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6. AUTHOR(S)
Alice L. Alldredge

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Marine Science Institute
University of California
Santa Barbara, California 93106

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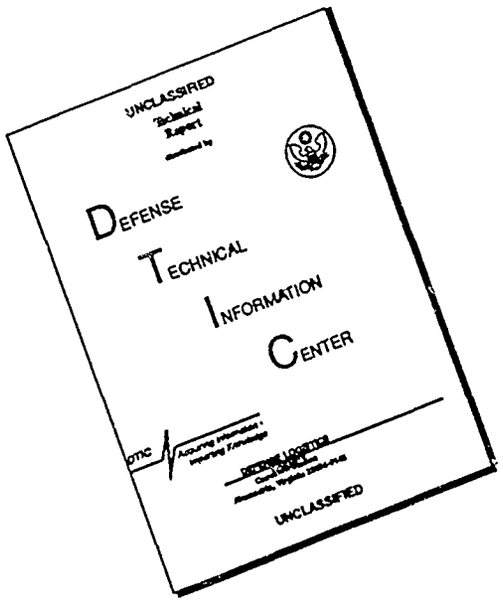
Much of the suspended particulate matter in the ocean exists as aggregates of smaller particles of algae, bacteria, organic detritus and inorganic particles. The characteristics and abundances of these aggregates affect the trophic interactions, chemistry and optical properties of the water column. The goal of this research was to quantify several processes governing the rates of production, breakdown and loss of marine aggregates, particularly those larger than 500 um, known as marine snow. Our results indicate that gravitational settlement is considerably more significant than disaggregation as a process of aggregate loss. Settling velocities of natural aggregates measured directly in situ increased with increasing aggregate size and ranged from 50 to 200 md⁻¹ for aggregates up to 75mm in length. Moreover, aggregates were very strong and resistant to disaggregation by fluid shear. High energy storm events or current shears equivalent to those in tidal channels would be required to fragment even the most fragile organic aggregates in the upper ocean. The process of aggregate formation via particle collision and subsequent attachment occurs at rates up to an order of magnitude higher than previously assumed because the attachment probabilities of colliding marine snow aggregates approaches 100%. Coagulation of diatom blooms is a significant source of marine snow in many ocean regimes.

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FINAL REPORT - ONR N00014-85-K-0771

PARTICLE DYNAMICS IN THE SEA: PROCESSES OF PRODUCTION AND LOSS GOVERNING THE ABUNDANCE OF MARINE SNOW

JULY 1, 1985 - SEPT. 30, 1989
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Principal Investigator:

Dr. Alice L. Alldredge
Department of Biological Sciences and
Marine Science Institute
University of California
Santa Barbara, CA 93106
805-961-3997; Omnet - A.Alldredge

ABSTRACT

Much of the suspended particulate matter in the ocean exists as aggregates of smaller particles of algae, bacteria, organic detritus and inorganic particles. The characteristics and abundances of these aggregates affect the trophic interactions, chemistry and optical properties of the water column. The goal of this research was to quantify several processes governing the rates of production, breakdown and loss of marine aggregates, particularly those larger than 500 um, known as marine snow. Our results indicate that gravitational settlement is considerably more significant than disaggregation as a process of aggregate loss. Settling velocities of natural aggregates measured directly *in situ* increased with increasing aggregate size and ranged from 50 to 200 md^{-1} for aggregates up to 75 mm in length. Moreover, aggregates were very strong and resistant to disaggregation by fluid shear. High energy storm events or current shears equivalent to those in tidal channels would be required to fragment even the most fragile organic aggregates in the upper ocean. The process of aggregate formation via particle collision and subsequent attachment occurs at rates up to an order of magnitude higher than previously assumed because the attachment probabilities of colliding marine snow aggregates approaches 100%. Coagulation of diatom blooms is a significant source of marine snow in many ocean regimes.

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BACKGROUND

Much of the suspended particulate matter in the ocean exists as aggregates of smaller particles of algae, bacteria, organic detritus, and inorganic particles. These aggregates range from tens of microns to many centimeters in diameter and compose the majority of particles in the larger size categories of the particle size spectrum in the ocean. Marine aggregates larger than 500 μm, known as marine snow, are formed by two major pathways. Primary particles, including phytoplankton, bacteria, and detritus are repackaged into fecal pellets, mucus feeding structures, molts and animal biomass via biological processes of animal grazing or they are coagulated into aggregates by processes of physical collision and attachment. Once formed, aggregate are lost or become reduced in size by gravitational settlement, animal consumption, dissolution, microbial decomposition, or physical disaggregation by fluid motion.

Thus, these competing processes of aggregate formation, breakdown and loss govern the characteristics and abundances of aggregated particulate matter in the ocean and affect the abundances of primary particles as well. They alter the oceanic particle size spectrum in ways which may significantly impact the trophic structure, microbial activity, particulate flux, chemistry and optical properties of the water column.

OBJECTIVES

The long term goal of my research is to understand and quantify the processes governing the rates of production, breakdown and loss of aggregated particulate matter in sufficient detail to predict variability in the distribution, abundance and size frequency of marine snow in the ocean. The following specific objectives were pursued as part of the attainment of this goal:

1. Prioritize the major pathways of marine snow formation and loss as to likely importance. Formulate testable hypotheses based on this prioritization.

2. Quantify two major processes of aggregate loss; gravitational settlement and physical disaggregation due to fluid motion.

3. Begin quantification of physical coagulation as a processes governing aggregate formation. Especially determine attachment probabilities of colliding aggregates as a function of aggregate origin, size, and velocity

4. Develop, test and deploy an underwater video imaging system for determination of the abundances and size distributions of marine snow *in situ*. Quantitative measurements of aggregate sizes and abundances are required to assess the impact of the various processes governing aggregate formation and loss in nature.

SUMMARY OF ACCOMPLISHMENTS

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Complete details of the results of this contract appear in the 8 publications and manuscripts appended to this report. However, the following abstract summarizes the most significant of our findings:

Processes of Aggregate Loss

Gravitational settlement - The settling velocities of undisturbed macroscopic aggregates of marine snow were measured with scuba in surface waters off southern California and analyzed as a function of aggregate mass, size, and density. The mean settling velocity was 74±39 m d^{-1} for aggregates ranging from 2.4 to 75 mm in maximum length. Sinking rates in the field varied exponentially with aggregate size and dry weight and were consistently up to 4 times slower than rates measured in the laboratory.

The excess densities of the 80 aggregates examined were calculated from volume and dry weight and ranged over 4 orders of magnitude with a median of 1.4 X 10^{-4} g cm^{-3}. Aggregates of marine snow sank more slowly than predicted for either sold or porous spheres of equivalent volume and density, although their velocities were within the range expected for equivalent sinking prolate ellipsoids. No relationship between settling velocity and either excess density or particle shape was found. Drag coefficients of marine snow were also higher than predicted by theory for spheres of equivalent volume and density. These deviations from theoretical expectations may be partially explained by errors in the estimation of the excess density of aggregates. Variability in the densities of the heterogeneous primary particles comprising marine snow (fecal pellets, clay-mineral particles, phytoplankton, molts etc.) and the potential for buoyancy regulation by individual phytoplankton cells inhabiting aggregates make determination of excess density especially problematic.

Disaggregation by fluid shear - Abiotic fragmentation of large, rapidly sinking aggregates into smaller, suspended particles by fluid shear has been suggested as an important process governing particle size distributions in the ocean and as one explanation for the exponential decrease in the flux of particulate organic matter with depth below the euphotic zone. We investigated this process by quantifying the small scale energy dissipation rates required to fragment or disaggregate fragile, macroscopic aggregates of particulate matter, known as marine snow. The fate of individual, hand-collected aggregates was videorecorded as they settled through a gradient of turbulent kinetic energy generated by a calibrated oscillating grid system in a laboratory tank.

Amorphous aggregates of detrital debris, gelatinous houses of larvacean tunicates, and aggregates of the sewage flocculating bacteria, *Zoogloea ramigera*, all ranging up to 4 mm in diameter, did not break apart at energy dissipation rates far in excess of 1 $cm^2 s^{-3}$. The rate of energy dissipation required to disaggregate fragile flocs of chain-forming diatoms up to 25 mm in length ranged from 10^{-3} to greater than 1 $cm^2 s^{-3}$ and increased exponentially with decreasing maximum aggregate diameter. Seventy percent of disaggregating particles fragmented into two subunits. Aggregates aged 5 days in the laboratory were significantly stronger than identical unaged particles. Our experiments

have been limited to a few types of marine snow, including some among the most fragile, and to small scales of shear. However, they indicate that high energy storm events or current shears equivalent to those reported from tidal channels would be required to fragment even the most fragile organic aggregates in the upper ocean. Thus, disaggregation by fluid motion appears to be a relatively insignificant processes of aggregate loss.

Processes of Aggregate Formation

Attachment probabilities - The rate at which suspended particles in the ocean coagulate to form larger, more rapidly sinking aggregates is directly related to the efficiency with which the particles stick together once collided. Many previous models of coagulation in the ocean have assumed that the attachment probability of natural suspended particles is low, based on data for marine sediments. We determined the attachment probabilities of natural macroscopic aggregates as a function of aggregate type, size, and collision velocity by observing and videorecording individual particle-particle interactions between 660 pairs of aggregates collided together via gravitational settlement. Attachment probabilities of marine macroaggregates in the size range of 0.2 to 7.6 mm are the highest yet measured ranging from 0.60 (i.e. 60% of collisions result in attachment) for amorphous detrital aggregates to 0.88 for flocculated diatoms. Attachment probabilities increased with increasing particle volume, the surface area of contact, and collision velocity. Large size and surface complexity resulting in multi-point contact between colliding particles and the abundance of sticky, microbially-produced exopolymers on the aggregate surfaces probably increase aggregation efficiency. The high attachment probabilities of suspended organic macroaggregates suggest that particle aggregation rates due to physical coagulation in the ocean may be many times higher than previously predicted.

Diatom blooms as sources of marine snow - Blooms of chain-forming marine diatoms were observed in the process of aggregating into centimeter-sized flocs of marine snow in surface waters of the Santa Barbara Channel, California. These aggregates were composed of a rich assemblage of living, actively photosynthesizing diatoms dominated by the setose genus Chaetoceros and by chain-forming Nitzschia spp. Flocculation of one bloom occurred in as little as 24 hours and bloom flocculation apparently was not triggered by nitrogen-limitation. Marine snow of diatom origin was also abundant during spring, summer and early autumn throughout the Southern California Bight, suggesting that diatom flocculation is a seasonally significant source of marine snow. Resting spores rarely occurred within either newly formed or aged diatom flocs. The mean in situ settling velocity (±S.D.) of newly formed flocs was 117 ± 56 m d-1, two orders of magnitude faster than unaggregated Chaetoceros. Rapid, episodic export of surface derived primary production to the ocean bottom via mass flocculation and settlement of diatom blooms can occur prior to consumption by pelagic grazers and significantly effects marine food webs, ocean flux processes, diatom biology, and optical properties of the water column.

Measurement of Aggregate Size and Abundance In Situ

We have developed and ocean tested an underwater video imaging system designed to produce quantitative data on the size distributions and abundances of aggregates larger than 500 μm in diameter. This system is a substantial modification of the configuration used by Honjo et al. (Deep Sea Res. 31:67-76, 1984). While their system used a still camera and strobe lighting, our system uses continuous light and a CCD video camera to photograph the particles in a defined volume of seawater. In this type of video camera light impinges directly on a computer chip. There is no video tube and thus, no ghosting. The camera produces sharp, bright images of aggregates > 500 μm in diameter which are contained in a volume defined by the slab of light. This slab has a minimum size of 12 X 15 X 5 cm and can be enlarged to considerably greater volumes, although some loss of resolution results. Video was chosen because of the ease with which modern computerized image analysis systems can handle images on video tape. The marine snow video camera system also contains a CTD and yields vertical profiles of aggregate abundance to greater than 200 m. The camera will be deployed in our future ONR research, especially that involving the Accelerated Research Initiative on Aggregate Dynamics.

SPECIFIC ACCOMPLISHMENTS

A. *Publications* - Research presented in the following publications, and manuscripts was partially or totally supported by ONR Contract N00014-K-0771. These documents present the detailed findings of this contract and are appended to this report:

1. Alldredge, A.L., C.C. Gotschalk, and S. MacIntyre 1987. Evidence of sustained residence of macrocrustacean fecal pellets in surface waters off Southern California. Deep-Sea Research.. 34:1641-1652.

2. Alldredge, A.L. and M. W. Silver 1988. Characteristics, dynamics and significance of marine snow. Progress in Oceanography 20:41-82.

3. Alldredge, A.L. and C. C. Gotschalk 1988. In situ settling behavior of marine snow. Limnology and Oceanography 33:339-351.

4. Alldredge, A.L. and C. C. Gotschalk 1989. Direct observations of the mass flocculation of a diatom bloom: Characteristics, settling velocities and formation of diatom aggregates. Deep-Sea Research 36: 159-171.

5. Logan, B. E. and A. L. Alldredge 1989. Potential for increased nutrient uptake of flocculating diatoms. Marine Biology 101: 443-450.

6. Alldredge, A.L. and P. McGillivary. The attachment probabilities of colliding macroscopic aggregates

(marine snow). Manuscript to be submitted to Deep-Sea Research (appended).

7. Alldredge, A.L., T. C. Granata, C. C. Gotschalk and T. D. Dickey. The physical strength of marine snow and its implications for particle disaggregation processes in the ocean. Manuscript to be submitted to Limnology and Oceanography (appended).

B. *Reports* - The following published reports resulted from this contract:

1. Alldredge, A.L. and E. O. Hartwig 1986. Aggregate Dynamics in the Sea. ONR Workshop Report, AIBS

2. Biological processes which form, alter, and destroy aggregate in the ocean. In Aggregate Dynamics in the sea, ONR Workshop report, AIBS, pp 109-130.

C. *Presentations at Scientific Meetings* - The following presentations as scientific meetings and conferences reported Research findings supported by this ONR contract.

1. Alldredge, A.L. Aggregate dynamics: Biological processes which form, alter, and destroy aggregate in the ocean. Aggregate Dynamics in the sea, ONR Workshop; Asilomar Conference Center, Sept. 1986.

2. Alldredge, A.L. In situ settling behavior of marine snow. AGU-ASLO Ocean Sciences Meeting, Jan. 1988

3. P.A. McGillivary and A.L. Alldredge. Attachment probabilities of natural particles on collision. AGU-ASLO Ocean Sciences Meeting, Jan. 1988.

4. Alldredge, A.L. Mass flocculation and settlement of diatoms: Significant source of marine snow? AGU-ASLO Ocean Sciences Meeting, Jan. 1988.

5. Alldredge, A.L. Characteristics and particle dynamics of marine snow. Keynote address, Workshop on marine aggregates, Alfred-Wegner Institute for Polar Research, Bremerhaven, Germany, June 1988.

6. Logan, B.E. and A.L. Alldredge. The potential for increased nutrient uptake of flocculating diatoms. AGU-ASLO, Dec. 1988.

7. Alldredge, A.L., T. C. Granata, C.C. Gotschalk. The physical strength of marine snow: Implications for particle disaggregation processes in the ocean. AGU-ASLO Ocean Sciences meeting, Feb. 1990.

D. *Organization of Marine Snow Workshops and Symposia by PI*

1. Organized ONR Workshop on Aggregate Dynamics in the Sea, Asilomar Conference Center, Pacific Grove, California, Sept. 1986. 39 participants.

2. Organized a Symposium on "Marine Aggregates", AGU-ASLO Fall Meeting, Dec., 1988.

E. *Associated personnel*

Dr. Philip McGillivary, Postdoctoral Fellow (1986-1988)
Chris C. Gotschalk, Staff Research Associate (1985-89)
3-4 undergraduate assistants per year, part time

APPENDICES

A. Alldredge, A.L., C.C. Gotschalk, and S. MacIntyre 1987. Evidence of sustained residence of macrocrustacean fecal pellets in surface waters off Southern California. Deep-Sea Research 34:1641-1652.

B. Alldredge, A.L. and M. W. Silver 1988. Characteristics, dynamics and significance of marine snow. Progress in Oceanography 20:41-82.

C. Alldredge, A.L. and C. C. Gotschalk 1988. In situ settling behavior of marine snow. Limnology and Oceanography 33:339-351.

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E. Logan, B. E. and A. L. Alldredge 1989. Potential for increased nutrient uptake of flocculating diatoms. Marine Biology 101: 443-450.

F. Alldredge, A.L. and P. McGillivary. The attachment probabilities of colliding macroscopic aggregates (marine snow). Manuscript to be submitted to Deep-Sea Research

G. Alldredge, A.L., T. C. Granata, C. C. Gotschalk and T. D. Dickey. The physical strength of marine snow and its implications for particle disaggregation processes in the ocean. Manuscript to be submitted to Limnology and Oceanography

H. Alldredge, A.L. and E. O. Hartwig 1986. Aggregate Dynamics in the Sea. ONR Workshop Report, AIBS Technical Reprot

Deep-Sea Research, Vol. 34, No. 9, pp. 1641–1652, 1987.
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Evidence for sustained residence of macrocrustacean fecal pellets in surface waters off Southern California

ALICE L. ALLDREDGE*†, CHRIS C. GOTSCHALK† and SALLY MACINTYRE†

(*Received* 11 *November* 1986; *in revised form* 20 *March* 1987; *accepted* 24 *March* 1987)

Abstract—Large fecal pellets produced by macrocrustaceans, probably euphausiids, were observed frequently in the upper 20 m of the Santa Barbara and Santa Cruz basins off southern California at abundances ranging from 500 to 98,000 pellets m^{-3}. Although sinking rates of these pellets, ranging from 18 to 170 m day^{-1}, were rapid enough to remove the pellets from surface waters within hours, up to 40% of the pellets in the field had peritrophic membranes which were partially or totally decayed. Laboratory aging studies indicate that these decomposing pellets were from 4 to 10 days old. Moreover, the daily calculated flux of pellets from surface water, based on sinking rate measurements, was many times the photosynthetic carbon production of the euphotic zone, suggesting that sustained daily production of pellets at the abundances we observed would not be possible. We hypothesize that a proportion of fecal pellets produced by vertically migrating macrocrustaceans at night do not sink immediately, but accumulate in surface waters. Turbulent mixing processes, which increase the residence time of fecal pellets in the mixed layer, partially explain the observed accumulation.

INTRODUCTION

THE sinking of fecal pellets is a major pathway by which surface-derived material reaches the sea floor [see ANGEL (1984) for review]. Up to 90% of particulate flux may be in the form of fecal pellets in some coastal areas (DUNBAR and BERGER, 1981), and fecal pellets represent the bulk of the flux at some oceanic sites as well (HONJO and ROMAN, 1978; SPENCER *et al.*, 1978). Despite their abundance in sediment trap material (ANGEL, 1984), fecal pellets are considered to be a negligible component of the water column itself because of their relatively high settling velocities and potentially short residence time (MCCAVE, 1975; BISHOP *et al.*, 1977). Fecal pellets of adult zooplankton sink at rates of 10 to several 1000 m day^{-1} in the laboratory (BRULAND and SILVER, 1981), suggesting that they would remain only a short time in surface waters. Moreover, large discrete fecal pellets are rarely collected in water bottles and other devices which dircctly sample the water column (FELLOWS *et al.*, 1981).

However, recent research suggests that small, relatively slowly sinking zooplankton fecal pellets can be abundant in surface waters. KRAUSE (1981) found consistently high concentrations of copepod fecal pellets in the upper 30 m of the North Sea over a 2.5 month period, and concluded that the pellets could not be sinking in nature as rapidly as sinking rates determined in the laboratory would indicate. Sinking rates determined in

* Department of Biological Sciences and † Marine Science Institute, University of California, Santa Barbara, CA 93106, U.S.A.

the laboratory represent maximum potential rates and do not account for physical processes which may retard sinking or advect pellets upward in nature. In this study we report the frequent occurrence of large, rapidly sinking macrocrustacean fecal pellets in the surface waters of coastal California and present evidence suggesting that these fecal pellets may have longer residence times in surface waters than previously hypothesized.

MATERIALS AND METHODS

Field sampling

We observed abundant, large, strand-like fecal pellets in epipelagic waters off southern California during numerous scuba dives over a 2-year period. Fecal pellets were collected by hand on three of these dives in Santa Cruz Basin in the autumn and winter of 1985–1986 (Fig. 1). Divers collected 50–100 fecal pellets individually in 6 ml syringes and seawater in 4-l polyethylene bottles from depths of 7–12 m at each station. Abundances of fecal pellets at 10 m were determined from three replicate visual counts of the number of pellets passing through a 5.7 cm hoop attached to a hand-held flow meter as described in ALLDREDGE (1979).

Primary production and light attenuation of seawater were also measured at each station. Six replicate, 60 ml samples of surrounding seawater (containing no fecal pellets) collected at 10 m were each spiked with 10 μCi ^{14}C bicarbonate as described in STRICKLAND and PARSONS (1972) and incubated on the deck of the ship or in an environmental chamber at *in situ* temperature and light intensities for 2 h at mid-day. Three replicates served as dark controls. Light profiles were determined with a Licor Model LI-185A light

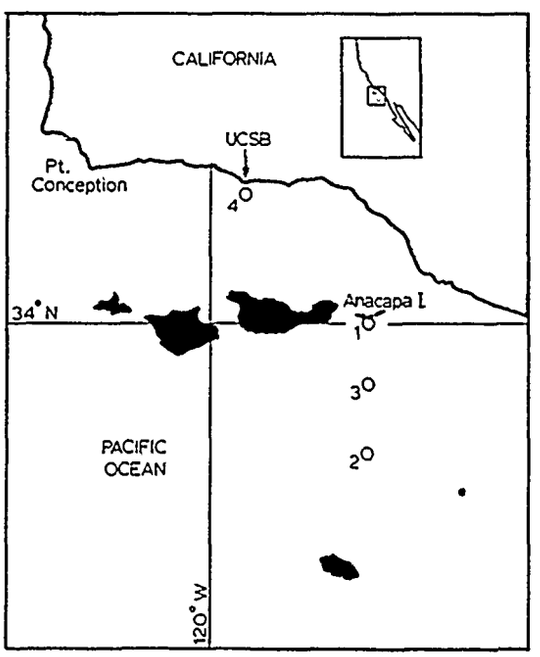


Fig. 1. Sampling stations in Santa Cruz (Stas 1–3) and Santa Barbara (Sta. 4) basins off southern California.

meter and a LI-192S underwater quantum sensor. Continuous wind speed records were obtained at one station (30 April) with a Qualimetric Weathermeasure Anemometer (Series 200SD).

Laboratory analysis

Following collection, the length and width of each pellet were measured under a dissecting microscope. We calculated pellet volume from these measurements assuming pellets to be cylinders. The condition of the peritrophic membrane of each pellet was categorized as being either intact, partially disrupted or totally decomposed. Intact peritrophic membranes were continuous sheaths containing no tears, splits or areas where the contents of the pellet spilled through. Partially disrupted membranes contained tears or holes and the membrane itself appeared thin and tattered. Fecal pellets with totally decomposed membranes had no discernible membranes, and the pellets had lost their smooth surfaces and cylindrical appearance. Representative pellets of each membrane type were fixed as described in Gowing and Silver (1983) and examined under a Hitachi S-415A Scanning Electron Microscope to determine general contents of the pellets and the location of bacteria populations inhabiting the pellets.

We measured the abundances of bacteria per mm of pellet length for pellets in each membrane category. Fecal pellets, previously fixed in 2% formalin, were disrupted with a sonicator (Alldredge *et al.*, 1986), stained and counted using standard acridine orange techniques (Hobbie *et al.*, 1977). We also estimated the densities of macrocrustacean fecal pellets collected in the Santa Barbara Channel in February 1987, by observing the behavior of pellets settling through density gradients in the laboratory. Seawater density was measured with a hygrometer to the nearest 0.001 g cm^{-3} and increased by the addition of NaCl and sucrose.

We determined the time required for the peritrophic membranes of pellets to decompose in the laboratory at *in situ* temperatures. Fecal pellets were collected individually in sterile 6 ml syringes in the Santa Barbara Channel and maintained in these syringes in the dark at 15°C. Each day 15 fecal pellets which had intact peritrophic membranes on the day of collection were pipetted with a sterile pippette onto a slide and examined under a dissecting microscope for signs of membrane decomposition.

Sinking rate vs pellet size was determined both in the laboratory and the field for pellets observed on 11 October 1985 in the Santa Barbara Channel. In the laboratory method, individual pellets were removed from the syringe with a pipette and placed gently at the top of a graduated cylinder (8 × 50 cm) containing seawater collected at the same depth and time as the pellets. This seawater was 14°C and had a salinity of 33.66‰. The settling chamber was located on a table in a 14°C walk-in environmental chamber. Observation of a solution of fluorescein dye added to the settling chamber revealed no advective water movement. We timed the sinking of each pellet past external markings on the graduate cylinder with a stop watch. At least four replicate measurements were made on each pellet. Each pellet was then removed from the chamber with a pipette and measured under a dissecting microscope.

Some measurements of the sinking rates of totally undisturbed fecal pellets were made directly in the field by scuba divers. One diver, floating 5–10 m away from the other divers for reduced turbulence, delivered a tiny spot of fluorescein dye (mixed dry at depth with seawater to insure a density and temperature identical to seawater) at a point 3 cm below a fecal pellet located approximately 1.5 m in front of him. The dye was

delivered from a spring loaded syringe through a capillary tube to a hypodermic needle attached to the end of a 1 m rod. A fine wire "site" attached to the rod tip 3 cm above the delivery point of the dye marked the settling distance. The time required for the pellet to sink to the dye spot was determined with an underwater stop watch and the pellet was then collected. The dye spot did not diffuse appreciably for several minutes, and with care, the diver produced no turbulence (observed via deformation of the dye spot) which would interfere with an accurate measurement.

Organic carbon and nitrogen contents of fecal pellets were also determined for pellets collected in the Santa Barbara Channel. Forty to 60 pellets from each station were measured and split between two replicate pre-ashed Whatman GF/F glass fiber filters. Organic carbon and nitrogen were measured on a Perkin–Elmer CHN Analyzer, Model 240B as described by SHARP (1974) using the temperature modification suggested by TELEK and MARSHALL (1974) to reduce carbonate interference.

RESULTS

The presence of a peritrophic membrane, the large size, and the physical characteristics of the fecal pellets we observed *in situ* indicated that they were produced by one or more species of macrocrustaceans, probably the euphausiid species *Euphausia pacifica* or *Nematocilis difficilis* or the sergestid *Sergestes similis*. These are the most numerous macrocrustaceans in the Santa Barbara and Santa Cruz basins (EBELING *et al.*, 1970). Specimens of *E. pacifica* freshly collected in the Santa Barbara Channel and held in beakers of seawater in the laboratory produced fecal pellets of the same appearance, width and range of lengths as we observed in naturally occurring fecal pellets.

We observed abundant fecal pellets on 42% of our dives in the Santa Barbara Channel and Santa Cruz Basins during 1985 and 1986. The abundances of fecal pellets in surface waters at the six stations we sample ranged from 500 to 98,000 m^{-3}. Three of these stations were sampled on three consecutive days along a 50 km transect in the Santa Cruz Basin (Fig. 1) indicating that high abundances of fecal pellets can occur over large geographic areas and for extended periods of time. Mean wind speed was 5 m s^{-1} at the Santa Cruz Basin stations. Wind speed was low at night and early morning, reaching maximum speeds of 9 m s^{-1} in late afternoon and early evening.

The fecal pellets collected on all six sampling dates and from a variety of locations (Fig. 1) were similar in appearance and size. Cross-sectional diameter averaged 0.08 ± 0.04 mm at all stations while length ranged from 0.3 to 7.5 mm (Table 1). Length to width ratios ranged from 19:1 to 52:1. Fecal pellets were yellow brown in color and

Table 1. *Mean abundances and physical characteristics* (±1 S.D.) *of macrocrustacean fecal pellets observed on six dates in surface waters of coastal California. SCB, Santa Cruz Basin; SBB, Santa Barbara Basin. Station locations are shown in Fig.* 1. *L = length, W = width.*

Date	Location–Sta. no.	Abundance (no. l^{-1})	Mean length (mm)	Mean volume (10^{-3} mm)	L:W
30 April 1985	SCB–1	4.8 ± 2.2	3.7 ± 2.3	19 ± 11	46:1
1 May 1985	SCB–3	4.6 ± 0.9	2.5 ± 1.8	7 ± 4	41:1
2 May 1985	SCB–2	12.0 ± 5.7	4.2 ± 2.6	21 ± 13	52:1
11 Oct. 1985	SBB–4	1.4 ± 0.1	2.2 ± 1.2	11 ± 6	28:1
23 Jan. 1986	SBB–4	98.0 ± 17	1.5 ± 1.2	7 ± 5	19:1
11 Feb. 1986	SBB–4	0.5 ± 0.1	2.2 ± 1.5	11 ± 7	28:1

contained abundant diatom frustules, primarily centric diatoms, and unidentifiable digested detrital debris. Armored dinoflagellates, pennate diatoms and coccolithophorids occurred occasionally within the pellets. Intact pellets had a density of approximately 1.25 g cm^{-3}.

The sinking rates of fecal pellets were directly proportional to the length of the fecal pellet and ranged from 18 to 170 m day^{-1}. The correlation coefficients for the relationship between sinking rate and pellet length determined in the field did not differ statistically from that of laboratory measurements ($P > 0.5$; ZAR, 1974) so field and laboratory measurements were combined (Fig. 2). The rapid sinking rates of fecal pellets implied that the fecal pellets we observed at 10 m depth had been produced recently, probably within the previous 12 h since those produced prior to this time would have sunk well below the depth of collection.

However, examination of the decompositional state of the peritrophic membranes of the pellets indicated that many were considerably older than 12 h. Fecal pellets maintained in the laboratory at 15°C required 7 ± 3 days for the peritrophic membrane to decompose from the "intact" to the "partially disrupted" state and an additional 3 ± 2 days to decompose to the "totally decomposed" state. In the field up to 40% of the pellets at some stations had peritrophic membranes which were either partially or total decomposed (Fig. 3). The proportion of pellets exhibiting some membrane decomposition varied with station and was not correlated with distance from shore (Fig. 3). Fecal pellets with intact peritrophic membranes were significantly longer than those with partially or totally decomposed membranes ($P < 0.02$; one-way ANOVA) suggesting that fecal pellets break with age. However, intact pellets were not different in width from those with partially decomposed membranes ($P > 0.2$) while pellets with totally decomposed membranes were significantly wider and looser in appearance ($P < 0.01$) (Fig. 4a,b).

The concentration of bacteria within fecal pellets in the field also increased significantly as pellets reached higher degrees of decomposition. Intact fecal pellets contained as few as 6×10^7 bacteria mm^{-3} while fecal pellets with totally decomposed membranes contained up to 53×10^7 bacteria mm^{-3} (Fig. 4c). Examination of the fecal pellets with scanning electron microscopy indicated that the majority of bacteria were contained within the pellets, rather than on the surfaces of the peritrophic membranes.

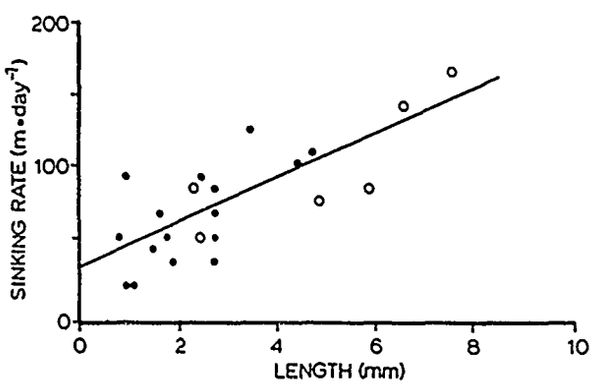


Fig. 2. Sinking rate as a function of fecal pellet length. Closed circles, measurements made in the laboratory. Open circles, measurments made *in situ*. (Sinking rate) = 15.7 (length) + 30.5, correlation coefficient = 0.77; $P < 0.001$.

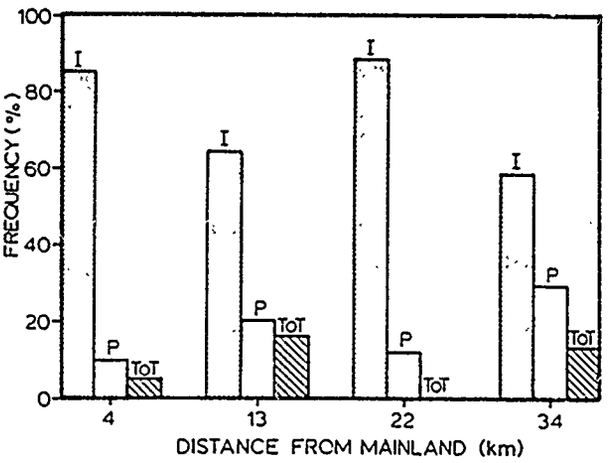


Fig. 3. Frequency of occurrence of pellets with intact (I; stippled bars), partially disrupted (P; open bars) and totally decomposed (TOT; striped bars) peritrophic membranes in surface waters of the four sampling stations as a function of distance from the California mainland. Station 4 (4 km from shore) was sampled 11 February 1986. The other three stations were sampled 30 April–2 May 1985.

Fecal pellets contained from 0.7 to 2.27 μg of organic carbon pellet^{-1} and from 0.10 to 0.26 μg of organic nitrogen pellet^{-1}. Pellets contained a mean of 0.46 μg carbon and 0.079 μg nitrogen per mm of length. C:N ratios averaged 8.9 ± 2.4. Total particulate organic carbon in fecal pellets ranged from 0.7 to 68.6 mg m^{-3} (Table 2). We calculated the mean predicted flux of fecal pellets by multiplying the mass of organic carbon in fecal pellets per m^{-3} by the sinking rate of a pellet of mean size (from Fig. 2) at each station. This calculation assumes that fecal pellets were, in fact, sinking in nature. The mean calculated flux was very high due to the abundance of fecal pellets and ranged from 46 to 2615 mg carbon m^{-2} day^{-1}. This flux represented > 100% of the daily primary production on all but one sampling day (Table 2). Our calculations indicate that a minimum of from 8 to 1614% of the primary production of surface waters would be lost from the euphotic zone daily as fecal pellets, if pellets were sinking at empirically determined rates. These calculations are deliberately conservative. We assumed that primary production was equal to that found at 10 m throughout the water column down to the 1% light level. Such an assumption overestimates primary production, thus minimizing the impact of fecal flux. Yet the assumed sinking of fecal pellets still produced a potential flux >100% of the primary production m^{-2} day^{-1}. Primary production was relatively low at our stations averaging 1.7 ± 1.9 mg m^{-3} h^{-1} at 10 m.

DISCUSSION

The fecal pellets observed in this study were very similar to pellets produced by euphausiids. *Meganyctiphanes norvegica*, *Euphausia krohnii*, and *Nematoscelis megalops* produce pellets ranging from 1 to 7 mm in length, from 0.048 to 0.176 mm in width and having length to width ratios of 9:1 to 65:1 (FOWLER and SMALL, 1972). The natural fecal pellets we observed fell well within these size limits. Moreover, the relationship between

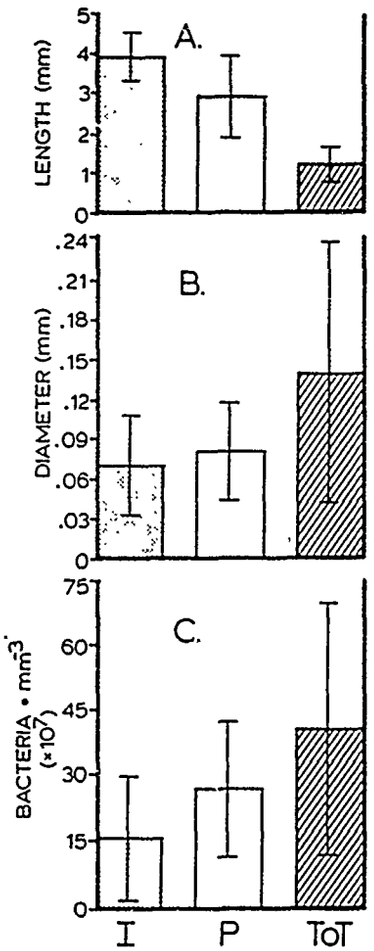


Fig. 4. Characteristics of fecal pellets with intact (I; stippled bars), partially disrupted (P; open bars) and totally decomposed (TOT; striped bars) peritrophic membranes averaged over all sampling stations. Error bars represent ±1 S.D. (A) Mean pellet length of pellets in each membrane category. (B) Mean diameter of pellets in each membrane category. (C) Mean abundance of bacteria per unit volume within pellets in each membrane category.

Table 2. Mean particulate organic carbon (POC) and nitrogen (PON) content of fecal pellets and estimated flux of pellets on six sampling dates in surface waters of coastal California. Flux was calculated by multiplying the carbon or nitrogen in fecal pellets per cubic meter by the sinking rate of the mean-sized pellet on each day

	μg pellet^{-1}		mg m^{-3} in pellets		Sinking rate	Flux (mg m^{-2} d^{-1})		% of 1°
Date	POC	PON	POC	PON	(m d^{-1})	POC	PON	production
30 April 1985	2.0	0.24	9.6	1.2	89	854	102	395
1 May 1985	1.4	0.16	6.2	0.7	70	435	52	241
2 May 1985	2.3	0.26	27.2	3.1	96	2615	300	1614
11 Oct. 1985	1.2	0.14	1.7	0.2	65	109	13	8
23 Jan. 1986	0.7	0.12	68.6	11.8	54	3708	635	114
11 Feb. 1986	1.4	0.10	0.7	0.1	65	46	3	N.D.

sinking rate and pellet size which we observed was very similar to that reported for euphausiid pellets by FOWLER and SMALL (1972). These data, coupled with the usually high abundance of *E. pacifica* and *N. difficilis* at our study sites in the Santa Barbara and Santa Cruz basins (BRINTON, 1962; EBELING *et al.*, 1970), and the visual similarity of our pellets with those produced by *E. pacifica* in the laboratory strongly support the identification of these pellets as euphausiid fecal pellets.

Although copepod fecal pellets may occur abundantly in surface water (KRAUSE, 1981; HOFFMAN *et al.*, 1981), only one other study documents the occurrence of macrocrustacean fecal pellets in the water column. YOUNGBLUTH *et al.* (1985) observed pellets identified as those of euphausiids or sergestiids at densities of 100–1000 pelles m^{-3} in the Gulf of Maine from a manned submersible. These fecal pellets were especially abundant at night within the thermocline at 15–30 m.

Data from sediment traps indicate that macrocrustacean fecal pellets may be common, particularly in neritic waters of southern California. DUNBAR and BERGER (1981) deployed a sediment trap for 4 months in the Santa Barbara Basin and found a flux of 660 g m^{-2} y^{-1} to the sediments, of which 60–90% was fecal pellets. The most common pellets were large, "tabular" forms similar in diameter to the pellets we observed in surface waters, although shorter. DUNBAR and BERGER (1981) suggested that these tabular pellets were derived from salps. However, salps are relatively uncommon and patchy in the Santa Barbara Basin (ALLDREDGE, unpublished data). It is more likely that the tabular pellets observed by DUNBAR and BERGER (1981) were broken macrocrustacean pellets. The total yearly flux calculated by DUNBAR and BERGER (1981) was 75% of the yearly average of 900 g m^{-2} y^{-1} for the Santa Barbara Basin over 25 years as determined by KRISHNASWAMI *et al.* (1973) using varied sediment cores of modern sedimant. Thus, DUNBAR and BERGER (1981) did not sample during a period of anomalously high fecal pellet abundance.

Two independent types of evidence support the conclusion that many of the fecal pellets we observed in nature were not sinking immediately from surface waters. First, up to 40% had peritrophic membranes which were partially or totally decayed. Our laboratory aging observations indicate that pellets with partially disrupted peritrophic membranes would be at least 4 days old at 15°C. This degradation rate is within the range of that for copepod pellets which require from 3 to 35 days for degradation of the peritrophic membrane, depending on temperature (HONJO and ROMAN, 1978; TURNER, 1979). Moreover, this age is probably conservative as fecal pellets appear to age much more rapidly under laboratory conditions than they do in nature (GOWING and SILVER, 1983).

Secondly, the organic carbon content of fecal pellets sinking from surface waters was generally many times the daily carbon fixed in the euphotic zone by phytoplankton. Although some macrocrustaceans are omnivorous, *E. pacifica*, the most probable source of our pellets, obtains most of its daily ration from phytoplankton (OHMAN, 1984). If, as suggested by laboratory sinking rates, all the fecal pellets we observed in surface waters had been produced in the previous 12 h, then primary production would have had to have been much greater than we observed to sustain the production of these pellets via macrocrustacean grazing. This argument is further strengthened by the fact that not all the phytoplankton was available for consumption by macrocrustaceans. Herbivorous copepods alone usually have a biomass equal to or greater than that of euphausiids at our study sites (FLEMINGER *et al.*, 1974). Since we observed abundant fecal pellets over three

consecutive days in the same, large geographic area it is unlikely that the high abundances of fecal pellets we observed at each station were episodic events of only a few hours duration resulting from patchy distributions of macrocrustaceans. Moreover, the high abundances of fecal pellets observed in sediment traps deployed for 4 months in the Santa Barbara Basin (DUNBAR and BERGER, 1981) indicate that macrocrustacean fecal pellets must occur frequently in high abundances. Primary production was inadequate to sustain the daily production of pellets in the abundances we observed at most stations.

Thus, we hypothesize that some pellets do not sink immediately, but rather accumulate in surface waters as they are produced nightly by vertically migrating macrocrustaceans feeding at the surface. Such an accumulation over time would explain the very high densities of fecal pellets we observed relative to primary production and the highly decomposed state of the peritrophic membranes of many of the pellets.

Accumulation of large, rapidly sinking fecal pellets in surface water could result from four physical processes common to the continental shelf and slope areas sampled here. Langmuir circulations and turbulence both prolong the residence time of particles by redistributing them throughout the mixed layer. Particles accumulating within the thermocline could be entrained back into the mixed layer during deep mixing events, and the upward component of velocity during upwelling events could counteract the sinking of particles. This last mechanism is unlikely at our study site since our low productivity measurements do not suggest upwelling conditions had been present for any appreciable length of time. We include consideration of Langmuir circulations in our discussion of turbulent mixing. Langmuir cells have upward velocities sufficient to keep fecal pellets in suspension (DENMAN and GARGETT, 1983; WELLER *et al.*, 1985), but based on calculations of the time required for them to cycle particles in the upper mixed layer, DENMAN and GARGETT (1983) concluded that they are comparable to turbulent eddies as a vertical transport mechanism.

Whether turbulent mixing maintains particles in suspension can be determined by comparing the characteristic time for settling, $t_s = z/w_s$, where z is depth and w_s is sinking rate, to the characteristic time for turbulent diffusion, $t_d = z^2/2k_z$, where k_z is the coefficient of vertical diffusivity (LICK, 1982). If $t_d/t_s \gg 1$, settling is the dominant mechanism of vertical transport. If $t_d/t_s \ll 1$, turbulent diffusion will govern movement of particles.

We found the ratio $t_d/t_s \approx 5$ using a settling velocity of 90 m d^{-1}, that of the mean size of pellet we observed, a mixed layer depth of 50 m, and an eddy diffusivity of 50 cm^2 s^{-1}. This value of the coefficient of eddy diffusivity is moderate. Measured values of eddy coefficients for the upper mixed layer range from 0.1 to 1400 cm^2 s^{-1}, being highly dependent upon wind speed, stability of the water column, and time of day (KONDO and SASANO, 1979; POLLARD, 1981). During our study, wind speeds averaged 5 m s^{-1} and based on multi-year CALCOFI (California Cooperative Oceanic Fisheries Investigations) records of temperature near our stations for the month of April we assume stability of the water column was low and the thermocline was approximately 50 m. Under these conditions, an average eddy diffusivity in the upper mixed layer of 50–100 cm^2 s^{-1} is not unreasonable. Two different approaches for computing eddy diffusivity from wind speed support estimates of this magnitude. FENNEL *et al.* (1983) compute k_z from $c^2U^3/\pi^2 t_m$, where c is a constant equal to 1.3 when length is given in meters and time in seconds, t_m is the time of mixed layer mixing, and U is wind speed. For 5 m s^{-1} winds and assuming $t_m = 1$ h, $k_v = 60$ cm^2 s^{-1}. In the other approach,

applicable to turbulent boundary layers, $k_z \approx 0.15\ u_* l$, where u_* is the water friction velocity and l is the depth of the boundary layer, in this case approximately 10 m (IMBERGER and HAMBLIN, 1982). The water friction velocity is the square root of the wind stress divided by the density of water $(\rho_a C_D U^{-2}/\rho_w)^{1/2}$, where ρ_a is density of air and C_D is drag coefficient taken to be 1.3×10^{-3}. Following this approach, $k_v \approx 75\ cm^2\ s^{-1}$.

The ratio of t_d/t_s that we calculated implies that the effects of diffusion and settling are similar in magnitude. In fact, the intensity of mixing varies with time since the processes driving turbulence are not steady, whereas the settling rate of intact pellets is constant. For particles to remain in suspension, mixing events of an intensity sufficient to keep the particles in suspension need to occur on a time scale shorter than the time required for all the particles to settle out of the mixed layer. During our observations, wind speeds had a diurnal cycle and were greatest in late afternoon. By this time, pellets defecated the previous night would have sunk nearly to the base of the mixed layer. The occurrence of wind-driven mixing at this time would redistribute throughout the mixed layer any pellets not yet lost from the mixed layer and would prolong their residence time.

REYNOLDS (1984) and SMITH (1982) provide analytical expressions to compute the fractional retention of particles in the mixed layer as a function of the number of mixing events in the time required for a particle to sink out of the mixed layer. When the water column is continuously mixing, the number of particles remaining in suspension at a time t is $M = M_0 \exp(-tw/l)$, where M_0 is the initial number of particles, w is sinking rate, and l is depth of the mixed layer. Assuming the production of fecal pellets to be at steady state, our data on fecal pellet decay indicate that 10–30% of the pellets persist in the mixed layer for 4–10 days and, of that population, 0–80% persist for another 1–5 days. For 10% of the pellets to persist in the water column the 4 days or more required for their peritrophic membrane to decay, REYNOLDS (1984) and SMITH's (1982) model indicates that the water column would need to mix continuously and the sinking rate of the pellets would have to be $<29\ m\ d^{-1}$. However, very few intact pellets were small enough to have sinking rates $<29\ m\ d^{-1}$, and thus the abundance and size distribution of pellets with partially decomposed membranes cannot be explained by turbulent mixing alone. However, turbulent mixing is sufficient to explain the abundance of pellets with totally disrupted membranes. Pellets with totally disrupted membranes result from aging of pellets with partially disrupted membranes; they are smaller than intact fecal pellets and sink more slowly. Assuming that their sinking rate ranges from 10 to 80 m day^{-1}, REYNOLDS (1984) and SMITH's (1982) model of turbulent mixing does explain the persistence of the partially intact fecal pellets in the water column long enough for the entire membrane to decay. When 80% of the pellets with partially decomposed membrane persisted, their model indicates that only the small pellets would have remained unless the density of fecal pellets decreases as they decompose. This assumption is not unreasonable because their composition would change with the invasion of bacteria and with the leakage of water. Although we did not measure the sinking rates of pellets in different states of decomposition, the larger diameter and fluffy appearance of decomposing pellets suggests they may have a lower density and thus, sink more slowly than intact pellets.

The turbulent mixing model only partially explains the prolonged residence times of fecal pellets. We have assumed, however, that the production of fecal pellets is at steady state and that sinking rates of partially decomposed pellets are identical to those of similarly sized intact pellets. If sinking rate slows with age, then turbulence may more adequately explain the observed accumulations.

Entrainment of fecal pellets that have accumulated in the thermocline is another possible source of fecal pellets to the mixed layer. Fecal pellet density determined in salt gradients and by calculations based on KOMAR *et al.*'s (1981) semi-empirical relationship between sinking rate and dimension indicate that the density difference between the mixed layer and the pycnocline is insufficient to reduce sinking velocity and thereby cause accumulations in the pycnocline. Fecal pellets have been observed at high abundances in the pycnocline at night due to nocturnal feeding of upwardly migrating euphausiids and sergestids (YOUNGBLUTH *et al.*, 1985; YOUNGBLUTH, personal communication). If thermocline waters were entrained into the upper mixed layer by mixing occurring in the early morning, these fecal pellets could be injected into the mixed layer.

Turbulence maintains particles in the water column for a longer time than would be predicted based on their sinking rates, but does not fully explain the accumulation of macrocrustacean fecal pellets in the mixed layer. Although the mechanisms maintaining and supplying fecal pellets in the mixed layer need further investigation, the sustained presence of large, abundant fecal pellets in surface waters must have a significant impact on the ecology of the pelagic zone. Smaller fecal pellets are recycled and readily consumed in the euphotic zone [see PAFFENHÖFER and KNOWLES (1979) and TURNER and FERRENTE (1979) for review]. Likewise, large pellets may be available to fish and zooplankton, such as salps, some euphausiids and pteropods, capable of feeding on macroscopic food. Moreover, many fish capable of feeding upon marine snow (ALLDREDGE, 1976, 1979) might also eat fecal pellets. The pellets we observed had mean C:N ratios of 9, suggesting that they may be a reasonable food source. The repackaging of phytoplankton by macrocrustacean grazers into large, heavily pigmented particles may also impact the bulk optical properties of seawater. Furthermore, such distinctive particles may serve as natural tracers useful in investigating a variety of physical mixing processes in surface waters. The potential for the sustained residence of large fecal pellets in the mixed layer suggests that other macroscopic particles exhibiting relatively high sinking rates but low effective densities, especially aggregates of marine snow, may also be days to weeks old before they settle from the mixed layer.

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REFERENCES

ANGEL M. V. (1984) Detrital organic fluxes through pelagic ecosystems. In. *Flows of energy and materials in marine ecosystems*, M. J. R. FASHAM, editor, Plenum, New York, pp. 475–516.

ALLDREDGE A. L. (1976) Discarded appendicularian houses as sources of food, surface habitats, and particulate organic matter in planktonic environments. *Limnology and Oceanography*, 21, 14–23.

ALLDREDGE A. L. (1979) The chemical composition of macroscopic aggregates in two neritic seas. *Limnology and Oceanography*, 24, 855–866.

ALLDREDGE A. L., J. J. COLE and D. A. CARON (1986) Production of heterotrophic bacteria inhabiting macroscopic organic aggregates (marine snow) from surface waters. *Limnology and Oceanography*, 31, 68–78.

BISHOP J. K. B., J. M. EDMOND, D. R. KETTEN, M. P. BACON and W. B. SILKER (1977) The chemistry, biology, and vertical flux of particulate matter from the upper 400 m of the equatorial Atlantic Ocean. *Deep-Sea Research*, 24, 511–548.

BRINTON E. (1962) Distribution of Pacific euphausiids. *Bulletin of the Scripps Institution of Oceanography*, 8, 51–270.

BRULAND K. W. and M. W. SILVER (1981) Sinking rates of fecal pellets from gelatinous zooplankton (salps, pteropods, doliolids). *Marine Biology*, 63, 295–300.

DENMAN K. L. and A. E. GARGETT (1983) Time and space scales of vertical mixing and advection of phytoplankton in the upper ocean. *Limnology and Oceanography*, 28, 801–815.

DUNBAR R. B. and W. H. BERGER (1981) Fecal pellet flux to modern bottom sediment of Santa Barbara Basin (California) based on sediment trapping. *Geological Society of America Bulletin*, 92, 212–218.

EBELING A. W., G. W. CAILLIET, R. M. IBARA and F. A. DEWITT (1970) Pelagic communities and sound scattering off Santa Barbara, California. *Proceedings of an International Symposium on Biological Sound Scattering in the Ocean*, G. BROOK, editor, pp. 1–19.

FELLOWS D. A., D. M. KARL and G. A. KNAUER (1981) Large particle fluxes and the vertical transport of living carbon in the upper 1500 m of the northeast Pacific Ocean. *Deep-Sea Research*, 28, 921–936.

FENNEL W., H. PRANDKE and H. U. LASS (1983) On the penetration depth of wind wave mixing. *Tropical Ocean-Atmosphere Newsletter*, 22, 12–13.

FLEMINGER A., J. D. ISSACS and J. G. WYLLIE (1974) Zooplankton biomass measurement from Cal COFI Cruises of July 1955 to 1959 and remarks on comparisons with results from October, January and April cruises of 1955 to 1959. California Cooperative Fisheries Investigations Atlas No. 21. Marine Research Committee State of California.

FOWLER S. W. and L. S. SMALL (1972) Sinking rates of euphausiid fecal pellets. *Limnology and Oceanography*, 17, 293–296.

GOWING M. M. and M. W. SILVER (1983) Origins and microenvironments of bacteria mediating fecal pellet decomposition in the sea. *Marine Biology*, 73, 7–16.

HOBBIE J. E., R. J. DALEY and S. JASPER (1977) Use of nucleopore filters for counting bacteria by fluorescence microscopy. *Applied Environmental Microbiology*, 33, 1225–1228.

HOFFMAN E. E., J. G. M. KLINCK and G.-A. PAFFENHOFER (1981) Concentrations and vertical fluxes of zooplankton fecal pellets on a continental shelf. *Marine Biology*, 61, 327–335.

HONJO S. and M. R. ROMAN (1978) Marine copepod fecal pellets: production, preservation and sedimentation. *Journal of Marine Research*, 36, 45–57.

IMBERGER J. and P. F. HAMBLIN (1982) Dynamics of lakes, reservoirs, and cooling ponds. *Annual Review of Fluid Mechanics*, 14, 153–187.

KONDO J. and Y. SASANO (1979) On wind-driven current and temperature profiles and diurnal period in the oceanic planetary boundary layer. *Journal of Physical Oceanography*, 9, 360–372.

KOMAR P. D., A. P. MORSE and L. F. SMALL (1981) An analysis of sinking rates of natural copepod and euphausiid fecal pellets. *Limnology and Oceanography*, 26, 172–180.

KRAUSE M. (1981) Vertical distribution of fecal pellets during FLEX '76'. *Helgolaender Wissenschaftliche Meeresuntersuchungen*, 34, 313–327.

KRISHNASWAMI S., D. LAL, B. S. AMIN and A. SOUTAR (1973) Geochronological studies in Santa Barbara Basin: ^{55}Fe as a unique tracer for particulate settling. *Limnology and Oceanography*, 18, 763–770.

LICK W. (1982) Entrainment, deposition, and transport of fine-grained sediments in lakes. *Hydrobiologia*, 91, 31–40.

MCCAVE I. N. (1975) Vertical flux of particles in the ocean. *Deep-Sea Research*, 22, 491–502.

OHMAN M. D. (1984) Omnivory by *Euphausia pacifica*: the role of copepod prey. *Marine Ecology Progress Series*, 19, 125–131.

PAFFENHÖFER G.-A. and S. C. KNOWLES (1979) Ecological implications of fecal pellet size, production and consumption by copepods. *Journal of Marine Research*, 37, 35–49.

POLLARD R. T. (1981) Observations of models of the structure of the upper ocean. In: *Modelling and prediction of the upper layers of the ocean*, E. B. KRAUS, editor, Pergamon Press, Oxford, pp. 475–516.

REYNOLDS C. S. (1984) *The ecology of freshwater phytoplankton*, Cambridge University Press, Cambridge, 384 pp.

SHARP J. H (1974) Improved analysis for particulate organic carbon and nitrogen from seawater. *Limnology and Oceanography*, 19, 984–989.

SMITH I. R. (1982) A simple theory of algal deposition. *Freshwater Biology*, 12, 445–449.

SPENCER D. W., P. G. BREWER, A. FLEER, S. HONJO, S. KRISHNASWAMI and Y. NOZAKI (1978) Chemical fluxes from a sediment trap experiment in the deep Sargasso Sea. *Journal of Marine Research*, 36, 493–523.

STRICKLAND J. D. H. and T. R. PARSONS (1972) *A practical handbook of seawater analysis*, Fisheries Research Board of Canada, Ottawa, 310 pp.

TELEK G. and N. MARSHALL (1974) Using a CHN analyser to reduce carbonate interference in particulate organic carbon analysis. *Marine Biology*, 24, 219–221.

TURNER J. T. (1979) Microbial attachment to copepod fecal pellets and its possible ecological significance. *Transactions of the American Microscopical Society*, 98, 131–135.

TURNER J. T. and J. G. FERRANTE (1979) Zooplankton fecal pellets in aquatic ecosystems. *Bioscience*, 29, 670–677.

WELLER R. A., J. P. DEAN, J. MARRA, J. F. PRICE, E. A. FRANCIS and D. C. BOARDMAN (1985) Three-dimensional flow in the upper ocean. *Science*, 227, 1552–1556.

YOUNGBLUTH M. J., T. G. BAILEY and P. J. DAVOL (1985) Downward flux of fecal strands in the Gulf of Main. *EOS*, 66, 1264 (Abstr.).

ZAR J. H. (1974) *Biostatical analysis*, Prentice-Hall, Englewood Cliffs, New Jersey, 620 pp.

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Characteristics, Dynamics and Significance of Marine Snow

ALICE L. ALLDREDGE* and MARY W. SILVER**

*Department of Biological Sciences, University of California, Santa Barbara, CA 93106, U.S.A.
**Institute of Marine Sciences, University of California, Santa Cruz, CA 95064, U.S.A.

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ABSTRACT

Macroscopic aggregates of detritus, living organisms and inorganic matter known as marine snow, have significance in the ocean both as unique, partially isolated microenvironments and as transport agents: much of surface-derived matter in the ocean fluxes to the ocean interior and the sea floor as marine snow. As microhabitats, marine snow aggregates contain enriched microbial communities and chemical gradients within which processes of photosynthesis, decomposition, and nutrient regeneration occur at highly elevated levels. Microbial communities associated with marine snow undergo complex successional changes on time scales of hours to days which significantly alter the chemical and biological properties of the particles. Marine snow can be produced either *de novo* by living plants and animals especially as mucus feeding webs of zooplankton, or by the biologically-enhanced physical aggregation of smaller particles. By the latter pathway, microaggregates, phytoplankton, fecal pellets, organic debris and clay-mineral particles collide by differential settlement or physical shear and adhere by the action of various, biologically-generated, organic compounds. Diatom flocculation is a poorly understood source of marine snow of potential global significance. Rates of snow production and breakdown are not known but are critical to predicting flux and to understanding biological community structure and transformations of matter and energy in the water column. The greatest challenge to the study of marine snow at present is the development of appropriate technology to measure abundances and characteristics of aggregates *in situ*.

CONTENTS

1	Introduction		43
2	Sampling problems		44
3	Abundance		46
4	Characteristics		50
	4.1	Organic content	51
	4.2	Associated organisms	52
	4.3	Photosynthesis and microbial production	58
	4.4	Successional patterns	59
	4.5	Chemical microenvironment	60
5	Origins		61
	5.1	*De novo* production	62
		5.1.1 Zooplankton	62
		5.1.2 Phytoplankton	64
	5.2	Biologically enhanced physical aggregation	65
		5.2.1 Bringing particles together	67
		5.2.2 Bonding particles together	68
		5.2.2.1 Biological glues	68
		5.2.2.2 Biologically enhanced particle size	70
6	Breakdown and Loss		71
	6.1	Consumption	71
	6.2	Decomposition	71
	6.3	Sinking	72
	6.4	Lateral advection	74
7	Conclusions		74
8	Acknowledgements		75
9	References		76

"When I think of the floor of the deep sea, the single, overwhelming fact that possesses my imagination is the accumulation of sediments. I see always the steady, unremitting, downward drift of materials from above, flake upon flake, layer upon layer - a drift that has continued for hundreds of millions of years, that will go on as long as there are seas and continents ... For the sediments are the materials of the most stupendous snowfall the earth has ever seen ..." Rachael Carson, *The Sea Around Us*.

1. INTRODUCTION

Much of the suspended matter in the ocean exists as aggregates of organic detritus, microorganisms and clay minerals. These particles range from a few microns to many centimetres in size and are abundant and ubiquitous in the pelagic zone throughout the world's oceans. Marine snow is herein defined as those aggregated particles in the ocean larger than 500 µm in length. Marine snow originates from diverse sources and is a major component of the material caught in sediment traps. The sinking of marine snow is a primary mechanism by which surface derived material reaches deep water and the ocean floor (see FOWLER and KNAUER, 1986, for extensive review). Furthermore, these macroscopic aggregates harbour rich detrital communities of bacteria, phytoplankton, flagellates, and protozoans, generally at concentrations many orders of magnitude greater than found in the surrounding seawater (SILVER, SHANKS and TRENT, 1978), suggesting that marine snow may be an important site for biological processes of production, decomposition and nutrient recycling in the water column. Aggregates provide not only persistent chemical microhabitats for microorganisms (ALLDREDGE and COHEN, 1987) but are also food sources for large particle feeders including fish and zooplankton (ALLDREDGE, 1972, 1976).

Advances in our understanding of the characteristics and abundance of marine snow have been hindered by problems associated with sampling and quantifying these fragile aggregates in nature. Historically, studies of naturally occurring aggregates in seawater developed simultaneously in two distinctive schools. One is based on a tradition of *in situ* observations of particles, exemplified by Japanese researchers who in the 1950s called attention to the large flocs readily visible from submersibles in both coastal and deep water. They named these "marine snow" (SUZUKI and KATO, 1953) after the "long snowfall" of sedimentary material described by CARSON (1951). Particles were photographed underwater (SUZUKI and KATO, 1953; NISHIZAWA, FUKUDA and INOUE, 1954), gently collected and associated organisms described (TSUJITA, 1952). Sinking rates of submersible collected flocs were measured (KAJIHARA, 1971) and their origins and importance discussed as unique microenvironments in the pelagic zone (SUZUKI and KATO, 1953; NISHIZAWA, 1966).

The second tradition, carried out primarily by North American scientists in the 1960s and 1970s, studied particles obtained from water bottles. These researchers examined cleared filter preparations and described at least three particle classes: "organic aggregates", flakes, and debris from organisms (RILEY, 1963, 1970; GORDON, 1970; WIEBE and POMEROY, 1972). The term "organic aggregate" was chosen by RILEY (1963) to describe flocculent conglomerates of smaller particles, generally in the size range of 25-50μm, but which could reach sizes up to a millimetre or more. These stained primarily with carbohydrate stains and were more abundant near the surface than at depth. "Flakes" tended to be transparent, small (rarely >50μm), thin and scale-like, and stained mostly with protein stains. Their abundances changed little with depth.

In the late 1970s and 1980s the two traditions of studying oceanic particles were combined in a series of investigations on the large flocs known to divers and submersible users. These workers determined abundances of marine snow in shallow water with *in situ* observations and hand-collected fragile particles, allowing the first quantitative measurements of aggregate contents (e.g. TRENT, SHANKS and SILVER, 1978; SILVER, SHANKS and TRENT, 1978). These original investigations were soon augmented by a variety of studies, discussed below, and some of these carried the basic methodology to mesopelagic and even bathypelagic depths, using manned submersibles.

In this paper we summarise our present knowledge of the characteristics, distribution, abundance, sources and significance of marine snow in the sea. Two excellent reviews on detrital fluxes in the sea also discuss some aspects of marine snow and should be consulted (ANGEL, 1984; FOWLER and KNAUER, 1986).

2. SAMPLING PROBLEMS

Difficulties in studying large aggregates were acknowledged even in the earliest work and by researchers using both *in situ* observations and water bottle sampling. The existence of marine snow passed largely unnoticed until the advent of direct undersea observation because marine snow is fragile and is commonly broken up by routine methods of collection and subsequent handling (NISHIZAWA, FUKUDA and INOUE, 1954; RILEY, 1963). A variety of steps in routine handling of particles have been identified which cause aggregate disruption or loss. If samples are obtained using water bottles, large particles may be missed because they tend to settle in the quiet water inside the water bottle and sink below the spigot (CALVERT and McCARTNEY, 1979). Particles that are still suspended may break apart when they pass through the spigot of the water sampling bottle (GIBBS and KONWAR, 1983). Alternatively, particles obtained by pumps are often fragmented in passage through the hoses and pump (GIBBS, 1981). Transport and storage of water samples containing the particles also result in either disaggregation or clumping of aggregates (ALLDREDGE and SILVER, personal observation).

Processing of water samples for counting can cause particle breakage. If particles are to be collected on filters, some aggregates break apart while being pipetted onto or drawn

through the sampling orifice of the counter (GIBBS, 1982a; GIBBS, 1982b). Much of our modern understanding of the size spectrum of particles in the sea is based on these latter, disruptive methods of automated counting (SIMPSON, 1982).

Lastly, should aggregates survive these various assaults during collection and handling, they are unlikely to be found in most samples because of the comparatively small water volumes usually examined. In surface waters, where typically snow particles may number a few per litre (see 3, below), only a few tens or hundreds of mililitres are generally processed for microscopic or particle analysis. The problem is more severe in deep water, where snow abundances are often reduced to a few tens per cubic metre or less. Such volume-related problems of assaying the abundance of the millimetre-sized particles, have been recognised even in earlier studies (SHELDON, PRAKASH and SUTCLIFFE, 1972).

The combined effect of these sampling problems is to underestimate the abundance of marine snow. Very recently, two studies have made comparisons between the size spectra of particles measured *in situ* with those of the same water analysed in the laboratory (EISMA, 1987; BALE and MORRIS, 1987). Both studies showed that the number of large particles observed in laboratory samples were lower than in the *in situ* measurements and there was a corresponding increase in the abundance of the small size classes in the laboratory samples. Consequently, the authors of both studies concluded that *in situ* methods are required to assess particle size distributions in aquatic environments.

Much of our modern understanding of marine snow has resulted from *in situ* observations and collections by divers. Aggregate abundances are determined by divers, who count the number of particles passing through a hand-held ring as they swim horizontal transects underwater (TRENT, SHANKS and SILVER, 1978). This method is limited to surface waters, and subject to some variability related to the ability of the diver to both discriminate the particles (related to ambient light, diver's visual acuity, size and colour of the aggregates, etc.) and to correctly assess particles sizes as >0.5mm.

Recently, several instruments have been developed which assess particle spectra directly in the water column. The "marine snow camera", developed by HONJO, DOHERTY, AGRAWAL and ASPER (1984) surveys the largest volume, about $0.7m^3$, of any system to date, and allows sizing of particles >0.2mm. The camera system of JOHNSON and WANGERSKY (1985) is a higher resolution system which sizes particles to a minimum limit of 50µm in diameter, but the concomitant restriction in its depth of field reduces the volume of water it can survey to a few tens of millimetres (see CARDER, COSTELLO and STEWARD, 1986). Both camera systems supply data records in the form of photographic images, whose interpretation can be intensive in both time and labour, so the results are available only some time after the survey has been completed rather than in "real time". BALE and MORRIS (1987) describe a submersible laser diffraction instrument for work in estuaries that interfaces with a microcomputer, to provide *in situ* monitoring of particles ranging in size from 5-500µm. Its viewing area is relatively small, and because it requires water to flow between two windows, more fragile particles are likely to be disrupted.

Ideally, a monitoring system for snow should provide not only information about the particle size spectra *in situ* but will also sample the particles. Such a system has been partially achieved by imaging devices associated with sediment traps and by large volume pumping systems. CARDER, STEWARD and BETZER (1982) describe a holographic device (HMV = "holographic microvelocimeter": COSTELLO, YOUNG, CARDER and BETZER, 1986) that records sizes, shapes, orientations and sinking rates of 15-250μm diameter particles that settle at modest rates (about 16-200m d^{-1}) into sediment traps. The particles are sensed and photographed as they enter a viscous solution that slows their descent. Such a device will be useful for recording sizes and settling rates of those marine snow particles that settle at the appropriate rates, but probably is not a device for measuring the full size spectrum of aggregates in the water column. The trap associated with the HMV collects the snow particles, but only the cumulative properties of the particles can be determined, since the individual, sticky particles partially coalesce during deployment and recovery of the trap (see 4.2 below). ASPER (1987) describes a combined camera and sediment trap system, the "marine snow flux camera", that photographs the collecting plate of a sediment trap, so that the material can be sized as it is being collected. The device was constructed primarily to assess the contribution of marine snow to the total particle flux. These collections are also mixtures which provide only information about the bulk properties of all the materials that have been collected.

Large volume *in situ* filtration systems ("LVFS" - BISHOP and EDMOND, 1976) provide an alternative collection system for marine snow, since they filter up to tens of cubic metres of water, which are the volumes needed for assaying marine snow in nature. However, much of the marine snow collected by the LVFS (e.g. BISHOP, COLLIER, KETTEN and EDMOND, 1980), is subject to some particle disruption. In the studies of BISHOP and his colleagues, the particles of concern to them were the denser, more inclusion-rich fraction of the aggregate spectrum, particles that are likely to be the critical ones for their flux predictions; thus they have not sought to assay the full array of loosely populated marine snow particles (BISHOP, STEPIEN and WIEBE, 1987).

3. ABUNDANCE

Measurements of marine snow abundance are now available from a variety of near-surface locations. Abundances of particles per litre in the upper 30m range from none to a maximum of about 500; common neritic values are 1-10 per litre (Table 1). There is considerable variability in both the numbers and sizes of aggregates over time at individual sites (eg Monterey Bay values, Table 1), including over the tidal cycle in shallow water environments (WELLS and SHANKS, 1987). Individual snow aggregates in surface waters range in volume from 10^{-3} to 6ml, with the particles occupying between 0.003 and 0.7% of the total water volume (Table 2). Even larger mucus flocs are known to occur (JOHANNES, 1967; GILMER, 1972) and can be abundant (ALLDREDGE, personal observation). Currently data on the size spectra and volumes of marine snow are available from only a few neritic sites and thus may not be representative of the full range of pelagic environments. Moreover, all near-surface data are based on

TABLE 1

Abundances of Marine Snow

Number l^{-1}	Location	Reference
Nearsurface (upper 30 m)		
1.9-2.8	Monterey Bay, Calif.	TRENT et al., 1978
0-8.0	Santa Barbara, Calif.	ALLDREDGE, 1979
0-3.7	Gulf of California	ALLDREDGE, 1979
0.7-14	Monterey Bay, Calif.	SHANKS and TRENT, 1980
1.0-7.0	N.E. Atlantic	SHANKS and TRENT, 1980
0.1-1.1	So. California	ALLDREDGE and COX, 1982
6.6-12	Monterey Bay, Calif.	KNAUER et al., 1982
35	Monterey Bay, Calif.	HEBEL, 1983
9.4-12	Pt. Sur, Calif.	HEBEL, 1983
1-79	Santa Barbara, Calif	PREZELIN and ALLDREDGE, 1983
2.8-5.6	So. Calif. Bight	BEERS et al., 1986
0.1-1.0	N.E. Atlantic	ALLDREDGE et al., 1986
1.9-4.0	So. California	ALLDREDGE et al., 1986
291-489	Cape Lookout Bight, North Carolina	WELLS and SHANKS, 1987
Deeper Waters		
.001-5.0	Sargasso Sea	HONJO and ASPER, 1982
0.2-7.5	California Current (off Monterey)	HONJO and ASPER, 1982
0.2-0.6	So. California (60 m depth)	ORZECK and NIELSEN, 1984
0.0005-.004	Subtropical NW Atlantic (130-650 m)	ALLDREDGE and YOUNGBLUTH, 1985
0.016-.038	Central Mexico Slope waters (80-900 m)	ALLDREDGE and SILVER, unpub.
0.13-.005	Central Mexico, oceanic waters 0-400 m	ALLDREDGE and SILVER, unpub.
0.014-.001	400-3000 m	ALLDREDGE and SILVER, unpub.
0.5-2.5	Panama Basin (100-3000 m)	ASPER, 1986
.0005-.01	NE Atlantic, warm core ring, 100-1000 m	BISHOP et al., 1980

direct visual counts, generally of aggregates >3mm, so that they underestimate the abundance of marine snow <3mm.

Marine snow is not only a prominent feature of near-surface waters, but has long been noted in deeper environments as well. Methods to quantify concentrations of aggregates in deep water include observation from submersibles (SILVER and ALLDREDGE, 1981; YOUNGBLUTH, 1984), deep saturation divers in the lower euphotic and upper mesopelagic zone (TRENT and ORZECK, 1984), *in situ* large-volume pumps (BISHOP, EDMOND, KETTEN, BACON and SILKER, 1977), and remote cameras (HONJO, DOHERTY, AGRAWAL and ASPER, 1984; JOHNSON and WANGERSKY, 1985). In general, marine snow abundances in the deep sea are considerably lower than in the surface waters (Table 1).

In the most extensive deep-water study to date, ASPER (1986) presented vertical oceanographic sections of particles >1mm in the Panama Basin and the North Atlantic, using the HONJO, DOHERTY, AGRAWAL and ASPER (1984) camera system. These data, presented as total aggregate

TABLE 2

VOLUME OF MARINE SNOW FROM SURFACE WATERS

Month	Location	Aggregate Volume (ml)	% of water column	Reference
June	Point Sur	0.025-0.08	<0.1	HEBEL, 1983
June	Monterey Bay	0.15	<0.1	HEBEL, 1983
July-Sept	Monterey Bay	0.003-2.24	0.01-0.67	TRENT et al., 1978
March-April	So. Calif. Bight	0.1-1.0	0.01-0.15	ALLDREDGE and COX, 1982
April	Santa Barbara	0.034-1.0	0.1-0.27	PREZELIN and ALLDREDGE, 1983
June-Aug	Monterey Bay	0.01-0.29	0.006-0.33	SILVER et al., 1978
Feb	So. Calif. Bight	0.08-0.2	0.02-0.04	BEERS et al., 1986
March	So. Calif. Bight	0.01-0.05	0.002-0.009	BEERS et al., 1986
Aug	So. Calif. Bight	0.002-0.2	0.001-0.1	BEERS et al., 1986
Apr-June	Monterey Bay	0.0012-0.015	—*	DAVOLL and SILVER, 1986
—	Cape Lookout Bight	0.0001-0.0002	0.02-0.003	WELLS and SHANKS, 1987
March-July	So. Calif. Bight	0.0001-6.0	—	ALLDREDGE and GOTSCHALK, in press

* - no data

volumes (sum of particle volumes for all size classes - in mm^3), show midwater maxima, which probably resulted from resuspension on the shelf in the Atlantic (Fig.1a) and from resuspension from the sides and bottom in the Panama Basin (Fig.1b). Repeated sampling at the same sites showed horizontal patchiness of aggregates on scales of 10^2m; otherwise, profiles of abundance were relatively stable over the time scales of sampling.

Available information on the abundance of macroscopic aggregates is largely biased toward larger particles and coastal environments. Considerably more information on the size spectra of aggregates measured *in situ* is required before the distribution, particle dynamics, and full significance of marine snow in the world's oceans can be appreciated.

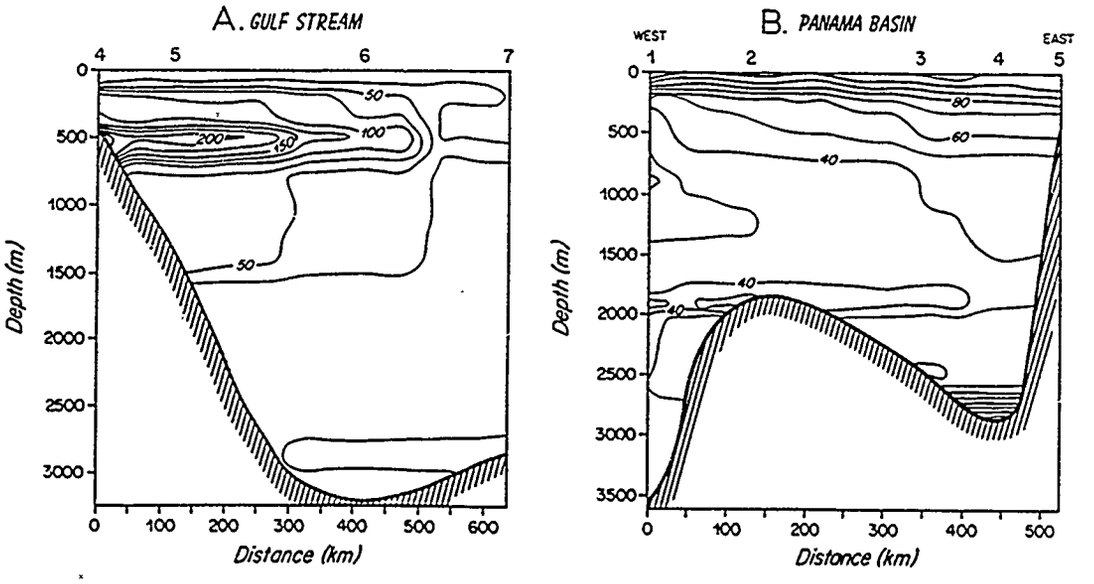


FIG.1 Vertical cross sections of the water column showing abundance of marine snow as aggregate volume ($mm^3 l^{-1}$) for (A) the Gulf Stream and (B) the Panama Basin. (A) shows a midwater plume of snow, likely resuspended by the Gulf Stream as it meanders over the shelf and slope. (B) shows resuspension from the basin sides and floor (from ASPER, 1986).

4. CHARACTERISTICS

Marine snow is a generic category which encompassed aggregates of highly diverse origins, morphologies and characteristics. The structure of aggregates, therefore, varies along a continuum from fragile, porous, loose associations of smaller particles and organisms (Fig.2a) to highly cohesive, robust, gelatinous structures produced by zooplankton (Fig.2b). Many contain obvious mucus matrices in which are embedded detritus and fecal pellets (Fig.2c,d). Shapes range from compact spheres (Fig.2b) to comets (Fig.2c), strands and plates. Because of its diverse origins, the characteristics of marine snow are highly variable.

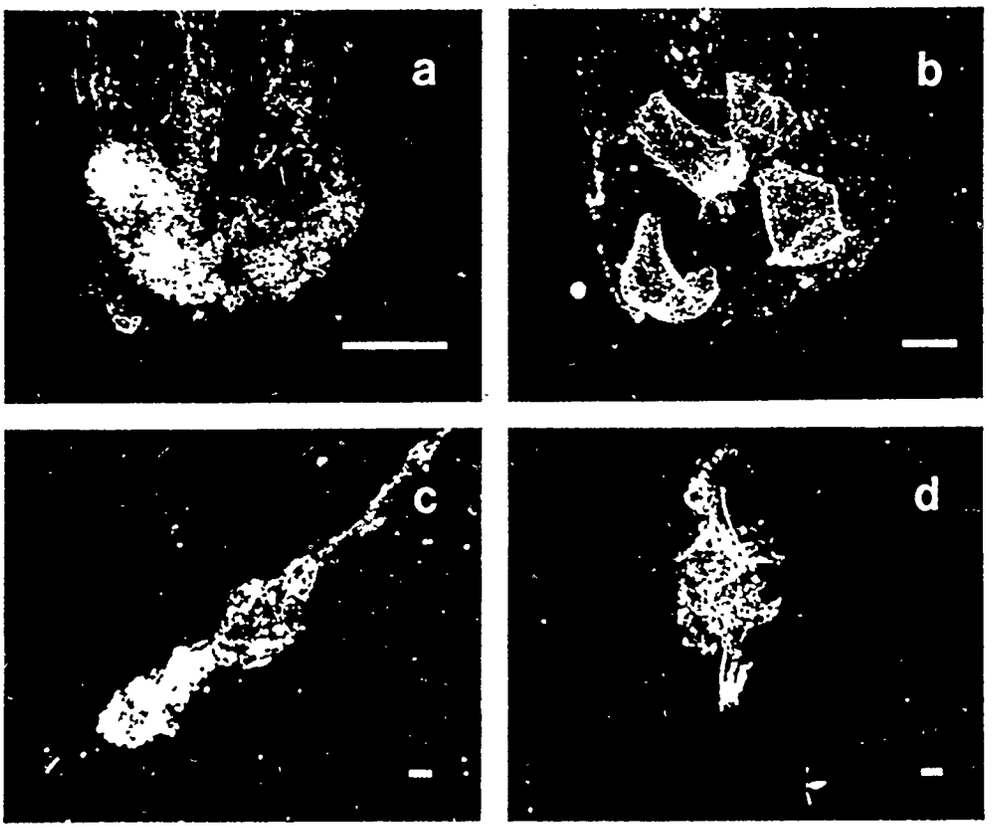


FIG.2 Examples of marine snow. (a) loosely associated aggregate formed by the flocculation of living, chain-forming diatoms. Scale = 1cm; (b) abandoned filter net or "house" of an appendicularian identifiable by the presence of 2 incurrent filters and a large, U-shaped internal filter surrounded by an envelope of particle-studded mucus; (c) typical comet-shaped aggregate; (d) irregularly-shaped aggregate of unknown origin containing numerous macrocrustacean fecal pellets. Scale of b-d = 1mm.

4.1 *Organic content*

Various investigators have measured the organic contribution of diver-collected aggregates to the total suspended pool of particulate matter in surface waters (Table 3). These collections indicate that marine snow can compose up to 63% of the total particulate organic carbon in neritic waters. As expected for detrital material, the carbon:nitrogen ratios of snow aggregates are high, usually ranging from 7:1 to 10:1 (Table 3). Observed organic carbon and nitrogen contents respectively range from 0.1 to 7µg C and from 0.03 to 1.1µg N per aggregate (Table 4), but these ranges probably do not reflect the full variability in nature. ALLDREDGE and GOTSCHALK (in press) found that the dry weight of marine snow is directly proportional to both particle length and volume, ranging from 1 to 2800µg per aggregate for aggregates with maximum lengths of 2.4 to 75mm. Although they did not measure carbon content, marine snow particles are about 20% carbon (ALLDREDGE, 1979) suggesting that maximum values of 500 to 600µg carbon per aggregate probably occur in nature. Discarded appendicularian houses, one type of macroscopic aggregate, contain up to 36µg carbon per aggregate (ALLDREDGE, 1976).

TABLE 3

CARBON:NITROGEN RATIOS OF MARINE SNOW FROM SURFACE WATERS

Month	Location	% of total POC on snow	C:N	Reference
July-Aug	Gulf of California	0.2-5.1	9.4:1	ALLDREDGE, 1976
July-Aug	Gulf of California	0-20	11.3:1	ALLDREDGE, 1979
Oct-March	Santa Barbara Channel	0-63	9.4:1	ALLDREDGE, 1979
June-July	Monterey Bay	—*	7.5:1	SHANKS and TRENT, 1980
June	Pt. Sur	5	7.1:1	HEBEL, 1983
June	Monterey Bay	9	6.2:1	HEBEL, 1983
April	Santa Barbara Channel	0.7	2.8:1	PREZELIN and ALLDREDGE 1983
Various	No. Atlantic	—	8.9:1	CARON et al., 1986

* - no data

TABLE 4
PARTICULATE ORGANIC CARBON (POC) AND NITROGEN (PON) CONTENT OF MARINE SNOW FROM SURFACE WATERS

Month	Location	Mean POC $\mu g\ C\ agg^{-1}$	Mean PON $\mu g\ N\ agg^{-1}$	References
July-Aug	Gulf of California	6.9	1.1	ALLDREDGE, 1976
July-Aug	Gulf of California	3.37	0.29	ALLDREDGE, 1979
Oct-March	Santa Barbara Channel	4.32	0.46	ALLDREDGE, 1979
June-July	Monterey Bay	1.36	0.33	SHANKS and TRENT, 1980
June	Pt. Sur	3.21	0.48	HEBEL, 1983
June	Monterey Bay	1.23	0.24	HEBEL, 1983
April	Santa Barbara Channel	0.1	0.03	PREZELIN and ALLDREDGE, 1983
July	N.E. Atlantic	0.71	0.10	PREZELIN and ALLDREDGE, 1983

4.2 *Associated Organisms*

From their studies in the Peru Current, POMEROY and JOHANNES (1968) suggested that "organic aggregates appear to be the locus of much of the metabolic activity in the ocean". Work over the last several decades has provided many more examples of aggregate enrichment but has also demonstrated a wide range in variability in the colonization of marine snow. This range can be most easily explained as resulting from the differing origins and ages of the particles. For example, snow particles that originated as feeding structures, such as the webs of pteropods or houses of larvaceans, are "precharged" with microorganisms as a result of the food collecting activity of the zooplankton that produced them. On the other hand, snow particles that form from the disintegration of fecal pellets have been seeded with enteric bacteria and various digestion resistant algae and bacteria (POMEROY and DEIBEL 1980; SILVER and BRULAND, 1981; GOWING and SILVER, 1983). The numbers and types of microorganisms populating marine snow change with the age of the particle, undergoing succession as occurs within any detrital community. Furthermore, the sticky snow scavenges particles, including organisms, during its residence in the water column (McCAVE, 1984). Many organisms that colonize marine snow are also likely to be actively attracted to particles: recently evidence has been presented that microflagellates can use ammonia gradients, which would be present in most snow particles (see 4.5 below), to locate feeding sites (SIBBALD, ALBRIGHT and SIBBALD 1987).

Organisms found on marine snow include bacteria, algae, protozoans, and even metazoans (Figs 3 and 4), but some of these organisms differ in their growth habits when they occur on aggregates. For example, bacteria can attach to the aggregate substrate by means of stalks, fibrils or other capsular materials (e.g. SIEBURTH, 1979; BIDDANDA, 1985). Bacteria associated with particles can also be considerably larger than those freely suspended in the surrounding water (eg ALLDREDGE and YOUNGBLUTH, 1985). Some types of organisms may occur preferentially on particles; for example FENCHEL (1982) suggested that attachment to a substrate may be

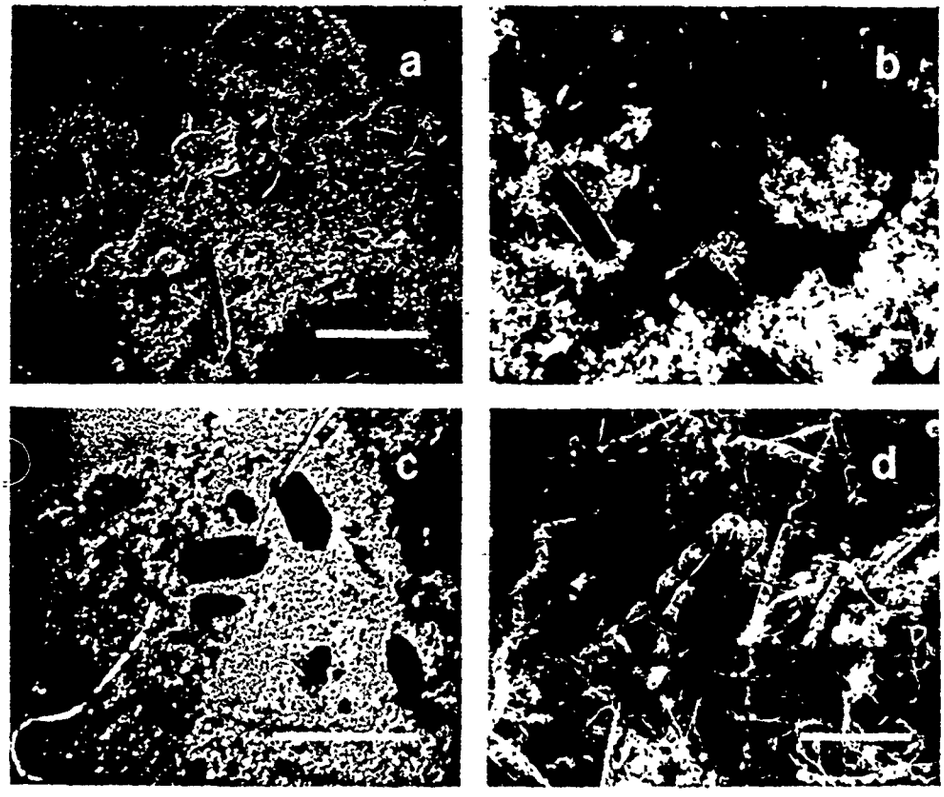


FIG.3 Micrographs of marine snow. (a) low magnification view of diver-collected marine snow from 10m in Monterey Bay, California. Particles include a nauplius and fecal pellet. (b) material from a 120m sediment trap from water off central Mexico (18°N, 108°W) containing miscellaneous marine snow, a fecal pellet of the swimming crab, *Pleuroncodes planipes*, and centric diatoms; (c) diver collected marine snow from Monterey Bay, California containing numerous fecal pellets; (d) scanning electron micrograph (SEM) of the interior of a large floc formed by the aggregation of living diatoms, dominated by various species of *Chaetoceros*. Scale: a-c=300μm; d=50μm.

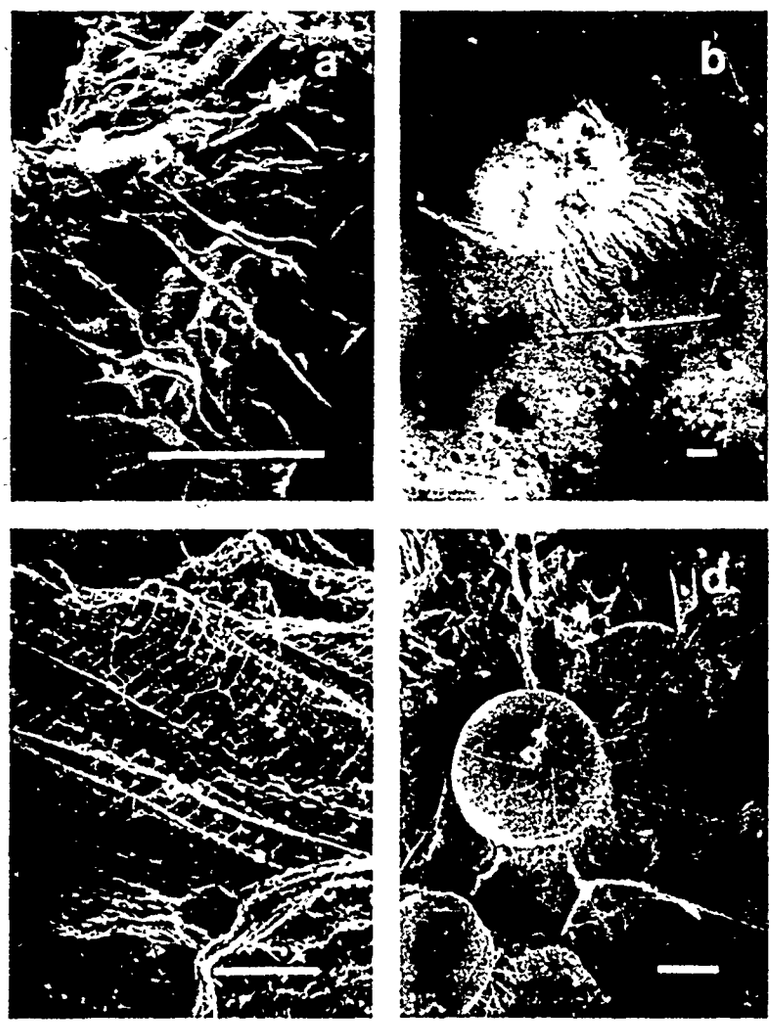


FIG.4. Micrographs of marine snow. (a) SEM of typical sheet mucus with diatom fragments found abundantly on many aggregates; (b) ciliate on marine snow collected in a sediment trap at 1400m off central Mexico (18°N, 108°W); (c) typical filter web of an appendicularian house found on a diver-collected aggregate. Mucus in marine snow often has distinct patterns that suggest zooplankton origin; (d) SEM of the centric diatom *Thalassiosira* sp. and its associated fibrils and mucus which contribute to marine snow production (sample from sediment trap at 50m off central California, 136°N, 124°W). Scale = 10 μm.

important for suspension feeding protozoans because they generate more effective water currents when anchored than when they are free swimming. Recently CARON (1987) showed that some microflagellates show strong preferences for feeding on attached cells. The dependence on particles may be so strong, that the pelagic existence of particular groups of microflagellates may depend on bacteria colonizing particles (CARON, DAVIS, MADIN and SIEBURTH, 1986). Larger animals, including crustaceans that feed by scraping, may also be dependent on surfaces that snow and other particles provide in the pelagic zone (ALLDREDGE, 1972; HAMNER, MADIN, ALLDREDGE, GILMER and HAMNER, 1975).

The types of microorganisms associated with diver or submersible-collected aggregates from various sites and depths are shown in Table 5. Microorganisms commonly occur at concentrations from 1 to 3 orders of magnitude higher on marine snow than in equal volumes of surrounding seawater. These observations indicate that marine snow acts as a centre of microbial activity in the water column and concentrates some classes of microorganisms more than others.

Collections of marine snow have also been made in deep water using sediment traps. Sediment trap samples contain mixtures of marine snow-like aggregates, fecal pellets, and a wide range of biogenic and lithogenic debris (Fig.3a-c). Since sediment trap collections are deployed for periods of days to weeks, particles arriving later during the deployment settle on top of those which had arrived previously, and will tend to coalesce. Aggregates will further fragment or coalesce as the traps are recovered. Thus the precise size and content of individual particles that arrive in traps are nearly impossible to reconstruct from trap collections.

Contents of sediment traps, however, can provide quantitative and qualitative information on the composition of sinking marine snow, because snow often appears to be the dominant material entering traps (FOWLER and KNAUER, 1986). ASPER (1987) photographed particles entering sediment traps in the Panama Basin and concluded that essentially all the material entering the traps arrived in association with marine snow. The only other method that allows quantification of the contributions made by individual particles to particulate flux are large volume, *in situ* filtration systems. Data collected by these systems indicate that "fecal aggregates", a broad size range of concentrated, marine snow-like particles, are usually the dominant contributors to mass flux in the sea (eg BISHOP, EDMOND, KETTEN, BACON and SILKER 1977; BISHOP, KETTEN and EDMOND, 1978; BISHOP, STEPIEN and WIEBE, 1987).

The particles collected by sediment traps are also greatly enriched in microorganisms. The metabolic rates of microbial populations inhabiting detritus collected by traps are considerably higher than those of the free-living communities through which the particles settle (FELLOWS, KARL, and KNAUER, 1981; KARL and KNAUER, 1984). Organisms associated with decomposition, namely bacteria and protozoa, are also found to be as abundant and active on the trap collected particles as on marine snow from surface waters (eg SILVER, GOWING, BROWNLEE and CORLISS, 1984; DUCKLOW, HILL and GARDNER, 1985; TAYLOR, KARL and PACE, 1986). Furthermore, some of the trap evidence suggests that these sinking detrital particles form local "hotspots"

TABLE 5

Marine Snow Content – Intact Cells

Organism	Locality	Cells per aggregate	% of total suspended population	Enrichment over surrounding water	Reference
I. Algae (photoautotrophs)					
Near Surface (0-35 m)					
phytoplankton >2 µm	So. Calif.	1.0×10^4	–*	3.2×10^2	TRENT, 1985
phytoplankton >2 µm	So. Calif. Bight	$6\text{-}1.3 \times 10^3$	0.2-2.5	$6.7 \times 10^2\text{-}3.0 \times 10^5$	BEERS et al., 1986
phytoplankton <5 µm	Monterey Bay, CA	$8.0 \times 10^2\text{-}2.2 \times 10^4$	–	$1.0 \times 10^2\text{-}1.8 \times 10^2$	DAVOLL and SILVER, 1986
phytoplankton >5 µm	Monterey Bay, CA	$6.3 \times 10^1\text{-}4.1 \times 10^3$	–	$7.5 \times 10^1\text{-}1.1 \times 10^3$	DAVOLL and SILVER, 1986
phytoplankton <2 µm	NW Atl-shelf and slope	–	–	$1.9 \times 10^1\text{-}4.3 \times 10^1$	CARON et al., 1986
	NW Atl warm core ring	–	–	1.9×10^1	CARON et al., 1986
	Gulf Stream	–	–	4.2×10^1	CARON et al., 1986
	Sargasso Sea	–	–	4.2×10^1	CARON et al., 1986
phytoplankton 2-20 µm	NW Atl-shelf and slope	–	–	$7\text{-}2.3 \times 10^1$	CARON et al., 1986
	NW Atl-warm core ring	–	–	2.4×10^1	CARON et al., 1986
	Gulf Stream	–	–	6.7×10^1	CARON et al., 1986
	Sargasso Sea	–	–	5.8×10^1	CARON et al., 1986
phytoplankton >20 µm	NW Atl-shelf and slope	–	–	$2.4 \times 10^2\text{-}2.7 \times 10^2$	CARON et al., 1986
	NW Atl-warm core ring	–	–	2.0×10^1	CARON et al., 1986
	Gulf Stream	–	–	1.3×10^3	CARON et al., 1986
	Sargasso Sea	–	–	7.0×10^2	CARON et al., 1986
monads and flagellates	So. Calif.	5.0×10^3	–	–	TRENT, 1985
	So Calif Bight	$5.5 \times 10^2\text{-}4.7 \times 10^3$	–	$5.5 \times 10^2\text{-}4.7 \times 10^3$	BEERS et al., 1986
diatoms	Monterey Bay, CA	$0\text{-}5.2 \times 1^3$	0-16	$0\text{-}2.7 \times 10^1$	SILVER et al., 1978
	So. Calif.	$2.4 \times 10^3\text{-}3.1 \times 10^4$	11-14	$5.9 \times 10^1\text{-}1.1 \times 10^2$	PREZELIN and ALLDREDGE, 1983
diatoms-pennate	So. Calif.	2.4×10^3	–	–	TRENT, 1985
diatoms-centric	So. Calif.	2.3×10^3	–	–	TRENT, 1985
diatoms-pennate	So. Calif.	$2.7 \times 10^1\text{-}4.1 \times 10^3$	–	$2.8 \times 10^1\text{-}6.0 \times 10^3$	BEERS et al., 1986
diatoms-centric	So. Calif.	$1.4 \times 10^1\text{-}7.9 \times 10^2$	–	$3.9 \times 10^1\text{-}4.2 \times 10^3$	BEERS et al., 1986
dinoflagellates	Monterey Bay, CA	$0\text{-}1.2 \times 10^3$	0-100	$0 \text{ to } >2.1 \times 10^3$	SILVER et al., 1978
	So. Calif.	1.3×10^2	25	1.2×10^3	PREZELIN and ALLDREDGE, 1983
dinoflagellates-thecate	So. Calif.	3.7×10^1	–	–	TRENT, 1985
dinoflagellates-athecate	So. Calif.	2.6×10^2	–	–	TRENT, 1985
dinoflagellates-thecate	So. Calif.	$4\text{-}1.2 \times 10^2$	–	$4.5\text{-}8.0 \times 10^2$	BEERS et al., 1986
dinoflagellates-athecate	So. Calif.	$1.8 \times 10^1\text{-}2.0 \times 10^2$	–	$3.6\text{-}1.4 \times 10^2$	BEERS et al., 1986
coccolithophores	So. Calif.	9.8×10^1	–	–	TRENT, 1985
	So. Calif.	$1.8 \times 10^1\text{-}8.7 \times 10^2$	–	$9.1\text{-}1 \times 10^3$	BEERS et al., 1986

TABLE 5 (cont.)

		Marine Snow Content – Intact Cells			
Deep Water					
cyanobacteria	So. Calif. (1000-1650 m)	1.8×10^4-3.0×10^4	–	1.9×10^3-2.7×10^3	SILVER and ALLDREDGE, 1981
algae 1-2 μm	(1000-1650 m)	2.3×10^3-3.8×10^5	–	–	SILVER and ALLDREDGE, 1981
diatoms	(1000-1650 m)	2×10^3-1×10^5	–	3.3×10^2-7.2×10^3	SILVER and ALLDREDGE, 1981
flagellates and monads	So. Calif. (75-260 m)	1.2×10^3-4.0×10^4	–	–	TRENT, 1985
diatoms-pennate	(75-260 m)	$7\text{-}9.3 \times 10^2$	–	–	TRENT, 1985
diatoms-centric	(75-260 m)	1.6×10^2-4.6×10^3	–	–	TRENT, 1985
dinoflagellates thecate	(75-260 m)	4.7×10^1-2.8×10^2	–	–	TRENT, 1985
dinoflagellates-athecate	(75-260 m)	2.5×10^2-6.8×10^2	–	–	TRENT, 1985
coccolithophores	(75-260 m)	1.1×10^2-3.4×10^3	–	–	TRENT, 1985
cyanobacteria	Bermuda 640 m	–	–	$>2.5 \times 10^2$	SILVER et al., 1986
<5 μm eukaryotes	Bermuda	–	–	$>1.7 \times 10^2$	SILVER et al., 1986
II. Bacteria					
Near Surface (0-25 m)					
	Sargasso Sea	6.6×10^5-3.3×10^2	–	$2\text{-}1 \times 10^2$ (or more)	CARON et al., 1982
	So. Calif.	1.2×10^7-2.5×10^7	7-78	6.7×10^1-1.2×10^3	PRETZELIN and ALLDREDGE, 1983
	So. Calif.	1.3×10^6-1.7×10^6	0.9-3.0	3.0×10^1-3.7×10^1	ALLDREDGE et al., 1986
	NW Atl (oceanic)	1.8×10^6-2.8×10^6	0.2-4.4	$2\text{-}5.5 \times 10^1$	ALLDREDGE et al., 1986
	Monterey Bay, CA	4.2×10^5-6.7×10^6	–	8.3×10^1-3.0×10^2	DAVOLL and SILVER, 1986
Deep Water					
	So. Calif. (1000-1650 m)	1.0×10^5-1.7×10^5	–	—	SILVER and ALLDREDGE, 1981
	NW Atlantic (oceanic) (30-650 m)	3×10^6-3×10^7	<.05	up to 10^2	ALLDREDGE and YOUNGBLUTH, 1985
III. Protozoa					
Near Surface (0-35 m)					
ciliates	Monterey Bay, CA	$0\text{-}1.3 \times 10^2$	0-100	$5\text{-}8.6 \times 10^3$ or more	SILVER et al., 1978
2-20 μm cells mostly flagellate	NW Atl-shelf and slope	–	–	1.7×10^1-2.7×10^1	CARON et al., 1986
	NW Atl-warm core ring	–	–	3.1×10^1	CARON et al., 1986
	Gulf Stream	–	–	1.1×10^2	CARON et al., 1986
	Sargasso Sea	–	–	5.2×10^2	CARON et al., 1986
bactivorus flagellates	NW Atl-shelf and slope	–	–	4.8×10^2-5.1×10^2	CARON et al., 1986
	NW Atl-warm core ring	–	–	2.7×10^2	CARON et al., 1986
	Gulf Stream	–	–	7.6×10^4	CARON et al., 1986
bactivorous amoeba	No. Atlantic	–	–	4.1×10^2-6.2×10^3	CARON et al., 1986
ciliates	Monterey Bay, Ca	$6\text{-}7.4 \times 10^1$ d	–	1.1×10^2-2.1×10^3	DAVOLL and SILVER, 1986
microflagellates	Monterey Bay, Ca	1.8×10^2-5.5×10^3	–	1.1×10^2-9.9×10^2	DAVOLL and SILVER, 1986

• - no data

of metabolic activity, and are islands of chemosynthetic productivity at certain depths in the aphotic water column (KARL and KNAUER, 1984; KARL, KNAUER, MARTIN and WARD, 1984).

4.3 *Photosynthesis and microbial production*

One of the most conspicuous features of near surface particles noted by early observers (TSUJITA, 1952; RILEY, 1963) is their accompanying algal cells. Chlorophyll contents of photoautotrophs inhabiting marine snow range from 0.002 to 3μg Chl a per aggregate in neritic waters (Table 6). Individual particles show 3-750 fold enrichments of chlorophyll pigment relative to equal volumes of surrounding seawater and the chlorophyll on snow particles amounts to from 0.1 to 34% of the total chlorophyll content of the bulk seawater (Table 6).

TABLE 6

CHLOROPHYLL *A* CONTENT OF MARINE SNOW

Month	Location	ng Chl. *a* agg.$^{-1}$	% of total on snow	Enrichment factor	Reference
July.-Aug.	Monterey Bay	2.3-590	0.1-7.2	4-750	TRENT et al., 1978
March-April	Southern California Bight	40-3410	0.6-34	67-442	ALLDREDGE and COX, 1982
April	Santa Barbara Channel	20-200	0.3-20	3-74	PREZELIN and ALLDREDGE, 1983
March	Southern California Bight	0.2-9	0.1-1.0	27-540	BEERS et al., 1986
August	Southern California Bight	0.4-3	1.3-1.6	15-72	BEERS et al., 1986
April	Southern California Bight	9-321	73	—*	ALLDREDGE and GOTSCHALK, unpublished

* - no data

Carbon-14 incubations (ALLDREDGE and COX, 1982; KNAUER, HEBEL and CIPRIANO, 1982; PREZELIN and ALLDREDGE, 1983) and oxygen electrode data (ALLDREDGE and COHEN, 1987) indicate that algal populations concentrated on marine snow actively fix carbon. Autotrophic populations on marine snow contribute up to 58% of the total primary production in the water (KNAUER, HEBEL and CIPRIANO, 1982) depending on the numbers and sizes of the snow particles, and the physiological conditions of the associated algal populations (see discussion in PREZELIN and ALLDREDGE, 1983). Photosynthesis appears to occur primarily on the surface of the particle (ALLDREDGE and COHEN, 1987). Internal chemical conditions and shading may reduce photosynthesis in the particle centres and relative production rates (i.e. production per unit

chlorophyll a) occasionally can be lower on snow than in the surrounding water (ALLDREDGE and COX, 1982; PREZELIN and ALLDREDGE, 1983).

The abundance of bacteria on marine snow, generally 2 to 5 orders of magnitude higher than in the surrounding seawater (Table 5), and high levels of hydrolytic enzymes within marine snow (AMY, CALDWELL, SOELDNER, MORITA and ALBRIGHT, 1987) indicate that aggregates may be sites of intense heterotrophic activity. Recent studies of both surface (ALLDREDGE, COLE and CARON, 1986) and mesopelagic aggregates (ALLDREDGE and YOUNGBLUTH, 1985) demonstrate that bacteria on marine snow are more abundant, significantly larger, and metabolically active. However, growth rates based on incorporation of ^{3}H-Thymidine per bacterium are only occasionally higher, and often lower than those of bacteria free-living in the surrounding seawater, indicating that attached bacteria are not consistently growing more rapidly than free-living forms. The contribution of bacteria inhabiting the aggregates to total bacterial production in the mesopelagic zone appears to be insignificant, i.e. < 1% (ALLDREDGE and YOUNGBLUTH, 1985), because large aggregates are rare. In surface waters, contributions by marine snow of up to 26% of total bacterial production have been observed, although the contribution is generally less than 10% (ALLDREDGE, COLE and CARON, 1986).

The microbial activity on marine snow is highly variable and probably dependent upon aggregate age. Rapid successional changes in microbial populations suggest that any labile matter available in newly formed aggregates is quickly utilized by bacteria. So while most particles are considerably more active biologically on a per volume basis than the surrounding seawater, they may still be relatively inactive during most of their existence in comparison with their maximum potential rates.

4.4 *Successional Patterns*

Marine snow communities undergo predictable successional changes in their species composition and physical/chemical microenvironment from their time of formation to their final disruption or destruction. Similar changes occur in a variety of detrital communities (see summary by NEWELL, 1984). For example, POMEROY and DEIBEL (1980) and POMEROY, HANSON, McGILLIVARY, SHERR, KIRCHMAN and DEIBEL (1984) described microbial succession on marine snow of fecal origin. A rapid burst of bacterial growth upon extrusion of the fecal aggregates is followed by increases in populations of microflagellates and ciliates. These organisms graze the growing bacteria resulting in decline of the bacterial populations after a few days. Finally the fragmenting remnants of the fecal material are inhabited by sparse communities of microorganisms. Likewise, rates of metabolic activity and biomass are highest when pellets are fresh and decline with time (ANDREWS, KARL, SMALL and FOWLER, 1984). Similar sequences have been described for communities that develop on mucus derived from zooplankton in oceanic waters (CARON, DAVIS, MADIN and SIEBURTH, 1986).

The sequence of colonization on larvacean houses has also been described (DAVOLL and SILVER, 1986). Three phases were evident. An inoculation phase occurs as the larvacean pumps water and microorganisms through the house filter system. A second stage occurs after house

abandonment, when resident microbial populations multiply and mobile immigrants enter and change the relative abundances of different trophic groups. The third and final phase takes place as the house matrix is exhausted and the house fragments.

Successional changes in populations on marine snow and consequent alterations in the chemistry of the colonized aggregates can be expected both in particles that remain suspended in the mixed layer and in those that sink into deep water. Changes in the chemistry of settling materials are also being studied using sediment traps (FOWLER and KNAUER, 1986). Unfortunately the organisms and the biological processes causing many of the changes are still poorly known. However, evidence indicates that microbial utilization and substrate decomposition occurs as detritus settles through the water (ITURRIAGA, 1979; GARDNER, HINGA and MARRA, 1983; LORENZEN, WELSCHMEYER and COPPING, 1983; DUCKLOW, HILL and GARDNER, 1985; see also 6.2, below).

4.5 *Chemical Microenvironment*

The abundance of microorganisms on marine snow would suggest that concentrations of metabolically active substances, both those produced and those consumed, would be different in aggregates than in the surrounding seawater. It is difficult to measure these concentrations, however, because, inevitably, aggregate collections include contamination with surrounding water. Seawater background values can be subtracted out of aggregate samples yielding reasonable measures for substances occurring at elevated concentrations within marine snow. However, estimates of concentration factors in the soluble phase inside marine snow are subject to error because the true volume of water associated with the individually variable aggregates usually is only known approximately and sorption onto the matrix is not yet considered.

Trace metals, including Al, Fe, Mn, Ni, Zn, Cd, and Pb can show disproportionately high concentrations in marine snow relative to other particles in the surrounding seawater (HEBEL, KNAUER and MARTIN, 1986). The impact of this trace metal enrichment on the communities living within marine snow is not known, but sinking marine snow may be a major transporter of trace metals out of the euphotic zone (HEBEL, KNAUER and MARTIN, 1986).

Ammonia is the most consistently concentrated of the dissolved nutrients measured within marine snow (SHANKS and TRENT, 1979). Ammonium concentrations as high as 0.5mM were observed (SHANKS and TRENT, 1979), and even these may be underestimates because of dilution. Such high values begin to approach the concentrations at which some phytoplankton are inhibited (about 1mM (SYRETT, 1962)). PREZELIN and ALLDREDGE (1983), found that snow particles contained all the measurable ammonia in seawater at one of their study sites. They suggest that chemoautotrophs, possibly nitrifiers, utilize these nutrients in the microenvironment of the aggregate. They provide evidence for substantive dark fixation of carbon that would be expected of nitrification in the ammonia-enriched aggregates. Chemoautotrophy also may occur as decomposing detrital aggregates settle through the water column. High concentrations of nitrifiers on sediment trap collected particles, with concomitant depth changes in microbial biomass and ammonia concentrations suggest that significant *in situ* carbon fixation occurs in the mesopelagic zone (KARL, KNAUER, MARTIN and WARD, 1984; KARL and KNAUER, 1984).

The elevated nutrient concentrations found within aggregates are a subject of considerable ecological importance. McCARTHY and GOLDMAN (1979) stressed the potential importance of nutrient-enriched microenvironments in pelagic near-surface communities where biolimiting nutrients are present in vanishingly small concentrations. Predictions of available nutrient concentrations rely on appropriate models of the diffusive regime around aggregates. JACKSON (1980) calculated that nutrient pulses introduced by single releases from zooplankters would diffuse to background levels very quickly. MITCHELL, OKUBO and FUHRMAN (1985) similarly calculated only µm sized zones of enrichment could exist around phytoplankton cells excreting dissolved materials. However, chemical gradients around and within marine snow particles, where molecular diffusion may be constrained, should be considerably different from the environment surrounding small, solid particles (GOLDMAN, 1984; PAERL, 1984).

Recently, ALLDREDGE and COHEN (1987) presented the first experimental evidence that persistent microzones could be maintained in colonized particles of marine snow and fecal pellets, even in turbulent environments. Gradients of oxygen and pH were detectable within a zone 1mm wide surrounding marine snow particles 1-4mm in diameter maintained in the laboratory, even when the aggregates were in diffusive and advective flow regimes like those in the sea. Moreover, internal oxygen concentrations within 4mm aggregates held in the dark were reduced by 48%, suggesting that marine snow may sustain microenvironments in which processes requiring low oxygen conditions, such as denitrification or nitrogen fixation, may occur.

Marine snow aggregates, as we presently understand them, are loosely organised, physically semi-enclosed structures consisting of clusters of individual particles. Such aggregates may correspond to physical structures known as fractals (see Fig.3b), exemplified by soot and snowflakes - structures that are presently of considerable interest to chemists and physicists (WITTEN and CATES, 1986). Such fractals can develop as random aggregates of individual particles or clusters of particles. They have loose and semi-open structures and are individually unpredictable in their shapes, but their average properties can be surprisingly well described. Such particles act as traps for dissolved molecules that adsorb on their surfaces. The paths of substances diffusing under Brownian motion are so long that molecules rarely escape to the outside of the lattice before contacting an internal surface (WITTEN and CATES, 1986). They will effectively trap not only substances that may bond with the many charged organic molecules present in the matrix, such as ammonium ions (see GOLDMAN's 1984 discussion) but also the dissolved gasses that may be utilised by organisms in the aggregate. The same argument may be applied to the molecules diffusing into the aggregate which are likely to be trapped well before they reach the aggregate's core. This would greatly slow diffusive processes between the inside and outside of the aggregate and intensify concentration gradients.

5. ORIGINS OF MARINE SNOW

Despite their highly variable physical characteristics, appearance, and composition marine snow originates from only two general pathways of formation: (1) Aggregates which are produced

de novo by mucus-producing marine organisms, especially by certain zooplankton and phytoplankton; (2) Aggregates which result from the biologically-enhanced physical aggregation of smaller component particles (Fig.5). At present we know little about the mechanisms by which marine snow is formed and even less about the rates of aggregate formation and what environmental factors influence those rates. Quantitative information is required on: (a) the environmental constraints of aggregate formation, (b) the rate of aggregate production under various conditions and (c) the relative significance of each source in different oceanographic regimes, before predictions can be made about the abundances and size distributions of aggregates likely to be encountered at any time or place in the ocean.

5.1 *De novo production of macroaggregates by marine organisms*

Mucus feeding structures of zooplankton and the gelatinous sheaths produced by some marine phytoplankton become aggregates of marine snow once they are abandoned or begin to decay. Some flocculent fecal pellets can also be classified as marine snow.

5.1.1 *Zooplankton and other animal sources.* Zooplankton can be the major source of marine snow at certain times and locations (PREZELIN and ALLDREDGE, 1983; CARON, DAVIS, MADIN, and SIEBURTH, 1982). Appendicularians, which are abundant in the plankton, feed by secreting a gelatinous "house" composed of mucopolysaccharides, which contains a complex array of filters and passages (Fig.2b, 4c). Phytoplankton, bacteria, fecal pellets and microaggregates are collected on the external filters and surface of the house or within the internal filter. Individual houses can vary in diameter from a few hundred microns to 30 or more cms (BARHAM, 1979), although most are about 1 to 20mm in diameter (ALLDREDGE and MADIN, 1982).

Individual appendicularians produce and discard from 4-16 houses per day (TAGUCHI, 1982; GORSKY, FISHER and FOWLER, 1984; FENAUX, 1985). These discarded houses become microaggregates which contain diverse detrital populations derived both from the growth of the microorganisms collected on the filters when the house was still occupied and by later colonization from the surrounding seawater (ALLDREDGE, 1972; DAVOLL and SILVER, 1986). The rate of house production increases linearly with increasing temperature and is higher at higher food concentrations (FENAUX, 1985).

Larvaceans are important sources of marine snow not only in the euphotic zone, where they are most abundant, but also at aphotic depths. The giant larvacean, *Bathochordaeus* produces 30-100cm houses in the lower euphotic zone and down to depths of at least 700m in the mesopelagic zone (BARHAM, 1979; YOUNGBLUTH, 1984). Observations from submersibles reveal densities of these abandoned houses up to several per cubic metre off Mexico (BARHAM, 1979). Smaller species of larvaceans also occur at depth: YOUNGBLUTH (1984) and DAVOLL (1986) noted several species numbering up to 10 m^{-3} in mesopelagic waters near Bermuda.

The high daily production rate of houses indicates that discarded appendicularians houses will be an important source of snow wherever appendicularians are abundant. Discarded houses

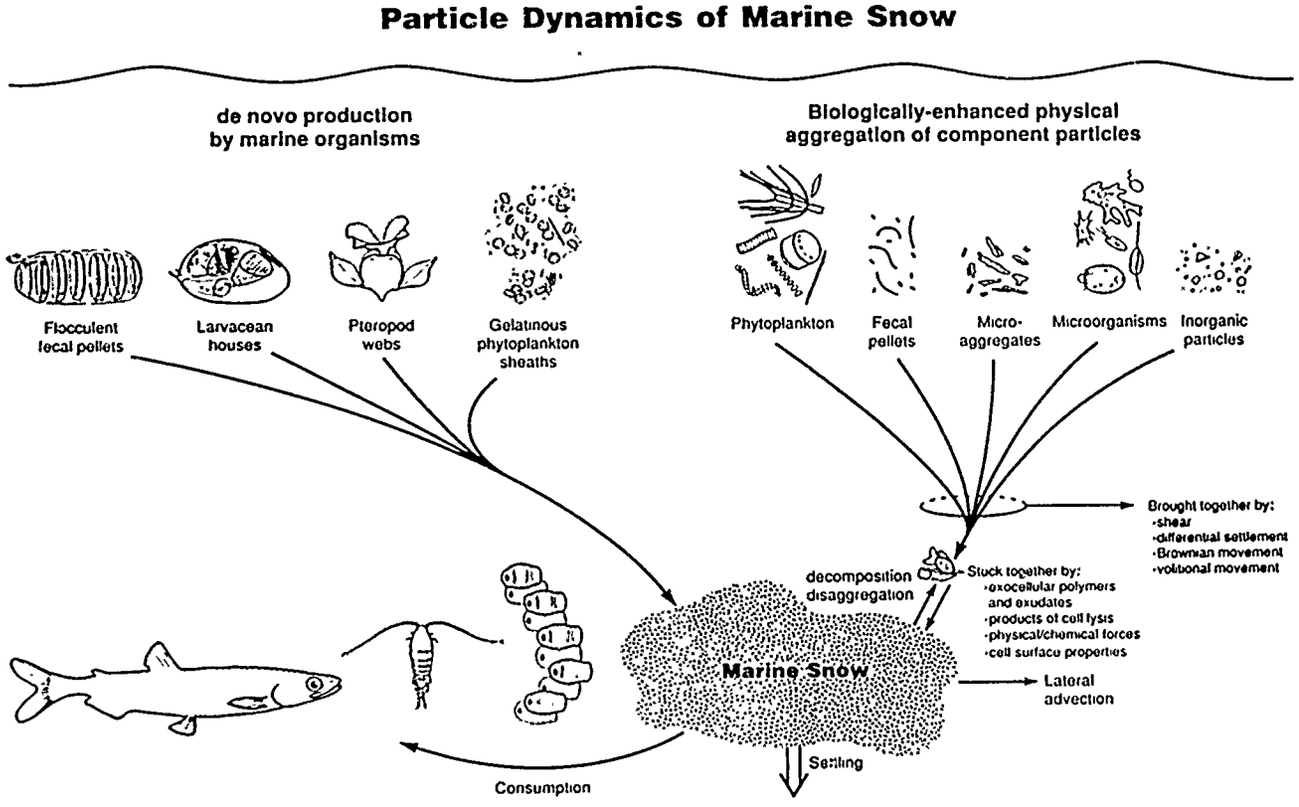


FIG.5. Major processes by which marine snow is produced, broken down and lost from the pelagic zone. Marine snow is produced by two major pathways. First, marine plankton produce marine snow aggregates *de novo* as mucus webs, houses, sheaths, and flocculent fecal pellets. Second, smaller component particles, including phytoplankton, fecal pellets, microaggregates, bacteria and inorganic particles, collide together via physical processes and become stuck together, facilitated by biological "glues". Snow is broken down or lost by processes of decomposition, disaggregation, consumption, lateral advection and settlement.

occur at densities up to 80 l^{-1} off California (PREZELIN and ALLDREDGE, 1983) and in Kaneohe Bay, Hawaii, flux rates of 8.9 x 10^4 houses m^{-2} d^{-1} have been reported (TAGUCHI, 1982). Six percent and 24% of aggregates sampled over several seasons in the Santa Barbara Channel and the Gulf of California, respectively, were identifiable appendicularian houses. Abundance ranged from 0-1 house l^{-1} at these study sites (ALLDREDGE, 1979).

The mucus feeding webs produced by some thecosomateous pteropods (GILMER, 1972) are occasionally abundant in oceanic surface waters (CARON, DAVIS, MADIN and SIEBURTH, 1982) and at mesopelagic depths (YOUNGBLUTH, 1984), although the rates of web production and their significance as a source of marine snow is not known. Foraminifera also produce mucus flocs at lower euphotic and upper mesopelagic depths (YOUNGBLUTH, 1984; ALLDREDGE and YOUNGBLUTH, 1985), and can be significant contributors to sediment trap collections at these depths (GOWING and SILVER, unpublished).

Mucus produced by a variety of other animals may also serve as the nucleus for marine snow aggregates. Sources of mucus include sloughed coral mucus exported from coral reefs (COLES and STRATHMAN, 1973), decomposing gelatinous plankton and egg masses, and mucus sloughed by coelenterates and other animals during feeding or defense. The quantitative significance of these sources of marine snow is unknown but it is likely to be small.

Fecal material produced by doliolids may be a significant source of marine snow, particularly in neritic waters where doliolids are abundant. This flocculent fecal material contains no peritrophic membrane (POMEROY and DEIBEL, 1980) and sinks about 10 times more slowly than similarly sized fecal pellets produced by other zooplankton (BRULAND and SILVER, 1981). Doliolids have been reported in swarm densities up to 1600 animals m^{-3}, at which times they remove most of the particulate matter from seawater (DEIBEL, 1985) and repackage it as marine snow. Although no data on the fecal matter production of doliolids are available, snow production must be significant during such blooms.

Other types of fecal material also form marine snow. Some midwater fish produce loose fecal material unbound by a peritrophic membrane. Although this material sinks very rapidly, its irregular structure and glutinous qualities make it difficult to identify among aggregated material of other origins within sediment traps (ROBISON and BAILEY, 1981). In addition, the larvae of the pelagic penaeid shrimp, *Solenocera atlantidis*, tows an undetached peritrophic membrane several times longer than itself which harbours a variety of microorganisms, fecal pellets and detritus on which the larvae feeds. Once detached, this fecal mass forms a large aggregate of marine snow (YOUNGBLUTH, 1982).

5.1.2 *Phytoplankton.* Many species of phytoplankton produce mucus sheaths around their colonies. While the phytoplankton are healthy, these mucus structures are technically not marine snow. However, when the colonies die, senesce, or begin to decay they contain the mucus matrix needed for aggregate formation. The gelatinous sheaths of twelve species of the diatom genus *Thalassiosira* may be sheet-like or tubular and can be up to several centimetres in length (FRYXELL, GOULD, and WATKINS, 1984). The tangled fibrils in these sheaths

(Fig.4d) were conspicuous components of the particulate flux observed in sediment traps deployed from the base of the euphotic zone to 2000m off California (SILVER, unpublished observation).

Many of the prymnesiophytes, a group of golden algae that includes the coccolithophores, produce gelatinous colonial stages which sink rapidly carrying other pelagic debris along to depth. One common world-wide contributor of phytoplankton mucus is the prymnesiophyte species, *Phaeocystis pouchetii.* The colonies of healthy, actively growing individuals are normally bacteria-free. However, as growth slows, bactericidal compounds normally secreted by the alga are reduced so that the colonies develop extensive bacterial floras, the cells begin to senesce, and the colonies decompose (BATJE and MICHAELIS, 1986; DAVIDSON and MARCHANT, 1987). These colonies were the main component of sedimenting material in the Barents Sea (WASSMANN, 1987). In the Panama Basin, HONJO (1982a) found a massive flux of a seasonal bloom of the coccolithophorid *Umbellicosphaera sibogae.* The mucus colonies sank rapidly carrying a variety of biogenic and lithogenic debris to depths of about 4000m. In the North Sea mucus aggregates of the ubiquitous *Emiliani huxleyii* dominated the particulate material settling into sediment trap collections after a brief bloom on the surface (CADEE, 1985). A large pulse of sinking material was also produced by another prymnesiophyte, the colonial organic-scaled *Corymbellus aureus,* at the end of its surface bloom in the North Sea (CADEE, 1986). Blooms of non-sheath forming diatoms are also a globally significant source of marine snow (SMETACEK, 1985), but such diatom aggregates are not formed *de nova* but rather through physical collision of cells and chains. Thus, they are discussed in the next section. In general, the quantitative significance of gelatinous phytoplankton as a source of marine snow is poorly known because episodic snow production by blooming phytoplankton is easily missed in routine sampling surveys. However, the settlement of gelatinous phytoplankton may represent a significant mechanism by which surface derived material reaches the ocean floor.

Benthic macroalgae are also likely, but probably minor, sources of marine snow. Mucus sluffed by macroalgae, particularly floating *Sargassum* sp., (ALLDREDGE, personal observation) and kelp (LINLEY, NEWELL and BOSMA, 1981) can provide the matrix for aggregate formation.

5.2 *Biologically enhanced physical aggregation*

The exact mechanisms by which marine snow is formed via aggregation of component particles in nature has not been studied extensively. However, a large body of literature on particle-particle interactions in aqueous solutions (see STUMM and MORGAN, 1981; O'MELIA, 1987), coagulation in natural waters (see LERMAN, 1979; McCAVE, 1984; SHOLKOVITZ, 1976; EISMA, 1986), and flocculation in waste water systems (PAVONI, TENNEY and ECHELBERGER, 1972; ADAMSE, DEINEMA and ZEHNDER, 1984) serves as a foundation upon which understanding and future research may be built.

Five classes of component particles aggregate to form marine snow (Fig.4). These include phytoplankton, microorganisms, fecal pellets, inorganic particles (especially clay-minerals),

and microaggregates. The factors governing the production, abundance and size distribution of each of these categories of component particles is far beyond the scope of this review. However, as we shall see, the abundance of marine snow may be highly dependent upon the availability and characteristics of these component particles.

Microaggregates, the organic aggregates of RILEY (1963), are significant building blocks in marine snow formation. They are produced by many poorly understood processes including spontaneous formation from dissolved organics in standing seawater, adsorption of dissolved organic matter onto colloidal sized particles (JOHNSON and COOKE, 1980; JENSEN and SONDERGAARD 1982), adsorption of organic matter into dissolving bubbles (BAYLOR, SUTCLIFFE and HIRSCHFELD 1982; JOHNSON, 1976; JOHNSON and COOKE, 1980); salt flocculation of humic materials when freshwater mixes with seawater (SHOLKOVITZ, 1976), and bacterial aggregation (SHELDON, EVELYN and PARSONS, 1967; LINLEY and FIELD, 1982; BIDDANDA, 1985).

Living phytoplankton, particularly diatoms, are also particularly significant component particles in the formation of marine snow via biologically enhanced physical aggregation. SMETACEK (1985) suggested that nutrient stressed diatom blooms aggregate into large flocs which settle in mass rapidly to the sea floor. He speculates that mass flocculation may transport diatom resting stages to the deep sea and to the sediments, insuring survival of the species via the maintenance of seed populations at depth.

Using SCUBA, ALLDREDGE (personal observation) has observed blooms of living, chain-forming diatoms aggregating into centimeter-sized flocs of marine snow in the Southern California Bight (Fig.2a). These flocs were composed of a rich assemblage of diatom genera, dominated by the setose genus *Chaetoceros* (Fig.3d). Nine species of *Chaetoceros,* 12 other diatom genera including *Nitzschia* and *Bacteriastrum,* fecal pellets, flagellates and protozoans also occurred within flocs. Resting spores were rarely found. Sinking velocities of diatom flocs measured directly *in situ* ranged from 50-200m d^{-1} (ALLDREDGE and GOTSCHALK, in press), 1 to 2 orders of magnitude faster than single *Chaetoceros* chains (SMAYDA and BOLEYN, 1966). Thus flocculation would promote rapid export of diatom blooms to the deep sea.

Floc formation by diatoms and some other shelled phytoplankton may help to explain a biogeographical problem known to marine micropaleontologists. Diatom shells and the skeletons of other small organisms are often distributed in deep water sediments directly below their surface populations. This is surprising given the comparatively slow individual settling rates of shells, which would result in horizontal displacements by underlying currents to sites far from their surface origins, and their chemical dissolution during the long settling interval in some cases (eg the calcareous coccoliths, HONJO, 1976). Fecal pellets, which sink relatively rapidly and protect inclusions from dissolution (SCHRADER, 1971) have been invoked as the mechanism for delivering biogenic material to depth (see ANGEL, 1984, for review).

The importance of marine snow vs fecal transport is not yet known. However, new evidence suggests that phytoplankton aggregates settle rapidly to the seafloor, in many cases, without

passing through a grazer's digestive tract (RICE, BILLETT, FRY, JOHN, LAMPITT, MANTOURA and MORRIS, 1986). The digestive versus non-digestive transport mechanism is important to resolve because gut passage breaks, erodes, or dissolves skeletal materials and alters the chemical nature of organic cellular components. The non-fecal exodus of algae from the euphotic zone appears to be pulsed or highly seasonal and may occur before zooplankton become abundant. For example, camera observations of bathyl sediments led LAMPITT (1985) and BILLETT, LAMPITT, RICE and MANTOURA (1983) argue for transport of algal flocs up to centimetres in size early in the growth season, with fecal mediated transport later in the year. Sediment trap collections similarly suggested to TAKAHASHI (1986) and GERSONDE and WEFER (1987) that marine snow must be the agent to transport some of the seasonal blooms to depth because of the integrity and condition of diatom frustules; these snow pulses could be the mass sinking of aggregating diatoms (SMETACEK, 1985).

Diatoms, microaggregates, and other types of component particles are only the building blocks for aggregate formation. Aggregation of these component particles to form marine snow is accomplished in two steps. First component particles must be brought together; second they must become stuck together. These two processes act independently of each other. Processes which bring component particles together are largely physical. Mechanisms which stick these particles together and result in aggregation are governed largely by biological and chemical properties and processes. We shall examine each of these mechanisms in turn.

5.2.1 *Bringing particles together.* McCAVE (1984) evaluated the four major mechanisms which bring particles together in the ocean; Brownian motion, fluid shear (both laminar and turbulent), differential settlement, and animal feeding. He concluded that animal feeding must be the dominant mode by which particles are aggregated into particles large enough to contribute to material flux in the sea. Of the physical mechanisms, Brownian motion dominates interactions of fine particles, and differential settlement should dominate coagulation between similarly sized particles between 1 and 100μm in surface waters (McCAVE, 1984).

McCAVE's (1984) calculations indicate that collisions of small particles with larger ones, resulting in the formation of marine snow-sized aggregates, should be controlled primarily by shear. Shear both collides similarly-sized particles and leads to scavenging of small particles by large ones more effectively than differential settling. Thus we would predict increased collision frequencies and increased rates of marine snow formation, in areas of the ocean such as the upper mixed layer, exhibiting both high shear and high concentrations of component particles. We do, in fact, find abundances of marine snow an order of magnitude higher in surface waters than in the deep sea.

Differential settlement may be as important as shear in special cases of marine snow formation such as diatom flocculation. SMETACEK (1985) proposed that nutrient-stressed diatoms within blooms experience accelerated sinking and become entangled with cells around them as they settle via their setae, fibrils, or exuded mucus. Newly formed diatom flocs nearly always have a trailing edge of vertically aligned, captured diatom chains and a comet-like shape when observed in the field (Fig.2a, ALLDREDGE, personal observation), suggesting that more

slowly sinking chains are captured as they are swept into the wake of a more rapidly sinking aggregate. EISMA (1986) suggested that flocculation in estuaries occurs predominantly under conditions of viscous flow, and that turbulence, which can break apart as well as aggregate particles, largely determines the maximum size of macroflocs. No empirical data on the relationship between shear, concentration of component particles, and the rate of marine snow formation presently exist for the ocean. McCAVE's and EISMA's conclusions represent testable hypotheses for future research.

5.2.2 *Bonding particles together.* Once brought together, particles must stick together. The physical and chemical mechanisms of colloidal particle-particle interaction are the subject of an extensive literature (see STUMM and MORGAN, 1981; O'MELIA, 1987). In seawater suspended particles contain a coating of absorbed, negatively-charged organic matter (NEIHOF and LOEB, 1972, 1974). Thus, they repel each other. These repulsive, electrostatic forces can be offset by attractive Van der Waal forces, which increase rapidly as the interparticle separation approaches zero (O'MELIA, 1987).

The attachment probability of colliding particles of natural sediment, as determined by measuring the rate of change in particle number in a suspension under agitation, is generally considerably less than 10% (ALI, O'MELIA and EDZWALD, 1984; ALI, 1985). However, particle interaction theory treats particles as discrete spheres with distinct boundaries. Natural marine aggregates are not colloidal, discretely bounded, nor spherical. Moreover, colloidal-sized, clay-mineral particles have little or no biological component, while the classes of component particles which aggregate to form marine snow are either organisms themselves (phytoplankton, bacteria) or contain abundant, attached detrital communities (fecal pellets, microaggregates, many clay-minerals). Although the 20 year old controversy regarding the need for bacteria for the formation of microaggregates is still raging (KRANCK and MILLIGAN, 1980; BIDDANDA, 1985; JOHNSON, ZHOU and WANGERSKY, 1986), this controversy is irrelevant to the formation of marine snow in the sea, since all natural microaggregates appear to contain attached bacteria, small algae and sometimes protozoa (RILEY, 1970). Even microaggregates formed without apparent bacterial contribution have attached bacteria within 3 hours of formation (JOHNSON, ZHOU, WANGERSKY, 1986).

Two biologically-mediated pathways appear to enhance marine snow formation via physical aggregation: (1) production of sticky mucus, exopolymers, or products of cell lysis which increase the attachment probability of colliding particles; and (2) biological alteration of the effective size and surface characteristics of component particles which potentially increase collision probabilities. Although our understanding of these enhancement processes in the ocean is poor, it is hoped that the somewhat speculative nature of the following section will help stimulate further research.

5.2.2.1 Biological glues: Extracellular polymeric material exuded from living or lysed cells is ubiquitous in most natural systems. Macromolecules, including complex mucopolysaccharides, are excreted at the exposed surfaces of bacteria, especially during declining growth and death (see HARRIS and MITCHELL, 1973; CALLEJA, 1984 for extensive reviews). In

aquatic systems these mucopolysaccharides and structurally related glycoproteins occur in a wide variety of polymeric forms and serve many purposes. Extracellular polymers attach bacteria to surfaces as adhesive fibres and webs and form sticky capsular secretions (HARRIS and MITCHELL, 1973; PAERL, 1975). Attached bacteria also remove dissolved organic matter from seawater and convert it to particulate matter via growth and extracellular excretion (PAERL, 1973, 1978). Aggregation of microaggregates into macroaggregates has been clearly demonstrated by this method (PAERL, 1973, 1978).

Extracellular polymers produced by attached bacteria may greatly increase the probability of adhesion when natural particles collide and form marine snow. Flocculation of microbes in waste water provides a mechanism for this process. Flocculation of microorganisms in wastewater involves the interaction of polymers excreted at the cell surfaces. Attachment results from specific adsorption of polymer segments and from bridging of polymers between cells (BUSCH and STUMM, 1968). For polymer bridging to occur, polymers must sorb to a solid surface with segments extending into the bulk media so that sorption to adjacent particles, leading to aggregate formation, is facilitated. Although aggregating particles have like charges (negative), reduction of this surface potential is not a prerequisite of flocculation (BUSCH and STUMM, 1968; PAVONI, TENNEY and ECHELBERGER, 1972). These polymers are very effective flocculation agents. Well flocculated cells can be dispersed to form a stable suspension by extraction of their exocellular polymer coatings. Moreover, addition of extracted microbial polymer to stable dispersions of kaolinite, silica or alumina results in substantial flocculation of these inorganic particles (BUSCH and STUMM, 1968).

Although aggregation of microorganisms has been observed at all growth states, most flocculation occurs during states of low or no growth (CALLEJA, 1984). Bacteria in porous flocs have the potential to experience greater uptake of high molecular weight molecules, perhaps explaining the adaptive value of flocculation under nutrient stress (LOGAN and HUNT, 1987). HARRIS and MITCHELL (1973) attribute flocculation of nutrient stressed cells to both increased exopolymer secretion and to cell lysis. Cell lysis may be a significant part of some aggregation processes. Not only do released polysaccharides, proteins and other cell components produce polymer bridging, but DNA, which survives breakdown and polymerisation following cell lysis, is an especially effective flocculating agent when added to various microbial systems (VALLOM and McLOUGHLIN, 1984).

Some bacteria produce more effective flocculating agents than others. The "quality" rather than quantity of bacterial exudates may be critical to bioflocculation efficiency (AL-SHAHWANI, JAZRAWI and AL-RAWI, 1986). Moreover, strains of *Pseudomonas* which secreted floc-producing exopolymers are also capable of producing an exoenzyme which brings about deflocculation (TAGO and AIDA, 1977). Such findings suggest that the role of bacterial exudates in processes of aggregation in the ocean may be very complex.

Although abundant bacterial aggregates have been occasionally reported (SEKI, 1971), concentrations of bacteria similar to those found in waste water systems rarely exist in natural ocean waters. However, exopolymers produced by bacteria attached to aggregates, probably

form polymer bridges with surrounding particles by mechanisms similar to those observed to flocculate waste water suspensions. The high abundance of bacteria on aggregates, often in a state of little or no growth (ALLDREDGE, COLE and CARON, 1986; ALLDREDGE and YOUNGBLUTH, 1985), suggests that exopolymeric material must also be abundant. Moreover, this polymeric material is largely resistant to microbial attack (HARRIS and MITCHELL, 1973). The presence of such material would greatly facilitate particle adhesion following collision. Attachment probabilities as high as 100% may be possible.

Considerably less is known about phytoplankton exudates as agents facilitating flocculation. The production of extracellular mucus by phytoplankton increases under nutrient stress (MYKLESTAD, 1974; DEGENS and ITTEKOT, 1984) and these polymers may stick cells together as they collide (SMETACEK, 1985). For example, some diatoms in the surf zone excrete an organic layer capable of cementing clay particles to their surfaces (LEWIN, COLVIN and McDONALD, 1980). Phytoplankton exudates are known to be surface-active (WILSON and COLLIER, 1972; ZUTIC, COSOVIC, MARCENKO and BIHARI, 1981). Surfactants absorb and accumulate at marine interfaces such as particle surfaces and are implicated in flocculation processes (HUNTER and LISS, 1979). Although flocculation occurs commonly in senescent phytoplankton cultures in the laboratory, the frequency with which diatom and other phytoplankton exudates serve as flocculation agents in the water column remains largely unknown.

Phytoplankton death and cell lysis may also release flocculating agents such as DNA (VALLOM and McLOUGHLIN, 1984). GIESKES and ELBRACHTER, (1986) present evidence that diatom cells can break apart and release cellular components (chloroplasts) into the water. Superfluous feeding by zooplankton may also break cells and release their soluble and particulate constituents. The role of cell lysis in the rapid flocculation of diatom blooms is unknown, but potentially important.

4.2.3.2 Biologically increased size in aggregates: Although there are now some biological models explaining aggregation in aquatic systems, the physical descriptions of the aggregates are presently inadequate. While theory regarding particle-particle interactions has been developed primarily for colloidal-sized particles with smooth, regular profiles, natural aggregates often have highly convoluted, irregular surfaces. Setae and fibrils of diatoms, bacterial fibrils, capsular material, and exopolymer chains extend out from the surfaces of colonized aggregates (PAERL, 1975; BIDDANDA, 1986) increasing the total effective size of the particles. These extensions may increase the potential numbers of collisions with surrounding particles. MASSALSKI and LEPPARD (1979) and LEPPARD (1984) report the existence of fibrillar colloids emerging from the surfaces of both living phytoplankton and detrital particles in freshwater lakes. Although colloidal fibrils have not been reported to coat marine particles and microorganisms, some electron micrographs of marine microbial flocs (BIDDANDA, 1986) suggest that they may occur in the ocean as well.

On a molecular level, bacterially produced fibrils and exopolymers apparently alter the surface charge characteristics in ways that may favour aggregation. The convoluted shapes and protuberances of the aggregates coupled with their rapid settlement at Reynolds numbers of

1 to 30 (ALLDREDGE and GOTSCHALK, in press) may also cause complex flow patterns around the sinking particles. Velocity gradients generated in the wake of sinking aggregates may enhance capture of surrounding particles. Excreted mucus may also alter the surface chemistry and effectively extend aggregate surfaces. The physical boundaries of aggregates then become difficult to measure and the flow regimes, particularly as they are effected by viscosity changes due to release of exudates, become difficult to predict. New models and descriptions of the flow field around such gel and solute-releasing particles may be required before their surface properties and settling regimes can be predicted.

6. BREAKDOWN AND LOSS

Two biological processes contribute to the removal or size reduction of aggregates; consumption by zooplankton or nekton and decomposition by microorganisms. Additional physical processes resulting in aggregate loss include settlement, lateral advection, and particle fragmentation via turbulence and mixing.

6.1 *Consumption.*

Consumption reduces the size and alters the physical and chemical characteristics of marine snow. While most zooplankton repackage small particles into larger ones, some zooplankton and nekton, including salps, doliolids and fish, consume large macroaggregates, repackaging them into smaller, but more compact and dense fecal pellets containing less labile organic material (ALLDREDGE and MADIN, 1982). Small copepods and euphausiid larvae also feed on the surfaces of macroaggregates and produce small fecal pellets (ALLDREDGE, 1972, 1976). No quantitative information yet exists regarding the significance of marine snow consumption by large particle feeders to either oceanic food webs or to particle dynamics in the ocean. However, the order of magnitude reduction in the abundance of marine snow below the epipelagic zone suggests that consumption needs to be quantified: either the aggregates are consumed by detritivores or they are broken apart at the base of the mixed layer, reducing their apparent abundance at depth. Below the depth of diel vertical migration (i.e. 1000-1500m) the bathypelagic and abyssalpelagic communities must rely on marine snow and fecal pellets as the primary source of organic material. Consumers may be aided in locating marine snow by bioluminescence of attached microorganisms, which serves to "advertise" the particles (ORZECH and NEALSON, 1984).

6.2 *Decomposition*

The role of microorganisms as decomposers in the pelagic zone and the rates at which decomposition occurs have been the subject of considerable study. Bacterial decomposition primarily alters the chemical composition and nutritional value of aggregates. The C:N ratios and percentage of refractory matter in small aggregates (RILEY, 1970) and in the large particle flux (SEUSS, 1980; MARTIN, KNAUER, KARL and BROENKOW, 1987) increases with depth, suggesting that aggregates and other sinking detritus become nutritionally depleted with age.

However, decomposition may not be a major pathway by which aggregates become fragmented or reduced in size in nature. Less than 10% of heterotrophic activity in seawater is associated with attached bacteria (AZAM and HODSON, 1977; DUCKLOW and KIRCHMAN, 1983), and these attached forms are only rarely more metabolically active than free-living bacteria (ALLDREDGE, COLE and CARON, 1986). Moreover, utilization of labile material on marine aggregates occurs very rapidly, often within the first 48 hours, following formation (POMEROY *et al.* 1984). The majority of marine aggregates in nature appear to be nutritionally spent. Although some fragmentation of very flocculent aggregates may occur as labile matter is decomposed, microbial activity appears as likely to aggregate (PAERL, 1973, 1974) as to fragment marine snow.

6.3 *Sinking*

Settlement is a major mechanism by which aggregates are removed from the pelagic zone. Particles resembling marine snow are the most abundant components of many sediment trap collections (FOWLER and KNAUER, 1986) and are the dominant material entering traps (ASPER, 1987). Major interest in marine snow has focused on the role these particles play in carrying adsorbed and associated materials into the deep sea, but predictions of the behaviour of marine snow are still limited because its sinking characteristics are poorly known.

Numerous measurements of the sinking rates of many types of marine snow have been made in both the laboratory and the field (Table 7) These range from 1-368 m d^{-1}. Laboratory measurements tend to be artificially high in many cases, probably because aggregates collapse and compress during collection and handling (ALLDREDGE and GOTSCHALK, in press). ASPER (1986) estimated snow sinking rates from *in situ* measurements of both flux and snow photographed accumulating in a sediment trap (sinking rates calculated as the quotient of flux and concentration). His results suggest that there are several kinds of snow, with some settling more rapidly than others. Fresh, rapidly sinking particles may descend from the surface, accreting the slower particles at depth, and older, more refractory and lighter aggregates may be derived from resuspension at continental margins and advected at middepths to more oceanic environments. In his Panama Basin observations, the former would be smaller aggregates (1-2.5mm) that sink more rapidly (36 m d^{-1}) than the larger (4-5mm) particles that sink slowly (1m d^{-1}). ASPER's suggestion of slow settling for the marine snow in the Panama Basin is at variance with the prediction of LAL (1977) that only very small particles (ones < 5μm) are transported significant distances from nearshore environments to oceanic regions.

ALLDREDGE and GOTSCHALK (in press) conducted the only study of the size-specific sinking rates of undisturbed, uncontained aggregates directly *in situ*. They measured the sinking rates of free-floating aggregates relative to a spot of neutrally buoyant dye placed below the particle. The mean sinking rate of aggregates ranging from 2.4 to 75mm in maximum length was 74 ± 39m d^{-1}. Sinking rate was an exponential function of aggregate diameter and dry weight. Excess density, the difference between the density of the aggregate and that of the surrounding seawater, ranged over 4 orders of magnitude with a median of 0.14 kg m^3. ALLDREDGE and GOTSCHALK (in press) suggest that the excess density of marine snow consisting largely of living organisms, such as diatom flocs, may be effected by the buoyancy regulation mechanisms of these organisms.

TABLE 7

SINKING RATES OF MARINE SNOW

Type Material	Method of Measurement	Sinking Rate ($m\ d^{-1}$)	Site	Reference
Reaggregated, field collected marine snow from submersible	laboratory settling chamber	17-260	Japan neritic	KAJIHARA ,1971
Field collected marine snow (3mm, spherical)	calculated	91	California, neritic	ALLDREDGE, 1979
Natural marine snow	*In situ* settling chamber	68±18 (43-95	Monterey Bay	SHANKS and TRENT, 1980
Field collected larvacean houses	laboratory settling chamber	57-64	California neritic	SILVER and ALLDREDGE, 1981
Field collected larvacean houses	laboratory settling chamber	103-368	neritic, Hawaii	TAGUCHI, 1982
aggregates of phytoplankton detritus from sea floor (2000 m)	calculated from time lapse *in situ* photography	100-150	north-east Atlantic	BILLET et al., 1983
larvacean houses from lab cultured larvaceans	laboratory settling chamber	26-157	Monaco	GORSKY et al., 1984
aggregates of phytoplankton detritus from sea floor	calculated from time lapse *in situ* photography	100-150	north-east Atlantic	LAMPITT, 1985
sediment trap samples from deep water (to 3560 m)	indirect calculation using *in situ* flux (trap) data and particle concentration data (*in situ* camera)	1, 26 and 36	Panama Basin	ASPER, 1987
Sediment trap samples from deep water (to 3800 m)	calculated time lag from trap collections at different depths	175	North Pacific (Sta. Papa)	ASPER, 1986
Natural marine snow	*In situ* visual measurements of undisturbed particles	74±38 (16-200)	Southern Calif. Bight	ALLDREDGE and GOTSCHALK in press

Excess density may also decrease as aggregates sink into higher density waters at depth. This may result in decreased settling velocities with depth and accumulation of marine snow, such as observed by ASPER (1986) at discontinuity layers. It has been predicted that such accumulations might also result from decreases in fluid turbulence at these discontinuities (HUNT, 1980).

Considerable field evidence exists to show that some marine snow particles are sinking rapidly through the water column, as discussed above. Evidence also comes from accounts describing the rapid sedimentation of phytoplankton blooms in shallow seas (eg BODUNGEN, BROCKEL, SMETACEK and ZEITZSCHEL, 1981; SMETACEK, 1985; SKJOLDAL and WASSERMANN, 1986) and some deep ocean basins, (BILLETT, LAMPITT, RICE and MANTOURA, 1983; LAMPITT, 1985; TAKAHASHI, 1986).

Further evidence that near-surface material settles rapidly into deep water is provided by the strongly seasonal inputs found in bathypelagic environments, inputs that reflect the production and populations of overlying waters (eg DEUSER, ROSS and ANDERSON, 1981; HONJO, 1982a).

Rapid sinking rates do not necessarily mean that all particles settle from surface waters immediately, however. Models (LANDE and WOOD, 1987) and field data on fecal pellets (ALLDREDGE, GOTSCHALK and MacINTYRE, 1987) suggest that many aggregates may be retained in the mixed layer for days to weeks or accumulate at the thermocline. This is consistent with the calculations of EPPLEY, RENGER and BETZER (1983) which indicate that the residence time of particles in surface waters is on the order of weeks or more. Considerably more information on the effects of physical mixing processes on aggregate abundance, depth distributions and sinking is needed before the role of sedimentation as a mechanism of aggregate loss to the water column can be adequately assessed.

6.4 *Lateral Advection*

Lateral advection of marine snow, particularly from aggregate rich shelf and slope waters, or from suspended sediments found there, may be a major factor determining vertical and horizontal distributions of marine snow in some regions of the sea (ASPER, 1986). Certainly, lateral advection from slope and shelf sources has been widely invoked to explain plumes for a variety of materials at mid-depth (eg HONJO, 1982b; MARTIN and KNAUER, 1985). Elucidation of the significance of lateral advection in determining the distribution of marine snow awaits development of adequate methods for assessing snow abundance and size distributions rapidly in three dimensions and in "real time".

7. CONCLUSIONS

Marine snow has significance both as a unique, partially isolated physical environment in the water column and as a transport agent that redirects living and nonliving materials in their transit through the ocean. As a microhabitat, it presents a complex, solid interface with a semi-isolated internal environment that can differ chemically and physically from the water column outside. This microcosm has its own intensified communities, chemical gradients and solid-liquid interfaces. Materials and organisms enclosed in this microcosm are also moving through the water column in trajectories defined by the physical characteristic of their substrate; no longer is their motion and fate controlled by their individual motions or physical properties. Thus association with the larger snow particle can result in accelerated or decelerated descent from the surface to depth.

Photosynthesis, decomposition and nutrient regeneration are enhanced on marine snow. Elevated concentrations of algae and microorganisms produce ammonia and carbon dioxide and utilize oxygen, likely producing redox gradients in larger aggregates, especially at night or at aphotic depths. These conditions could affect the redox chemistry of many substances (PAERL,

1984) and may account for observations of diagenesis (LEE and CRONIN, 1982) and dramatic changes in the composition of organic matter in particles sinking through deep water (e.g. WAKEHAM, FARRINGTON, GAGOSIAN, LEE, DEBARR, NIGRELLI, TRIPP, SMITH and FREW, 1980; WAKEHAM, LEE, FARRINGTON and GAGOSIAN, 1984).

High variability of naturally occurring marine snow particles, resulting from rapid microbial succession on time scales of hours to days certainly affects the extent to which marine snow serves as a locus for metabolic activity in the water column. Older aggregates should be chemically more refractory and less populated. The properties of aggregates will be difficult to predict unless their sources and ages are known. Thus, marine snow systems likely share features expected from ecological studies of other communities, namely that variability and change are troublesome but entirely expected attributes of complex natural detrital microcosms.

The greatest challenge to the study of marine snow at the present time is the development of appropriate technology to measure the abundances and characteristics of marine snow *in situ*. Needed are new instruments that will allow aggregate counting and sizing, measurement of sinking speeds, and gentle collection of undisrupted aggregates directly in the water column. Questions regarding the origins, temporal variability, contribution to vertical flux and physical, chemical and biological properties of marine snow await development of such new systems.

Although marine snow is ubiquitous in the ocean, its origins and fate are still poorly understood. The rates at which marine snow is produced by zooplankton or by biologically-enhanced physical aggregation in the ocean are not known but are critical to predicting the flux of materials to depth, a subject of great interest among the oceanographic community. Clearly the composition of the phytoplankton community and its physiological health and sinking behaviour are central to the processes of floc formation and marine snow genesis. The mechanisms of aggregate formation suggest that at some times the rate of formation of marine snow is directly related to the magnitude and scale of local shear and to the abundance and biological characteristics of colliding component particles. Biological glues, including bacterial polymers, phytoplankton exudates, and products of cell lysis, such as DNA, may be particularly significant in this process. Considerably more information is necessary if we are to clearly understand aggregate dynamics and make meaningful predictions regarding the abundance, age, biological inhabitants, rates of biological processes, and size distributions of marine snow on meaningful space and time scales in the ocean.

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9. REFERENCES

ADAMSE, A.D., M.H. DEINEMA and A.J.B. ZEHNDER (1984) Studies on bacterial activities in aerobic and anaerobic waste water purification. *Antonie van Leeuwenhoek,* 50, 665-682.

ALI, W. (1985) *Chemical aspects of coagulation in lakes.* Doctoral dissertation, The John Hopkins University, Baltimore, Maryland.

ALI, W., C.R. O'MELIA and J.K. EDZWALD (1984) Colloidal stability of particles in lakes: Measurement and significance. *Water Science and Technology,* 17, 701-712.

ALLDREDGE, A.L. (1972) Abandoned larvacean houses: A unique food source in the pelagic environment. *Science,* 117, 885-887.

ALLDREDGE, A.L. (1976) Discarded appendicularian houses as sources of food, surface habitats, and particulate organic matter in planktonic environments. *Limnology and Oceanography,* 21, 14-23.

ALLDREDGE, A.L. (1979) The chemical composition of macroscopic aggregates in two neritic seas. *Limnology and Oceanography,* 24, 855-866.

ALLDREDGE, A.L., J.J. COLE and D.A. CARON (1986) Production of heterotrophic bacteria inhabiting macroscopic organic aggregates (marine snow) from surface waters. *Limnology and Oceanography,* 31, 68-78.

ALLDREDGE, A.L. and Y. COHEN (1987) Can microscale chemical patches persist in the sea? Microelectrode study of marine snow, fecal pellets. *Science,* 235, 689-691.

ALLDREDGE, A.L. and J.L. COX (1982) Primary productivity and chemical composition of marine snow in surface waters of the Southern California Bight. *Journal of Marine Research* 40, 517-527.

ALLDREDGE, A.L. and C. GOTSCHALK (in press) *In situ* settling behaviour of marine snow. *Limnology and Oceanography,*

ALLDREDGE, A.L., C. GOTSCHALK and S. MacKINTYRE (1987) Evidence for sustained residence of macrocrustacean fecal pellets in surface waters off southern California. *Deep-Sea Research,* 34, 1641-1652

ALLDREDGE, A.L. and L.P. MADIN (1982) Pelagic tunicates: Unique herbivores in the marine plankton. *Bioscience,* 32, 655-661.

ALLDREDGE, A.L. and M.J. YOUNGBLUTH (1985) The significance of macroscopic aggregates (marine snow) as sites for heterotrophic bacterial production in the mesopelagic zone of the subtropical Atlantic. *Deep-Sea Research,* 32, 1445-1456.

AL-SHAHWANI, M.F., S.F. JAZRAWI and E.H. AL-RAWI (1986) Effects of bacterial communities on floc size and numbers in industrial and domestic effluents. *Agricultural Wastes* 16, 303-311.

AMY, P.S., B.A. CALDWELL, A.H. SOELDNER, R.Y. MORITA and L.J. ALBRIGHT (1987) Microbial activity and ultra structure of mineral-based marine snow from Howe Sound, British Columbia. *Canadian Journal of Fisheries and Aquatic Science,* 44, 1135-1142.

ANDREWS, C.C., D.M. KARL, L.F. SMALL and S.W. FOWLER (1984) Metabolic activity and bioluminescence of oceanic fecal pellets and sediment trap particles. *Nature, London,* 307, 539-541.

ANGEL, M.V. (1984) Detrital organic fluxes through pelagic ecosystems. In: *Flows of Energy and Materials in Marine Ecosystems, Theory and Practice,* Ed. M.J.R. FASHAM, Plenum Press, New York, 475-516.

ASPER, V.L. (1986) *Accelerated settling of marine particulate matter by "marine snow" aggregates.* PhD Thesis, Massachusetts Institute of Technology/Woods Hole Oceanographic Institution, WHOI 96-12, 189pp.

ASPER, V.L. (1987) Measuring the flux and sinking speed of marine snow aggregates. *Deep-sea Research,* 34, 1-17.

AZAM, F. and R.E. HODSON (1977) Size distribution and activity of marine microheterotrophs. *Limnology and Oceanography,* 22, 492-501.

BALE, A.J. and A.W. MORRIS (1987) *In situ* measurement of particle size in estuarine waters. *Estuarine and Coastal Shelf Science,* 24, 253-263.

BARHAM, E.G. (1979) Giant larvacean houses: Observations from deep submersibles. *Science,* 205, 1129-1131.

BATJE, M. and H. MICHAELIS (1986) *Phaeocystis pouchetii* blooms in the East Frisian coastal waters (German Bight, North Sea). *Marine Biology,* 93, 21-27.

BAYLOR, E.R., W.H. SUTCLIFFE and D.S. HIRSCHFELD (1962) Adsorption of phosphates onto bubbles *Deep-Sea Research,* 9, 120-124.

BEERS, J.R., J.D. TRENT, F.M.H. REID and A.L. SHANKS (1986) Macroaggregates and their phytoplanktonic components in the Southern California Bight*Journal of Plankton Research,* 8, 475-487.

BIDDANDA, B.A. (1985) Microbial synthesis of macroparticulate matter. *Marine Ecology - Progress Series,* 20, 241-251.

BIDDANDA, B.A. (1986) Structure and function of marine microbial aggregates. *Oceanologica Acta,* 9, 209-211.

BILLETT, D.S.M , R.S. LAMPITT, A.L. RICE and R.F.C. MANTOURA (1983) Seasonal sedimentation of phytoplankton to the deep sea benthos. *Nature, London,* 302, 520-522.

BISHOP, J.K.B., R.W. COLLIER, D.R. KETTEN and J.M. EDMOND (1980) The chemistry, biology and vertical flux of particulate matter from the upper 400m of the Panama Basin. *Deep-Sea Research,* 27, 615-640.

BISHOP, J.K.B. and J.M. EDMOND (1976) A new, large volume *in situ* filtration system for sampling oceanic particulate matter. *Journal of Marine Research,* 34, 181-198.

BISHOP, J.K.B., J.M. EDMOND, D.R. KETTEN, M.P. BACON and W.B. SILKER (1977) The chemistry, biology and vertical flux of particulate matter from the upper 400m of the equatorial Atlantic Ocean. *Deep-Sea Research,* 24, 511-548.

BISHOP, J.K.B., D.R. KETTEN and J.M. EDMOND (1978) The chemistry, biology and vertical flux of particulate matter from the upper 400m of the Cape Basin in the Southeast Atlantic Ocean. *Deep-Sea Research,* 25, 1121-1161.

BISHOP, J.K.B., J.C. STEPIEN and P.H. WIEBE (1987) Particulate matter distributions, chemistry and flux in the Panama Basin: response to environmental forcing. *Progress in Oceanography,* 17, 1-59.

BODUNGEN, B.V., K.V. BROCKEL, V. SMETACEK and B. ZEITZSCHEL (1981) Growth and sedimentation of the phytoplankton spring bloom in the Bornholm Sea (Baltic Sea). *Kieler Meeresforschung, Sonderheft,* 5, 49-60.

BRULAND, K.W. and M.W. SILVER (1981) Sinking rates of fecal pellets from gelatinous zooplankton (salps, pteropods, doliolids). *Marine Biology,* 63, 295-300.

BUSCH, P.L. and W. STUMM (1968) Chemical interactions in the aggregation of bacteria bioflocculation in waste treatment. *Environmental Science and Technology,* 2, 49-53.

CADEE, G.C. (1985) Macroaggregates of *Emiliana huxleyi* in sediment traps. *Marine Ecology - Progress Series,* 24, 193-196.

CADEE, G.C. (1986) Organic carbon in the water column and its sedimentation, Fladen Ground (North Sea), May 1983. *Netherlands Journal of Sea Research,* 20, 347-358.

CALLEJA, G.B. (1984) *Microbial Aggregation.* CRC Press Inc., 276pp.

CALVERT, S.E. and M.J. McCARTNEY (1979) The effect of incomplete recovery of large particles from water samplers on the chemical composition of oceanic particulate matter. *Limnology and Oceanography,* 24, 532-536.

CARDER, K.L., R.G. STEWARD and P.R. BETZER (1982) *In situ* holographic measurements of the sizes and settling rates of oceanic particulates. *Journal of Geophysical Research,* 87, 5681-5686.

CARDER, K.L., D. COSTELLO and R.G. STEWARD (1986) State-of-the-art instrumentation for measuring ocean aggregates. In: *Aggregate Dynamics in the Sea, Workshop Report* A.L. ALLDREDGE and E.O. HARTWIG, eds., American Institute of Biological Sciences, Washington, D.C. 131-185.

CARON, D.A. (1987) Grazing of attached bacteria by heterotrophic microflagellates. *Microbial Ecology,* 13, 203-218.

CARON, D.A., P.G. DAVIS, L.P. MADIN and J.McN. SIEBURTH (1986) Enrichment of microbial populations in macroaggregates (marine snow) from surface waters of the North Atlantic. *Journal of Marine Research,* 44, 543-565.

CARON, D.A., P.G. DAVIS, L.P. MADIN and J.McN. SIEBURTH (1982) Heterotrophic bacteria and bacterivorous protozoa in oceanic macroaggregates. *Science,* 218, 795-797.

CARSON, R. (1951) *The Sea Around Us,* Oxford University Press, 230pp.

COLES, S.L. and R. STRATHMANN (1973) Observations on coral mucus flocs and their potential trophic significance. *Limnology and Oceanography,* 18, 673-678.

COSTELLO, D.K., R.W. YOUNG, K.L. CARDER and P.R. BETZER (1986) Multiple-sample sediment traps with *in situ* holographic imaging of settling particles. *EOS,* 67, 899.

DAVIDSON, A.T., and H.J. MARCHANT (1987) Binding of manganese by Antarctic *Phaeocystis pouchetii* and the role of bacteria in its release. *Marine Biology,* 95, 481-487.

DAVOLL, P.J. (1986) Production and heterotrophic activity of macroaggregates in mesopelagic regions. *EOS,* 65, 904.

DAVOLL, P.J. and M.W. SILVER (1986) Marine snow aggregates: life history sequence and microbial community of abandoned larvacean houses from Monterey Bay, California. *Marine Ecology - Progress Series,* 33, 111-120.

DEIBEL, D. (1985) Blooms of the pelagic tunicate, *Dolioletta gegenbauri:* Are they associated with Gulf Stream frontal eddies? *Journal of Marine Research,* 43. 211-235.

DEGENS, E.T. and V. ITTEKOT (1984) A new look at clay-organic interactions. *Mitteilungen Geologische-Paleontologische Institut, Universitat Hamburg,* 56, 229-248.

DEUSER, W.G., E.H. ROSS and R.F. ANDERSON (1981) Seasonality in the supply of sediment to the deep Sargasso Sea and implications for the rapid transport of matter to the deep ocean. *Deep-Sea Research,* 28, 495-505.

DUCKLOW, H.W., S.M. HILL and W.D. GARDNER (1985) Bacterial growth and the decomposition of particulate organic carbon collected in sediment traps. *Continental Shelf Science,* 4, 445-464.

DUCKLOW, H.W. and D.L. KIRCHMAN (1983) Bacterial dynamics and distribution during a diatom bloom in the Hudson River Plume, USA. *Journal of Plankton Research,* 5, 333-355.

EISMA, D. (1986) Flocculation and de-flocculation of suspended matter in estuaries. *Netherlands Journal of Sea Research,* 20, 183-199.

EPPLEY, R.W., E.H. RENGER and P.R. BETZER (1983) The residence time of particulate organic carbon in the surface layer of the ocean. *Deep-Sea Research,* 30, 311-323.

FELLOWS, D.A., D.M. KARL and G.A. KNAUER (1981) Large particle fluxes and the vertical transport of living carbon in the upper 1500m of the northeast Pacific Ocean. *Deep-Sea Research,* 28A, 921-936.

FENAUX, R. (1985) Rhythm of secretion of Oikopleurid's houses. *Bulletin of Marine Science,* 37, 498-503.

FENCHEL, T. (1982) Ecology of heterotrophic microflagellates. I. Some important forms and their functional morphology. *Marine Ecology - Progress Series* 8, 211-212.

FOWLER, S.W. and G.A. KNAUER (1986) Role of large particles in the transport of elements and organic compounds through the oceanic water column. *Progress in Oceanography,* 16, 147-194.

FRYXELL, G.A., R.W. GOULD Jr. and T.P. WATKINS (1984) Gelatinous colonies of the diatom *Thalassiosira* in the Gulf Stream warm core rings, including *T. fragilia* sp. nov. *British Phycology Journal,* 19, 141-156.

GARDNER, W.D., K.R. HINGA and J. MARRA (1983) Observations on the degradation of biogenic material in the deep ocean with implications on the accuracy of sediment trap fluxes. *Journal of Marine Research,* 41, 195-214.

GERSONDE, R. and G. WEFER (1987) Sedimentation of biogenic siliceous particles in Antarctic waters from the Atlantic sector. *Marine Micropaleontology,* 11, 311-332.

GIBBS, R.J. (1981) Floc breakage by pumps. *Journal of Sedimentary Petrology,* 51, 670-672.

GIBBS, R.J. (1982a) Floc breakage during HIAC light-blocking analysis. *Environmental Science and Technology,* 16, 298-299.

GIBBS, R.J. (1982b) Floc stability during Coulter Counter analysis. *Journal of Sedimentary Petrology,* 52, 657-670.

GIBBS, R.J. and L.N. KONWAR (1983) Sampling of mineral flocs using Niskin Bottles. *Environmental Science and Technology,* 17, 374-375.

GIESKES, W.W.C. and M. ELBRACHTER (1986) Abundance of nanoplankton-size chlorophyll-containing particles caused by diatom disruption in surface waters of the southern ocean (Antarctic Peninsula Region). *Netherlands Journal of Sea Research,* 20, 291-303.

GILMER, R. (1972) Free-floating mucus webs: A novel feeding adaptation for the open ocean. *Science,* 176, 1239-1240.

GOLDMAN, J.C. (1984) Conceptual role for microaggregates in pelagic waters. *Bulletin of Marine Science,* 35, 462-476.

GORDON, D.C. (1970) A microscopic study of organic particles in the North Atlantic Ocean. *Deep-Sea Research,* 17, 175-185.

GORSKY, G., N.S. FISHER and S.W. FOWLER (1984) Biogenic debris from the pelagic tunicate *Oikopleura dioica,* and its role in the vertical transport of a transuranium element. *Estuarine, Coastal, and Shelf Science,*18, 13-23.

GOWING, M.M. and M.W. SILVER (1983) Origins and microenvironments of bacteria mediating fecal pellet decomposition in the sea. *Marine Biology,*73, 7-16.

HAMNER, W.M., L.P. MADIN, A.L. ALLDREDGE, R.W. GILMER and P.P. HAMNER (1975) Underwater observations of gelatinous zooplankton: sampling problems, feeding biology, and behaviour. *Limnology and Oceanography,* 20, 907-917.

HARRIS, R.H. and R. MITCHELL (1973) The role of polymers in microbial aggregation. *Annual Review of Microbiology,* 27, 27-50.

HEBEL, D.V.W. (1983) *Concentration and flux of trace metals, carbon-nitrogen, and particulate matter in marine snow.* Master's Thesis, San Francisco State University, 69pp.

HEBEL, D.V.W., G.A. KNAUER and J.H. MARTIN (1986) Trace metals in large agglomerates (marine snow). *Journal of Plankton Research,* 8, 819-824.

HONJO, S. (1976) Coccoliths: production, transportation and sedimentation. *Marine Micropaleontology,* 1, 65-79.

HONJO, S. (1980) Material fluxes and modes of sedimentation in the mesopelagic and bathypelatic zones. *Journal of Marine Research,* 38, 53-97.

HONJO, S. (1982a) Seasonality and interaction of biogenic and lithogenic particulate flux at the Panama Basin. *Science,* 218, 883-884.

HONJO, S. (1982b) Deep advective transport of lithogenic particles in Panama Basin. *Science,* 216, 516-518.

HONJO, S., K.W. DOHERTY, Y.C. AGRAWAL and V. ASPER (1984) Direct optical assessment of large amorphous aggregates (marine snow) in the deep ocean. *Deep-Sea Research,* 31, 67-76.

HONJO, S., and V.L. ASPER (1982) Deep water marine snow concentrations in two oceans. *EOS,* 63, 1016.

HUNT, J.R. (1980) Prediction of oceanic particle size distributions from coagulation and sedimentation mechanisms. In: *Particles in water; characteristics, fate, effects, and removal,* M.C. KAVANAUGH and J.O. LECKIE, editors, *Advances in Chemistry Series,* 189. American Chemistry Society, Washington DC, 243-257.

HUNTER, K.A. and P.S. LISS (1982) Organic matter and the surface charge of suspended particles in estuarine waters. *Limnology and Oceanography,* 27, 322-335.

ITURRIAGA, R. (1979) Bacterial activity related to sedimenting particulate matter. *Marine Biology,* 55, 157-169.

JACKSON, G.A. (1980) Phytoplankton growth and zooplankton grazing in oligotrophic oceans. *Nature, London,* 284, 439-441.

JENSEN, L.M. and SONDERGAARD (1982) Abiotic formation of particles from extracellular organic carbon released by phytoplankton. *Microbial Ecology,* 8, 47-53.

JOHANNES, R.E. (1967) Ecology of organic aggregates in the vicinity of a coral reef. *Limnology and Oceanography,* 12, 189-195.

JOHNSON, B.D. (1976) Non-living organic particle formation from bubble dissolution *Limnology and Oceanography,* 21, 444-447.

JOHNSON, B.D. and R.C. COOKE (1980) Organic particle and aggregate formation resulting from the dissolution of bubbles in seawater. *Limnology and Oceanography,* 25, 653-661.

JOHNSON, B.D. and WANGERSKY (1985) A recording backscattering meter and camera system for examination of the distribution and morphology of macroaggregates *Deep-Sea Research,* 32, 1143-1150.

JOHNSON, B.D., X. ZHOU, and P.J. WANGERSKY (1986) Surface coagulation in the sea. *Netherlands Journal of Sea Research,* 20, 201-210.

KAJIHARA, M. (1971) Settling velocity and porosity of large suspended particles. *Journal of the Oceanographic Society of Japan,* 22, 158-161.

KARL, D.M. and G.A. KNAUER (1984) Vertical distribution, transport, and exchange of carbon in the northeast Pacific Ocean: evidence for multiple zones of biological activity. *Deep-Sea Research,* 31, 221-243.

KARL, D.M., G.A. KNAUER, J.H. MARTIN and B.B. WARD (1984) Bacterial chemolithotrophy in association with sinking particles. *Nature, London,* 309, 54-56.

KNAUER, G.A., D. HEBEL and F. CIPRIANO (1982) Marine snow: major site of primary production in coastal waters. *Nature, London,* 300, 630-631.

KRANCK, K. and T. MILLIGAN (1980) Macroflocs: production of marine snow in the laboratory. *Marine Ecology - Progress Series,* 3, 19-24.

LAL, D. (1977) The oceanic microcosm of particles. *Science,* 198, 997-1009.

LAMPITT, R.S. (1985) Evidence for the seasonal deposition of detritus to the deep-sea floor and its subsequent resuspension. *Deep-Sea Research,* 32, 885-897.

LANDE, R. and A.M. WOOD (1987) Suspension times of particles in the upper ocean. *Deep-Sea Research,* 34, 61-72.

LEE, C. and C. CRONIN (1982) The vertical flux of particulate organic nitrogen in the sea: decomposition of amino acids in the Peru upwelling area and the equatorial Atlantic. *Journal of Marine Research,* 40, 227-251.

LEPPARD, G.G. (1984) Organic coatings on suspended particles in lake water. *Archives fur Hydrobiologie,* 102, 265-269.

LERMAN, A. (1979) *Geochemical processes: water and sediment environments.* Wiley, 481pp.

LEWIN, J., J.R. COLVIN and K.L. McDONALD (1980) Blooms of surf-zone diatoms along the coast of the Olympic Peninsula, Washington. XII The clay coat of *Chaetoceros armatum* T. West. *Botanica Marina,* 23, 333-341.

LINLEY, E.A.S. and J.G. FIELD (1982) The nature and ecological significance of bacterial aggregation in a nearshore upwelling ecosystem *Estuarine, Coastal and Shelf Science,* 14, 1-11.

LINLEY, E.A.S., R.C. NEWELL and S.A. BOSMA (1981) Heterotropic utilization of mucilage released during fragmentation of kelp *(Ecklonia maxima* and *Laminaria pallida).* I. Development of microbial communities associated with degradation of kelp mucilage *Marine Ecology - Progress Series* 4, 31-41.

LOGAN, B.E. and J.R. HUNT (1987) Advantages of microbial growth in permeable aggregates in marine systems. *Limnology and Oceanography,* 32, 1034-1048.

LORENZEN, C.J., N.A. WELSCHMEYER and A.E. COPPING (1983) Particulate organic carbon flux in the subarctic Pacific. *Deep-Sea Research,* 30, 639-643.

MARTIN, J.H. and G.A. KNAUER (1985) Lateral transport of Mn in the north-east Pacific Gyre oxygen minimum. *Nature, London,* 314, 524-526.

MARTIN, J.H., G.A. KNAUER, D.M. KARL and W.W. BROENKOW (1987) VERTEX: Carbon cycling in the northeast Pacific. *Deep-Sea Research,* 34, 267-286.

MASSALSKI, A. and G.G. LEPPARD (1979) Morphological examination of fibrillar colloids associated with algae and bacteria in lakes. *Journal of the Fisheries Research Board of Canada,* 36, 922-938.

McCARTHY, J.J. and J.C. GOLDMAN (1979) Nitrogenous nutrition of marine phytoplankton in nutrient depleted waters. *Science,* 203, 670-672.

McCAVE, I.N. (1984) Size spectra and aggregation of suspended particles in the deep ocean. *Deep-Sea Research,* 31,. 329-352.

MITCHELL, J.G., A. OKUBO and J.A. FUHRMAN (1985) Microzones surrounding phytoplankton form the basis for a stratified marine microbial ecosystem. *Nature, London,* 316, 58-59

MYKLESTAD, S. (1974) Production of carbohydrates by marine planktonic diatoms. I. Comparison of nine different species in culture. *Journal of Experimental Marine Biology and Ecology,* 15, 261-274.

NEWELL, R.C. (1984) The biological role of detritus in the marine environment. In: *Flows of energy and materials in marine ecosystems, theory and practice,* M.J.R. FASHAM, editor, Plenum Press, 317-343.

NEIHOF, R.A. and G.I. LOEB (1972) The surface charge of particulate matter in seawater. *Limnology and Oceanography,* 17, 7-16.

NEIHOF, R.A. and G.I. LOEB (1974) Dissolved organic matter in sea water and the electric charge of immersed surfaces. *Journal of Marine Research,* 32, 5-12.

NISHIZAWA, S. (1966) Suspended material in the sea: from detritus to symbiotic microcosmos. *Bulletin of the Plankton Society of Japan,* 13, 1-33.

NISHIZAWA, S., M. FUKUDA and N. INOUE (1954) Photographic study of suspended matter and plankton in the sea. *Bulletin of the Faculty of Fisheries of Hokkaido University,* 5, 36-40.

O'MELIA, C.R. (1987) Particle-particle interactions. In: *Aquatic Surface Chemistry,* W. STUMM, editor, Wiley-Interscience, 385-403.

ORZECH, J.K. and K.H. NEALSON (1984) Bioluminescence of marine snow: its effect on the optical properties of the sea. In: *Ocean Optics VII,* M.A. BLIZARD, editor, Proceedings of the SPIE, 489, SPIE, Bellingham, 100-106.

PAERL, H.W. (1973) Detritus in Lake Tahoe: Structural modification by attached microflora. *Science,* 180, 496-498.

PAERL, H. (1974) Bacterial uptake of dissolved organic matter in relation to detrital aggregation in marine and freshwater systems. *Limnology and Oceanography,* 19, 966-972.

PAERL, H.W. (1975) Microbial attachment to particles in marine and freshwater ecosystems. *Microbial Ecology,* 21, 73-83.

PAERL, H.W. (1978) Microbial organic carbon recovery in aquatic ecosystems. *Limnology and Oceanography,* 23, 927-935.

PAERL, H.W. (1984) Alteration of microbial metabolic activities in association with detritus *Bulletin of Marine Science,* 35, 393-408.

PAVONI, J.L., M.W. TENNEY and W.F. ECHELBERGER Jr (1972) Bacterial exocellular polymers and biological flocculation. *Journal of the Water Pollution Control Federation* 44, 414-431.

POMEROY, L.R. and D. DEIBEL (1980) Aggregation of organic matter by pelagic tunicates. *Limnology and Oceanography,* 25, 643-652.

POMEROY, L.R., R.B. HANSON, P.A. McGILLIVARY, B.F. SHERR, D. KIRCHMAN and D. DEIBEL (1984) Microbiology and chemistry of fecal products of pelagic tunicates: Rates and fates. *Bulletin of Marine Science,* 35, 426-439.

POMEROY, L.R. and R.E. JOHANNES (1968) Occurrence and respiration of the ultraplankton in the upper 500m of the ocean. *Deep-Sea Research,* 15, 381-391.

PREZELIN, B.B. and A.L. ALLDREDGE (1983) Primary production of marine snow during and after an upwelling event. *Limnology and Oceanography,* 28, 1156-1167.

RICE, A.L., D.S.M. BILLETT, J. FRY, A.W.G. JOHN, R.S. LAMPITT, R.F.C. MANTOURA and R.J. MORRIS (1986) Seasonal deposition of phytodetritus to the deep-sea floor. *Proceeding of the Royal Society of Edinburgh,* 88, 265-279.

RILEY, G.A. (1963) Organic aggregates in seawater and the dynamics of their formation and utilization. *Limnology and Oceanography,* 8, 372-381.

RILEY, G.A. (1970) Particulate matter in seawater. *Advances in Marine Biology,* 8, 1-118.

ROBISON, B.H. and T.G. BAILEY (1981) Sinking rates and dissolution of midwater fish fecal matter. *Marine Biology,* 65, 135-142.

SCHRADER, H-J. (1971) Fecal pellets: role in sedimentation of pelagic diatoms. *Science,* 174, 55-57.

SEKI, H. (1971) Microbial clumps in seawater in the euphotic zone of Saanich Inlet (British Columbia). *Marine Biology,* 9, 4-8.

SEUSS, E. (1980) Particulate organic carbon flux in the oceans - surface productivity and oxygen utilization. *Nature, London,* 288, 260-263.

SHANKS, A.L. and J.D. TRENT (1979) Marine snow: microscale nutrient patches. *Limnology and Oceanography,* 24, 850-854.

SHANKS, A.L. and J.D. TRENT (1980) Marine snow: Sinking rtes and potential role in vertical flux. *Deep-Sea Research,* 27, 137-144.

SHELDON, R.W., T.P.T. EVELYN and T.R. PARSONS (1967) On the occurrence and formation of small particles in seawater. *Limnology and Oceanography,* 12, 367-375.

SHELDON, R.W., A. PRAKASH and W.H. SUTCLIFFE (1972) The size distribution of particles in the ocean. *Limnology and Oceanography,* 17, 327-340.

SHOLKOVITZ, E.R. (1976) Flocculation of dissolved organic and inorganic matter during the mixing of river water and seawater. *Geochemica et Cosmochemica Acta,* 40, 831-845.

SIBBALD, M.J., L.J. ALBRIGHT and P.R. SIBBALD (1987) Chemosensory responses of a heterotrophic microflagellate to bacteria and several nitrogen compounds. *Marine Ecology - Progress Series,* 36, 201-204.

SIEBURTH, J.McN. (1979) *Sea Microbes,* Oxford University Press, New York, 491pp.

SILVER, M.W. and A.L. ALLDREDGE (1981) Bathypelagic marine snow: deep-sea algal and detrital community. *Journal of Marine Research,* 39, 501-530.

SILVER, M.W. and K.W. BRULAND (1981) Differential feeding and fecal pellet composition of salps and pteropods, and the possible origin of the deep water flora and olive-green "cells". *Marine Biology,* 62, 263-273.

SILVER, M.W., M.M. GOWING and P.J. DAVOLL (1986) The association of photosynthetic picoplankton and ultraplankton with pelagic detritus through the water column (0-2000m) *Canadian Bulletin of Fisheries and Aquatic Science,* 214, 311-341.

SILVER, M.W., M.M. GOWING, D.C. BROWNLEE and J.O. CORLISS (1984) Ciliated Protozoa associated with oceanic sinking detritus, *Nature, London,* 309, 246-248.

SILVER, M.W., A.L. SHANKS and J.D. TRENT (1978) Marine snow: microplankton habitat and source of small-scale patchiness in pelagic populations. *Science,* 201, 371-373.

SIMPSON, W.R. (1982) Particulate matter in the oceans - sampling methods, concentration, size distribution and particle dynamics. *Annual Review of Oceanography and Marine Biology,* 20, 119-172.

SKJOLDAL, H.R. and P. WASSERMANN (1986) Sedimentation of particulate organic matter and silicium during spring and summer in Lindaspollene, Western Norway. *Marine Ecology - Progress Series,* 30, 49-63.

SMAYDA, T.J. and B.J. BOLEYN (1966) Experimental observations of the flotation of marine diatoms. III. *Bacteriastrum hyalinium* and *Chaetoceros lauderi. Limnology and Oceanography,* 11, 35-43.

SMETACEK, V.S. (1985) Role of sinking diatom life-history cycles: ecological, evolutionary and geological significance. *Marine Biology,* 84, 239-251.

STUMM, W. and J.P. MORGAN (1981) *Aquatic Chemistry,* Wiley-Interscience, 731pp.

SUZUKI, N. and K. KATO (1953) Studies on suspended materials. Marine snow in the sea. I. Sources of marine snow. *Bulletin of the Faculty of Fisheries of Hokkaido University,* 4, 132-135.

SYRETT, P.J. (1962) Nitrogen assimilation. In: *Physiology and Biochemistry of Algae,* R.A. LEWIN, editor, Academic Press, 171-188.

TAGO, Y. and K. AIDA (1977) Exocellular mucopolysaccharide closely related to bacterial floc formation. *Applied and Environmental Microbiology,* 34, 308-314.

TAGUCHI, S. (1982) Seasonal study of fecal pellets and discarded houses of appendicularia in a subtropical inlet, Kaneoha Bay, Hawaii. *Estuarine, Coastal and Shelf Science,* 14, 545-555.

TAKAHASHI, K. (1986) Seasonal fluxes of pelagic diatoms in the subarctic Pacific, 1982-1983. *Deep-Sea Research,* 33, 1225-1251.

TAYLOR, G.T., D.M. KARL and M.L. PACE (1986) Impact of bacteria and zooflagellates on the composition of sinking particles: an *in situ* experiment. *Marine Ecology - Progress Series,* 29, 141-155.

TRENT, J.D. (1985) *A study of macroaggregates in the Marine Environment,* PhD thesis, Scripps Institution of Oceanography, University of California, San Diego, 254pp.

TRENT, J.D. and J.K. ORZECK (1984) The use of a US Navy Deep-Diving System for marine biological research. In: *Divers, submersibles and marine science.* N.C. FLEMMING, editor, Memorial University of Newfoundland, Occasional Papers in Biology, 9, 35-43.

TRENT, J.D., A.L. SHANKS and M.W. SILVER (1978) *In situ* and laboratory measurements on macroscopic aggregates in Monterey Bay, California. *Limnology and Oceanography,* 23, 626-635.

TSUJITA, T. (1952) A preliminary study on naturally occurring suspended organic matter in water adjacent to Japan. *Journal of the Oceanographic Society of Japan,* 8, 3-4

VALLOM, J.K. and A.J. McLOUGHLIN (1984) Lysis as a factor in sludge formation. *Water Research,* 18, 1523-1528.

WAKEHAM, S.G., J.W. FARRINGTON, R.B. GAGOSIAN, C. LEE, H. DEBARR, G.E. NIGRELLI, B.W. TRIPP, S.O. SMITH and N.M. FREW (1980) Organic matter fluxes from sediment traps in the equatorial Atlantic Ocean. *Nature, London,* 286, 798-800.

WAKEHAM, S.G., C. LEE, J.W. FARRINGTON and R.B. GAGOSIAN (1984) Biogeochemistry of particulate organic matter in the oceans: results from sediment trap experiments. *Deep-Sea Research,* 31, 509-528.

WASSMANN, P. (1987) Sedimentation of organic matter and silicate out of the euphotic zone of the Barents Sea. *EOS,* 68, 1728.

WELLS, J.T. and A.L. SHANKS (1987) Observations and geological significance of marine snow in a shallow water, partially-enclosed marine embayment. *Journal of Geophysical Research,* 92, 13,185 - 13,190.

WIEBE, W.J. and L.R. POMEROY (1972) Microorganisms and their association with aggregates and detritus in the sea: a microscopic study. *Memorie dell' Instituto Italiano di Idrobiologia,* 29, Suppl. 325-352.

WILSON, W.B. and A. COLLIER (1972) The production of surface-active materials by marine phytoplankton cultures. *Journal of Marine Research,* 30, 15-26.

WITTEN, T.A. and M.E. CATES (1986) Tenuous structures from disorderly growth processes. *Science,* 232, 1607-1611.

YOUNGBLUTH, M.J. (1982) Utilization of a fecal mass as food by the pelagic mysis larva of the Penaeid shrimp *Solenocera atlantidis. Marine Biology,* 66, 47-51.

YOUNGBLUTH, M.J. (1984) Water column ecology: *in situ* observations of marine zooplankton from a manned submersible. In: *Divers, Submersibles and Marine Science.* N.C. FLEMMING, editor, Memorial University of Newfoundland Occasional Papers in Biology, 9, 45-57

ZUTIC, V., E. COSOVIC, E. MARCENKO and N. BIHARI (1981) Surfactant production by marine phytoplankton. *Marine Chemistry,* 10, 505-520.

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In situ settling behavior of marine snow[1]

Alice L. Alldredge and Chris Gotschalk
Department of Biological Sciences and Marine Science Institute, University of California, Santa Barbara 93106

Abstract

The settling velocities of undisturbed macroscopic aggregates known as marine snow were measured with SCUBA in surface waters off southern California and analyzed as a function of aggregate size, mass, and density. The mean settling velocity was 74±39 m d^{-1} for aggregates ranging from 2.4 to 75 mm in maximum length. Sinking rates in the field varied exponentially with aggregate size and dry weight and were consistently up to four times slower than rates measured in the laboratory.

The excess densities of the 80 aggregates examined were calculated from volume and dry weight and ranged over four orders of magnitude with a median of 1.4×10^{-4} g cm^{-3}. Aggregates of marine snow sank more slowly than predicted for either solid or porous spheres of equivalent volume and density, although their velocities were within the range expected for equivalent sinking prolate ellipsoids. No relationships between settling velocity and either excess density or particle shape were found. Drag coefficients of marine snow were also higher than predicted by theory for spheres of equivalent volume and density. These deviations from theoretical expectations may be partially explained by errors in the estimation of the excess densities of aggregates. Variability in the densities of the heterogeneous primary particles comprising marine snow (fecal pellets, clay-mineral particles, phytoplankton, molts, etc.) and the potential for buoyancy regulation by individual phytoplankton cells inhabiting aggregates make determination of excess density especially problematic.

Large, rapidly sinking particles are far less numerous than fine suspended particles in the pelagic zone of the sea. However, recent studies suggest that large particles are primarily responsible for the vertical transport of biogenic materials and elements through the water column (*see* Fowler and Knauer 1986). Although fecal pellets are a major source of large, rapidly sinking particles in some regions of the world's oceans (Angel 1984), in most other areas flocculent amorphous aggregates >0.5 mm in diameter, known as marine snow, appear to be the major source of particulate flux (Fowler and Knauer 1986).

Sinking aggregates transfer energy and nutrients from the surface mixed layer into the ocean interior and to the seafloor. The rate at which this transfer occurs depends primarily on the composition, size, abundance, and sinking rate of the particles. Although settling velocities of marine snow, ranging from 1 to 370 m d^{-1}, have been measured directly in both the laboratory (Silver and Alldredge 1981; Taguchi 1982; Gorsky et al. 1983) and the field (Shanks and Trent 1980) and estimated from in situ photographs (Billett et al. 1983; Lampitt 1985; Asper 1987), the relationships between settling velocity and aggregate properties such as size, mass, and density are not known. Accurate estimates of flux based on particle abundances in nature require information on size-specific sinking rates. Moreover, data on the settling behavior of aggregates are necessary in order to understand the quantitative impact of processes that alter aggregate size and density (consumption by grazers, dissolution, disaggregation, etc.) on the biogeochemical processes associated with particles in the water column. In this paper we present the first data on the settling behavior of undisturbed aggregates of marine snow in situ as a function of aggregate size, mass, and density. We discuss variations in this settling behavior from predicted theory and provide evidence that laboratory studies substantially overestimate sinking rates of marine snow in nature.

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Methods

Theoretical considerations—When a particle settles at a constant, or terminal, velocity through a fluid, the force of gravity pulling the particle downward is exactly balanced by the retarding drag force of the fluid flowing around the particle. The resulting force balance equation takes the form

$$V(\rho_a - \rho_f)g = \tfrac{1}{2}C_D A \rho_f U^2 \qquad (1)$$

where V is the volume of the particle in cm^3, ρ_a the density of the particle in g cm^{-3}, ρ_f the density of the fluid in g cm^{-3}, g the acceleration due to gravity or 980 cm s^{-2}, A the maximum cross-sectional area of the particle perpendicular to the direction of sinking in cm^2, U the settling velocity of the particle in cm s^{-1}, and C_D (the drag coefficient) a dimensionless number. For spherical particles, C_D is a function of Reynolds number (Re = dU/ν, where d is particle diameter in cm and ν is the kinematic viscosity of the fluid). At Reynolds numbers <0.5, Stokes' expression for a settling sphere is valid and $C_D \cong 24/\mathrm{Re}$ (White 1974). For nonspherical particles, such as marine snow, however, the drag coefficient becomes a complicated function of both shape and Reynolds number. This function must usually be determined empirically (*see* Tietjens 1957; Graf 1971; Komar and Reimers 1978). Rearranging Eq. 1 yields

$$U = (2g\Delta\rho V/\rho_f C_D A)^{1/2} \qquad (2)$$

where $\Delta\rho = (\rho_a - \rho_f)$. From Eq. 2 we would expect the terminal settling velocity of an aggregate of marine snow to be a function of the excess density of the particle, the ratio of volume and projected area (in the direction of settling), and the drag coefficient. We measured the physical properties of marine snow appropriate for elucidating these relationships.

Since the drag coefficient and, thus, settling velocity are a function of shape, we also required a coefficient that adequately describes the shape of an aggregate and how it departs from spherical. Most previous studies of the effects of shape on the settling of natural particles, including sediment grains (Komar and Reimers 1978) and small animals such as foraminifera (Fok-Pun and Komar 1983), have used the Corey shape factor (CSF) (Albertson 1953; *see* McNown and Malaika 1950):

$$\mathrm{CSF} = \frac{D_s}{(D_l D_i)^{1/2}} \qquad (3)$$

where D_s, D_l, and D_i are the smallest, largest, and intermediate axial diameters of the particle. For a spherical shape, CSF = 1. The further from spherical a particle becomes, the closer to 0 CSF becomes. McNown and Malaika (1950) found that the ratio of the principal-axis lengths was the best predictor for determining the effect of shape on the settling velocities of small ellipsoids, cones, cylinders, and prisms up to Re of ~10.

The simplest way to consider the effects of shape on settling velocity is to consider a sphere deformed to form a new shape of equivalent volume and density, encountering a different resistance from the fluid flow past it. This resistance differs from that of the original sphere by k, the coefficient of form resistance (also called the dynamic shape factor) where

$$k = \frac{U_s}{U} \qquad (4)$$

with U_s the sinking velocity of a sphere of equivalent volume and density and U the settling velocity of the particle. Theoretical derivation of k and further discussion of the effects of particle shape on it can be found elsewhere (McNown and Malaika 1950; Davis 1979; Hutchinson 1967). For ellipsoids of regular shape, k varies as a direct function of CSF. Most prolate (largest axial diameter parallel to flow) ellipsoids and all oblate (largest axial diameters perpendicular to flow) ellipsoids have a $k > 1$ and sink more slowly than equivalent spheres. The further from spherical the particles become the larger k becomes (McNown and Malaika 1950).

Empirical measurements—Settling velocities of individual aggregates of marine snow were measured both in situ and in the laboratory. Field measurements were made at depths of 10–15 m during 25 SCUBA

dives in the San Pedro Basin, California (4 km due east of Two Harbors, Catalina Island), in March and June 1986 and during two dives in the Santa Barbara Channel (6 km due south of the University of California, Santa Barbara) during July 1986. All dives were in late morning. We measured the settling velocities of 80 undisturbed aggregates of marine snow relative to a spot of dilute, neutrally buoyant fluorescein dye placed 3 cm below each particle. The powdered dye was mixed with seawater at depth so as to produce a solution of the same density as the seawater surrounding the aggregates. A SCUBA diver delivered the spot of dye (a few millimeters in diameter) from a dye ejector consisting of a hypodermic needle mounted on a 1-m-long, 2.4-cm-diameter plastic pipe (Fig. 1). The stock of this dye ejector rested against the diver's shoulder to stabilize the ejector and reduce vibration at its tip.

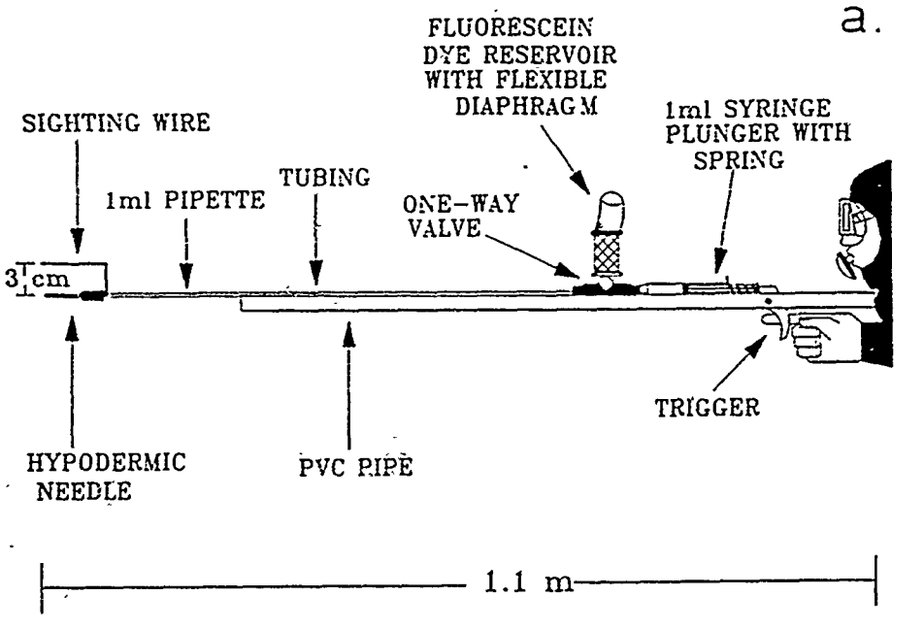
The 3-cm distance was determined by siting the bottom of the aggregate at the tip of a thin wire attached to the ejector exactly 3 cm above the release point of the dye (Fig. 1a). The dye spot congealed and stabilized in shape and size within 1–2 s after delivery. Several minutes were required for it to diffuse. With care, a diver could deliver a spot of dye, slowly pull the ejector back, and hang suspended 2–3 m from the aggregate without producing turbulence near the aggregate. Turbulence was easily detected by observing deformation of the dye spot. A second diver, located 7–8 m away, measured with a stopwatch the time required for the particle to sink to the dye spot, relying on visual cues from the first diver. This second diver then photographed the still undisturbed aggregate to provide a record of its size and shape using a Nikonos camera with a 1 : 1 or 3 : 1 close-up extension tube and framer. The aggregate was then collected in a 6-ml plastic cylinder for later determination of aggregate dry weight.

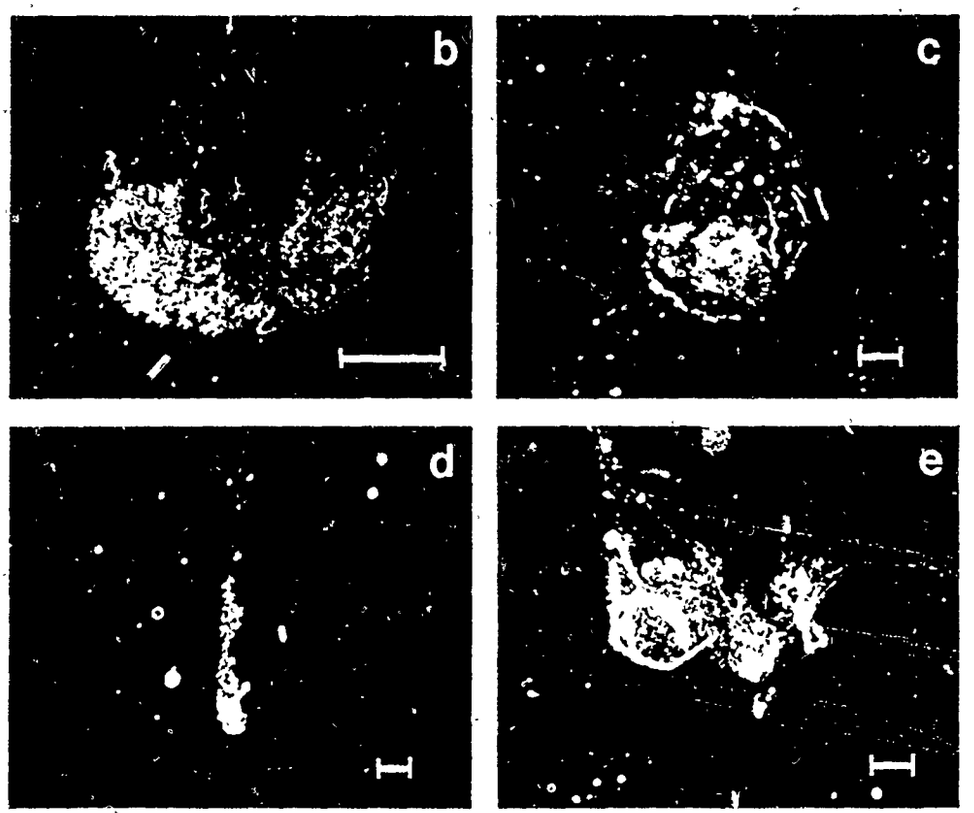
A single photograph was taken in a plane parallel to the direction of sinking (i.e. a side view) by orienting the particle at a predetermined focal distance from the camera lens demarcated by a thin wire frame. A transparent metric ruler photographed in the frame yielded scale. Turbulence produced by moving the camera after the first photograph altered the aggregate's shape and in some cases threatened to break the particle apart. These factors thwarted our attempts to obtain additional photographs in other planes. Direct observation of many aggregates in the field indicated, however, that most sinking aggregates are shaped like comets or prolate ellipsoids and are nearly symmetrical about their polar axes (parallel to the direction of sinking). Thus, a photograph oriented parallel to the plane of sinking allowed for the most accurate estimation of volume.

The settling velocities of 37 different aggregates were determined in the laboratory for comparison with field measurements. Aggregates of marine snow collected from 10-m depths in the Santa Barbara Channel were allowed to sink slowly out of the open bottom of their collecting cylinders into the top of an 8-cm-diameter, 2,000-ml graduated cylinder containing seawater from the depth of collection. Both the samples and the graduated cylinder were maintained in an environmental chamber at ambient seawater temperature (16°C), and settling rates were determined within 4 h of sample collection. Periodic injection of fluorescein dye into the settling chamber indicated that no convective currents were present. We timed the sinking of each aggregate past external markings on the graduated cylinder with a stopwatch. Each aggregate was then removed from the chamber with a pipette and placed on a filter for dry weight determination. Dry weight was used as the property of marine snow potentially least affected by collection and handling.

Physical characteristics of each sinking aggregate were determined as follows—

Dry weight: Each individual aggregate was filtered with 3 ml of surrounding seawater onto a preweighed Nuclepore filter (2.4-cm diameter, 0.40-μm pore size), rinsed quickly with distilled water and dried for a minimum of 24 h in a desiccator. Filters were reweighed to the nearest 0.1 μg on a Cahn electrobalance and the dry weights were corrected with 3-ml seawater blanks. Reweighing of some filters 10 d after placement in the desiccator indicated that all water was lost within the first 24 h.


a.
FLUORESCEIN DYE RESERVOIR WITH FLEXIBLE DIAPHRAGM
1ml SYRINGE PLUNGER WITH SPRING
SIGHTING WIRE
TUBING
1ml PIPETTE
ONE-WAY VALVE
3 cm
TRIGGER
HYPODERMIC NEEDLE
PVC PIPE
1.1 m


b
c
d
e

Diameter: The maximum diameter perpendicular to the direction of sinking was measured to the nearest 0.1 mm on the photographs.

Maximum length: The maximum length was measured to the nearest 0.1 mm on the photographs.

Projected area: Drag on a sinking particle may be correlated with the maximum cross-sectional area perpendicular to the direction of sinking. We calculated this projected area with the measured maximum cross-sectioned diameter assuming that this area was a circle. Photographs taken perpendicular to the direction of sinking would have yielded the projected area. Photographing small, fragile objects from directly above or below, however, is nearly impossible for a diver floating in open water. Moreover, such photographs would have yielded underestimates of volume since most aggregates were elongated along their polar axes.

We estimated the error involved in calculating the projected area from the maximum cross-sectional diameter using 30 three-dimensional clay models resembling the shapes of aggregates in our photographs. These models were 4–5 cm long, radially symmetrical, and molded to approximate the shape of the aggregates as seen from the side view in the photographs of the natural aggregates. The projected area of each model was determined from its maximal cross-sectional shadow perpendicular to the polar axis. That area was then compared with the calculated area of a circle having a diameter equal to the maximum cross-sectional diameter of the model. The 95% C.L. of the mean on our projected area measurements was ±19%.

Volume: Volume was calculated from the photograph of each aggregate, assuming that aggregates were symmetrical about their polar axis and that their volumes approximated ellipsoids or spheres. The few irregularly shaped aggregates, such as that shown in Fig. 1e, were divided into subunits resembling spheres, cylinders, or ellipsoids, and total volume was estimated by adding the volumes of these subunits. We also estimated the error of calculating volume from two-dimensional photographs using the clay models. We calculated the volume of these clay models from their two-dimensional shadows projected in the plane parallel to their polar axes and compared these calculated volumes with the actual displacement volumes of the models in water. These trials yielded a 95% C.L. on volumes of ±30%.

Porosity: Porosity is the fraction of an aggregate not occupied by solid matter and was needed to determine aggregate density. We calculated porosity, P, directly from the measurements of volume and dry weight with the equation:

$$P = 1 - \frac{W/\rho_s}{V} \tag{5}$$

where W is dry weight in g and ρ_s the density of the solid hydrated matter within the aggregate. We assumed $\rho_s = 1.23$ g cm^{-3} which is the wet density of euphausiid fecal pellets (Komar et al. 1981). Since zooplankton fecal pellets contain a representation of many of the types of particles found in marine snow including diatom frustules, clay-mineral particles, and intact cells, their wet density seemed a reasonable choice for the density of the solid matter within aggregates. By comparison, the density of dry cellulose is about 1.5 g cm^{-3} and that of living phytoplankton may be equal to seawater, about 1.025 g cm^{-3} (Smayda 1970). Since aggregates were generally >99% porous, our calculated porosities were not particularly sensitive to the value of ρ_s. Values of ρ_s 0.2 g cm^{-3} higher or lower than the value used altered porosity of our aggregates only negligibly.

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Fig. 1. Measurement of sinking rates of marine snow in situ. a. Dye ejector used by SCUBA diver to deliver neutrally buoyant dye spot below aggregate. b. Aggregate formed from senescent diatoms and diatom frustules (scale = 1 cm). c. Spherical mucus aggregate formed from the decomposing house of an appendicularian. d. Comet-shaped aggregate of unknown origin. e. Irregularly shaped aggregate of unknown origin containing numerous macrocrustacean fecal pellets (scale of c–e = 1 mm).

Excess density ($\Delta\rho$): The difference between the density of the aggregate and that of the surrounding seawater was calculated from

$$\Delta\rho = \frac{W}{V}\left(1 - \frac{\rho_f}{\rho_s}\right). \quad (6)$$

Seawater density was determined from ambient temperature and salinity according to Mamayev (1975). Salinity was measured with a Plessey Environmental Systems laboratory salinometer (model 6230N).

Significant functional relationships between the above variables were determined with methods of standard linear regression (Sokal and Rohlf 1969).

Results

Characteristics of marine snow—Of the 80 aggregates of marine snow studied in the field, 68 were collected in the San Pedro Basin at a salinity of 33.570‰, a temperature of 15.0°C, and a seawater density of 1.02488 g cm^{-3}. The remaining 12 were from the Santa Barbara Basin at a salinity of 33.642‰, a temperature of 16.0°C, and a seawater density of 1.02466 g cm^{-3}. Data from the two study sites were pooled.

The 80 aggregates of marine snow were highly variable in size, shape, and general appearance. The 12 aggregates from the Santa Barbara Basin were all flocculent conglomerates of living senescent diatoms, particularly chain-forming species, and frustules (Fig. 1b) which formed following a diatom bloom (*see* Smetacek 1985). Aggregates from the San Pedro Basin were of diverse origins and appearance. Some were the remains of appendicularian houses containing considerable gelatinous mucus (Fig. 1c). Most were aggregates of smaller particles, detritus, and fecal pellets. Shapes ranged from comets (Fig. 1d) to spheroids (Fig. 1c) to oblate spheres (Fig. 1b). Some of the aggregates had irregular shapes or contained abundant macrocrustacean (primarily euphausiid) fecal pellets (Fig. 1e). The shapes of some aggregates appeared to have been deformed by the flow of fluid around them as they sank (Fig. 1b, d). Sinking aggregates maintained a stable orientation in the water, and we observed no twisting or rotating as they sank.

Diameters of the aggregates ranged from 0.5 to 25.5 mm and maximum lengths from 2.4 to 75 mm. Aggregate volumes ranged from 3 to 6,000 mm^3 and were related to approximately the cube of aggregate diameter (Fig. 2A). Dry weights varied from 2 to 1,110 μg $aggregate^{-1}$ and also increased significantly with aggregate diameter (Fig. 2B). Projected areas ranged from 0.1 to 511 mm^2. Reynolds numbers ranged from 0.4 to 32.

The aggregates studied had very high porosities ranging from 97 to 99.9% with a mean of 99.5%. Porosity increased significantly with increasing particle diameter (Fig. 2C). We plotted the log of (1 − porosity), as did Kajihara (1971), in order to reveal the large range of porosities encountered (Fig. 2C).

The excess density ($\Delta\rho$) of the aggregates ranged over four orders of magnitude from 2.2×10^{-2} to 1.3×10^{-5} g cm^{-3} (Fig. 2D). The median was 1.4×10^{-4} g cm^{-3}. Only 20% of the aggregates had a $\Delta\rho > 1 \times 10^{-3}$ g cm^{-3} (Fig. 2D). If we assume that the interstitial water within the aggregates had the same density as the surrounding seawater, or 1.02488 g cm^{-3}, the median absolute density of the aggregates of marine snow collected at our study sites was 1.02502 g cm^{-3}. Excess density was highly correlated with aggregate size (Fig. 2D) despite the variable nature of the primary particles comprising the aggregates—including varying proportions of fecal pellets, mucus, molts, frustules, and other components. Although it appeared that diatom flocs might have a different excess density to size relationship than other types of marine snow, the slope of the regression line describing that relationship was not significantly different (ANCOVA test for equality of slope: Sokal and Rohlf 1969) from the slope of the regression line describing the excess density to size relationship for all of the other aggregates (Fig. 2D). The data set for diatom snow was small with high variability, however, so additional data may reveal a significant difference.

Settling velocities—Figure 3 displays the settling velocities of 80 aggregates of marine

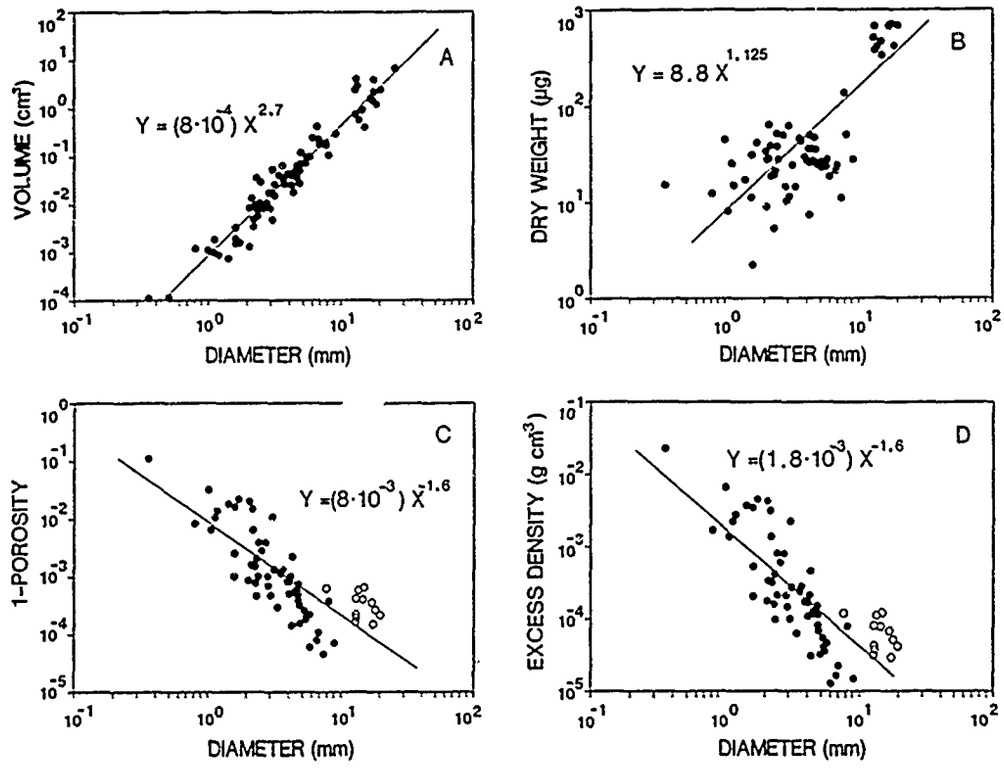


Fig. 2. Size characteristics of marine snow. A. Aggregate volume as a function of diameter (regression coefficient, rc, = 0.97; $P < 0.001$). B. Aggregate dry weight as a function of diameter (rc = 0.71; $P < 0.001$). C. Aggregate porosity as a function of diameter: O—diatom flocs; ●—all other marine snow regardless of origin (rc = 0.79; $P < 0.001$). D. Aggregate excess density as a function of diameter (rc = 0.79; $P < 0.001$), symbols as in panel C.

snow in situ as a function of various particle characteristics. Mean settling rate was 74±39 m d^{-1}. Sinking speed increased exponentially with particle diameter (Fig. 3A). Settling velocities increased with the increasing ratio of volume to projected area, as predicted by settling theory (Fig. 3B).

Settling rate in situ increased exponentially with aggregate dry weight (Fig. 3C). We compared the size-specific settling rates of marine snow determined in the laboratory with rates for similarly sized and shaped aggregates determined in situ with dry weight as an accurate measure of aggregate size. Despite minimal handling of particles, settling velocities measured in the laboratory were consistently higher, by up to four times, than those of similarly sized aggregates measured in situ (Fig. 3C). No significant statistical correlation could be found between sinking rate and dry weight of aggregates studied in the laboratory.

Although settling theory predicts that the sinking rate of an object settling in a fluid is a function of the excess density of the object, our data did not yield a significant relationship between excess aggregate density, as calculated by our methods, and sinking rate (Fig. 3D).

We measured or derived all of the dimensional terms in the force balance Eq. 1 for a settling object. Thus, we can directly calculate the drag coefficient, C_D, for each sinking aggregate. Calculations of C_D for our nonspherical aggregates can provide insight into the effects of shape and other variables that potentially alter the settling behavior of marine snow relative to sinking spheres.

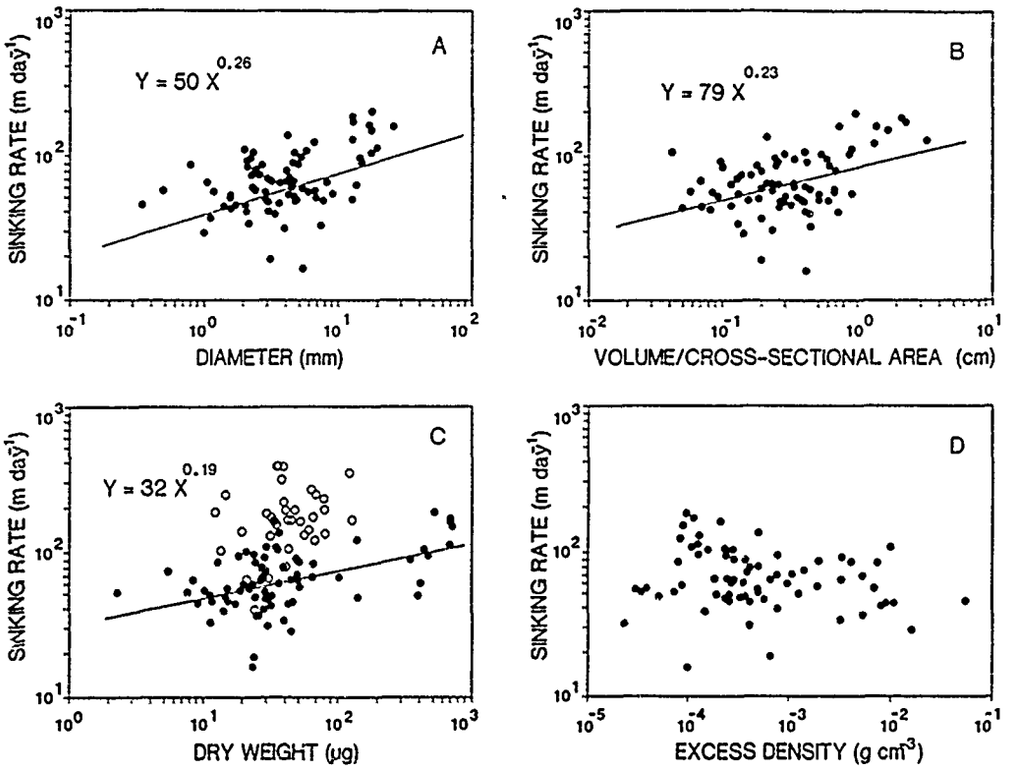


Fig. 3. Sinking rates of marine snow in situ (●) as a function of: A—aggregate diameter (regression coefficient, rc, = 0.61; $P < 0.001$); B—aggregate volume divided by projected area (rc = 0.42; $P < 0.001$); C—aggregate dry weight (rc = 0.60; $P < 0.001$) (O—sinking velocities determined in the laboratory); D—aggregate excess density.

Figure 4A presents C_D as a function of Reynolds number. Also plotted on Fig. 4A are the predicted curves for spheres assuming Stokes settling ($C_D = 24/\mathrm{Re}$) and an empirically determined relationship,

$$C_D = \frac{24}{\mathrm{Re}} + \frac{6}{1 + (\mathrm{Re})^{1/2}} + 0.4, \quad (7)$$

for solid spheres at higher Reynolds numbers (White 1974).

The drag coefficients of marine snow were consistently higher than those of spheres of equivalent Reynolds number (Fig. 4A), indicating that marine snow sank more slowly than equivalent spheres. Spheres sink more rapidly than most other shapes (Simpson 1982). Moreover, for nonspherical particles, C_D is a function of both Re and shape. Therefore, we investigated shape as a factor affecting settling velocity.

We hypothesized that the coefficient of form resistance, k, would also increase with increasing nonsphericity for marine snow particles. We determined the Corey shape factor, CSF, assuming that the particles were symmetrical about their polar axis; thus the two smallest axial diameters, D_s and D_i, were equal for prolate aggregates while D_i and D_l were equal for oblate aggregates. We calculated U_s, the settling velocity of a sphere of equivalent volume and density to each aggregate, with the force balance Eq. 2. In solving this equation for equivalent spheres, we used the equation for C_D empirically derived by White (Eq. 7) for spheres outside the Stokes range. Since excess density was size-specific, we used the empirically derived function of Fig. 2D to calculate the excess density of sinking spheres as a function of sphere diameter. Substitution of these parameters into the force balance Eq. 2 en-

abled us to obtain a solution for the settling velocity of a sphere with a volume and density equivalent to each aggregate of marine snow.

We found no significant relationship between k and the shapes of the aggregates (Fig. 4B). We also found no relationship when the analysis was restricted to oblate aggregates or prolate aggregates only. Aggregates whose shapes varied greatly from spherical, including long comets, had values of k very similar to those of nearly spherical particles. Some near-spherical aggregates sank considerably slower than equivalent spheres, with values of $k \gtrsim 3$, rather than the predicted value of 1. Previous studies on the effects of shape on C_D predict that particles with highly nonsperhical shapes would have higher drag coefficients (Komar and Reimers 1978), but we found no significant relationship between shape and C_D (Fig. 4C).

The C_D of marine snow was higher than predicted for sinking spheres of equivalent Reynolds number, since the settling velocity of marine snow was slower than that of equivalent spherical particles. Although we found no relationship between either drag coefficient or the coefficient of form resistance and the Corey shape factor, shape might still partially explain the high C_D observed. Other factors including permeability and surface roughness might also increase drag.

In order to elucidate these issues, we plotted the sinking velocity of particles of several different shapes and porosities having volumes and excess densities equivalent to those of our aggregates (Fig. 5). The equations for the settling velocities of a sphere, and a prolate ellipsoid with an aspect ratio of 4 : 1 [prolate ellipsoid (a) based on Stokes' law, Fig. 5] were obtained from Lerman et al. (1974). The settling velocities of equivalent spheres at Reynolds numbers outside the Stokes range (Re > 0.5) were obtained from White (1974) as described previously. The empirically derived curve for the settling velocity of equivalent prolate ellipsoids with aspect ratio of 4 : 1 at Re > 0.5 [prolate ellipsoid (b), Fig. 5] was obtained by solving Eq. 4 for the settling velocity, U, of a prolate ellipsoid by using the settling

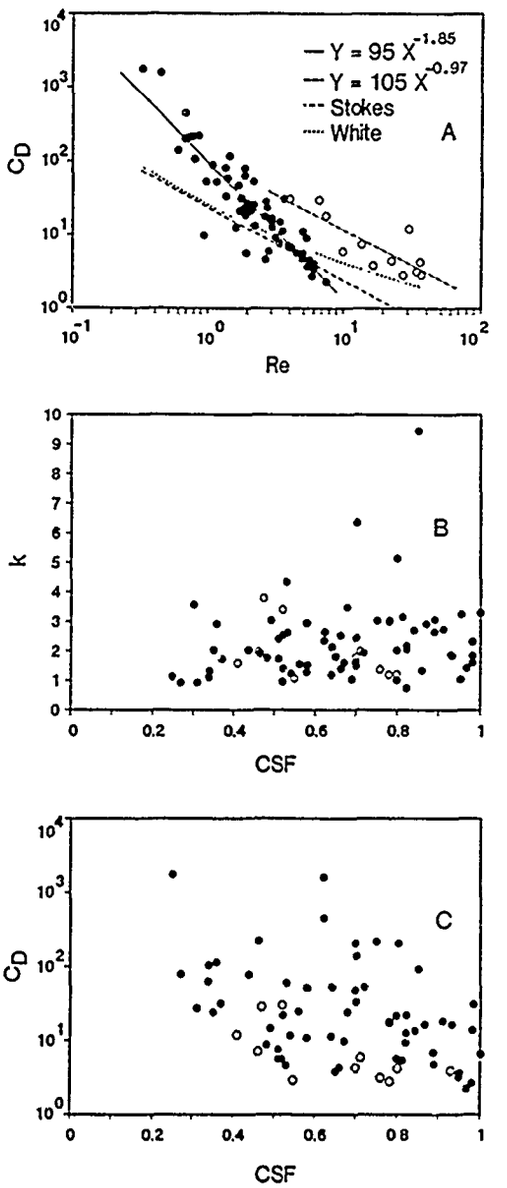


Fig. 4. Drag coefficient (C_D) and effects of shape (O—diatom snow; ●—marine snow of all other origins). A. C_D vs. Reynolds number (Re); White—C_D of sinking spheres determined empirically from White (1974); Stokes—C_D, as predicted by Stokes' equation. B. The dynamic shape factor, k, as a function of the Corey shape factor (CSF). CSF should equal 1 for perfect spheres (*see text for definitions*). C. Drag coefficient as a function of the Corey shape factor.

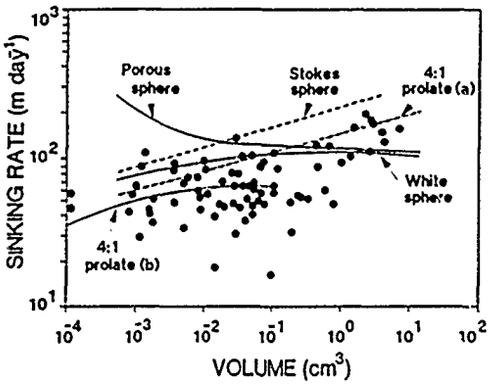


Fig. 5. Settling velocities of marine snow (●) and of various spheres and prolate ellipsoids with volumes and excess densities equal to those of the aggregates studied. Dashed lines are theoretical settling rates predicted by Stokes' ("Stokes sphere") or variations of Stokes' law for prolate ellipsoids, prolate 4:1 (a). Solid lines are settling velocities derived from empirical studies. "White sphere," solid spheres according to White (1974). Porous spheres predicted from empirical data of Matsumoto and Suganuma (1977). Prolate 4:1 (b) predicted from empirical data of White (1974) with k values from McNown and Malaika (1950) to correct for nonspherical shape.

velocities of sinking spheres (U_s) from White (1974) and k values for a prolate ellipsoid of 4 : 1 aspect ratio from McNown and Malaika (1950) who empirically determined k up to Re of ~10.

In order to estimate the potential effects of permeability on settling velocities of marine snow, we used data on permeable flocs of steel wool ranging in porosity from 90 to 99.7% and in size from 3 to 100 mm studied by Matsumoto and Suganuma (1977). The settling velocities of permeable steel wool flocs having volumes and densities equivalent to those of the marine snow were calculated by correcting sinking rates of solid equivalent spheres as determined with White's equation, using the size-specific correction factor, F, developed empirically by Matsumoto and Suganuma (1977).

Figure 5 demonstrates that aggregates sink considerably more slowly than do spheres and 4 : 1 prolate spheres of equivalent volume and excess density as predicted with Stokes' law. Aggregates sink, on average, only about half as fast, however, as would be expected for equivalent spheres at Reynolds numbers > 1. Porosity appears to increase, rather than decrease, sinking velocities within the range studied. The porous spheres of Matsumoto and Suganuma (1977) had rough, convoluted surfaces analogous to the surfaces of marine snow aggregates. Such convoluted surfaces might increase skin friction and thus total drag on the particle. Neither surface roughness nor permeability, however, appears to have increased the drag of Matsumoto and Suganuma's particles. Masliyah and Polikar (1980) also investigated the settling velocities of permeable spheres of milled plastic up to 2.5 cm in diameter and at Re up to 120. These spheres were 97% porous with highly convoluted and prickly surfaces. Their settling velocities also deviated only slightly from the settling velocities of equivalent impermeable spheres. Thus permeability and surface roughness probably have relatively little effect on the settling velocities of marine snow. Logan and Hunt (1987) concluded that surface roughness and flow through microbial aggregates probably did not contribute to observed deviations in settling velocity compared to predictions for impermeable spheres.

Discussion

Many different methods have been used to estimate the sinking rates of marine snow. Our sinking rates tended to be lower than those estimated from time-lapse photography of the seafloor (100–150 m d^{-1}: Billett et al. 1983; Lampitt 1985) and lower than those measured by ourselves and others in settling chambers in the laboratory (Silver and Alldredge 1981; Taguchi 1982; Gorsky et al. 1983). Collection and gentle transfer of fragile aggregates in the laboratory apparently result in slight collapse of the aggregate, with concurrent decreases in porosity, increases in density, and increases in settling velocity. Our sinking rates were similar to the range of 43–95 m d^{-1} reported by Shanks and Trent (1980), who measured sinking rates of aggregates in large cylinders in situ. In general, we observed similar sinking rates to those calculated by Asper (1986) from sediment trap data and particle abundances in the water column, although we never observed rates as low as the 1 m d^{-1} he reported from deep water of the Panama Basin. The highly porous, flocculent nature

of the material he observed may explain its slow sinking rate.

Previous investigations of the settling velocities of natural aggregated matter as a function of aggregate diameter vary somewhat from our results. Kajihara (1971) found $U = 160d^{0.57}$ and Gibbs (1985) reported $U = 248d^{0.78}$ respectively for reaggregated and estuarine flocs of <1 mm; we report $U = 50d^{0.26}$ for marine snow aggregates of larger size.

Previous investigations of the porosity and excess density of natural and manmade flocs have yielded results similar to those reported here. Assuming Stokes' law, Kajihara (1971) claculated the porosity of natural marine flocs <1 mm from settling velocities measured in the laboratory. He found that porosity increased with increasing particle size, although he reported porosities lower than ours for similarly sized particles. His particles were formed by reaggregation of smaller component particles and were probably more dense than natural flocs. Gibbs (1985) found that excess density of estuarine flocs <1 mm decreased with increasing floc size. Tambo and Watanabe (1979) also found decreasing excess density with increasing size for clay-aluminum flocs in the laboratory, although the excess density of these inorganic flocs was about three times that of marine snow aggregates of equivalent size. Our empirical result that porosity of marine snow increases in proportion to $d^{-1.6}$ corroborates the independently derived assumption of Logan and Hunt (1987) that the porosity of microbial flocs increases in proportion to $d^{-1.6}$.

We observed a large range and high scatter of settling velocities when plotted against diameter and dry weight—parameters that could be measured with minimal error. This scatter most likely arose from error in measuring sinking rates in situ (variations in exact sinking distance, etc.) and from the highly heterogeneous nature of the aggregates themselves. Aggregate size, shape, composition (i.e. presence of fecal pellets, mucus, diatoms, etc.), porosity, and rigidity were all highly variable in the population of natural and randomly chosen particles studied here, resulting in a large range of sinking rates. Plots of settling velocity vs. size for natural microscopic particles of sediment of uniform composition show scatter similar to that which we observed for macroscopic aggregates (Hawley 1982).

Nonspherical shapes result in decreased settling velocities of aggregates in all the cases examined in Fig. 5. In fact, when nonspherical shape is taken into account, macroscopic aggregates appear to sink within the range predicted for similar nonspherical particles sinking outside the Stokes range [Fig. 5, curve 4:1 prolate (b)]. Thus, deviations in the settling rate of marine snow from that of spheres at Reynolds numbers >1 may result partly from deviations from nonspherical shape. Why then did we not obtain significant relationships between settling velocity and either shape or excess density?

The coefficient of form resistence (k) and settling velocity both depend on excess density. Excess density is directly dependent on the primary particle density (*see Eq. 6*). We assumed that this primary particle density was a constant for all aggregates and equal to the wet density of euphausiid fecal pellets—the only density value we could find in the literature for a natural marine particle with components similar to those of marine snow. This assumption probably resulted in sufficient error to obscure the expected relationship between sinking and shape and excess density of marine snow.

Assumption of a constant primary particle density for all marine snow aggregates is problematic for two major reasons. First, the primary particles composing marine snow aggregates are not homogeneous. Diatom frustules, clay mineral particles, fecal pellets, living phytoplankton, protozoa, crustacean carapaces, and the various unidentifiable debris making up marine snow each have their own densities. Each aggregate is composed of varying percentages of these and other components yielding its own, unique total excess density. To accurately determine the excess density of each aggregate we would have to know not only the exact composition and size of each component particle comprising it, but also the densities of those components. Reliable data of this sort are not currently available for any of the complex types of natural particles composing marine snow.

Second, the problem of determining the

density of the component particles in marine snow is further confounded by the sizable percentage of living organisms comprising some aggregates (Silver et al. 1978). Many of these organisms can regulate their individual buoyancies. Diatom flocs represent an extreme type of marine snow where >90% of the particle may be living cells (Alldredge unpubl.). The density of diatoms varies with their physiological state and even with the time of day (Eppley et al. 1967; Smayda 1970). When nutrient replete, diatom cells may be neutrally buoyant. When nutrient stressed their excess density ranges up to 0.08 g cm^{-3} (Eppley et al. 1967). It is probable that we overestimated the excess density of the diatom flocs because we assumed they had a constant primary particle density similar to other aggregates that contain a much lower proportion of living cells. This assumption may have produced the apparent deviations in porosity, excess density, and drag coefficient observed for this type relative to other types of marine snow. Aggregates are not composed solely of inanimate particles, and thus, we would expect their overall density to depend, in part, on the density of their living components. This density may vary on a scale as short as hours, depending upon the nature of the community on the snow and its physiological state. Clearly additional research on the density of natural marine particles is needed to refine the relationships between sinking and aggregate characteristics reported here.

Relationships between sinking and both excess density and shape may also have been obscured by high scatter in the data and by the compounding of error in the measurements. Excess density is dependent on volume and dry weight—each with its own corresponding errors. The odd finding that some of the values for the drag coefficients of marine snow are lower than those predicted by Stokes' law may also arise from compounding of random error since the calculation of drag coefficient depends on several empirically determined variables including settling velocity, projected area, and excess density.

Data provided herein may allow estimation of the characteristics and flux of natural particles based on their size distributions in situ generated from photographs and survey cameras (*see* Asper 1987; Johnson and Wangersky 1985). Estimates of particulate flux based on collection of particles in the water column with in situ pumps have already provided considerable information about flux (Bishop et al. 1977, 1980). Care must be taken in calculating flux from predicted settling rates and measured particle abundances in the water column, however. Just because large particles sink does not necessarily mean that they sink out of the water column at the predicted rate. Accumulation of marine snow has been documented at a well-developed pycnocline in the subtropical Atlantic (Alldredge and Youngbluth 1985). Marine snow accumulating at the top of a density discontinuity could be reinjected back into the mixed layer by wind-mixing events. Reinjection of some proportion of the marine snow population back into the mixed layer would result in accumulation of marine snow in surface waters and potential residence times for these particles longer than would be predicted based on their sinking rates alone. Macrocrustacean fecal pellets, particles with settling velocities and excess densities considerably greater than those of marine snow, are known to have residence times in surface waters up to 10 d or more (Alldredge et al. 1987). Moreover, lateral advection appears responsible for high snow abundances at certain depths in the Panama Basin (Asper 1986); aggregates are carried horizontally as well as sinking vertically. Since flux calculations often assume that the particles immediately sink out of the system, calculations of particulate flux based on particle abundances and size distributions in situ and on predicted settling velocities could overestimate flux to the ocean interior and to the seafloor.

References

ALBERTSON, M. 1953. Effects of shape on the fall velocity of gravel particles, p. 243–261. Proc. 5th Iowa Hydraul. Conf.

ALLDREDGE, A. L., C. C. GOTSCHALK, AND S. MACINTYRE. 1987. Evidence for sustained residence of macrocrustacean fecal pellets in surface waters off southern California. Deep-Sea Res. 34: 1641–1652.

———, AND M. J. YOUNGBLUTH. 1985. The significance of macroscopic aggregates (marine snow) as sites for heterotrophic bacterial production in the

mesopelagic zone of the subtropical Atlantic. Deep-Sea Res. 32: 1445–1456.

ANGEL, M. V. 1984. Detrital organic fluxes through pelagic ecosystems, p. 425–516. *In* Flows of energy and materials in marine ecosystems, theory and practice. NATO Conf. Ser. 4, Mar. Sci. V. 13. Plenum.

ASPER, V. L. 1986. Accelerated settling of marine particulate matter by "marine snow' aggregates. Ph.D. thesis, Mass. Inst. Technol./Woods Hole Oceanogr. Inst. WHOI-96-12. 189 p.

———. 1987. Measuring the flux and sinking speed of marine snow aggregates. Deep-Sea Res. 34: 1–18.

BILLETT, D. S. M., R. S. LAMPITT, A. L. RICE, AND R. F. C. MANTOURA. 1983. Seasonal sedimentation of phytoplankton to the deep-sea benthos. Nature 302: 520–522.

BISHOP, J. K. B., R. W. COLLIER D. R. KETTEN, AND J. M. EDMOND. 1980. The chemistry, biology and vertical flux of particulate matter from the upper 400 m of the Panama Basin. Deep-Sea Res. 27: 615–640.

———, J. M. EDMOND, D. R. KETTEN, M. P. BACON, AND W. B. SILKER. 1977. The chemistry, biology and vertical flux of particulate matter from the upper 400 m of the equatorial Atlantic Ocean. Deep-Sea Res. 24: 511–548.

DAVIS, C. N. 1979. Particle-fluid interaction. J. Aerosol Sci. 10: 477–513.

EPPLEY, R. W., R. W. HOLMES, AND J. D. H. STRICKLAND. 1967. Sinking rates of marine phytoplankton measured with a fluorometer. J. Exp. Mar. Biol. Ecol. 1: 191–208.

FOK-PUN, L., AND P. D. KOMAR. 1983. Settling velocities of planktonic foraminifera: Density variations and shape effects. J. Foram. Res. 13: 60–68.

FOWLER, S. W., AND G. A. KNAUER. 1986. Role of large particles in transport of elements and organic compounds through the oceanic water column. Prog. Oceanogr. 16: 147–194.

GIBBS, R. J. 1985. Estuarine flocs: Their size, settling velocity and density. J. Geophys. Res. 90: 3249–3251.

GORSKY, G., N. S. FISHER, AND S. W. FOWLER. 1983. Biogenic debris from the pelagic tunicate, *Oikopleura dioica*, and its role in the vertical transport of a transuranium element. Estuarine Coastal Shelf Sci. 18: 13–23.

GRAF, W. H. 1971. Hydraulics of sediment transport. McGraw-Hill.

HAWLEY, N. 1982. Settling velocity distribution of natural aggregates. J. Geophys. Res. 87: 9489–9498.

HUTCHINSON, G. E. 1967. A treatise on limnology. V. 2. Wiley.

JOHNSON, B. D., AND P. J. WANGERSKY. 1985. A recording backward scattering meter and camera system for examination of the distribution and morphology of macroaggregates. Deep-Sea Res. 32: 1143–1150.

KAJIHARA, M. 1971. Settling velocity and porosity of large suspended particles. J. Oceanogr. Soc. Jpn. 27: 158–162.

KOMAR, P. D., A. P. MORSE, AND L. F. SMALL. 1981. An analysis of sinking rates of natural copepod and euphausiid fecal pellets. Limnol. Oceanogr. 26: 172–180.

———, AND C. E. REIMERS. 1978. Grain shape effects on settling rates. J. Geol. 86: 193–209.

LAMPITT, R. S. 1985. Evidence for the seasonal deposition of detritus for the deep-sea floor and its subsequent resuspension. Deep-Sea Res. 32: 885–897.

LERMAN, A., L. DEVENDRA, AND M. F. DACEY. 1974. Stokes' settling and chemical reactivity of suspended particles in natural waters, p. 17–47. *In* R. J. Gibbs [ed.], Suspended solids in water. Plenum.

LOGAN, B. E., AND J. R. HUNT. 1987. Advantages to microbes of growth in permeable aggregates in marine systems. Limnol. Oceanogr. 32: 1034–1048.

MCNOWN, J. S., AND J. MALAIKA. 1950. Effects of particle shape on settling velocity at low Reynolds numbers. Trans. Am. Geophys. Union 31: 74–82.

MAMAYEV, O. I. 1975. Temperature-salinity analysis of world ocean waters. Elsevier.

MASLIYAH, J. H., AND M. POLIKAR. 1980. Terminal velocity of porous spheres. Can. J. Chem. Eng. 58: 299–302.

MATSUMOTO, K., AND A. SUGANUMA. 1977. Settling velocity of a permeable model floc. Chem. Eng. Sci. 32: 445–447.

SHANKS, A. L., AND J. D. TRENT. 1980. Marine snow: Sinking rates and potential role in vertical flux. Deep-Sea Res. 27: 137–144.

SILVER, M. W., AND A. L. ALLDREDGE. 1981. Bathypelagic marine snow: Deep-sea algal and detrital community. J. Mar. Res. 39: 501–530.

———, A. L. SHANKS, AND J. D. TRENT. 1978. Marine snow: Microplankton habitat and source of small-scale patchiness in pelagic populations. Science 201: 371–373.

SIMPSON, W. R. 1982. Particulate matter in the oceans—sampling methods, concentration, size distribution and particle dynamics. Oceanogr. Mar. Biol. Annu. Rev. 20: 119–172.

SMAYDA, T. R. 1970. The suspension and sinking of phytoplankton in the sea. Oceanogr. Mar. Biol. Annu. Rev. 8: 355 p. Allen & Unwin.

SMETACEK, V. S. 1985. Role of sinking in diatom life-history cycles: Ecological, evolutionary and geological significance. Mar. Biol. 84: 239–251.

SOKAL, R. R., AND F. J. ROHLF. 1969. Biometry. Freeman.

TAGUCHI, S. 1982. Seasonal study of fecal pellets and discarded houses of appendicularia in a subtropical inlet, Kaneohe Bay, Hawaii. Estuarine Coastal Shelf Sci. 14: 545–555.

TAMBO, N., AND Y. WATANABE. 1979. Physical characteristics of flocs—1. The floc density function and aluminum floc. Water Res. 13: 409–419.

TIETJENS, O. G. 1957. Applied hydro- and aeromechanics. Dover.

WHITE, F. M. 1974. Viscous fluid flow. McGraw-Hill.

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RAPID RESPONSE PAPER

Direct observations of the mass flocculation of diatom blooms: characteristics, settling velocities and formation of diatom aggregates

A. L. ALLDREDGE*† and C. C. GOTSCHALK†

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Abstract—Blooms of chain-forming marine diatoms were observed in the process of aggregating into centimeter-sized flocs of marine snow in surface waters of the Santa Barbara Channel, California. These aggregates were composed of a rich assemblage of living, actively photosynthesizing diatoms dominated by the setose genus *Chaetoceros* and by chain-forming *Nitzschia* spp. Flocculation of one bloom occurred in as little as 24 h, and bloom flocculation apparently was not triggered by nitrogen-limitation. Marine snow of diatom origin was also abundant during spring, summer and early autumn throughout the Southern California Bight, suggesting that diatom flocculation is a seasonally significant source of marine snow. Resting spores rarely occurred within either newly formed or aged diatom flocs. The mean *in situ* settling velocity (± S.D.) of newly formed flocs was 117 ± 56 m d^{-1}, two orders of magnitude faster than unaggregated *Chaetoceros*. Rapid, episodic export of surface-derived primary production to the ocean bottom via mass flocculation and settlement of diatom blooms can occur prior to consumption by pelagic grazers and significantly effects marine food webs, oceanic flux processes, and diatom biology.

INTRODUCTION

RECENT evidence from sediment traps (HONJO, 1982; SMETACEK, 1985; TAKAHASHI, 1986) and *in situ* photographs of the sea floor (BILLETT *et al.*, 1983; RICE *et al.*, 1986) suggests that significant vertical export of primary production from the upper ocean to the deep sea must occur as episodic, seasonal events following phytoplankton blooms. In temperate, polar, and coastal seas this rapidly sinking phytoplankton is often dominated by diatoms that reach the sea floor relatively intact without being ingested by zooplankton (TAKAHASHI, 1986; v. BODUNGEN *et al.*, 1986; see SMETACEK, 1985 for review). The arrival of uningested phytoplankton at depth often lags only days behind blooms at the ocean surface (BILLETT *et al.*, 1983). Since single cells and chains sink far too slowly for such rapid transport, it has been hypothesized that diatoms, in particular, must sink in the form of large, quickly settling flocs of marine snow, amorphous aggregates 0.5 mm or greater in diameter (SMETACEK, 1985; TAKAHASHI, 1986). This hypothesis has been confirmed by descriptions of diatom aggregates in nature (ALLDREDGE and SILVER, 1988) and by photographs taken *in situ* of a diatom bloom flocculating into millimeter-sized aggregates in a small coastal bay (KRANCK and MILLIGAN, 1988).

* Department of Biological Sciences and † Marine Science Institute, University of California, Santa Barbara, CA 93106, U.S.A.

Episodic removal of uningested phytoplankton from surface waters as large aggregates may have significant impacts on both pelagic and benthic food webs, and on oceanic flux processes. The rapid mass sedimentation of diatom blooms to the sea floor may also represent a major global sink for carbon (WALSH, 1983) and a significant, although as yet uninvestigated, aspect of diatom biology. Using SCUBA, we have observed blooms of living, chain-forming diatoms aggregating into centimeter-sized flocs of marine snow in surface waters off southern California. Herein, we present the first empirical descriptions of the taxonomic composition, characteristics, formation, and settling velocities of diatom flocs in nature, and discuss the significance of diatom flocculation as a source of marine snow.

METHODS

Using SCUBA (ALLDREDGE, 1979), we directly observed dense blooms of chain-forming diatoms in the process of flocculating into macroscopic aggregates of marine snow in surface waters of the Santa Barbara Channel, California, on four occasions during 1986 and 1988. On three of these sampling days the abundance of flocs larger than 2 mm was measured visually by divers as described in ALLDREDGE (1979), diatom flocs were hand-collected individually in 6 or 20 ml polypropylene cylinders from depths of 10–25 m. Surrounding aggregate-free seawater was collected in 20 ml cylinders.

At each station, primary production and Chl *a* content of diatom flocs and surrounding seawater was measured at midday within 90 min of collection. Multiple measurements on each floc were achieved by gently disrupting each floc in a tissue grinder and then splitting it into two, 2 ml aliquots. Comparisons of carbon fixation rates per unit dry weight of disrupted and intact diatom flocs, and SEM examination of cell integrity indicated that gentle disruption did not result in reduction of photosynthetic capacity or cell breakage. ^{14}C-bicarbonate was added to one aliquot of each of 30 individual aggregates and to five, 2 ml surrounding seawater samples at a final ^{14}C concentration of 0.4 μCi ml^{-1}. The samples were incubated for 2 h in an environmental chamber at ambient seawater surface temperature (11–15°C) and at light levels of 150 μEin m^{-2} s^{-1}. Following incubation, samples were filtered onto 25 mm diameter, 0.4 μm Nucleopore filters, rinsed, and placed in a scintillation vial for later ^{14}C determination on a LKB Liquid Scintillation Counter, Model 1217. Carbon fixation was corrected for dark fixation by subtracting the mean value of five controls each of seawater or aggregates incubated with DCMU (3-(3,4-dichlorophenyl)-1, 1, dimethylurea) as described in PREZELIN and ALLDREDGE (1983).

The remaining 2 ml aliquot of each sample was filtered onto a 25 mm Whatman GF/F glass fiber filter for determination of Chl *a* and phaeopigments using standard methods (PARSONS *et al.*, 1984). Background seawater blanks of ^{14}C uptake or Chl *a* were subtracted from all aggregate samples.

The dry weight of 30 individual aggregates, each in 2 ml of surrounding seawater, and of five, 2 ml seawater blanks was determined at each station by pipetting each sample onto a pre-weighed nucleopore filter (25 mm diameter, 0.4 μm pore size). Filters were rinsed rapidly with distilled water, dried for 2 weeks in a dessicator and reweighed to the nearest 0.1 μg on a Cahn Electrobalance, Model 4600.

Concentrations of nitrate and ammonium within diatom flocs and in the surrounding seawater also were determined at each station from replicated 15 ml samples collected

directly *in situ* in cleaned 20 ml syringes. Diatom floc samples for nutrient analysis contained eight aggregates each. Samples were filtered through clean, sterile 0.2 μm cellulose membrane filters within 30 min of collection to remove particulate matter. Filtrates for nitrate were frozen for later analysis using the flow injection method of JOHNSON and PETTY (1983). Filtrates for ammonia were immediately analysed spectrophotometrically with a 10 cm light path using standard methods (PARSONS *et al.*, 1984).

Fifty ml of surrounding seawater and 10 aggregates from each station were preserved in 2% buffered formalin for later microscopic examination. The taxonomic composition of diatom flocs was determined from microscopic examination of slides prepared according to HEWES and HOLM-HANSEN (1983), or mounted in Pleurax mounting media as described in CUPP (1943).

On 25 July 1986, we measured the size-specific settling velocity of 14 undisturbed, newly formed diatom flocs directly *in situ* by measuring the time required for each floc to sink to a spot of neutrally bouyant fluorescein dye placed 3 cm below it as described in detail in ALLDREDGE and GOTSCHALK (1988). Floc diameter was determined from *in situ* photographs of the undisturbed aggregates (ALLDREDGE and GOTSCHALK, 1988).

Although we observed diatom blooms during actual flocculation only in the Santa Barbara Channel, we encountered abundant marine snow of diatom origin at 5 of 14 stations in the Southern California Bight during two cruises of the R.V. *Point Sur* in April and September, 1987, and at one additional station in the Santa Barbara Basin. At each of these stations we measured floc abundances *in situ* and the primary production, pigments, dry weight, nitrate and ammonium content of flocs and surrounding seawater as described above. Incubations were done in flowing seawater at ambient seawater surface temperature (15–16°C) in natural light on deck using neutral density filters to reduce the light to 150 μm Ein m^{-2} s^{-1}.

RESULTS

Diatom blooms in the process of flocculating occurred as dense suspensions of living, chain-forming species near the surface. The chains became increasingly aggregated with depth, and at 10–25 m all the visible diatoms existed as mm to cm-sized flocs. Abundances of newly formed flocs at 10–25 m ranged from 0.5 to 12.9 flocs l^{-1} (Table 1).

We observed diatom blooms in the process of flocculating in the mixed layer in both the presence and absence of wind. However, in the absence of wind, flocculation was more cleanly and obviously stratified with depth. For example, on 25 July 1986, no wind was present and the surface was calm and glassy. Microscale turbulence, discernible by observing the positions of particles relative to each other in the water column, was not visually detectable by divers. At 5 m the bloom was completely suspended as single cells and chains of cells. At 10 m many of the suspended chains had begun to aggregate into small flocs up to 10 mm in diameter, although suspended chains were still visible and abundant in the seawater around the flocs. At 15 m, all of the visible chains were aggregated into cm-sized flocs and seawater between the flocs contained few visible diatom chains.

Newly formed diatom flocs sampled during all the blooms consisted of loose assemblages of living, chain-forming diatoms (Fig. 1A) dominated by the setose genus, *Chaetoceros*, especially by *Ch. debilis* and *Ch. radicans*, a species with bristles on its setae (Fig. 1D). Setae were usually tangled within the flocs. Additional *Chaetoceros* species

Table 1. Mean characteristics (±S.D.) *of diatom aggregates from surface waters off southern California sampled during and after bloom flocculation. UD, undetectable; agg., aggregate; – no data available*

	During bloom flocculation			Post bloom flocculation					
	Santa Barbara Basin*			San Nicholas Island†			Santa Cruz Basin‡		California Current§
	11 Feb.‖	10 May‖	13 May‖	4 March	6 April	7 April	8 April	9 April	29 Sept.
Abundance (agg. l^{-1})	1.0	13	10	0.5	1.0	1.1	1.2	0.8	1.7
1° production (ng C $agg.^{-1}$ h^{-1})	20 ± 13	460 ± 230	578 ± 111	591 ± 336	8 ± 33	49 ± 33	233 ± 124	37 ± 22	55 ± 57
Chl *a* (ng $agg.^{-1}$)	42 ± 49	244 ± 122	190 ± 40	124 ± 78	3 ± 1	13 ± 5	138 ± 106	96 ± 16	8 ± 8
1° prod./Chl *a* (ng C ng Chl a^{-1} h^{-1})	0.6 ± 0.7	1.9 ± 0.6	3.2 ± 0.7	4.7 ± 2.1	2.6 ± 0.6	2.3 ± 0.8	1.8 ± 0.6	0.4 ± 0.3	6.3 ± 2.2
% Phaeopigments (phaeo./total Chl)	28 ± 5	19 ± 1	8 ± 0.4	36 ± 5	32 ± 9	50 ± 11	68 ± 19	79 ± 30	47 ± 8
Dry weight (µg $agg.^{-1}$)	27 ± 18	55 ± 28	34 ± 2	106 ± 85	80 ± 7	36 ± 35	143 ± 76	61 ± 46	10 ± 7
NO_3^- (µg-at. N l^{-1})									
Surrounding seawater	UD	6.5	29	–	UD	UD	4.4	1.4	0.3
Aggregates	UD	–	22.5	–	0.05	UD	2.5	1.4	0.3
NH_4^+ (µg-at. N l^{-1})									
Surrounding seawater	0.4	–	0.6	0.2	UD	UD	0.4	0.4	UD
Aggregates	0.3	–	0.5	0.5	0.2	0.1	UD	UD	UD
Maximum potential flux (g dry wt m^{-2} d^{-1})	2.1	83.0	39.0	6.1	9.6	4.8	19.6	6.1	2.2

* Position (34°20′N, 119°49′W).
† 6 April position (32°37′N, 118°9′W); 7 April position (33°11′N, 119°10′W).
‡Position (33°43′N, 119°31′W).
§ Position (34°25′N, 121°1′W).
‖ 1988, all other dates in 1987.

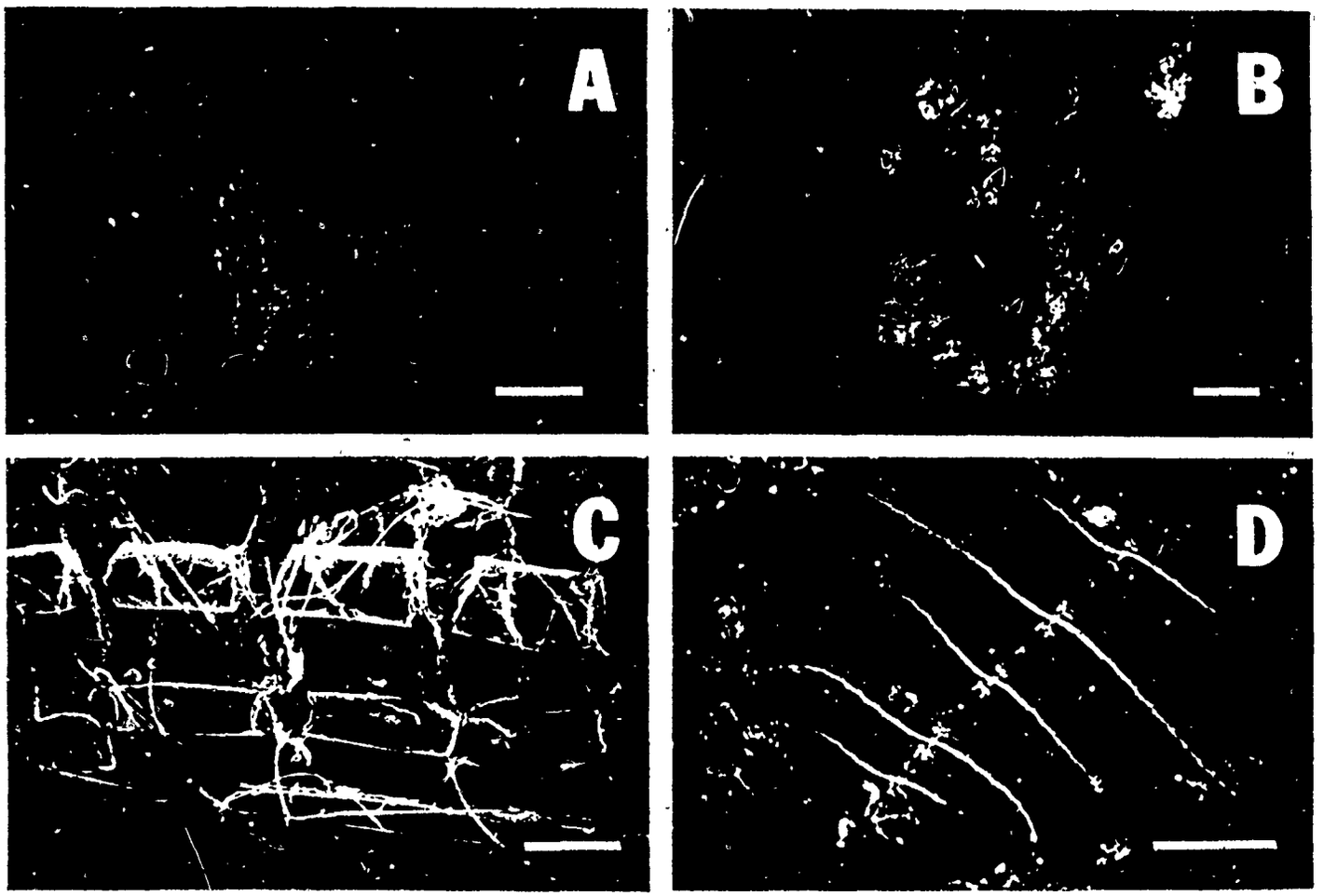


Fig. 1. Diatom flocs. (A) Newly formed floc with vertical aligned, captured chains trailing in its wake photographed *in situ*. Bar = 1 cm. (B) Compact, aged diatom floc containing scavenged microzooplankton fecal pellets. Bar = 1 cm. (C) Entangled spines of the dominant genus *Chaetoceros* facilitate aggregation. Bar = 10 μm. (D) Bristles on the setae of *Chaetoceros radicans*, the most abundant species observed in diatom flocs, facilitate entanglement. Bar = 30 μm.

Table 2. Taxonomic composition of diatom flocs sampled during and after bloom flocculation. Data expressed as mean (±S.D.) percent of total particles per aggregate (exclusive of bacteria). Miscellaneous particles included unidentifiable detritus, broken spines, armored dinoflagellates, zooplankton moults, and protozoans

	During bloom flocculation			Post bloom flocculation					
	Santa Barbara Basin*			San Nicholas Island			Santa Cruz Basin		California Current
	11 Feb.†	10 May†	13 May†	4 March	6 April	7 April	8 April	9 April	29 Sept.
Diatoms									
Chaetoceros spp.	52 ± 5	3[illegible] ± 6	68 ± 6	26 ± 3	26 ± 10	26 ± 13	73 ± 4	63 ± 15	47 ± 9
Bacteriastrum sp.	1	0	0	6 ± 2	1 ± 1	0	0	0	0
Nitzschia spp.	25 ± 7	51 ± 7	11 ± 3	10 ± 1	7 ± 4	8 ± 4	7 ± 3	3 ± 2	5 ± 4
Other centrics	13 ± 2	17 ± 1	14 ± 3	17 ± 3	<1	1 ± 1	5 ± 2	3 ± 2	7 ± 4
Other pennates	1 ± 1	0	0	6 ± 2	<1	<1	2 ± 2	1 ± 1	3 ± 1
Resting spores	1 ± 1	<1	5 ± 1	<1	2 ± 2	4 ± 3	1 ± 1	<1	<1
Total diatoms (%)	93 ± 1	99 ± 1	98 ± 1	65 ± 26	37 ± 4	40 ± 6	88 ± 4	70 ± 4	65 ± 4
Coccolithophorids	0	0	0	3 ± 2	3 ± 2	9 ± 7	1 ± 1	0	2 ± 1
Naked flagellates	8 ± 3	<1	<1	30 ± 12	48 ± 9	38 ± 15	3 ± 1	10 ± 5	29 ± 15
Fecal pellets	<1	<1	<1	1 ± 1	4 ± 2	4 ± 2	2 ± 1	11 ± 5	1 ± 1
Miscellaneous	<1	<1	<1	1 ± 1	8 ± 3	10 ± 5	6 ± 3	9 ± 3	3 ± 2

* Station positions same as Table 1.
† 1988, all other dates 1987.

included *Ch. affinis*, *Ch. didymus*, *Ch. curvisetus*, *Ch. peruvianus*, *Ch. concavicornis*, *Ch. subsecundus* and *Ch. difficilis*. *Ch. socialis*, a species embedded in a gelatinous matrix, was abundant on 10 and 13 May (Table 2).

The second most abundant genus in the flocs was chain-forming *Nitzschia*, including *N. pacifica*, *N. delicatissima* and *N. pungens*. Nine additional diatom genera, including *Bacteriastrum* spp. (also setose), *Skeletonema costatum*, *Thalassiosira* spp., *Thalassiothrix* spp., *Rhizosolenia hebetata*, *Schroderella delicatula*, *Eucampia* sp., *Cerataulina bergonii*, and *Actinoptychus* sp., coccolithophorids, naked flagellates, broken spines, and fecal pellets (Fig. 1) were also present within flocs (Table 2).

The mean Chl *a* content of newly formed flocs ranged from 42 to 244 ng aggregate^{-1} (Table 1). Phaeopigments ranged from 8 to 28% of total chlorophyll. High primary production per floc and high primary production per unit Chl *a* suggest that the diatoms within the newly formed flocs were healthy and metabolically active. Nitrate concentrations within the flocs and in the surrounding seawater were variable, ranging from undetectable to quite high. Ammonia concentrations were less variable ranging from undetectable concentrations to less than 1 µg-at. l^{-1} (Table 1).

We also encountered abundant marine snow of obvious diatom origin at 6 of 15 stations in the Southern California Bight and California Current (Tables 1 and 2). Although we did not observe diatom blooms in the process of flocculating at these stations, species of *Chaetoceros* and *Nitzschia* were always the dominant components within all the marine snow collected (Table 2). High phaeopigment ratios, up to 79% of total chlorophyll, indicated that most of the aggregates had not been formed recently. Moreover, most had higher proportions of both scavenged zooplankton fecal pellets and naked flagellates (Table 2; Fig. 1b) which are usually more abundant on aging marine snow (POMEROY *et al.*, 1984; see ALLDREDGE and SILVER, in press, for review). Resting spores, believed to form at the end of blooms (HARGRAVES and FRENCH, 1983), were rarely observed in either newly formed or aging diatom flocs from surface waters (Table 2).

The *in situ* sinking rate of newly formed diatom flocs increased exponentially with floc diameter (Fig. 2). The mean sinking velocity was 117 ± 56 m day^{-1} for flocs ranging from 19.5 to 75 mm in length. Sinking rates of flocs ranged from 50 to 200 m d^{-1}. We

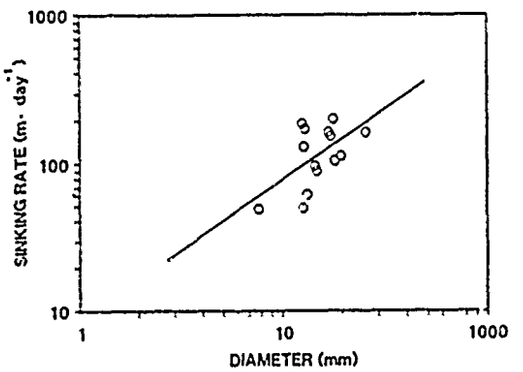


Fig. 2. Settling velocities of newly formed diatom flocs measured directly *in situ* as a function of the maximum diameter of the floc perpendicular to the direction of sinking. Regression equation: $Y = 8.4\ X^{0.95}$. Regression coefficient = 0.55, $P < 0.05$.

calculated the maximum potential vertical flux of diatom flocs possible at each station following bloom flocculation by multiplying the mean sinking rate per floc (117 m d^{-1}) by the mean floc abundance by the mean floc dry weight at each station. We assumed that all flocs would sink immediately out of the mixed layer, but since some flocs remain suspended, our calculations represent maximum potential rates. The maximum calculated flux at our stations ranged from 2.1 to 83.0 g dry wt m^{-2} d^{-1} (Table 1).

DISCUSSION

The existence of mass flocculation and settlement as a major stage in the successional sequence of diatom blooms was predicted by SMETACEK (1985) from evaluation of numerous sediment trap studies, *in situ* photographs of large flocs arriving at the sea floor (BILLETT *et al.*, 1983), and existing knowledge of diatom biology. KRANCK and MILLIGAN (1988) and ALLDREDGE and SILVER (1988) have since documented the existence of diatom flocculation with *in situ* photographs and direct observations of blooms in the process of flocculating. The results presented here are the first descriptions of the characteristics of these flocs and the conditions under which they form. Our observations indicate that mass flocculation of diatom blooms is a common occurrence off coastal California and a major source of marine snow in this area, especially during seasonal upwelling. Since diatom blooms occur over broad expanses of the ocean in association with upwelling and nutrient enrichment (GUILLARD and KILHAM, 1977), mass flocculation of diatom blooms is likely to have global significance.

The exact mechanism producing mass flocculation of diatom blooms are not yet clear. However, the extensive literature on particle aggregation in natural waters (STUMM and MORGAN, 1981; ALLDREDGE and SILVER, 1988) indicates that flocculation occurs in two steps: first, individual cells and chains must collide together, and second, following collision, they become stuck together. Brownian motion, differential settlement, and shear are the physical processes that collide all particles in the water column, including diatoms, together (MCCAVE, 1984). Diatom blooms may flocculate primarily via differential settlement. Nutrient-depleted cells generally sink more rapidly than nutrient-replete ones (SMAYDA, 1970), and SMETACEK (1985) suggested that those cells within a bloom which become nutrient depleted, sink differentially and become entangled with surrounding cells as they settle.

Our observations support differential settlement as a major process bringing diatoms together. We observed flocculation of blooms distinctly stratified with depth in the absence of visually detectable turbulence. Moreover, most newly formed flocs we observed in the field had a tail of vertically aligned, captured diatom chains and a cup-like or comet-like shape (Fig. 1), suggesting that slowly sinking suspended chains were captured as they were swept into the wakes of the more rapidly settling aggregates around them.

To form aggregates, colliding diatom cells also must bind or stick together. Setae, which both increase the effective size of the cells and enhance entanglement (especially those with bristles, Fig. 1D), appear to facilitate aggregation. Entangled setae bound many diatoms within flocs. Setose genera such as *Chaetoceros* and *Bacteriastrum*, the dominant components of diatom flocs off southern California, also dominate the second stage of diatom bloom succession, the stage immediately preceding rapid disappearance of diatoms from surface waters worldwide (GUILLARD and KILHAM, 1977). The presence

of setose species may be necessary for flocculation of diatom blooms. KRANCK and MILLIGAN (1988) also found *Chaetoceros* in diatom flocs in a coastal bay. Certainly this genus is a significant component of marine snow. BEERS *et al.* (1986) found *Chaetoceros* to be highly enriched on marine snow from the Southern California Bight, especially during late winter and early spring.

Nitzschia was the second most abundant genus within flocs and characteristic of all the flocs we observed. Although it has no setae, *Nitzschia* also may facilitate the sticking process. Diatom flocs containing high percentages of chain-forming *Nitzschia* visually appeared to contain more extracellular mucus. Perhaps copious exudate production by this and other diatom genera facilitates flocculation. Exopolymers are important flocculating agents in the formation of marine snow (ALLDREDGE and SILVER, 1988) and the production of extracellular polymers by phytoplankton increases under nutrient stress (MYKLESTAD, 1974; DEGENS and ITTEKOT, 1984). The role of exopolymer production in diatom flocculation remains to be investigated.

SMETACEK (1985) hypothesized that nutrient stress triggered diatom bloom flocculation. However, we found abundant nitrate both within flocs and in the surrounding seawater during two of the three flocculating blooms we sampled. Ammonia was detectable in the third. This suggests that flocculation may not be triggered by nitrogen limitation. This conclusion is supported by v. BODUNGEN *et al.* (1986), who found heavy sedimentation of diatoms, especially *Thalassiosira antarctica*, *Biddulphia* spp. and *Chaetoceros* spp. on the Northern Antarctic Peninsula Shelf in the presence of nutrients and by NOJI *et al.* (1986), who attributed abrupt sinking of a diatom bloom in the Kiel Bight to extremely low irradiance.

If differential settlement of nutrient-depleted cells is a major mechanism by which flocculation of the bloom begins, then silica limitation is one possible candidate requiring future investigation. BIENFANG *et al.* (1982) found that silica limitation, but not nitrogen or phosphorous limitation, resulted in increased sinking rates of three species of marine diatoms, including *Chaetoceros gracilis*. Although silica is rarely limiting (PAASCHE, 1980), it is known to become exhausted before N and P in intense diatom blooms during upwelling (WALSH *et al.*, 1971, 1977).

The highly stratified occurrence of diatom flocculation with depth in the absence of detectable turbulence in surface waters on one of our dives allows us to estimate the time required for flocculation to occur. Vegetative chains of *Chaetoceros* sink at maximum rates of approximately 4 m d^{-1} under nutrient stress (SMAYDA and BOLEYN, 1966). In the absence of turbulence a nutrient-depleted chain starting to sink differentially at a depth of 5 m, the depth where the bloom was observed to be completely suspended, would require about 18 h to sink to a depth of 8 m, the depth where some small flocs had begun to form. If, while sinking this distance, it became entangled with other chains, as we observed, its sinking rate would gradually accelerate until it reached the 120 m d^{-1} or more observed for cm-sized flocs. Since diatom flocs only 2–3 mm in diameter sink at rates of tens of meters per day (Fig. 2), only a few hours would be required for flocculating cells to settle the remaining distance from 8 to 15 m, the depth where nearly complete flocculation of the bloom was observed. These observations suggest that under some conditions diatom blooms may undergo mass flocculation in as little as 24 h.

We measured settling velocities of diatom flocs *in situ* that were two orders of magnitude faster than the mean sinking rate of 0.46–1.54 m d^{-1} reported for long chains of *Chaetoceros* in the laboratory (SMAYDA and BOLEYN, 1966). Our measured settling

velocities were very similar to the 175 m d^{-1} predicted for sedimenting diatoms by sediment trap studies (TAKAHASHI, 1986). Thus, mass flocculation of diatoms into large aggregates would facilitate rapid vertical transport of diatoms from surface waters at rates far higher than expected for unaggregated cells.

However, not all diatom flocs settle immediately from surface waters. Aging flocs, as evidenced by high abundances of naked flagellates and high concentrations of phaeopigments relative to newly-formed flocs, occurred at many of our stations. The presence of fecal pellets indicates that the flocs scavenge particles from the surrounding seawater as they form and settle. Turbulence may help retain some large aggregates in the mixed layer for many days where they age or disassociate (ALLDREDGE *et al.*, 1987).

We calculated the maximum potential flux expected at our stations assuming that all diatom flocs settle out immediately in order to determine if diatom flocculation could result in significant flux of primary production to the ocean bottom. The mean daily flux reported for waters off southern California ranges from 0.1 to 2 g dry wt m^{-2} d^{-1} (DUNBAR and BERGER, 1981; BRULAND *et al.*, 1981; NELSON *et al.*, 1987). This flux is one to two orders of magnitude lower than the maximum daily flux we predicted for the period immediately following bloom flocculation. The episodic nature of flocculation suggests that particulate flux from diatom blooms may be rarely sampled by sediment traps, perhaps explaining some of this discrepancy. However, the DUNBAR and BERGER (1981) traps were deployed for a 54 day period in the Santa Barbara Basin during March and April, a period of seasonal upwelling when diatom blooms would be expected to occur periodically. Yet 60–90% of the contents of their sediment traps were fecal pellets. Diatoms were common pellet components. Diatom flocs may be consumed in the water column or on the sea floor by vertical migrators such as euphausiids, which are capable of feeding on fluff on the benthos (MAUCHLINE and FISHER, 1969). Thus, despite the rapid settling rates of diatom aggregates, diatom production may be retained within the pelagic food web in coastal seas, such as the Southern California Bight, where some vertical migrators can forage on the bottom.

The significance of mass flocculation to diatom biology is not clear. SMETACEK (1985) hypothesized that flocculation maximized species survival over the long term. Aggregated cells sink out of warm nutrient-depleted water where their viability is low into dark, cold waters where they may remain viable for long periods of time as resting spores and vegetative resting stages. Later resuspension of these resting stages back into the mixed layer re-establishes surface populations. However, we observed very few resting cells within diatom flocs. Resting spore formation is triggered primarily by nitrogen limitation (HARGRAVES and FRENCH, 1983), a condition potentially existing within actively photosynthesizing diatom flocs in surface water. However, ammonia is generally highly enriched within marine snow in surface waters (SHANKS and TRENT, 1979; POMEROY *et al.*, 1984) and would become even more so as the aggregates sink into dark, deeper waters where their nitrogen-utilizing, algal inhabitants could not photosynthesize. Thus, resting spores would not necessarily be expected to form as flocs sink to depth.

Floc formation may be immediately adaptive to nutrient-stressed diatoms within blooms. The floc environment is probably a more favorable environment for nutrient-depleted cells than the surrounding seawater, since microbial communities within aggregates release abundant nutrients (ALLDREDGE and SILVER, 1988). Moreover, bacterial cells inhabiting porous sinking microbial aggregates have the potential for greater nutrient uptake than would be experienced were they freely suspended due to the

increased fluid flow past them (LOGAN and HUNT, 1987). This, and the occurrence of aggregation among a wide variety of organisms, including yeast and bacteria, in response to nutrient limitation (CALLEJA, 1984), suggests that diatom flocculation may confer some nutrient advantage as well. Since flocculation and mass settlement remove most of the diatoms from surface waters, the greatest advantage would be for those chains loosely caught in the wake of sinking flocs. These cells may become nutrient replete and fall off the flocs as they sink through the mixed layer and into the thermocline, thus re-establishing surface populations.

The predominance of diatom blooms and the abundance of diatomaceous sediments, particularly in temperate, subpolar and coastal seas (BERGER, 1976), indicate that the mass flocculation of diatoms into rapidly settling aggregates of marine snow is a phenomenon of potential global occurrence. In the open ocean rapid, episodic settlement of phytoplankton blooms may result in decoupling of pelagic food webs. Surface production settles as large flocs before it can be consumed by planktonic grazers and thus, becomes available primarily to near-bottom and benthic grazers and decomposers. Moreover, mass settlement produces episodic variation in the composition of particles contributing to vertical flux. The relatively unaltered phytodetritus reaching the sea floor following surface blooms varies significantly in composition from the ingested and recycled particulate matter present in the water column on most occasions (RICE *et al.*, 1986). The mass flocculation of diatom blooms has far-reaching implications for marine food webs, for oceanic flux processes, and for diatom ecology that are yet to be explored.

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REFERENCES

ALLDREDGE A. L. (1979) The chemical composition of macroscopic aggregates in two neritic seas. *Limnology and Oceanography*, 24, 855–866.

ALLDREDGE A. L. and C. GOTSCHALK (1988) *In situ* settling behavior of marine snow. *Limnology and Oceanography*, 33, 399–351.

ALLDREDGE A. L. and M. W. SILVER (1988) Characteristics, dynamics and significance of marine snow. *Progress in Oceanography*, 20, 41–82.

ALLDREDGE A. L., C. GOTSCHALK and S. MACINTYRE (1987) Evidence for sustained residence of macrocrustacean fecal pellets in surface waters off Southern California. *Deep-Sea Research*, 34, 1641–1652.

BEERS J. R., J. D. TRENT, F. M. H. REID and A. L. SHANKS (1986) Macroaggregates and their phytoplanktonic components in the Southern California Bight. *Journal of Plankton Research*, 8, 475–487.

BERGER W. H. (1976) Biogenous deep sea sediments: production, preservation and interpretation. In: *Chemical oceanography*, Vol. 5, J. P. RILEY and R. CHESTER, editors, Academic Press, pp. 265–388.

BIENFANG P. K., P. J. HARRISON and L. M. QUARMBY (1982) Sinking rate response to depletion of nitrate, phosphate, and silicate in four marine diatoms. *Marine Biology*, 67, 295–302.

BILLETT D. S. M., R. S. LAMPITT, A. L. RICE and R. F. C. MANTOURA (1983) Seasonal sedimentation of phytoplankton to the deep sea benthos. *Nature*, 302, 520–522.

BODUNGEN B. V., V. S. SMETACEK, M. M. TILZER and B. ZEITZSCHEL (1986) Primary production and sedimentation during spring in the Antarctic Peninsula region. *Deep-Sea Research*, 33, 177–194.

BRULAND K. W., R. P. FRANKS, W. M. LANDING and A. SOUTAR (1981) Southern California inner basin sediment trap calibration. *Earth and Planetary Science Letters*, 53, 400–408.

CALLEJA G. B. (1984) *Microbial aggregation*. CRC Press Inc., 276 pp.

CUPP E. E. (1943) *Marine phytoplankton diatoms of the west coast of North America*. University of California Press, 237 pp.

DEGENS E. T. and V. ITTEKOT (1984) A new look at clay-organic interactions. *Mitteilungen Geologische-Paleontologische Institut, Universitat Hamburg*, 56, 229–248.
DUNBAR R. B. and W. H. BERGER (1981) Fecal pellet flux to modern bottom sediment of Santa Barbara Basin (California) based on sediment trapping. *Geological Society of America Bulletin*, Part I, 92, 212-218.
GUILLARD R. R. L. and P. KILHAM (1977) The ecology of planktonic diatoms. In: *The biology of diatoms*, D. WERNER, editor, Blackwell Scientific, Oxford, pp. 372–469.
HARGRAVES P. and F. W. FRENCH (1983) Diatom resting spores: significance and strategies. In: *Survival strategies of the algae*, G. A. FRYXELL, editor, Cambridge University Press, pp. 49–68.
HEWES C. D. and O. HOLM-HANSEN (1983) A method for recovering nanoplankton from filters for identification with the microscope: The filter–transfer–freeze (FTF) technique. *Limnology and Oceanography*, 28, 389–394.
HONJO S. (1982) Seasonality and interaction of biogenic and lithogenic particulate flux at the Panama Basin. *Science*, 218, 883–884.
JOHNSON K. S. and R. L. PETTY (1983) Determination of nitrate and nitrite in seawater by flow injection analysis. *Limnology and Oceanography*, 28, 1260-1266.
KRANCK K. and T. G. MILLIGAN (1988) Macroflocs from diatoms: *in situ* photography of particles in Bedford Basin, Nova Scotia. *Marine Ecology Progress Series*, 44, 183–189.
LOGAN B. E. and J. HUNT (1987) Advantages of microbial growth in permiable aggregates in marine systems. *Limnology and Oceanography*, 32, 1034–1048.
MAUCHLINE J. and L. R. FISHER (1969) The biology of Euphausids. *Advances in Marine Biology*, 7, 1–421.
MCCAVE I. N. (1984) Size spectra and aggregation of suspended particles in the deep ocean. *Deep-Sea Research*, 31, 329–352.
MYKLESTAD S. (1974) Production of carbohydrates by marine planktonic diatoms. I. Comparison of nine different species in culture. *Journal of Experimental Marine Biology and Ecology*, 15, 261–274.
NELSON J. R., J. R. BEERS, R. W. EPPLEY, G. A. JACKSON, G. A. MCCARTHY and A. SOUTAR (1987) A particle flux study in the Santa Monica–San Pedro Basin off Los Angeles: particle flux, primary production, and transmissometer survey. *Continental Shelf Research*, 7, 307–328.
NOJI T., U. PASSOW and V. SMETACEK (1986) Interaction between pelagial and benthal during autumn in Kiel Bight. I. Development and sedimentation of phytoplankton blooms. *Ophelia*, 26, 333–349.
PAASCHE E. (1980) Silicon. In: *The physiological ecology of phytoplankton*, I. MORRIS, editor, University of California Press, pp. 259–284.
PARSONS T. R., Y. MAITA and C. M. LALLI (1984) *A manual of chemical and biological methods for seawater analysis*. Pergamon Press, New York, 173 pp.
POMEROY L. R., R. B. HANSON, P. A. MCGILLIVARY, B. F. SHERR, D. KIRCHMAN and D. DEIBEL (1984) Microbiology and chemistry of fecal products of pelagic tunicates: Rates and fates. *Bulletin of Marine Science*, 35, 426–439.
PREZELIN B. B. and A. L. ALLDREDGE (1983) Primary production of marine snow during and after an upwelling event. *Limnology and Oceanography*, 28, 1156–1167.
RICE A. L., D. S. M. BILLETT, J. FRY, A. W. G. JOHN, R. S. LAMPITT, R. F. C. MANTOURA and R. J. MORRIS (1986) Seasonal deposition of phytodetritus to the deep-sea floor. *Proceedings of the Royal Society of Edinburgh*, 88, 265–279.
SHANKS A. L. and J. D. TRENT (1979) Marine snow: microscale nutrient patches. *Limnology and Oceanography*, 24, 850–854.
SMAYDA T. J. (1970) The suspension and sinking of phytoplankton in the sea. *Oceanography and Marine Biology*, 8, 1–355.
SMAYDA T. J. and B. J. BOLEYN (1966) Experimental observations of the flotation of marine diatoms. III. *Bacteriastrum hyalinum* and *Chaetoceros lauderi*. *Limnology and Oceanography*, 11, 35–43.
SMETACEK V. S. (1985) Role of sinking in diatom life-history cycles. ecological, evolutionary and geological significance. *Marine Biology*, 84, 239–251.
STUMM W. and J. P. MORGAN (1981) *Aquatic chemistry*. Wiley-Interscience, New York, 731 pp.
TAKAHASHI K. (1986) Seasonal fluxes of pelagic diatoms in the subarctic Pacific, 1982–1983. *Deep-Sea Research*, 33, 1225–1251.
WALSH J. J. (1983) Death in the sea: Enigmatic phytoplankton losses. *Progress in Oceanography*, 12, 1–86.
WALSH J. J., J. C. KELLEY, R. C. DUGDALE and B. W. FROST (1971) Gross features of the Peruvian upwelling system with special reference to possible diel variation. *Investifacion pesq*, 35, 25–42.
WALSH J.J., T. E. WHITLEDGE, J. C. KELLEY, S. A. HUNTSMAN and R. D. PILLSBURY (1977) Further transition states of the Baja California upwelling ecosystem. *Limnology and Oceanography*, 22, 264–280.

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Potential for increased nutrient uptake by flocculating diatoms

B. E. Logan [1] and A. L. Alldredge [2]

[1] Environmental Engineering Program, Department of Civil Engineering, University of Arizona, Tucson, Arizona 85721, USA
[2] Department of Biological Sciences and Marine Science Institute, University of California, Santa Barbara, California 93106, USA

Abstract

Blooms of chain-forming diatoms commonly flocculate into centimeter-sized aggregates of living, vegetative cells following nutrient depletion in surface waters off southern California. We examined the hypothesis that diatom cells within aggregates experience increased nutrient uptake relative to unattached cells. We measured in situ settling velocities of 49 to 190 m d^{-1} and calculated porosities of 0.99931 to 0.99984 ($\pm < 0.03\%$) for 12, newly-formed diatom flocs ranging from 0.19 to 4.2 cm^3 in volume and 7 to 22 mm in equivalent spherical diameter. Using permeability–porosity relationships, we calculated intra-aggregate flow velocities of 20 to 160 $\mu m\ s^{-1}$. Although subject to considerable uncertainty, a Relative Uptake Factor analysis based on mass transfer equations suggests that diatoms fixed within aggregates undergoing gravitational settling can take up nutrients up to 2.1 ± 0.4 times faster than unattached diatoms experiencing laminar shear. Increased nutrient uptake by aggregated diatoms may be important in understanding the reasons for diatom floc formation.

Introduction

Blooms of chain-forming diatoms often disappear rapidly from surface ocean waters following nutrient depletion (Guillard and Kilham 1977, Smetacek 1985). This mass sedimentation occurs via flocculation of chains into loose, centimeter-sized aggregates of living, vegetative cells (Alldredge and Silver 1988, Kranck and Milligan 1988) which sink at rates of 50 to 200 m d^{-1}, one to two orders of magnitude higher than unaggregated chains (Alldredge and Gotschalk in press). Mass sinking of diatoms has been equated with mass mortality (Walsh 1983), and, at first glance, mechanisms resulting in the rapid settlement of viable cells out of the euphotic zone appear maladaptive. However, Smetacek (1985) suggested that mass flocculation removes diatoms from warm, nutrient-depleted surface waters, where their viability is low into dark, colder waters where they may remain viable for long periods of time as resting spores and vegetative resting stages. Later resuspension of these resting stages back into the euphotic zone would reseed surface waters with diatoms when conditions were again favorable for population growth.

While this evolutionary explanation of diatom flocculation is supported by existing literature on diatom biology, it does not preclude a more immediate adaptive advantage for mass flocculation. There are several possible immediate advantages for cell growth within the microhabitat of a porous aggregate, including interactions between adjacent microorganisms, (i.e., commensalism, mutualism, and exchange of genetic material) and potential protection from certain predators. The most important advantage in highly porous aggregates, however, may be increased nutrient uptake (Logan and Hunt 1987). Many types of cells, including yeasts and bacteria, aggregate when nutrients stressed (see Calleja 1984) and diatom flocculation in nature also appears to be triggered by nutrient limitation (Smetacek 1985). Moreover, cultures of *Chaetoceros debilis*, a representative of the most common genus in natural diatom flocs, flocculate under gentle rotation in the laboratory only when they reach stationary growth phase, (i.e., nutrient limitation) and not before (Alldredge unpublished data). Logan and Hunt (1987) predicted that advective flow through porous bacterial aggregates would increase the overall uptake of large molecular weight, dissolved organic molecules by attached, relative to unattached, bacteria. Moreover, Munk and Riley (1952) suggested that phytoplankton cells experiencing faster sinking velocities also have accelerated nutrient absorption and increased growth rates despite decreased concentrations of nutrients. Although Munk and Riley (1952) did not consider the case of phytoplankton in aggregates, recent experiments on the absorption of a large molecular weight dye by different types of marine snow support the existence of bulk fluid motion through natural marine aggregates (Logan 1987) and suggests that diatoms in sinking aggregates experience relatively more rapid fluid flow than unattached diatoms.

In this study we examined the hypothesis that diatom cells within aggregates experience increased overall transport of nutrients relative to unattached cells, i.e., that an immediate adaptive advantage of diatom flocculation is increased nutrient uptake by the aggregated cells. We used measured sinking velocities and porosities to calculate intra-aggregate flow velocities past cells fixed within natural diatom flocs. We then used mass transfer theory to predict the overall nutrient uptake of cells within natural diatom flocs relative to unattached cells.

Methods

Experimental

The settling velocities of 12 undisturbed, newly-formed diatom flocs were measured directly in situ by SCUBA divers in surface waters of the Santa Barbara Channel, California (34°23'N, 119°50'W) in July 1986. Settling velocities were determined, as described in Alldredge and Gotschalk (1988), by measuring the time required for each aggregate to sink to a spot of neutrally buoyant fluorescein dye placed 3 cm below the aggregate in the water column. Aggregate volume was determined from photographs taken in situ and each aggregate was collected for gravimetric determination of dry weight.

Porosity, p, was calculated directly from measurements of aggregate volume and dry weight using the equation

$$p = 1 - \frac{W}{PV}, \tag{1}$$

where W is the dry weight of the aggregate, V is aggregate volume and P is the density of the diatoms composing the aggregate, here assumed to be 1.1047 g cm^{-3}. This value was calculated from ambient seawater density (1.0247 g cm^{-3}, Alldredge and Gotschalk 1988) assuming an excess density for nutrient-depleted living diatom cells of 0.08 g cm^{-3} (Eppley et al. 1967). Species composition and mean cell sizes of diatoms in flocs were determined by counting and measuring cells in eight additional flocs collected at the same time.

Theoretical

Measured sinking velocities were compared to settling velocities of highly porous spherical aggregates, determined from a force balance as

$$U_p^2 = \frac{8\, g(P - P_f)\, d}{6\, C_D\, P_f}, \tag{2}$$

where U_p is the predicted settling velocity, g is the acceleration due to gravity, P is the particle density, P_f is the fluid density, d is the aggregate diameter, and C_D is the drag coefficient. For permeable aggregates with Reynolds numbers (Re) between 7 and 120 undergoing gravitational settling, Masliyah and Polikar (1980) determined the empirical expression of the drag coefficient as:

$$C_D = \frac{24\Omega}{\mathrm{Re}}\left[1 + 0.0853\,\mathrm{Re}^{(1.093 - 0.105\,w)}\right], \tag{3}$$

where $\mathrm{Re} = U_p d/\nu$, ν is the kinematic viscosity of the fluid, $w = \log_{10}(\mathrm{Re})$, and Ω is determined from

$$\Omega = \frac{2\xi^2[1 - \tanh\xi/\xi]}{2\xi^2 + 3[1 - \tanh\xi/\xi]}, \tag{4}$$

where ξ is the dimensionless size of the aggregate, defined as $\xi = a_f K^{-1/2}$, a_f is the aggregate radius, and K is the permeability of the aggregate.

The permeability of highly-porous aggregates was defined as a function of the aggregate structure and porosity using (Davies 1952):

$$K^{-1} = 16\, a_c^{-2}\, \phi^{1.5}(1 + 56\,\phi^3), \tag{5}$$

where a_c is the cell radius, and ϕ is the occupied volume fraction of the aggregate, equal to the quantity $(1 - p)$. We used the Davies correlation since this expression was used by Masilyah and Polikar (1980) in settling experiments to validate the existence of flow through permeable aggregates with $0.2 < \mathrm{Re} < 120$.

The average intra-aggregate volocity, u, through a permeable spherical aggregate undergoing gravitational settling (Adler 1981) is:

$$u = U\,\frac{a_f^*(\xi)}{a_f}, \tag{6}$$

where U is the measured in situ sinking velocity, and a_f^* is a function of the dimensionless variable ξ contained in Adler (1981). When a highly porous aggregate is permeable, streamlines cross the surface of the aggregate, and advect fluid past diatoms fixed within the interior of the aggregate. Therefore, a diatom within a rapidly sinking permeable aggregate potentially experiences higher fluid flow past its surface than does an unattached cell, which either sinks very slowly or moves entirely with the bulk fluid.

The rate of nutrient absorption by a cell is a function of nutrient concentration and flow field:fluid flow past a cell increases the rate of nutrient absorption by the cell (Munk and Riley 1952). Following the analysis of Logan and Hunt (1987), we incorporated this hydrodynamic effect into a first-order kinetic model using a mass transfer coefficient to increase cell kinetics with increased fluid flow past the surface of the cell. Since attached cells within aggregates are exposed to lower nutrient concentrations than unattached cells, nutrient removal by all cells within the aggregate was compared to nutrient removal by an equivalent number of cells freely dispersed in the bulk fluid using a Relative Uptake Factor, as described below.

The rate of mass transfer to a single cell, P_c, in any fluid environment (Logan and Hunt 1987) is:

$$P_c = 4\pi\, a_c\, D\, E_B\, \mathrm{Sh}\, C \tag{7}$$

where D is the nutrient diffusivity, assumed to be 10^{-5} cm^{-2} s^{-1}, and C is the nutrient concentration. The Sherwood number is a dimensionless ratio of the rate of mass transfer by advection to the rate of mass transfer by diffusion, and is defined here as $\mathrm{Sh} = \mathrm{k}\, a_c/D$, where k is the mass transfer coefficient. For a spherical object of radius a_c, the Sherwood number is unity for mass transfer by diffusion alone, and greater than unity for increased mass transfer due to fluid motion around the cell. The kinetics of nutrient uptake are incorporated in the transport model using a collector efficiency, E_B, which defines uptake as that fraction of collisions between substrate and cells that are successful; for instantaneous reactions, $E_B = 1$, and in the absence of nutrient uptake, $E_B = 0$. The mass transfer calculations presented below use $E_B = 0.025$, as determined by Logan (1986) from experimental data reported by Canelli and Fuhs (1976)

In order to examine mass transfer to attached and unattached diatoms, two Sherwood numbers are required: one for diatoms fixed in a flow field, and a second for unattached diatoms experiencing laminar shear. Sherwood numbers for diatoms within a permeable aggregate, or for unattached diatoms sinking in undisturbed fluid, were derived from data reported by Canelli and Fuhs (1976) on phosphorus uptake by cells of *Thalassiosira fluviatilis* fixed in a flow field. Using their data, we empirically determined the following correlation for the Sherwood number as a function of the Reynolds number:

$$\mathrm{Sh} = 1 + 45\,\mathrm{Re}^{0.57}. \tag{8}$$

Many mass transfer relationships indicate the Sherwood number is proportional to the Reynolds number to the 0.5 power, and our correlation is in good agreement with this value, since the standard error of the power in Eq. 8 is 0.08. In Fig. 1 we compare the phosphorus flux data reported by Canelli and Fuhs (their experiments 2 and 3, in Fig. 2) with fluxes predicted using the above correlation (Eq. 8). At lower concentrations of phosphorus (10 μg l^{-1}), flux values are less than 10^{-11} μg-P μm^{-2} min^{-1}, and the observed and predicted fluxes are in relatively close agreement. However, at larger phosphorus concentrations (100 μg l^{-1}), fluxes are

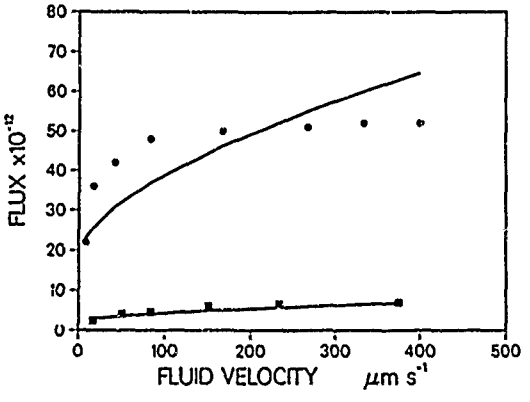


Fig. 1. Phosphorus fluxes (10^{-12} μg-P μm^{-2} min^{-1}) calculated using Eq. 8 (continous line) versus data reported by Canelli and Fuhs (1976): ■ – their experiment 2 ($a_c = 7.3$ μm, $C = 10$ μg-P l^{-1}); • – their experiment 3 ($a_c = 8.6$ μm, $C = 100$ μg-P l^{-1})

underestimated for fluid velocities less than 200 μm s^{-1}, and overestimated for velocities greater than 200 μm s^{-1}. Canelli and Fuhs' data suggest that a saturation value was reached in their experiments.

The fluid environment of an unattached diatom can be characterized as laminar shear, since diatoms freely suspended in the ocean are much smaller than the Kolmogorov microscale of turbulence. The Sherwood number for a sphere in laminar shear flow, Sh_G, (Frankel and Acrivos 1968) is:

$$\mathrm{Sh}_G = 1 + 0.26\,\mathrm{Pe}_G^{1/2} \tag{9}$$

where Pe is the dimensionless Peclet number, defined as $\mathrm{Pe}_G = a_c^2\, G/D$, and G is the fluid shear rate. Eq. 9 is valid for Peclet numbers much less than unity, and is only used for calculations of the rate of mass transfer to unattached diatoms.

The ratio of the overall nutrient uptake by aggregated cells to the nutrient uptake by an equivalent number of unattached cells is defined as the Relative Uptake Factor (Logan and Hunt 1987). For nutrient uptake by cells in a permeable aggregate undergoing gravitational settling, compared to unattached cells suspended in laminar shear flow, the Relative Uptake Factor, ν_a, is:

$$\nu_a = \frac{\mathrm{Sh}_u}{\mathrm{Sh}_G}\,\frac{[1-\exp(-\phi_a)]}{\phi_a}, \tag{10}$$

where ϕ_a, the dimensionless advective Thiele Modulus, is

$$\phi_a = \frac{2\,a_f\,k_u}{u}, \tag{11}$$

and a_f is the aggregate radius, and k_u is the first order uptake rate constant describing nutrient removal within the aggregate. From the rate of uptake per cell (Eq. 7), k_u is

$$k_u = \frac{3\,E_B\,\mathrm{Sh}_u\,D(1-p)}{a_c^2}, \tag{12}$$

The ratio of Sherwood numbers in Eq. 10 accounts for the different fluid mechanical environment of the unattached cells (laminar shear) and the cells within the aggregate (fixed in a flow field). The Thiele modulus, as defined in Eq. 11, is a ratio of the rate of mass transfer to attached diatoms, to the rate of fluid flow. Since nutrients are removed by cells as fluid flows through the aggregate, the Thiele modulus accounts for decreased nutrient concentrations in the aggregate interior.

For growth within the aggregate to be advantageous to all cells within the aggregate, the Relative Uptake Factor must be greater than unity. For $\nu_a < 1$, only cells near the surface of the aggregate would benefit from advective flow through the aggregate. Since first order kinetics are implied for all substrate concentrations below the bulk nutrient concentration, a Relative Uptake Factor analysis does not require that the bulk nutrient concentration be known since uptake is measured relative to unattached cells in the bulk fluid.

Results

Taxonomic composition of flocs expressed as percent of total cell number is shown in Table 1. Three species of diatoms, *Chaetoceros radicans*, *C. debilis*, and *Nitzschia* sp., comprised 86 ± 4% of the cells examined. The remaining cells were classified as centrics, pennates, or dinoflagellates. Aggregates were very loosely held together by tangled spines. Neither visual nor microscopic examination revealed the presence of abundant mucus exudates within the aggregates. The average cell volume of diatoms within the flocs was calculated based on the volumes of the three major diatom species, assuming their shapes to be cylinders. A cell with a volume equivalent to the average volume of cells within the flocs was calculated to have an average radius of 7 μm. This average radius was used in subsequent calculations for diatom characteristics.

The porosity of 12 diatom flocs is shown as a function of aggregate volume in Fig. 2. Aggregate volumes ranged between 0.19 and 4.2 cm^3; based on these volumes, the diameter of a spherical aggregate of equal volume varied between 7 and 20 mm. Porosity increased non-linearly with aggregate volume, ranging between 0.99931 and 0.99984. A maximum error in porosity, Δp, was determined using a first-term

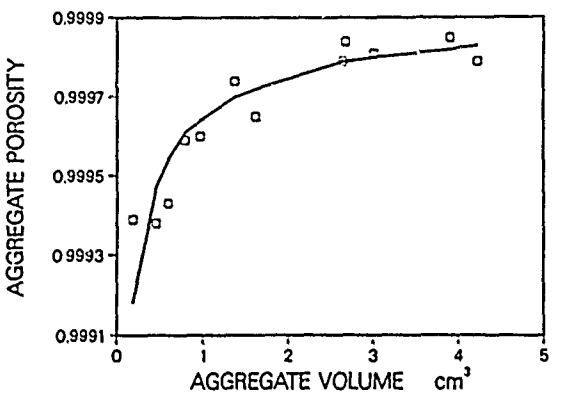


Fig. 2. Aggregate porosity (p) for 12 diatom flocs as a function of floc volume (V, cm^3), with regression line $p = 1 - 3.5 \times 10^{-4} V^{-0.50}$

Table 1. Percentage composition of diatom flocs collected from the Santa Barbara Channel, July 1986, by phytoplankton cell number. Reported percentages ignore whether cells present in chains. ($N = 10$, S.D. = standard deviation)

Species	Mean % (±S.D.)	Mean cell dimensions (diameter × height, μm)	Mean cell volume (μm)
Chaetoceros debilis	18±2	21×15	5440
Chaetoceros radicans	58±6	9×13	780
Nitzschia sp.	10+2	7×30	1150
Miscellaneous			
Centrics	8±3	15×15	
Pennates	3±1	10×30	
Dinoflagellates	4±2	12× 2	

Taylor Series expansion (Mickley et al. 1957) for porosity as a function of three variables, or

$$\Delta p = \left|\frac{\partial p}{\partial W}\right| \Delta W + \left|\frac{\partial p}{\partial V}\right| \Delta V + \left|\frac{\partial p}{\partial P}\right| \Delta P. \quad (13)$$

Using Eq. 1, this expression becomes:

$$\Delta p = \frac{1}{PV} \Delta W + \frac{W}{V_P^2} \Delta V + \frac{W}{V_P^2} \Delta P. \quad (14)$$

To calculate Δp, we used measured values, and assumed the following maximum errors based on data in Alldredge and Gotschalk (1988): $\Delta W = \pm 10\%$, $\Delta P = \pm 0.08$ g cm^{-3}, and $\Delta V = \pm 30\%$. As shown in Table 1, the errors in porosity are small and are $< 0.03\%$.

Measured settling velocities of diatom flocs in situ ranged between 49 and 190 m d^{-1}, with an average of 110 ± 40 m d^{-1} (Fig. 3). We also calculated the settling velocities using Eqs. 1 to 4. Predicted settling velocities of the 12 diatom flocs ranged between 73 and 120 m d^{-1} and were not statistically different (Students' t-test) from the observed settling velocities of these flocs, even though the calculated velocities did not appreciably increase with aggregate diameter. The average predicted settling velocity of 100 ± 12 m d^{-1} does not differs significantly from the in situ settling velocity of 110 m d^{-1}. Similar values for the observed and predicted settling velocities support the calculation of an equivalent aggregate radius used in this analysis, and the application of the permeable aggregate model for diatom flocs.

Measured sinking velocities were used in Eqs. 5 and 6 to calculate intra-aggregate flow velocities between 24 and 160 μm s^{-1} (2 to 14 m d^{-1}), with an average intra-aggregate velocity of 70 μm s^{-1} (6 m d^{-1}), or about 5% of the observed aggregate settling velocity for 12 diatom flocs (Table 2). A wide range of intra-aggregate velocities of 60 to 160 μm s^{-1} are predicted for aggregates in a narrow size range of 17 to 20 mm in diameter. This reflects the variable porosity, and therefore, permeability, of diatom flocs.

The overall rate of nutrient uptake by aggregated diatoms undergoing gravitational settling was compared to: (1) unattached cells in laminar shear flow and (2) unattached cells sinking in an undisturbed fluid, using a Relative Uptake Factor analysis. Fluid shear rates within the ocean mixed layer based on turbulent energy dissipation rates are highly variable, with ranges of 0.15 to 0.44 s^{-1} (Moum and Caldwell 1985), 0.001 to 1 s^{-1}, (Shay and Gregg 1984), and 0.01 to 0.04 s^{-1} (Oakey and Elliott 1982). The larger the shear rate, the greater the uptake of an unattached cell and the smaller the Relative Uptake Factor. In the first case, we assumed the largest fluid shear rate of 1 s^{-1} as an upper limit of fluid shear for unattached cells. This results in a conservative evaluation of the benefits of diatom nutrient uptake within a settling aggregate. For the 12 diatom flocs, we calculated Relative Uptake Factors between 1.0 and 2.1 (average of 1.4), indicating that diatoms within the aggregate could potentially utilize dissolved nutrients up to 2.1 times faster than unattached diatoms experiencing fluid shear in

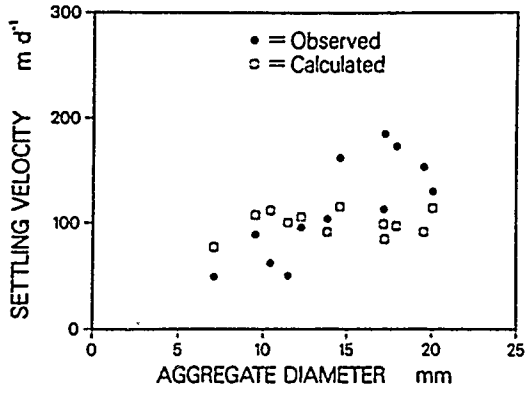


Fig. 3. Observed and calculated settling velocities of diatom flocs

Table 2. Properties of diatom flocs and predicted intra-aggregate velocities and relative uptake factors

Floc diam. (mm)	Floc porosity	Measured settling velocity ($m\,d^{-1}$)	Intra-aggregate velocity ($\mu m\,s^{-1}$)	Relative uptake factor
7.1	0.99939±0.00029	49	35	1.3±0.3
9.5	0.99938±0.00029	89	36	1.2±0.4
10.0	0.99943±0.00027	62	24	1.0±0.4
12.0	0.99959±0.00019	50	26	1.1±0.3
12.0	0.99960±0.00019	96	45	1.3±0.3
14.0	0.99974±0.00012	100	71	1.6±0.3
15.0	0.99965±0.00017	160	67	1.5±0.4
17.0	0.99979±0.00010	110	70	1.6±0.3
17.0	0.99984±0.00008	190	160	2.1±0.4
18.0	0.99981±0.00009	170	110	1.8±0.4
20.0	0.99985±0.00007	150	120	1.9±0.4
20.0	0.99979±0.00010	130	60	1.5±0.3

the water column (Table 2). This analysis accounts for nutrient depletion within the aggregate, and requires that both unattached diatoms and the diatom floc are exposed to low nutrient concentrations where a first order uptake model accurately describes nutrient uptake kinetics.

In case 2, Relative Uptake Factors were also calculated assuming unattached cells sank in undisturbed fluid. Smayda and Boleyn (1967) found that the mean sinking rate of chains of *Chaetoceros lauderi* up to 20 cells long ranged from 0.46 to 1.54 $m\,d^{-1}$, with no clear relationship between sinking speed and culture age. This species had a cell diameter ranging from 11 to 28 μm making it similar in size to the two *Chaetoceros* species that made up an average of 76% of the diatoms in our flocs. Assuming a sinking velocity of 1 $m\,d^{-1}$ for unattached cells, the Relative Uptake Factors of cells within aggregates ranged between 1.1 and 2.2. This suggests that consideration of unattached cells as either sinking or suspended within a laminar shear field is unimportant in obtaining Relative Uptake Factors greater than unity for diatom flocs.

The calculation of a Relative Uptake Factor is based on a series of measured values and equations. The maximum error in this calculation can be estimated using a Taylor series expansion about Eq. 10, by calculating errors in ϕ, using Eqs. 11 and 12, and Sh_u, using Eq. 8. An error for Sh_G was not determined since an upper limit of G was used in the calculation of this Sherwood number. The error in ϕ was determined for constant E_B, D, a_c, and v, with the following assumed errors: $\Delta W = \pm 10\%$, $\Delta P = \pm 0.08\,g\,cm^{-3}$, $\Delta V_f = \pm 30\%$, and $\Delta u = \pm 50\%$. These maximum errors are shown in Table 2 for each Relative Uptake Factor. On the average, $\gamma = 1.4 \pm 0.3$, which is larger than unity. Within these large error bounds, four Relative Uptake Factors were less than unity, indicating that within some aggregates, all cells may not have increased nutrient uptake compared to unattached cells.

Discussion

The porosities of diatom flocs were highly variable, but were in excess of 0.99910 for the 12 diatom flocs analyzed. These values are higher than average porosities estimated for aggregates found in engineered bioreactors. For example, porosities for activated sludge flocs range from 0.79 to 0.90, (Mueller et al. 1966), and porosities for mold pellets range from 0.800 to 0.988 (Yano et al. 1961). Since the size of an aggregate is a function of fluid shear (Hunt 1986), the high diatom floc porosities are reasonable for aggregates formed in low shear environments typical of natural systems. In engineered systems, such as wastewater treatment systems, shear rates are in the range of 100 to 1000 s^{-1}. Large shear rates contribute to aggregate breakup, re-compaction, and the formation of smaller aggregates with reduced porosities. Porosities of diatom flocs are similar to aggregate porosities determined using collision calculations based on random particle trajectories in computer models (Tambo and Watanabe 1979). These computer-generated aggregates, described as fractals (Witten and Cates 1986), typically neglect aggregate breakup.

The Relative Uptake Factors for the 12 diatom flocs were determined from several aggregate characteristics, and a series of relationships drawn from the literature, to be in the range of 1.0 ± 0.3 to 2.1 ± 0.4 (average 1.4 ± 0.3). This indicates flocculation can increase nutrient uptake by attached diatoms. In our error analysis, we estimated the cumulative effect of errors in measured parameters still resulted in Relative Uptake Factors greater than unity. Two equations were not included in the error analysis. Eq. 5, used to relate aggregate porosity and permeability, and Eq. 6, used to determine the intra-aggregate velocity. Several correlations have been found to provide good agreement between experimentally determined permeabilities and porosities for fibrous media at $Re < 10$ (Jackson and James 1986). However, we are unaware of correlations for high-porosity aggregates at the slightly larger Reynolds numbers ($3 \leq Re \leq 31$) determined for settling diatom flocs. As previously stated, we used the Davies correlation since this expression was supported by experiments conducted by Masilyah and Polikar (1980) for $0.2 < Re < 120$. Instead of performing an error analysis on Eqs. 5 and 6, we calculated

the error in the Relative Uptake Factor by assuming the intra-aggregate velocity obtained from these equations was only accurate within ± 50%. Even with this large variation in intra-aggregate velocity, only four of the Relative Uptake Factors, within a standard error, were less than unity. Therefore, while our hypothesis remains physically untested, our calculations provide strong evidence that diatom flocculation can increase nutrient uptake.

There are two defined limits to a Relative Uptake Factor analysis of mass transfer to attached diatoms. The lower limit results if the advective flow of nutrients into the aggregate is less than the diffusive flux. This occurs when the Peclet number for the floc, $Pe_f = a_f u_i D \ll 1$ (Logan and Hunt 1988). For the diatom flocs in this study, this would occur for $u \ll 0.01\ m\ d^{-1}$, a velocity much lower than calculated values (Table 2). However, since unattached cells settle at $\sim 1\ m\ d^{-1}$, intra-aggregate flows would have to be greater than $1\ m\ d^{-1}$ to confer any additional nutrient advantage to attached diatoms.

The upper limit of the Relative Uptake factor is defined by the ratio of Sherwood numbers in Eq. 10. As the intra-aggregate velocity increases, and the aggregate porosity decreases, the ratio $[1 - e^{-\phi}]/\phi$ approaches unity. Therefore, the overall uptake by attached cells cannot exceed the uptake by a cell fixed in a flow field of velocity u_i divided by the uptake of a cell in laminar shear (or sinking at $1\ m\ d^{-1}$). However, this ratio of Sherwood numbers may still underestimate uptake by attached cells since the high fluid velocities at an aggregate surface are not included in our calculations. We assumed the floc was homogeneous and spherical in shape, and that all cells within the aggregate resided in a fluid field described by the average intra-aggregate fluid velocity. This oversimplification of the structure and shape of a marine snow aggregate was necessary to obtain an analytical solution. Natural aggregates often have long comet-shaped tails and irregular shapes, the exact shape of the aggregate, however, is not expected to be important in mass transfer calculations (Aris 1975). More important to our calculations is the assumption of the homogeneity of the aggregate. Many aggregates contain internal voids (see Alldredge and Silver 1988, Fig. 2a, and Alldredge and Gotschalk 1988, Fig. 1b for visual examples). As a result, many cells (more than for a sphere) will be at the aggregate surface and will experience fluid velocities much larger than the average intra-aggregate velocity calculated for the homogeneous spherical aggregates in this study. These surface cells could remove nutrients much faster than cells within the aggregate interior. This effect would increase the benefits of attachment.

The maximum benefit of attachment for diatoms in permeable aggregates, for any model, is limited by the maximum possible increase in uptake with respect to fluid hydrodynamics. This hydrodynamic effect is described mathematically in terms of Sherwood number correlations for cells in laminar fluid shear and for spheres fixed in a fluid field. Despite work by Munk and Riley (1952) over three decades ago, little improvement has been made in quantifying the effect of hydrodynamics on nutrient uptake by phytoplankton. The physics of mass transfer to spheres and other objects is well understood in the field of chemical engineering, and kinetic models relating enzyme kinetics to bulk nutrient concentration are well studied by biologists. However, the increase in uptake kinetics as a result of fluid hydrodynamics in biological systems is not well understood.

To our knowledge, only two studies on the effect of hydrodynamics on nutrient uptake by marine diatoms can be used to calculate a Sherwood number. The first study, by Canelli and Fuhs (1976), investigated phosphorus uptake by cells of *Thalassiosira fluviatilis* fixed in a flow field and is used in our calculations (Eq. 8). In Fig. 4, two other Sherwood number correlations that have been used for similar purposes in other studies are compared to Eq 8 The first correlation, developed by Brian and Hales (Sherwood et al 1975), and used by Logan and Hunt (1987, 1988) to describe uptake by cells fixed in a flow field is:

$$Sh_u = (1 + 0.48\, Pe_u^{2/3})^{1/2}. \quad (15)$$

A second correlation was used by Munk and Riley (1952) in their classic study for sinking spheres, their correlation is.

$$Sh = 1 + 0.5\, Pe + 0.60\, Pe^2. \quad (16)$$

Fig. 4 shows that at velocities $\lesssim 160\ \mu m\ s^{-1}$ both Eqs 15 and 16 underestimate the effect of fluid flow when compared to the Sherwood number correlation derived using the experimental data of Canelli and Fuhs. All three correlations indicate Sherwood numbers should continue to increase with fluid velocities greater than $160\ \mu m\ s^{-1}$, but this observation is not supported by Canelli and Fuhs' data (Fig 1) These results suggest there is some effect of fluid velocity that is not adequately described in our mass transfer analysis. Since the calculated intra-aggregate velocities shown in Table 2 are less than $\lesssim 160\ \mu m\ s^{-1}$, the Relative Uptake Factors in Table 2 are conservative.

The second study that can be used to determine a Sherwood number correlation was reported by Pasciak and Gavis (1975, Fig. 5) on nitrate uptake by *Ditylum brightwelli*. Shown in Fig. 5 is a comparison of Sherwood numbers for a 41 μm cell (the equivalent spherical radius of *D brightwelli*) to Sherwood numbers calculated using Eq 9. Much greater uptake for unattached diatoms as a result of fluid shear is predicted from Eq. 9 than was observed by Pasciak and Gavis (1975). This suggests that we overestimated the uptake of unattached diatoms in our calculations, which would lead to a larger Relative Uptake ratio than shown in Table 2. Thus, experimental work by Pasciak and Gavis (1975), as well as by Canelli and Fuhs (1976), suggests that our comparison of the nutrient advantage experienced by aggregated over unattached diatoms is conservative.

Flocculation has historically been viewed as a disadvantage to attached cells for two reasons. First, aggregates have been viewed as impermeable, resulting in decreased nutrient availability to cells within the aggregate interior (Yano et al 1961). Second, since flocculation increases settling velocity, diatoms may be removed faster from the euphotic zone than unattached cells. Smetacek (1985), for example, has argued that aggregation and mass sinking represent a transition

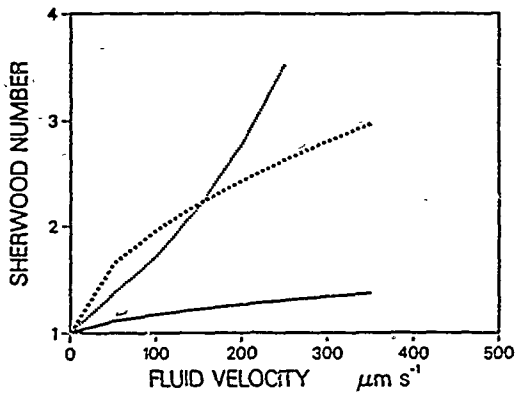


Fig. 4. Sherwood numbers of a cell 7 μm in radius fixed in a flow field, calculated using. Eq. 8, based on data in Canelli and Fuhs (1976) (dashed line), Eq. 16, the Brian and Hales Correlation (Sherwood et al. 1975) (continuous line); Eq. 15, a correlation used by Munk and Riley (1952) (dotted line)

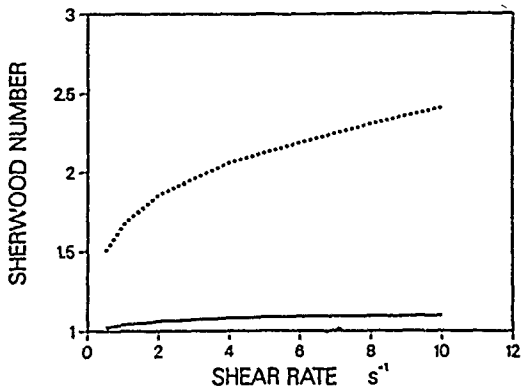


Fig. 5. Sherwood numbers calculated using Eq. 9 (dashed line) for a cell 41 μm in radius as a function of fluid shear rate versus results adapted from Pasciak and Gavis (1975) (continuous line)

from a growing to a resting stage in the life histories of diatoms. Aggregated cells sink out of nutrient-depleted surface waters into deep, nutrient-rich water and await resuspension back into the euphotic zone as resting stages. While this evolutionary explanation for the mass flocculation of diatom blooms may be correct, resting stages are rare in diatom flocs observed in surface waters (Alldredge and Gotschalk in press) although they may form at depth. Our data suggest that the flocculation of diatom blooms may be immediately adaptive because aggregation alters the fluid environment of a cell. A single unattached cell or chain is contained within a microscale eddy and must move with the bulk fluid; however, fluid flow around and through a rapidly sinking aggregate actually alters the fluid environment of associated cells, and increases nutrient uptake by attached cells compared to unattached cells. Flocculation may, therefore, be advantageous to nutrient-stressed diatoms by increasing the potential for uptake of scarce nutrients following an intense phytoplankton bloom.

Evolutionary theory predicts that, all else being equal, the genotype producing aggregation behavior will be selected for only if diatoms carrying that genotype remain in the mixed layer long enough to experience differential growth rates above those of non-aggregating genotypes of the same species. If the magnitude of this differential reproduction is very small, more time will be required to establish the genotype for aggregation within the species. However, as long as the differential reproduction of aggregating diatoms is greater than non-aggregating cells, i.e., the fitness of the aggregation genotype is greater than unity, then aggregation behavior will be selected for and the aggregation genotype will come to dominate the population (see Emlen 1973 for discussion). Phytoplankton cell growth and reproduction is directly related to nutrient uptake. Our finding that aggregated cells may take up nutrients as much as 2.1 times faster than unaggregated cells of the same species suggests that the differential production of aggregated cells has the potential to be quite high. However, even Relative Uptake Factors only slightly greater than unity could result in gradual selection for diatoms which aggregate.

We propose that some aggregating diatoms remain in the mixed layer long enough to experience differential reproduction because of two sequential processes. First, despite their rapid sinking rates, some diatom flocs remain suspended in the mixed layer for many days before they sink out of it. Lande and Wood (1987) calculated that slowly sinking particles may make many vertical excursions within the mixed layer before they are lost via settlement. Empirical evidence indicates that some rapidly settling particles also make such excursions. For example, 5 to 10% of macro-crustacean fecal pellets sinking at rates of 18 to 170 m d^{-1} have been observed suspended in the mixed layer 10 d after production (Alldredge et al. 1987). Moreover, diatom flocs several days old do indeed occur abundantly in surface waters off southern California (Alldredge and Gotschalk in press). Our calculations indicate that cells attached to these flocs, due to increased nutrient uptake, should have a selective advantage over nutrient depleted, unattached cells remaining an equal amount of time in the mixed layer. Second, once replete, at least some cells must fall off flocs before the flocs leave the mixed layer. Diatom flocs are fragile and erode or fragment at shear rates normally encountered in the ocean (McGillivary and Alldredge 1987). Single chains or floc fragments will more easily become suspended than the larger and heavier parent flocs. A cycle of repeated resuspension, coupled with gradual erosion or fragmentation of only a small percentage of diatom flocs formed after a bloom, would be adequate to reseed the mixed layer with unattached vegetative cells replete with nutrients due to their prior association with the flocs. It is these cells which may be capable of sustained survival following a bloom and which eventually re-establish diatom populations in surface waters when more favorable nutrient conditions reoccur.

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Literature cited

Adler, P. M. (1981). Streamlines in and around porous particles. J. Colloid Interface Sci. 81: 531–535

Alldredge, A. L., Gotschalk, C. C. (1988). In situ settling behavior of marine snow. Limnol. Oceanogr. 33: 339–351

Alldredge, A. L., Gotschalk, C. C. (In Press) Direct observations of the mass flocculation of diatom blooms: characteristics, settling velocities, and formation of diatom aggregates. J. mar. Res.

Alldredge, A. L., Gotschalk, C. C., MacIntyre, S. (1987). Evidence for sustained residence of macrocrustacean fecal pellets in surface waters off Southern California. Deep Sea Res. 34: 1641–1652

Alldredge, A. L., Silver, M. W. (1988). Characteristics, dynamics and significance of marine snow. Prog. Oceanogr. 20: 41–82

Aris R. (1975). The mathematical theory of diffusion and reaction in permeable catalysts. Vol. 1, the theory of the steady state. Clarendon Press. Oxford

Calleja, G. B. (1984). Microbial aggregation. CRC Press Inc., Boca Raton, FL.

Canelli, E., Fuhs, G. W. (1976). Effect of the sinking rate of two diatoms (*Thalassiosira* sp.) on uptake from low concentrations of phosphate. J. Phycol. 12: 93–99

Davies, C. N. (1952). The separation of airborne dust and particles. Proc., Inst. Mech. Eng., London B1: 185–213

Emlen, J. M. (1973). Ecology: an evolutionary approach. Addison Wesley, Reading, MA

Eppley, R. W., Holmes, R. W., Strickland, J. D. H. (1967). Sinking rates of marine phytoplankton measured with a fluorometer. J. exp. mar. Biol. Ecol. 1: 191–208

Frankel, N. A., Acrivos, A. (1968). Heat and mass transfer from small spheres and cylinders freely suspended in shear flow. Phys. Fluids 11: 1913

Guillard, R. R. L., Kilham, P. (1977). The ecology of marine planktonic diatoms. In: Werner, D. (ed.) The biology of diatoms. Blackwell Scientific, Oxford, p. 372–469

Hunt, J. R. (1986). Particle aggregate breakup by fluid shear. In: Mehta, A. J. (ed.) Estuarine cohesive sediment dynamics, lecture notes on coastal and estuarine studies. Springer-Verlag, Berlin, p. 85–109

Jackson, G. W., James, D. F. (1986). The permeability of fibrous porous media. Can. J. Chem. Eng. 64: 364–374

Kranck, K., Milligan, T. G. (1988). Macroflocs from diatoms: in situ photography of particles in Bedford basin, Nova Scotia. Mar. Ecol. Prog. Ser. 44: 183–189

Lande, R., Wood, A. M. (1987). Suspension times of particles in the upper ocean. Deep Sea Res. 34: 61–72

Logan, B. E. (1986). Mass transfer models for microorganisms in aggregates and biofilms. Ph.D. thesis. University of California, Berkeley

Logan, B. E. (1987). Advective flow through permeable aggregates. EOS 68: 1723

Logan, B. E., Hunt, J. R. (1987). Advantages to microbes of growth in permeable aggregates in marine systems. Limnol. Oceanog. 32(5): 1034–1048

Logan, B. E., Hunt, J. R. (1988). Bioflocculation as a microbial response to substrate limitations. Biotechnol. Bioeng. 31: 91–101

Masliyah, J. H., Polikar, M. (1980). Terminal velocity of porous spheres. Can. J. Chem. Eng. 58: 299–302

McGillivary, P. A., Alldredge, A. L. (1987). Mechanisms of marine snow production: attachment probabilities of natural particles on collision. EOS 68: 1715

Mickley, H. S., Sherwood, T. K., Reed, C. E. (1957). Applied mathematics in chemical engineering. McGraw Hill, New York, p. 53–58

Moum, J. N., Caldwell, D. R. (1985). Local influences on shear flow turbulence in the equatorial ocean. Science N.Y. 230: 315–316

Mueller, J. A., Voelkel, K. G., Boyle, W. C. (1966). Nominal diameter of floc related to oxygen transfer. ASCE J. San. Eng. Div. 92(SA2): 9–20

Munk, W. H., Riley, G. A. (1952). Absorption of nutrients by aquatic plants. J. mar. Res. 11: 215–240

Oakey, N. S., Elliott, J. A. (1982). Dissipation within the surface mixed layer. J. phys. Oceanogr. 12: 171–185

Pasciak, W. J., Gavis, J. (1975). Transport limited nutrient uptake rates in *Ditylum brightwellii*. Limnol. Oceanogr. 20: 604–617

Shay, T. J., Gregg, M. C. (1984). Turbulence in an oceanic convective mixed layer. Nature, Lond. 310: 282–285

Sherwood, T. K., Pigford, R. L., Wilke, C. R. (1975). Mass transfer. McGraw Hill, New York

Smayda, T. J., Boleyn, B. J. (1966). Experimental observations on the flotation of marine diatoms II, *Bacteriastrum hyalinum* and *Chaetoceros lauderi*. Limnol. Oceanogr. 11: 35–43

Smetacek, V. S. (1985). Role of sinking diatom life-history cycles: ecological, evolutionary and geological significance. Mar. Biol. 84: 239–251

Tambo, N., Watanabe, Y. (1979). Physical characteristics of flocs-I: the floc density function and aluminium floc. Wat. Res. 13: 409–414

Walsh, J. J. (1983). Death in the sea: Enigmatic phytoplankton losses. Prog. Oceanogr. 12: 1–86

Witten, T. A., Cates M. E. (1986). Tenuous structures from disorderly growth processes. Science, N.Y. 232: 1607–1612

Yano, T., Kodama, T., Yamada, K. (1961). Fundamental studies on the aerobic fermentation Part 8, oxygen transfer within a mold pellet. Agric. biol. Chem. 25: 580–584

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The attachment probabilities of colliding macroscopic marine aggregates (marine snow)

Alice L. Alldredge[1] and Philip McGillivary[2]

[1]Department of Biological Sciences and [2]Marine Science Institute

University of California

Santa Barbara, California, 93106 USA

Running head : Attachment probabilities of marine snow

ABSTRACT

The rate at which suspended particles in the ocean coagulate to form larger, more rapidly sinking aggregates is directly related to the efficiency with which the particles stick together once collided. Many previous models of coagulation in the ocean have assumed that the attachment probability of natural suspended particles is low, based on data for marine sediments. We determined the attachment probabilities of natural macroscopic aggregates as a function of aggregate type, size, and collision velocity by observing and videorecording individual particle-particle interactions between 660 pairs of aggregates collided together via gravitational settlement. Attachment probabilities of marine macroaggegates in the size range of 0.2 to 7.6 mm are the highest yet measured ranging from 0.60 (i.e. 60% of collisions result in attachment) for amorphous detrital aggregates to 0.88 for flocculated diatoms. Attachment probabilities increased with increasing particle volume, the surface area of contact, and collision velocity. Large size and surface complexity resulting in multi-point contact between colliding particles and the abundance of sticky, microbially-produced exopolymers on the aggregate surfaces probably increase aggregation efficiencies. The high attachment probabilities of suspended organic macroaggregates suggest that particle aggregation rates due to physical coagulation in the ocean may be many times higher than previously predicted.

INTRODUCTION

Extensive evidence from a variety of empirical and theoretical studies indicates that removal of particles from surface waters of the ocean to the deep sea requires their aggregation into larger particles with settling speeds greatly in excess of the original particles MCCAVE, 1975, see FOWLER and KNAUER, 1986 for review). This aggregation is accomplished by organisms, especially zooplankton which repackage fine suspended particles into fecal pellets, mucus feeding webs, and animal biomass, or by the process of physical coagulation. Coagulation, as used throughout this paper, is the process by which particles are brought into contact with each other by physical mechanisms of particle transport, including Brownian motion, fluid shear, and differential settlement, and subsequently become stuck together to form aggregates (O'MELIA and BOWMAN, 1984). The rate at which aggregation occurs by this second pathway in natural waters is a complex function of three variables; particle concentration, the intensity of the velocity gradient colliding the particles together, and the probability of attachment on collision (see STUMM and MORGAN, 1981).

Particle aggregation rates are potentially high when high particle concentrations or high shear result in increased frequencies of particle collision. However, even frequent collision will not result in high aggregation rates if the probability of attachment once particles come in contact is low. This factor, the attachment probability (α), also called the sticking factor (ALI et al., 1984), coalescence efficiency (MCCAVE, 1984), collision efficiency factor (GIBBS, 1983a) or the particle stability factor (see WEILENMANN et al., 1989) is defined by the relationship:

$$\alpha = \frac{\text{interparticle attachment rate}}{\text{interparticle collision rate}}$$

The attachment probability is thus the proportion of collisions which result in aggregation. When $\alpha = 1$, all collisions result in attachment. When $\alpha = 0$, no collisions result in attachment.

The attachment probability of colloidal-sized particles is a function of solution chemistry and the surface properties of the particles (O'MELIA, 1987). Previous models of coagulation in natural waters (ALI et al., 1984; O'MELIA and BOWMAN, 1984; MCCAVE, 1984; FARLEY and MOREL, 1986; WEILENMANN, et al., 1989) have assumed α to be constant and independent of particle size or collision velocity. This assumption arises, in part, from the method generally used to determine α. A suspended solution of particles is stirred or rotated in a reaction vessel at a known shear and the change in the number concentration of particles over time used to calculate an average α for the system . This method obscures differences in the attachment probabailities of particles in different size classes.

Attachment probabilities are not known for organic particles above colloidal size ranges. MCCAVE (1984) assumed an attachment probability of 0.1 for suspended marine particles, a value typical of most marine sediments (EDZWALD et al., 1974; GIBBS, 1983a). However, organic marine aggregates, especially aggregates > 500 μm in diameter, known as marine snow, contain abundant exopolymers and mucus exuded by the microbial communities inhabiting their surfaces (see ALLDREDGE and SILVER, 1988) which may greatly increase their stickiness (STUMM and

MORGAN, 1981). Most types of marine snow are produced by physical aggregation and are fractal in their geometry indicating that they are formed by cluster-cluster collisions (WILKONSON, 1989), primarily of particles in the size range of hundreds to thousands of μms (MCCAVE, 1984).

Rates of physical aggregation have not yet been quantified in the ocean. Some investigators have questioned the importance of coagulation in the ocean because the low particle concentrations and shears found there should result in low frequencies of collision and because they assumed that the frequency of successful collisions (i.e. α) was low (BRUN-COTTAN, 1976, LERMAN, 1979). Others have concluded that coagulation theory may reasonably predict observed particle size distributions in ocean waters (HUNT, 1980) . MCCAVE (1984), in the most recent and extensive theoretical treatment, concludes that aggregation rates in surface waters are largely determined by biological processes but he stressed our lack of basic empirical data with which to evaluate coagulation models.

The assumption that attachment probabilities are low may bias estimations of coagulation rates in the ocean. If attachment probabilities of organic marine aggregates are closer to 1, than coagulation rates in the ocean water column could be considerably higher than previously predicted. In the following study we observed and videorecorded the collision outcomes of individual pairs of marine aggregates in the marine snow size range which were collided together by differential settlement. Our goal was to determine the attachment probabilities of different types of marine snow and test the hypothesis

that α is independent of particle size and collision velocity for marine particles of macroscopic size.

MATERIALS AND METHODS

Particle collection: Intact aggregates of marine snow were collected by hand individually in 6 ml syringe barrels stoppered with a syringe plunger at each end by scuba divers at depths of 10 to 20 m. Samples were obtained at 13 stations in the southern California Bight and California Current during April and September, 1987 (see ALLDREDGE and GOTSCHALK, In Press, for station locations) and in the Santa Barbara Channel at 34° 15'N, 119 45' W. Aggregates were maintained at ambient surface temperature aboard ship or in a shore-based laboratory and their collision properties determined within 5 h after collection.

Aggregates were classified by the composition of their component particles as determined by microscopic examination of 10 aggregates from each station (ALLDREDGE and GOTSCHALK, In Press). Larvacean houses and large fecal pellets could be readily identified by external morphology. Ninety-five % of the aggregates occurring at any one station were of the same origin (ALLDREDGE and GOTSCHALK, In Press). Thus all collisions reported here were between aggregates of the same type.

Particle Collision: Individual pairs of aggregates were observed and videorecorded colliding together via differential settlement. Individual particle collisions were produced by dropping one particle from a pipette 2 to 3 cm directly above a second, stationary particle in a 1 X 1 X 5 cm clear plastic disposable cuvette filled with seawater collected at the same time as the particles and allowing the first particle to strike the second through gravitational settling. The second particle

rested on a layer of water-immiscible Freon which formed a concave, deformable meniscus below the seawater to abet particle collision and prevent particles from settling to the base of the chamber. Each collision event was recorded in 3 dimensions using two Newvicon video cameras oriented at 90° to each other and equipped with Nikon 55 mm macrolens to allow appropriate magnification of the settling chamber. A screen-splitter was used to record both video outputs simultaneously on the same video tape.

When particle trajectories did not coincide to produce collision (about 20% of attempts), one particle was resuspended and allowed to settle again. The small, 5 ml chambers used were sufficiently small to permit frequent, successful collisions with minimal particle manipulations. To minimize wall effects, particles were mainly of diameters less than 5 mm. We judged wall effects to be trivial based on observations of particle and fluid behavior within the chambers. However, the most likely result of minimal wall effects, if present, would have been to reduce particle velocities, thus merely broadening the range of collision velocities investigated.

Particle dimensions and impact velocities were measured and scaled directly from the screen using stop-action and tenth-speed video operation modes. Particle volumes were calculated from the three main particle axis lengths using the formula for the volume of an ellipsoid, the shape most closely approximating that of most of the aggregates studied.

Collision Outcomes: Within 5 to 10 seconds of collision, the collided aggregates were gently disturbed with a stream of water delivered near the lower side of the coalesced particle with a glass pipette. The eddy

produced by this disturbance slowly resuspended and rotated the aggregates allowing determination of their attachment state. Collision outcomes were classified in five commonly observed categories: 1) particle fusion - the two particles were fused into one indistinguishable aggregate, 2) multi-point attachment - the aggregates were attached at many points along their interface, 3) attachment by a filament - the aggregates were attached by one filamentous strand of material, 4) non-attachment - the particles were not attached and readily separated on disturbance, and 5) disintegration - one or both particles fragmented into many component particles upon impact or resuspension.

The frequency of attachment related to various variables (particle size, particle type, collision velocity etc.) was tested for statistical significance with R X C tests of independence using the G-statistic, a goodness of fit test or the test for equality of 2 percentages described in SOKAL and ROHLF (1969).

RESULTS

Six types of macroscopic particles were encountered in the Southern California Bight region; larvacean houses, diatom flocs, fecal aggregates, miscellaneous amorphous aggregates, pteropod webs, and large cylindrical fecal pellets produced by pelagic macrocrustaceans, probably the euphausiid, Euphausia pacifica (ALLDREDGE et al., 1987). All aggregates were composed primarily of organic matter including both living organisms and detrital debris. Most discarded larvacean houses were firm, gelatinous, spherical particles produced by *Oikopleura longicauda* or *O. dioica*. Diatom flocs were amorphous, porous, fragile

aggregations of chain forming diatoms dominated by *Chaetoceros* sp. and *Nitzschia* sp.. Fecal aggregates were composed primarily of numerous macrocrustacean and copepod fecal pellets embedded in a mucus matrix laden with bacteria and naked flagellates. Amorphous aggregates consisted of a variety of component particles, especially unidentifiable organic matter and debris, mucus and a few fecal pellets. Identifiable living cells, excepting bacteria, were a minor component of these aggregates. Pteropod webs were the feeding structures of pseudothecosomateous pteropods and consisted primarily of a mucus matrix with numerous smaller aggregates embedded in it. Extensive description of the biological characteristics of these particles, including community composition, chlorophyll *a* content, dry weight, and primary and bacteria production can be found in ALLDREDGE and GOTSCHALK (In Press).

Of the 660 individual collisions observed, 36% were between diatom flocs, 21% were between larvacean houses, 13% each were between amorphous aggregates, fecal aggregates, or fecal pellets and 5% were between pteropod feeding webs. The sample size of pteropod webs was too small to include them as a separate category in most analyses. Individual aggregates ranged from 0.2 to 7.6 mm in the diameter perpendicular to the direction of sinking and from 0.4 to 10.7 mm in maximum length. Settling velocities averaged 0.16 ± 0.11 cm s^{-1}. The mean Reynolds number (Re) of all aggregates was 3 ± 3, very similar to the range of 1 to 10 commonly observed for Reynolds numbers of undisturbed marine snow settling in situ (ALLDREDGE and GOTSCHALK, 1988) (Table 1).

The collision outcomes for each particle type are summarized in Table 2. Multipoint attachment and attachment by a filament were the most common outcomes observed for all particle types except diatom flocs, where a high percentage of collisions also resulted in fusion. Fewer than 7 % of the collisions resulted in disintegration except for diatom flocs. Diatom flocs were large, highly porous and fragile. Observations of diatom floc disintegrations in the collision chamber indicate that some disintegration of diatom flocs resulted from impact of the rapidly settling particle onto the stationary particle. However, no significant relationship was found between impact velocity and the probability that a collision would result in disintegration. Moreover, disintegration most commonly occurred from fluid shear produced when the coalesced aggregate was tested for attachment, making it impossible to identify a collision outcome. While disintegration may occur in nature, it appeared to be largely a result of our laboratory methods. Thus we eliminated disintegration as an outcome when calculating attachment probabilities.

Attachment probabilities (α) of the 6 types of marine snow investigated ranged from 0.60 to 0.88 with a mean of 0.77. The attachment probability of amorphous aggregates of 0.60 was significantly lower than that of other aggregates types ($p < 0.05$) while that of diatom flocs (0.88) was significantly higher ($p < 0.01$). The attachment probabilities of larvacean houses, fecal aggregates, pteropod webs and fecal pellets were not significantly different from each other.

Although attachment probability increased with increasing impact velocity for all aggregate types except fecal pellets (Fig. 1), this increase was significant at the 0.05 % probability level only for

amorphous aggregates. The probability that a increased with impact velocity was 0.07 % for all aggregate types combined, suggesting that additional data may yield a significant relationship since tests for goodness of fit are highly sensitive to sample size. This conclusion is further supported by comparing the attachment probabilities of all particles impacting at < 3 and > 3 cm s^{-1} using a statistical test for the equality of two percentages. The α of 0.67 for particles impacting at < 3 cm s^{-1} was significantly different ($p = 0.027$) from that of aggregates impacting at >3 cm s^{-1}, where $a = 0.81$.

Attachment probability also increased significantly with aggregate volume (Fig 2). This relationship was statistically significant only for all aggregate types combined. Aggregates with a volume larger than 0.5 mm^3 had an $\alpha = 0.83$, significantly higher ($p < .001$) than $\alpha = 0.71$ of all aggregates smaller than 0.5 mm^3.

The relative size of the two colliding particles had no effect on collision outcome. Particles which were very similar in volume (Fig. 3a) or in diameter (Fig. 3b) coalesced with the same probability as those that were highly dissimilar in either volume or diameter. However, the size of the surface area of contact between the two particles significantly effected collision outcome. Attachment probability increased as the area of contact between the particles increased for total aggregates, diatom flocs, larvacean houses and fecal aggregates, although sample sizes were large enough to yield statistically significant differences only for all particle types combined ($p < 0.05$) and fecal aggregates ($p < 0.05$). Attachment probability increased from a mean of 0.73 for all particles colliding

with a contact area < 4 mm^2 to 0.88 for all particles colliding with a contact area > 4 mm^2 (Fig. 4).

DISCUSSION

Most aggregates of marine snow are fractal in their geometry (WILKINSON, 1989) indicating that they have been formed by cluster-cluster collisions of smaller aggregates (MEAKIN, 1988). Coagulation theory predicts that aggregates in the marine snow size-range are formed primarily by collisions of particles about 50 μm or larger in diameter (MCCAVE, 1984). Most marine snow appears on microscopic examination to consist of many subunits, most on the order of hundreds of microns to several millimeters in size. Thus, in this study we focused on collisions between particles ranging from 200 to 7600 μm in diameter. This approximates the size range of clusters potentially colliding to form medium to large aggregates of marine snow in the ocean.

Although we collided aggregates via gravitational settlement, our results can be generalized to aggregation resulting from other transport modes as well. Attachment probability is independent of the mode of particle transport (DELICHATSIOS and PROBSTIEN, 1975; STUMM and MORGAN, 1981). In the ocean, aggregates in the marine snow size range are most efficiently aggregated by fluid shear (HUNT, 1982; MCCAVE, 1984) although differential settlement may also be important, especially in diatom flocculation (ALLDREDGE and GOTSCHALK, 1989).

Collision velocities observed in this laboratory study were slightly higher than the settling velocities of undisturbed marine snow sinking in situ. Settling velocities of marine snow sinking in nature range from 0.01 to 0.2 cm s^{-1} (ALLDREDGE and GOTSCHALK, 1988), while we observed

mean velocities of 0.1 to 0.24 cm s^{-1}. Aggregates may collapse slightly from collection and handling, increasing their excess density and sinking rates (ALLDREDGE and GOTSCHALK, 1988). However, the collision velocities we obseved are within the wider range of velocities expected to occur in nature due to a variety of particle transport modes including fluid shear.

The attachment probabilities of macroscopic marine aggregates observed in this study are higher than those reported for natural freshwater and marine particles of smaller size. Table 3 summarizes available data on the attachment probabilities of natural aquatic particles, most of which are sediments. Attachment probabilities of marine snow are generally 10 to 100 fold higher than those of freshwater sediments but only 2 to 4 fold higher than marine sediments. An extensive body of theory on colloidal aggregation has been applied to coagulation of sediments and may elucidate the process of marine snow formation as well.

Aggregation of colloids results from instability of the particle suspension. Particles in seawater bare a net negative charge (NEIHOF and LOEB, 1972) which is counterbalanced by positive counter-ions attracted electrostatically to it. The result is an electric double layer at the interface between the particle and the aqueous phase. A diffuse layer around the particle is established by the electrostatic attraction and the opposing process of counter-ion diffusion due to thermal motion. The electrostatic potential at the particle interface decreases with increasing distance from the particle. Two particles of the same sign approaching each other are repelled by repulsive forces which increase with decreasing distance between the particles. These

repulsive forces are counterbalanced by attractive van der Waal forces. Whether the net interaction between the particles is ultimately attractive or repulsive depends upon the difference between these opposing forces. In solutions of high ionic strength, such as seawater, the diffuse layer is compressed resulting in more fruitful collisions and greater instability of the colloidal solution. Absorbed organic coatings, including humic substances, decrease α and stabilize freshwater colloidal suspensions although this affect decreases with increasing salinity (STUMM and MORGAN, 1981; GIBBS, 1983b).

Aggregation of colloids may be explained by other mechanisms as well including adsorption followed by neutralization of charge, enmeshment of the particle in a precipitate of a coagulant, and interparticle bridging by polymers (O'MELIA, 1972) . This last mechanism may be most applicable to attachment of larger, organic aggregates. In this mechanism, one end of a polymer molecule absorbs onto a particle while the rest of the molecule is free to absorb onto another producing a particle-polymer-particle structure. Attached bacteria are ubiquitous on all marine organic aggregates (WEIBE and POMEROY, 1972, and see JOHNSON et al., 1986) and produce abundant exopolymers and sticky capsular secretions potentially available for polymer bridging (HARRIS and MITCHELL, 1973; CALLEJA, 1984). Microbial communities are particularly enriched on marine snow, with most of the aggregate surface coated with attached bacteria (CARON et al., 1986; ALLREDGE and SILVER, 1988). Fimbriae, adhesive fibers, and cell extensions of these attached bacteria may also form similar polymer-type bridges (PAERL, 1975). The frequent attachment of larger aggregates by elastic filaments observed

in this study supports polymer bridging as an important mechanism of attachments for organic macroaggregates.

While colloidal coagulation theory helps elucidate the attachment of macroaggregates, its usefulness is limited. The particles involved are much larger and more complex. Their diverse and abundant microbial populations may contain special recognition factors or appendages on their cell surfaces (CALLEJA, 1984) or produce coagulants which abet attachment (HARRIS and MITCHELL, 1973). The absorption concentrations of these exocellular polysaccharides vary among different strains of bacteria (PRINGLE and FLETCHER, 1986) and the polymers are largely resistant to microbial degradation (HARRIS and MITCHELL, 1973) attesting to the complexity of the chemistry involved.

Moreover, the large size and complex morphology of the aggregate surface itself results in intertwining or interlocking of portions of each colliding aggregate bringing the colliding particles into direct contact at many points simultaneously. Effective chemical attachment at only a few of these points coupled with physical interlocking of the fractal extensions emanating out from the irregular surface of the aggregates results in aggregation. The more points of contact between the two particles, the greater the probability of attachment. This is supported by our finding that multipoint attachment was the most common collision outcome observed. Moreover, α increased significantly as surface contact area increased. The observed increase in attachment probability with increased collision velocity among macroaggregates may also result from an increase in the number of contact points between the colliding aggregates. At higher velocities many of the aggregates

deformed and flattened slightly along the surface of impact, bringing the colliding particles into closer contact.

Thus, macroaggregate attachment is enhanced by 2 additional factors: 1) increased concentrations of microbial exudates available for polymer bridging and 2) increased surface area and surface complexity leading to multiple points of contact. This may explain why aggregates of marine snow have attachment probabilities several times higher than the highest values reported for marine sediments of microscopic size (see Table 3). Sediments have much less complex surfaces and small surface areas over which attachment may occur. Moreover attached communities and their associated exopolymers are more sparse on sediments and other inorganic particles than on marine snow.

Variations in the nature and complexity of the attached microbial community and in the surface morphology of macroaggregates may also explain variations in the attachment probabilities of different types of marine snow. Amorphous aggregates had the lowest attachment probabilities. They were small, presenting less potential surface area for contact. Moreover, they had fewer attached bacteria (ALLDREDGE and GOTSCHALK, In Press), and thus, potentially lower exopolymer concentrations to enhance attachment. The highest attachment probabilities were found among diatom flocs. These aggregates had irregular, highly convoluted and morphologically complex surfaces which may increase physical contact. Moreover, diatoms produce abundant exopolymers especially when nutrient stressed (DEGENS and ITTEKOT,1984) which may enhance flocculation of diatom blooms by increasing attachment probabilities (ALLDREDGE and GOTSCHALK, 1989; ALLDREDGE and SILVER, 1988).

Previous models of aggregation rates in natural waters (MCCAVE, 1984; ALI, et al, 1984; O'MELIA and BOWMAN, 1984; FARLEY and MOREL, 1986; WEILMANN et al.,1989) have assumed α to be constant across all size classes of aggregating particles primarily because the effect of particle size on α are poorly known and ambiguous. GIBBS (1983a) found natural sediments 2-4 um in diameter had attachment probabilities 25% higher than particles in the 0.5 to 1 um size range. However, this trend was reversed for particles of illite, a type of clay common in sediments. BURBAN et al. (1988) assume that α decreased as floc size of sediments increased. We found α increased significantly for particles larger than 0.5 Nl in volume, although the increase was only 16%. The high attachment probabilities we observed for marine snow may be primarily a function of large size. Information on attachment probabilities of organic particles of intermediate size, especailly in the 5 to 500 μm size range, are needed to accurately predict the rate of coagulation as a function of particle size in nature.

Our data indicate that the attachment probabilities of macroaggregates are significantly affected by particle type, size, collision velocity, and surface area of contact. However, the range of attachment probabilities we observed over these variables was actually quite narrow, varying only about 2 fold, in comparison with the order of magnitude differences reported for natural colloidal particles (see Table 3). Moreover, the attachment probabilities of marine snow are higher than any reported previously for natural particles. Mean attachment probabiltites of about 0.8 indicate that coagulation of organic particles in seawater may occur at rates an order of magnitude faster than predicted previously by aggregation models which assumed

considerably lower attchment probabilities (MCCAVE, 1984). These high attachment probabilities suggest that coagulation may be a significant process of particle aggregation, particularly in regions such as coastal oceans, where concentrations of particles available for collision are also high. They help explain the abundant and ubiquitous occurence of marine snow formed by particle coagulation throughout the worlds oceans.

REFERENCES

ALI, W. (1985) Chemical aspects of coagulation in lakes. Doctoral dissertation, The John Hopkins University, Baltimore, Maryland.

ALI, W., C. R. O'MELIA, and J. K. EDZWALD (1984) Colloidal stability of particles in lakes: Measurement and significance. *Water Science and Technology*, 17, 701-712.

ALLDREDGE, A. L. and C.C. GOTSCHALK (1988) In situ settling behavior of marine snow. *Limnology and Oceanography*, 33, 339-351.

ALLDREDGE, A. L., C. GOTSCHALK, and S. MACINTYRE (1987) Evidence for sustained residence of macrocrustacean fecal pellets in surface waters off southern California. *Deep Sea Research*, 34, 1641-1652.

ALLDREDGE, A.L. and C. C. GOTSCHALK (989) Direct observations of the mass flocculation of diatom blooms: characteristics, settling velocities and formation of diatom aggregates. *Deep-Sea Research*, 36, 159-171.

ALLDREDGE, A.L. and C. C. GOTSCHALK (1989) The relative contribution of marine snow of different origins to biological processes in coastal waters. Continental Shelf Research, IN PRESS.

ALLDREDGE, A.L. and M. W. SILVER (1988) Characteristics, dynamics and significance of marine snow. *Progress in Oceanography*, 20:41- 82.

BRUN-COTTAN J.-C. (1976) Stokes settling and dissolution rate model for marine particles as a function of size distribution. *Journal of Geophysical Research*, 81, 1601-1606.

BURBAN P. -Y., W. LICK and J. LICK (1988) The flocculation of fine-grained sediments in estuarine waters. *Journal of Geophysical Research*,

CALLEJA, G. B. (1984) *Microbial Aggregation*. CRC Press Inc., 276 pp.

CARON, D. A., P. G. DAVIS, L. P. Madin, and J. McN. SIEBURTH (1986) Enrichment of microbial populations in macroaggregates (marine snow) from surface waters of the North Atlantic. *Journal of Marine Research*, 44, 543-565.

DEGENS, E. T. and V. ITTEKOT (1984) A new look at clay-organic interactions. *Mitteilungen Geologische-Paleontologische Institut, Universitat Hamburg*, 56, 229-248.

DELICHATSIOS M. A. and R. F. PROBSTEIN (1975) Coagulation in turbulent flow: Theory and experiment. *Journal of Colloid and Interface Science*, 51, 394-405.

EDZWALD J. K., J. B. UPCHURCH and C. R. O'MELIA (1974) Coagulation in esturaies. *Environmental Science and Technology*, 8, 58-63.

FARLEY, K. J.and F. M. M. MOREL (1986) Role of coagulation in the kinetics of sedimentation. *Environmental Science Technology*, 20, 187-195.

FOWLER, S. W., and G. A. KNAUER (1986) Role of large particles in the transport of elements and organic compounds through the oceanic water column. *Progress in Oceanography*, 16, 147- 194.

GIBBS R. J. (1983a) Coagulation rates of clay minerals and natural sediments. *Sedimentary Petrology*, 53, 1193-1203.

GIBBS R. J. (1983b) Effect of natural organic coatings on the coagulation of particles. *Environmental Science and Technology*, 17, 237-240.

HARRIS, R. H. and R. MITCHELL (1973) The role of polymers in microbial aggregation. *Annual Review of Microbiology*, 27, 27-50.

HUNT, J. R. (1980) Prediction of oceanic particle size distributions from coagulation and sedimentation mechanisms. In: *Particles in*

water; characteristics, fate, effects, and removal, M. C. Kavanaugh and J. O. Leckie, 243-257. Advances in Chemistry Series #189. Am. Chem Soc, Washington D.C.

HUNT, J. R. (1982) Self similar particle-size distributions during coagulation: theory and experimental verification. *Journal of Fluid Mechanics*, 122, 169-185.

JOHNSON B. D., X. ZHOU and P. J. WANGERSKY (1986) Surface coagulation in sea water. *Netherlands Journal of Sea Research*, 20, 201-210.

LERMAN, A. (1979) *Geochemical processes: water and sediment environments*, Wiley, 481 pp.

McCAVE I. N. (1975) Vertical flux of particles in the ocean. *Deep-Sea Research*, 22, 491-502.

MCCAVE, I. N. (1984) Size spectra and aggregation of suspended particles in the deep ocean. *Deep-Sea Research*, 31, 329-352.

MEAKIN P. (1988) Fractal aggregates. *Advances in Colloid and Interface Science*, 28, 249-331.

NEIHOF, R. A. and G. I. LOEB (1972) The surface charge of particulate matter in seawater. *Limnology and Oceanography*, 17, 7-16.

O'MELIA, C. R. (1972) Coagulation and flocculation, in *Physicomechanical Processes for Water Quality Control*, Weber, W. J. Jr., Ed., Interscience, NY. 61- .

O'MELIA C. R. (1987) Particle-particle interactions. In: *Aquatic Surface Chemistry*, W. Stumm, editor, Wiley-Interscience, pp. 385-403.

O'MELIA C. R. and K. S. BOWMAN (1984) Origins and effects of coagulation in lakes. *Schweizerische Zeitschrift fur Hydrologie*, 46, 64-85.

PAERL, H. W. (1975) Microbial attachment to particles in marine and freshwater ecosystems. *Microbial Ecology*, 21, 73-83.

PRINGLE, J. H. and M. FLETCHER (1986) Absorption of bacterial surface polymers to attachment substrata. *Journal of General Microbiology*, 132, 743-749.

SOKAL R. R. and F. J. ROHLF (1969) *Biometry*. W. H. Freeman and Company, San Francisco, 776 pp.

STUMM, W. and J. P. MORGAN (1981) *Aquatic Chemistry*, Wiley-interscience, 731 p.

WEILENMANN U., C. R. O'MELIA and W. STUMM (1989) Particle transport in lakes: Models and measurements. *Limnology and Oceanography*, 34, 1-18.

WIEBE, W. K. and L. R. POMEROY (1972) Microorganisms and their association with aggregatesand detritus in the sea : a microscopic study. *Memorie dell' Instituto Italiano di Idrobiologia*, 29, Suppl. 325-352.

WILKINSON D. B. (1989) The fractal nature of biological aggregates. *M.S. Thesis. University of Arizona, Tucson.*

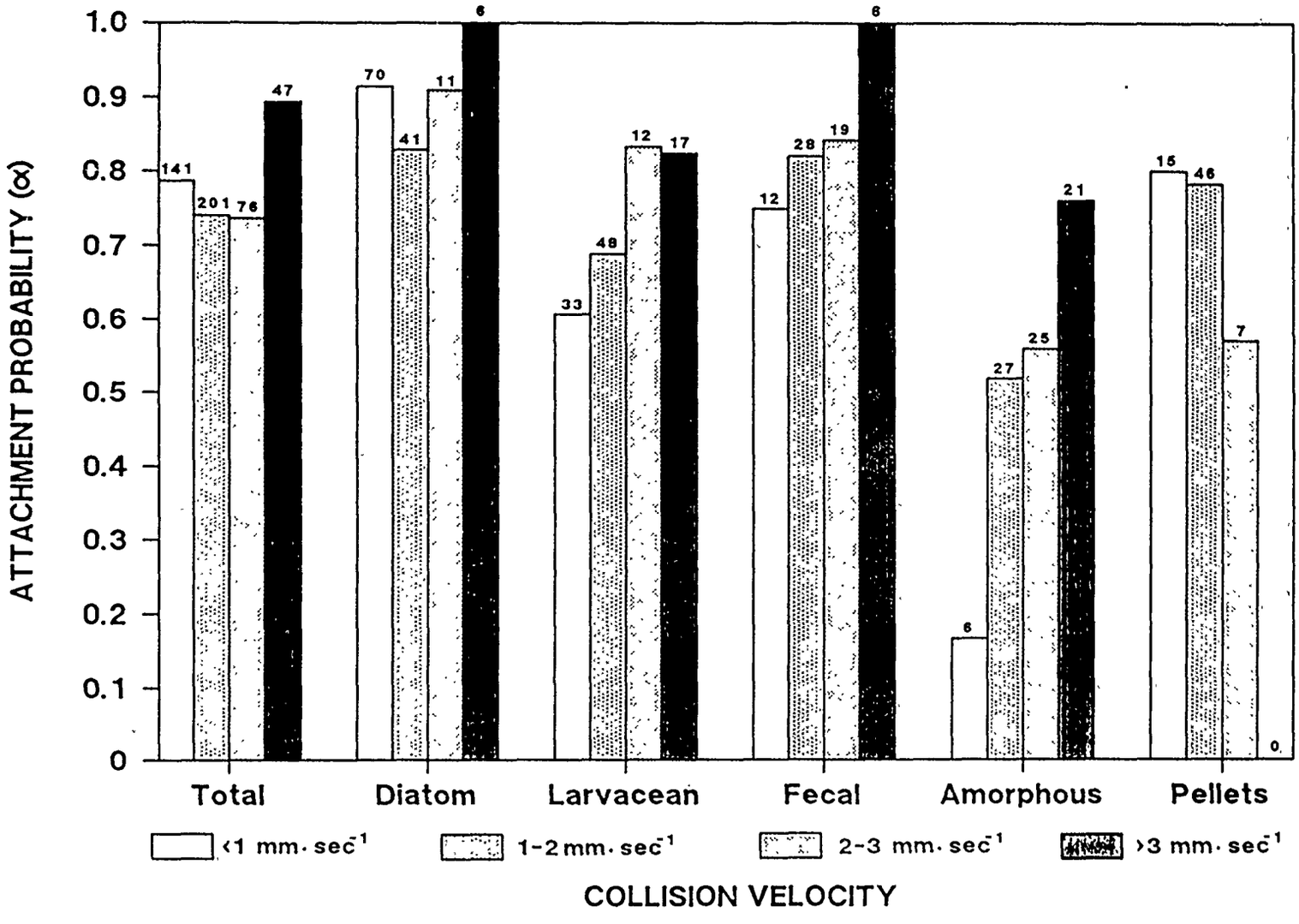
FIGURE LEGENDS

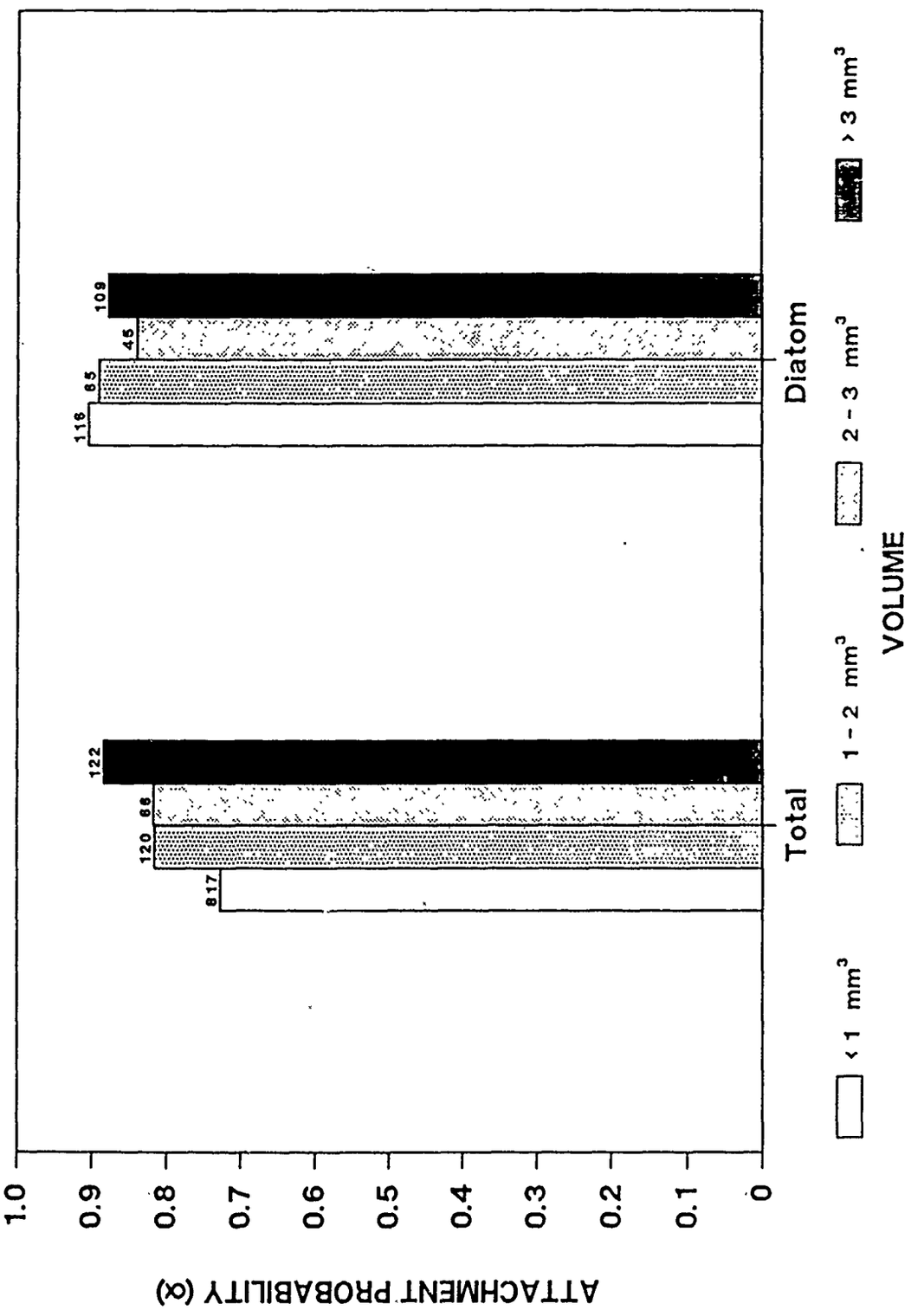
Figure 1: Effect of collision velocity on the attachment probabilities of 5 types of marine snow. Numbers above the bars are the number of collisions on which determination of α is based.

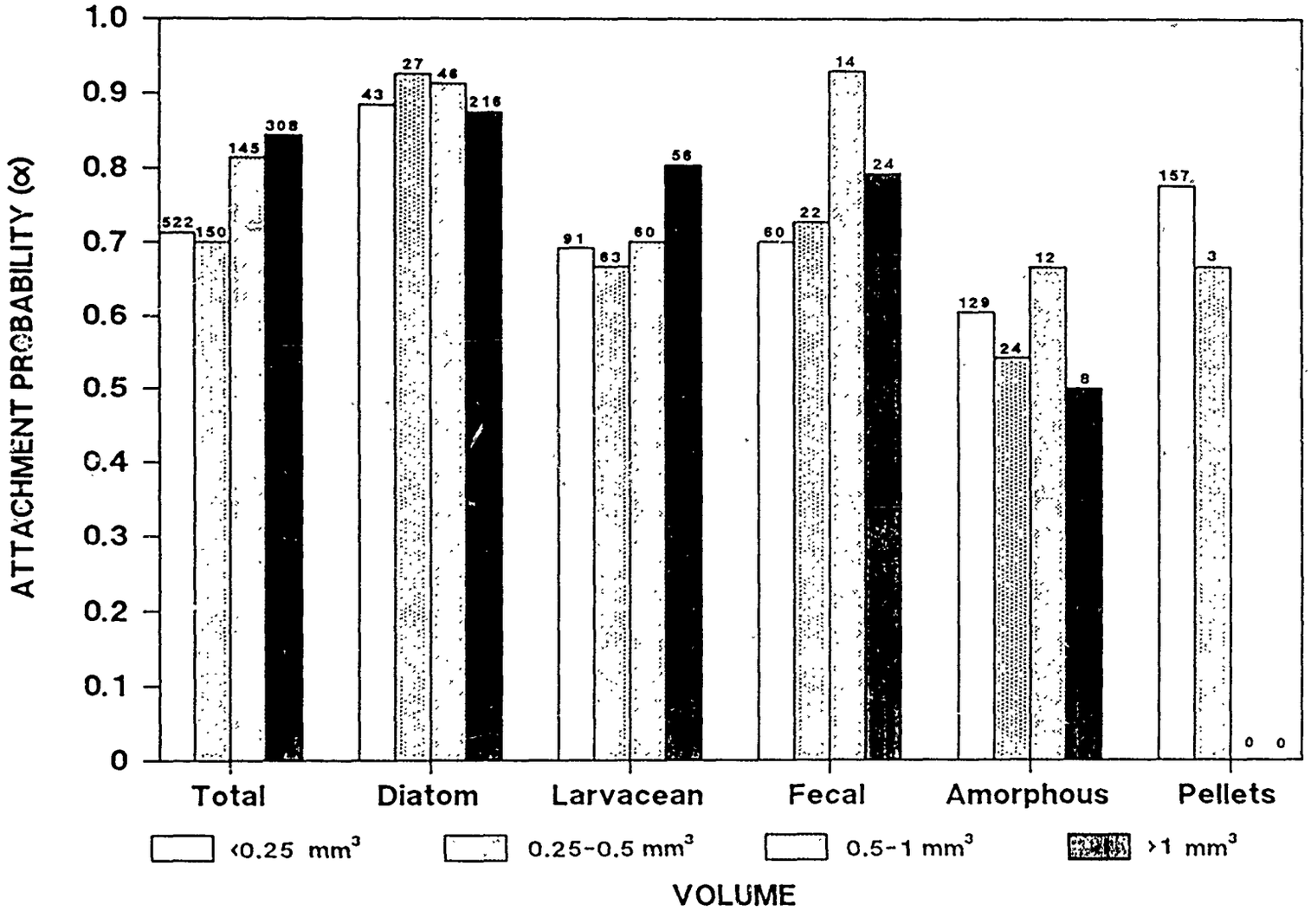
Figure 2: Effect of particle volume on the attachment probabilities of various types of marine snow. Numbers above the bars represent the number of particles observed. A) particle volume in 0.25 mm^3 increments. B) particle volume in 1 mm^3 increments. Only diatom flocs were consistently larger than 1 mm^3.

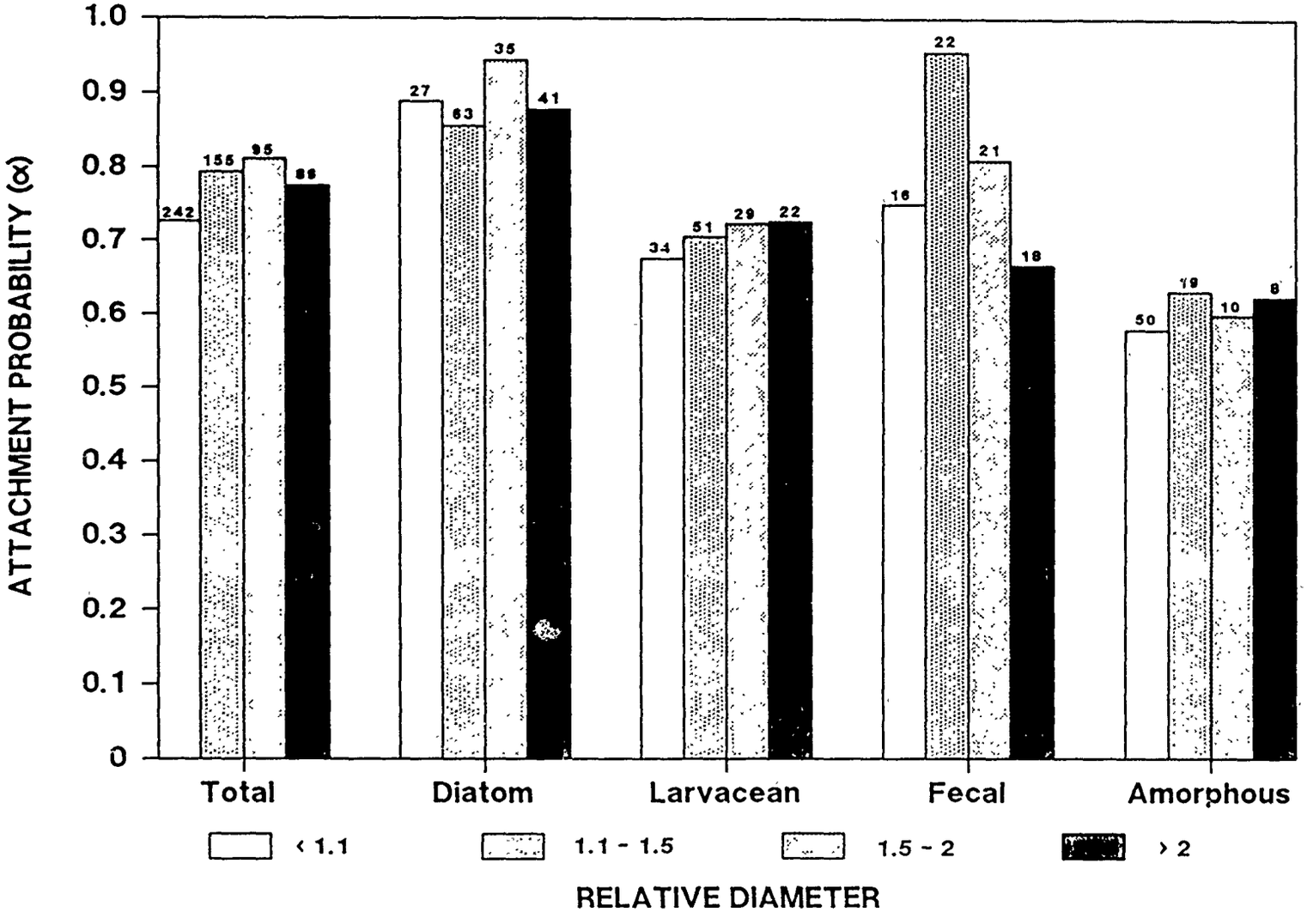
Figure 3: Effect of relative size on the attachment probabilities of various types of marine snow. Relative size of two colliding particles = (size of particle 1/ size of particle 2) where particle 1 is the larger particle. Numbers above bars represent the number of collisions on which determination of α is based. A) Relative diameter, B) Relative volume.

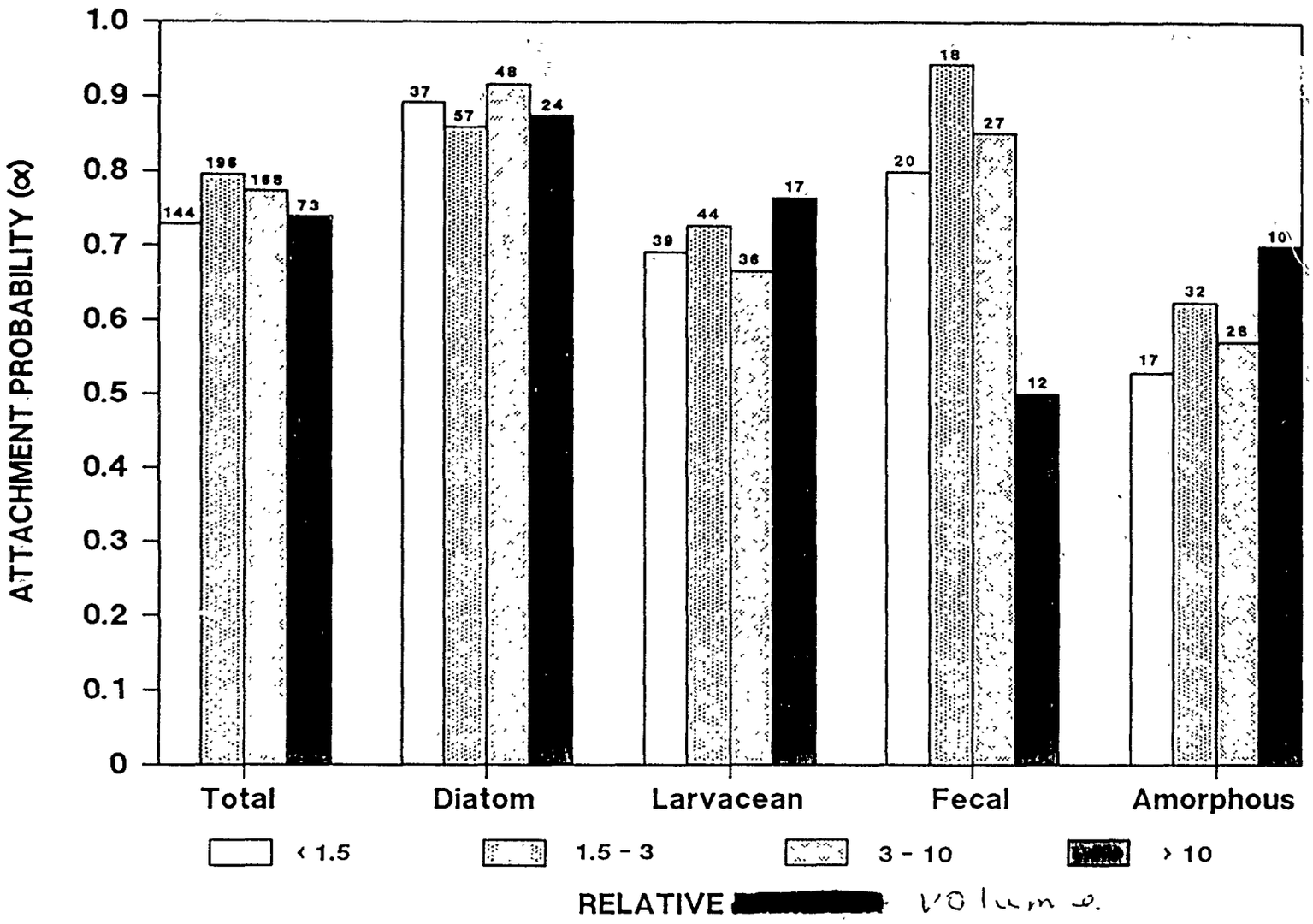
Figure 4: Effect of the surface area of contact between colliding particles on attachment probability of various types of marine snow. Numbers above the bars represent the number of collisions on which determination of α is based.


ATTACHMENT PROBABILITY (∝)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
141
201
76
47
70
41
11
6
33
48
12
17
12
28
19
6
6
27
25
21
15
46
7
0
Total
Diatom
Larvacean
Fecal
Amorphous
Pellets
<1 mm·sec⁻¹
1-2 mm·sec⁻¹
2-3 mm·sec⁻¹
>3 mm·sec⁻¹
COLLISION VELOCITY


ATTACHMENT PROBABILITY (∝)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Total
Diatom
817
120
88
122
116
65
45
109
< 1 mm³
1 - 2 mm³
2 - 3 mm³
> 3 mm³
VOLUME


ATTACHMENT PROBABILITY (α)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
522
150
145
308
43
27
46
216
91
63
60
56
60
22
14
24
129
24
12
8
157
3
0
0
Total
Diatom
Larvacean
Fecal
Amorphous
Pellets
<0.25 mm³
0.25-0.5 mm³
0.5-1 mm³
>1 mm³
VOLUME


ATTACHMENT PROBABILITY (α)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
242
155
95
88
27
63
35
41
34
51
29
22
16
22
21
18
50
19
10
8
Total
Diatom
Larvacean
Fecal
Amorphous
< 1.1
1.1 - 1.5
1.5 - 2
> 2
RELATIVE DIAMETER


ATTACHMENT PROBABILITY (α)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
144
196
168
73
37
57
48
24
39
44
36
17
20
18
27
12
17
32
28
10
Total
Diatom
Larvacean
Fecal
Amorphous
< 1.5
1.5 - 3
3 - 10
> 10
RELATIVE Volume

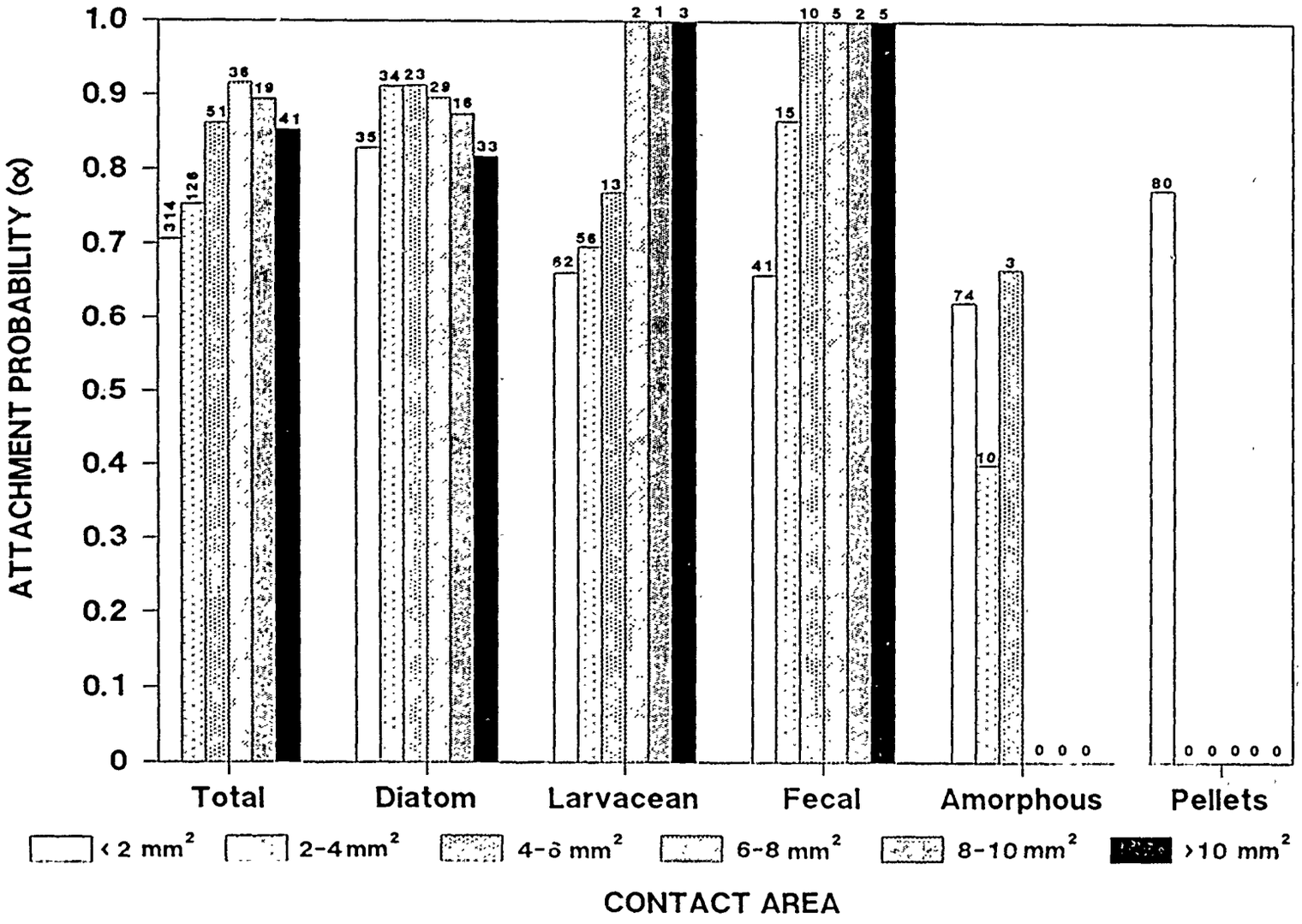

ATTACHMENT PROBABILITY (α)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
314 126 51 36 19 41
35 34 23 29 16 33
62 56 13 2 1 3
41 15 10 5 2 5
74 10 3 0 0 0
80 0 0 0 0 0
Total
Diatom
Larvacean
Fecal
Amorphous
Pellets
< 2 mm²
2-4 mm²
4-6 mm²
6-8 mm²
8-10 mm²
>10 mm²
CONTACT AREA

Table 1: Physical characteristics of colliding particles. Width = maximum diameter perpendicular to direction of sinking. Re = Reynolds number.

Particle type	n	Width (mm)	Max. length (mm)	Volume (mm^3)	Collision velocity ($cm \cdot sec^{-1}$)	Re
Diatom flocs	468	3.0 ± 1.3	4.4 ± 1.7	2.86 ± 3.25	0.11 ± 0.08	3.3 ± 3.4
Larvacean houses	272	1.8 ± ~~0.1~~ 0.7	2.9 ± 1.2	0.86 ± 0.91	0.18 ± 0.13	3.3 ± 3.0
Fecal aggregates	166	1.9 ± ~~0.1~~ 1.0	3.0 ± 1.4	0.90 ± 1.25	0.19 ± 0.09	4.0 ± 2.9
Amorphous aggregates	178	1.2 ± 0.~~1~~ 5	2.0 ± 0.9	0.20 ± 0.29	0.24 ± 0.11	3.2 ± 2.5
Fecal pellets	158	0.4 ± 0.2	2.3 ± 0.9	0.03 ± 0.05	0.14 ± 0.05	0.6 ± 0.4
Pteropod webs	68	1.4 ± 0.6	2.5 ± 1.0	0.38 ± 0.47	0.17 ± 0.10	2.3 ± 1.5
Total	1320	2.0 ± 1.3	3.2 ± 1.9	1.37 ± 2.54	0.16 ± 0.11	3.0 ± 3.0

62

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The physical strength of marine snow and its implications for particle disaggregation processes in the ocean

Alice L. Alldredge

Department of Biological Sciences, University of California, Santa Barbara, CA 93106

Timothy C. Granata

Ocean Physics Group, Department of Geology, University of Southern California, Los Angeles CA 90089

Chris. C. Gotschalk

Marine Science Institute, University of California, Santa Barbara,

and Thomas D. Dickey

Ocean Physics Group, University of Southern California

Running Head : Physical Strength of Marine Snow

ABSTRACT

Abiotic fragmentation of large, rapidly sinking aggregates into smaller, suspended particles by fluid shear has been suggested as an important process governing particle size distributions in the ocean and as one explanation for the exponential decrease in the flux of particulate organic matter with depth below the euphotic zone. We investigated this process by quantifying the small scale energy dissipation rates required to fragment or disaggregate fragile, macroscopic aggregates of particulate matter, known as marine snow. The fate of individual, hand-collected aggregates was videorecorded as they settled through a gradient of turbulent kinetic energy generated by a calibrated oscillating grid system in a laboratory tank.

Amorphous aggregates of detrital debris, gelatinous houses of larvacean tunicates, and aggregates of the sewage floccing bacteria, *Zoogloea ramigera*, all ranging up to 4 mm in diameter, did not break apart at energy dissipation rates far in excess of 1 cm^2s^{-3}. The rate of energy dissipation required to disaggregate fragile flocs of chain-forming diatoms up to 25 mm in length ranged from 10^{-3} to greater than 1 cm^2s^{-3} and increased exponentially with decreasing maximum aggregate diameter. Seventy percent of disaggregating particles fragmented into two subunits. Aggregates aged 5 days in the laboratory were significantly stronger than identical unaged particles. Our experiments have been limited to a few types of marine snow, including some among the most fragile, and to small scales of shear. However, they indicate that high energy storm events or current shears equivalent to those reported from tidal channels would be required to fragment even the most fragile organic aggregates in the upper ocean.

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INTRODUCTION

The magnitude of particulate flux to the ocean interior and the seafloor is largely determined by the abundance and sinking characteristics of particles in the larger size categories of the particle size spectrum (see Fowler and Knauer,1986 for review). Particles in these larger size classes are primarily aggregates of smaller particles of algae, microorganisms and detritus which have been repackaged into fecal pellets, mucus feeding webs and animal biomass via animal grazing, or coagulated into aggregates by physical processes of particle collision and attachment. Once formed, aggregates are lost or become reduced in size by gravitational settlement, animal consumption, dissolution, microbial decomposition to dissolved species, or physical disaggregation by fluid motion. These competing processes of aggregate formation, breakup and loss thus govern the characteristics and abundances of aggregated particulate matter in the ocean. They alter the oceanic size spectrum of particulate matter in ways which may significantly impact not only particulate flux but also the trophic structure, microbial activity, chemistry, and optical properties of the water column.

While processes of particle aggregation occur predominantly in the surface ocean, processes of particle loss occur throughout the water column. Numerous recent studies with sediment traps have revealed a consistent exponential decrease in the vertical flux of particulate organic matter (POM) with depth below the euphotic zone in all types of oceanic regimes (Berger et al., 1986). This decrease indicates that rapidly sinking, large particles must be converted to smaller, suspended particles or to dissolved constituents as they descend. Biological

processes of animal consumption, conversion of solubilized POM to suspended bacterial biomass (Cho and Azam, 1988), or bacterial decomposition may contribute to this decrease, although Karl et al. (1988) concluded that decomposition was unlikely to significantly decrease the flux of POM below the photic zone. They suggested a fourth alternative, abiotic fragmentation of fragile sinking aggregates by fluid shear, as a potentially significant physical processes responsible for the apparent shift in the particle size spectrum with depth.

Aggregates of POM larger than 500 um in diameter, known as marine snow, have been observed to break apart in water bottles and are generally considered to be quite fragile (Trent et al., 1978). Moreover, they form a major component of particulate flux (Fowler and Knauer, 1986) lending support to the physical disaggregation hypothesis. However, while indirect sampling and shipboard handling methods are vigorous and disruptive to marine snow (Alldredge and Silver, 1988), we have noticed that aggregates subjected by divers to levels of turbulence more similar to natural magnitudes do not always break apart. Moreover, aggregate strength has been shown to increase exponentially with decreasing aggregate size (Reich and Vold, 1959; Parker et al.., 1972; Smith and Kitchener, 1978; Tomi and Bagster, 1978b; Glasgow and Hsu, 1982) suggesting that aggregates in size classes smaller than those of marine snow would be even stronger. However, the strength of marine snow relative to the range of energy dissipation rates occurring in the natural ocean has not been quantified previously.

In the following study we measured the physical strength of marine snow as a function of aggregate size and composition by determining the magnitude of turbulent kinetic energy required to fragment, erode or

disrupt individual natural aggregates brought into the laboratory. We use these measurements to evaluate the possible significance of physical disaggregation by fluid shear as a process altering particle size distributions in the water column.

MATERIALS AND METHODS

Theoretical Considerations: The mechanisms by which aggregated particles are broken apart by physical processes depend upon the hydrodynamic regime which, in the ocean, is generally turbulent. Levich (1962) characterized eddies by their velocity and scale of turbulence (λ_e), the distance across which the velocity of an eddy changes. The scale of turbulence determines the energy content of an eddy. Large scale motions of scale L contain almost all the energy and are responsible for distribution of the energy through the system. However, they do not dissipate energy or disrupt aggregates. A scale of motion smaller than L is responsible for convective energy transfer to even smaller eddy scales, again with little energy dissipation. The range of scales of turbulence which dissipate energy and which have the potential to impact aggregates of the size range observed in the ocean (e.g microns to centimeters) is called the universal equilibrium range. It has been divided into a small eddy size region, the viscous dissipation subrange, and a larger eddy region, the inertial convection subrange. These subranges are divided by the Kolmogoroff microscale of turbulence (η) which is determined uniquely by the kinematic viscosity of the fluid (ν) and the rate of energy dissipation (ϵ):

$$\eta = (\nu^3/\epsilon)^{1/4} \qquad (1)$$

The relationship between ϵ and the root mean square velocity gradient (G) used in many previous disaggregation studies is

$$G = (\epsilon/\nu)^{1/2} \qquad (2)$$

Several mechanisms of aggregate breakup have been developed theoretically in the literature.

1) *Erosion* - Argaman and Kaufman (1970) and Parker et al. (1972) suggested that surface erosion of primary particles from the surface layers of the aggregate by turbulent drag is a principle mode of disaggregation. Surface shear stresses exceeding the shear strength of the polymer bridges bonding primary particles to the aggregate surface are produced by eddies which partially entrain the floc and exist on a scale approximating the aggregate diameter. Eddies that are large enough to fully entrain the aggregate produce zero relative velocity and no surface shear. Likewise eddies much smaller than the aggregate result in little surface shear. Surface shearing increases with eddy scale and with aggregate diameter. Parker et al. (1972) derived expressions for the maximum stable floc diameter (d_{max}) above which flocs were subject to disruption for aggregates both smaller and larger than the Kolmogoroff microscale. He assumed that aggregates smaller than the microscale were disrupted primarily by eddies in the viscous dissipation subrange while those larger than the microscale were disrupted primarily by eddies in the inertial convection subrange. These expressions take the form:

$$d_{max} = C\epsilon^{-\gamma} \qquad (3)$$

where C is the floc strength coefficient and the exponent γ is the stable floc size exponent. For erosion of aggregates larger than the Kolmogoroff microscale, Parker et al.. (1972) calculated that $\gamma = 1$; for erosion of flocs smaller than η, $\gamma = 0.5$.

2) *Instantaneous pressure fluctuations across the aggregate* - Based on the ideas of Thomas (1964), Tomi and Bagster (1978a) suggested that aggregate rupture resulted from instantaneous pressure differences on opposite sides of the floc produced by eddy motion. They defined the criterion for aggregate rupture as

$$p_d \geq \tau_{crit} \qquad (4)$$

where p_d is the instantaneous pressure fluctuation across a floc of size d and τ_{crit} is the limiting material strength due to attractive forces between primary particles of the aggregate. While Tomi and Bagster (1978a) assumed τ_{crit} was a constant independent of aggregate size, they acknowledged that, in practice, it would decrease with increasing aggregate size due to structural non-uniformities.

For large aggregates where $\eta << d << L$ the force balance between aggregate strength and induced stress yields $d_{max} \propto \epsilon^{-1}$. Where $d << \eta << L$; $d_{max} \propto \epsilon^{-2}$. They also derived an expression for an intermediate zone where $d \approx \eta$ and where both viscous and inertial effects might be significant. The value of γ derived for this region at the critical condition where $p_d = \tau_{crit}$ was $\gamma = 0.5$ yielding $d_{max} \propto \epsilon^{-0.5}$.

3) *Fragmentation due to filament fracture* - While most investigations of floc breakup have considered inorganic chemical flocs with relatively homogeneous interparticle bonding, Parker et al. (1972) considered the disaggregation of large biological flocs of activated sludge. He

predicted that maximum aggregate size would be limited by the tensile strength of the bacterial filament network binding the components of the aggregate together. For this filament network to fail, two eddies must act on the floc, simultaneously entraining and propelling the clusters in different directions. He predicted that the stable floc size exponent (γ) would be 0.25 in both the inertial convection and viscous dissipation subranges .

Additional theoretical and empirical studies support the relationship between energy dissipation and floc size described by equation (3). These are summarized in Table 1. The value of γ indicates the break-up mechanism which dominates. In many cases floc erosion and floc fragmentation occur simultaneously (Glasgow and Lueke, 1980; Pandya and Spielman, 1982). Some investigators have developed complex expression for calculating C as well (Parker et al., 1972; Tambo and Hozumi, 1979; Muhle et al., 1982)].

Empirical Measurements

Aggregate collection - Intact natural aggregates of marine snow for this study were collected individually in 6 ml polypropylene cylinders by SCUBA divers at depths of 10-15 m in the Santa Barbara Channel, California (34°20'N, 119°49'W) between February and June, 1989. Samples were stored undisturbed within their collecting cylinders at ambient seawater temperature (15-18 °C) and, except for the sample set collected June 9, their strength was determined within 18 to 40 hours of collection. The affects of aging on aggregate strength was determined for marine snow collected on June 9. The strength of one half of these samples was measured within 30 hours of collection while the strength of the other half was determined after they had been rotated within their

collecting cylinders end-over-end at 2 rev min^{-1} for 5 days in an environmental chamber at ambient seawater temperature (15 °C). Aggregates remained suspended within their slowly rotating cylinders simulating natural settlement in the water column (Gotschalk and Alldredge, 1989).

Almost all of the aggregates (>95%, see Alldredge and Gotschalk, In Press) collected at any one station were of the same type and composition. Fifteen samples from each collecting date were examined microscopically and identified as to origin based on their morphology, the presence of filtering nets, and on the identity of the dominant component particles forming the aggregate (e.g. diatoms, fecal pellets, unidentifiable debris, etc.).

We also compared the strength of marine snow with that of aggregates of *Zoogloea ramigera*, the slime-forming bacteria associated with activated sludge flocculating processes. Pure cultures of *Zoogloea ramigera* were grown in nutrient broth at 23 °C until they aggregated.

Aggregate Strength - Aggregate strength was determined by videorecording the fate of individual aggregates as they settled through a gradient of gradually increasing turbulent kinetic energy in the laboratory. Turbulence was generated by a stainless-steel grid oscillating vertically about a mean depth of 22.5 cm within a square plexiglass tank (Fig. 1). The tank was 62 cm X 62 cm X 76 cm in size and was filled with artificial seawater (Fig 1) . The grid was composed of 24 stainless steel tubes (1 cm O.D. X 61 cm in length) spot welded together at right angles with 5 cm separation midpoint to midpoint (Fig. 1). This system produced horizontal, isotropic turbulence with turbulence decreasing exponentially with increasing distance from the

grid vertically (Fig. 2). Various turbulent flow conditions could be created by adjusting oscillation frequency and amplitude of the grid. Generally we used frequencies from 2.4 to 4.9 Hz. Stroke length (grid amplitude) was held constant at 6 cm.

Dickey (1975), using a motion analysis technique, established that turbulent characteristics of flow in a tank can be determined using small (360 μm diameter), passive particles to follow the smallest scales of turbulent motions. Hartman (1983) and Isenogle (1985) used this technique in our tank to calculate energy dissipation rates at 5, 7, 9, 11, and 13 cm above the top stroke of the gird for frequencies of 0.50, 2.0, 3.5, and 4.5 Hz. Energy dissipation rates for our experiments were determined by calibrating our grid frequencies to those of Hartman (1983) and Isenogle (1985) using their data fit to the function:

$$\epsilon\ (z,\omega) = 10^{(0.56867\ -\ 0.22754z\ +(0.20455z)\log\omega)} \qquad (5)$$

where z is the distance from the grid in centimeter (cm) and ω is the grid frequency in hertz (Hz). Equation (5) regressed against the data of Hartman (1983) and Isenogle (1985) accounted for greater than 99% of the variance of energy dissipation at any given frequency.

The salinity of the seawater in the grid-turbulence tank was monitored with a YSI Model 33 salinity-conductivity-temperature meter and adjusted to match ambient seawater salinity around the aggregates by the addition of NaCl or dilution with freshwater. The tank and aggregate samples were equilabrated to room temperature (21-24°C). Each individual aggregate was then released 4 to 5 cm below the surface at a point in the center of the tank by gently immersing and inverting the

seawater-filled cylinder in which it had been collected and allowing the aggregate to exit slowly via gravitational settlement (Fig. 1). This method resulted in minimum manipulation and disturbance of the aggregates.

The behavior of each aggregate was videorecorded from the point of its initial release in the tank until it disaggregated or passed through the oscillating grid. Each aggregate was followed and kept in focus manually using a 55 mm Nikon macrolens attached to a Panisonic video camera, Model WV-1550 on a tripod. The vertical distance of the particle above the maximum upward stroke position of the oscillating grid was measured with a second video camera positioned below the first. This camera was also affixed to the vertically adjustable tripod and remained focused on a ruler showing the position of the particle above the grid to the nearest mm (Fig. 1). The images from both cameras were merged with a screen splitter and recorded simultaneously on 1/2 inch VHS videotape.

Data Analysis - Video tapes were analyzed on a MegaVision 1024 XM Image Processing System. Aggregate size was determined by averaging the areas and maximum diameters of three different orientations of each aggregate immediately after it had settled out of the collecting cylinder. The size of each particle was scaled using the diameter of the collecting cylinder as a size reference. Equivalent spherical volume was calculated from average area. The distance above the grid and the numbers and relative sizes of the daughter particles produced when the aggregate fragmented, eroded or disintegrated was also recorded. We were unable to measure absolute fragment sizes directly because we did not know the distance of the floc from the camera in the y direction at the

point of aggregate rupture (see Fig. 1). Fragment sizes were calculated by measuring the area of the parent floc immediately before rupture and then determining the proportion of this parent floc area represented by each fragment immediately after rupture. This proportion was then multiplied by the calibrated parent floc volume determined when the floc was first introduced into the tank in order to obtain absolute fragment sizse. Length measurements were recalculated immediately prior to disaggregation in the small number of trials (about 5%) where the aggregates deformed appreciably as they sank. A component particle within the floc whose shape and size did not change was used as a size reference in these caes. Trials where the aggregate disintegrated upon release, encountered wall effects, or otherwise exhibited aberrant behavior were discarded prior to image processing and were not included in our analysis.

RESULTS

We determined the strength of 337 individual aggregates representing 4 types of natural marine snow. One type, collected on both March 16 and June 9, was dominated primarily by chains, spines and frustules of the setose centric diatom genera *Chaetoceros*, especially *Chaetoceros debilis*, *Ch. peruvianus*, *Ch. socialis* and *Ch. radicans*. Diatoms of the *genera Nitzschia*, *Eucampia* and *Rhizosolenia* also occurred in low abundance. A second type of marine snow composed predominantly of the pennate chain forming diatom genus *Nitzschia*, especially *Nitzschia delicatissima* nd *N. pacifica*, was collected on May 19. Other species of diatoms were rare within these flocs. Both types of diatom aggregates also contained abundant unidentifiable debris, mucus, and occasional fecal pellets. The third type of aggregate investigated was composed

primarily of miscellaneous, unidentifiable debris and bacteria embedded in a mucus media. These aggregates were small, contained few fecal pellets or identifiable algal cells, and were typical of aggregates we have commonly observed previously in oligotrophic open ocean regimes. The fourth type of marine snow was not formed by coagulation processes. These aggregates were the spherical, discarded, gelatinous feeding structures, or houses, of the planktonic larvacean tunicates *Oikopleura dioica* and *O. longicauda*. They contained numerous fecal pellets, algae and debris within their filters. We also studied a fifth type of biological aggregate formed by the sewage bacteria *Zoogloea ramigera*. These flocs were small and bound together by numerous internal fibrils.

The sizes and disaggregation outcomes of the 5 types of aggregates, ranging from 1.8 to 25.0 mm in maximum diameter and from 0.8 to 198 mm^3 in volume, are summarized in Table 2. We have expressed aggregate size as maximum diameter since this is the dimension which actually encounters eddy motion. This is consistent with most previous studies of aggregate strength (see Table 3). Aggregates of miscellaneous debris, larvacean houses and *Zoogloea* flocs were so strong that they could not be disaggregated by our experimental apparatus (Table 2). All passed through the openings in grid and only ruptured if directly struck by a grid bar . Many of these aggregates were captured by circular flows and twirled rapidly around the grid bars before sinking intact to the bottom of the tank. Larvacean houses fragmented only when struck repeatedly by the grid bars. Their spherical shapes were deformed to flat plates prior to fragmentation. The highest rate of energy dissipation occurring in the calibrated portion of the tank, 5 cm above the grid, was 1 $cm^2 s^{-3}$. Since energy dissipation increased

exponentially nearer the grid, aggregates passing through the grid encountered energy dissipation rates considerably above this value without disaggregating.

The majority of both types of diatom flocs disaggregated within the calibrated range of our tank, at energy dissipation rates less than 1 cm^2s^{-3}. However, 7 to 44% pass through the grid indicating that many were strong enough to withstand energy dissipation rates of considerably greater magnitude (Table 2). Ninety-eight percent of all *Nitzschia* flocs and 90% of all *Chaetoceros* flocs investigated disaggregated at energy dissipation rates above 10^{-2} cm^2s^{-3}. The rate of energy dissipation required to fracture *Chaetoceros* aggregates was an exponential function of maximum aggregate diameter (Fig. 3A). Disaggregation occurred well within the inertial convection subrange. Marine snow is fractal in its geometry (Logan and Wilkonson, 1989), resulting in length dimensions which vary by ± 20% depending upon the plane in which the fractal aggregate is viewed (Meakin, 1988). This uncertainty in size introduced considerable scatter in our plots. In order to more clearly ascertain the relationship between energy dissipation rate and aggregate size we grouped the data into 24 equal bins based on maximum length. The mean maximum size versus the mean energy dissipation rate at disaggregation within each bin is plotted in Fig. 3B, yielding an significant exponential relationship between energy dissipation and maximum length ($P< 0.001$), and a stable floc size exponent (γ) of 0.30, quite close to the 0.25 predicted by Parker et al. (1972) for biological flocs breaking via filament fracture. Visible filaments occasionally separated fragments of disassociating diatom snow and were observed to stretch and snap.

The rate of energy dissipation required to fragment diatom aggregates composed predominantly of *Nitzschia* was also an exponential function of maximum aggregate diameter. The γ of these flocs was -0.62, indicating that larger aggregates tended to be stronger while smaller ones tended to be weaker than similarly sized aggregates of *Chaetoceros* (Fig 4A,B).

No significant difference in the relationship between maximum diameter and energy dissipation was observed between 1 day old and 5 day old *Chaetoceros* flocs for either unbinned (Fig 3A) or binned data (Fig 5). The two populations were not statistically different in length or volume (student's t-test for comparison of population means; Table 2). However, a significantly higher proportion of aged aggregates (44% vs 7%) was able to pass through the grid without disaggregating ($P<0.001$, test for the equality of two percentages, Sokal and Rohlf, 1969) and a significantly lower fraction of aged aggregates (53% versus 84%) fragmented at energy dissipation rates below 1 cm^2s^{-3} ($P<0.001$), indicating that short term aging increases the strength of aggregates appreciably (Table 2).

Seventy-one % of disaggregating particles broke into two fragments, while about 11% broke into more than 10 fragments (Fig. 6). The number of fragments produced increased with increasing parent floc size (Fig 7A) and decreased with increasing energy dissipation rate (Fig. 7B), although the number of fragments produced was highly variable among aggregates of similar size. In order to test the significance of these trends we compared the mean size and energy dissipation rate at break-up of the population of aggregates breaking into 2 fragments with that breaking into more than 10 fragments using a students-t test for the

comparison of population means. Both trends were significant at $P<0.001$.

Although the mean size of the fragments produced per aggregate was also highly variable, larger parent flocs tended to produce significantly larger fragments ($P<0.001$; Fig. 8A). Larger fragments were also produced significantly more often when disaggregation occurred at lower rates of energy dissipation ($P<0.01$; Fig. 8B). This would be expected since flocs disaggregating at lower rates of energy dissipation tended to be larger.

We calculated a relative fragment volume (RFV) for those trials which resulted in two fragments where:

$$RFV = \frac{\text{volume of the smaller fragment}}{\text{volume of the larger fragment}} \qquad (6)$$

Aggregates with relative fragment volumes near 1 broke into two equally-sized flocs while those with RFV nearer to 0 broke into fragments which were highly dissimilar in size. While relative fragment volume was highly variable, larger flocs did tend to disaggregate into more equally sized fragments than did smaller flocs (Fig. 9). No significant relationship was found between relative fragment size and the rate of energy dissipation at disaggregation.

DISCUSSION

Strength of marine snow

The approach used in this study varies considerably from the approach used in previous investigations of aggregate strength. We directly observed the process of disaggregation of individual natural aggregates while previous studies have examined the average strengths of

large populations of aggregates generated in the laboratory. In these studies flocs produced by agitation of uniform suspensions of organic or inorganic particles (see Table 3) within laboratory reaction vessels were subjected to quantified rates of turbulent shear generated by propellers, turbines or paddle stirrers. The mean or maximum particle diameter attainable at a variety of magnitudes of shear was determined once the system had reached steady state. Some studies also examined disaggregation under laminar flow (Stevenson,1972). This approach gives statistically valid average floc strengths but obscures variability among particles. It assumes all aggregates are uniform and homogeneous in structure, a condition not applicable to most natural aggregates. Maintenance of uniform, quantifiable shear throughout all parts of the reaction vessel is also a major problem in many of these studies.

Empirically determined values of the stable floc size exponent, γ, of a variety of organic and inorganic aggregates investigated in laboratory reactors fall within the range of 0 to 1 predicted by theory (Table 3). The stable floc size exponent of *Chaetoceros* aggregates of 0.3 is near the 0.25 predicted by Parker et al. (1972) for aggregates breaking via filament fracture, a special case of fragmentation. *Nitzschia* aggregates also broke via fragmentation with $\gamma = 0.6$, close to the 0.5 predicted by Tomi and Bagster (1978a) for fragmentation of aggregates approximating the Kolmogoroff microscale in size (Table 1). The small magnitude of γ suggests that errosion was a less common mode of disaggregation. However, smaller aggregates were more likely to fragment into disparately sized fragments suggesting that they were affected by smaller eddies acting more as agents of particle erosion than fragmentation.

Rupture into a few large fragments is consistent with the fractal geometry of marine snow (Logan and Wilkinson, In Press). This geometry indicates that aggregates have been formed primarily via collisions of clusters of particles rather than by attachment of primary particles to the aggregate surface one at a time (Meakin, 1988). Cluster-cluster collisions result in an inhomogeneous floc structure and increase the potential for fragmentation between adjoining clusters (Franscois and van Haute, 1984) .

We observed high variability in strength between individual aggregates of the same type and size. Some of this variability resulted from the stochastic nature of turbulence with the tank, but the aggregates themselves are also variable in composition. Although marine snow from any one sampling station is composed of similar types of primary particles (Alldredge and Gotschalk, In Press), the proportions of these components will vary according to the previous history of the aggregate and the nature of its attached microbial community. Microbial exopolymers and capsular material, which are significant binding agents within aggregates (Paerl, 1973; Alldredge and Silver, 1988), vary both between different aggregates and within the same aggregate depending upon the identity, abundance, and internal distribution of attached bacteria. Variations in the properties of algal exopolymers (Alldredge and Silver, 1988) and the presence of entwining setae within *Chaetoceros* flocs may also explain the higher strength of these flocs relative to those dominated by *Nitzschia*, a non-setose genus.

Aged aggregates were able to withstand considerably higher rates of energy dissipation than unaged aggregates without disaggregating. Since the physical properties of the aggregates remained unchanged over the

aging period, biological and related chemical changes associated with aging are likely to be responsible. The growth of microbial populations inhabiting marine snow occurs rapidly in the first 72 to 96 hours following aggregate formation (Pomeroy et al., 1984). The quantity or binding effectiveness of microbial exudates and capsular material produced by this dynamic microbial community may increase with aggregate age, serving to bind clusters together more effectively. Attached bacteria also produce fimbriae and fibrils which form a network of intertwining strands and potentially strengthen the aggregates (Paerl, 1973 ; Alldredge and Silver, 1988). Bacterial filament networks of this sort are responsible for the high strength of activated sludge flocs (Parker et al., 1972).

Although aged diatom flocs were able to withstand significantly higher turbulence, the stable floc size exponent and strength coefficient were not statistically different between aged and unaged populations. This undoubtedly results from the high scatter and relatively small sample size of our data set.

Larvacean houses, aggregates formed of amorphous debris, and aggregates of *Zoogloea ramagera* could not be disrupted by our experimental apparatus. Larvacean houses are composed of mucopolysaccharides secreted by the epithelial cells of the animals trunk (Korner, 1952). Algae and bacteria become attached to the house by filtering activities of the animals. Thus, these aggregates are not formed initially by cluster-cluster collisions and are not fractal in geometry. Once the houses are discarded, particles may collide and stick to the outer surfaces. However, the gelatinous framework maintains the integrity of the house for many days (Davoll and Silver, 1986)

suggesting that these aggregates are unlikely to fragment from fluid shear unless considerably decomposed.

The strength of aggregates formed of amorphous, unidentifiable debris may results, in part, from of their small size and abundant bacterial communities (Alldredge and Gotschalk, In Press). All natural biological aggregates may contain fibrilar networks somewhat similar to those found in activated sludge flocs. Bundles of such filaments must snap in order to fragment the floc (Parker et al., 1972).

Although we have not investigated all types of marine snow, most notably aggregates composed primarily of fecal material (Alldredge and Gotschalk, In Press) or of other types of algae (Alldredge and Silver, 1988), our previous observations of marine snow *in situ* indicate that diatom flocs are among the most fragile. Overall, our results indicate that most types of natural aggregates of marine snow, including a significant fraction of diatom snow (14 to 50 % depending upon sampling date) fragment at energy dissipation rates greater than 1 cm2s-3.

Implications for Particle Disaggregation in situ

Energy dissipation rates in most regions of the ocean most of the time appear too low to disaggregate even the most fragile marine snow. Energy dissipation rates in the upper mixed layer under low wind conditions range from 10^{-2} to 10^{-6} cm^2s^{-3} (Gargett et al., 1979; Dillon and Caldwell, 1980; Lueck and Reid, 1984; Shay and Greg; 1986; Peters et al., 1988). Even under high wind conditions of 15 m s^{-1}, ϵ ranges only from 10^{-2} to 10^{-4} cm^2s^{-3} in the upper 10 to 20 m of the water column (Dillon and Caldwell, 1980; Oakey and Elliot, 1982). Particles sinking through current boundaries or intrusions will also generally encounter low shear. For example, ϵ ranged from 10^{-4} to 10^{-5} cm^2s^{-3} in the

intrusion region between the California Current and the California Undercurrent (Yamazaki and Lueck, 1987); and from 10^{-2} to 10^{-3} cm^2s^{-3} in the Equatorial Undercurrent (Crawford and Osborne, 1979). Bottom stresses in many parts of the ocean may also be too low to disaggregate marine snow sinking through the benthic boundary layer. Energy dissipation rates of 10^{-2} to 10^{-4} cm^2s^{-3} are reported at 15 cm above the bottom in coastal regions (Dewey and Crawford, 1988).

The highest rates of energy dissipation reported in some regions of the ocean are adequate to disaggregate diatom aggregates. Storm events with winds exceeding 20 m s^{-1} produce energy dissipation rates ranging from 10^{-1} to 10^{-2} cm^2s^{-3} in the upper 25 m of the water column, rates sufficient to disaggregate about 78% of *Chaetoceros* snow and about 94% of *Nitzschia* flocs assuming they were similar to those investigated here. Energy dissipation rates in tidal channels of 10^{-3} to 1 cm^2s^{-3} (Grant, 1962) would disaggregate most diatom snow. Marine snow sinking through the boundary layer of some tidal currents could experience energy dissipation rates as high as 10^{-1} to 1 cm^2s^{-3} within 1 m of the bottom (Gross and Nowell, 1985), resulting in disruption. However, the other types of marine snow we investigated, including marine snow of miscellaneous debris, bacterial flocs and larvacean houses are sufficiently strong to withstand even these high rates of fluid shear.

Implications for oceanic flux processes and particle size spectra

Much of the particulate organic matter (POM) reaching the ocean interior and the seafloor does so in the form of large, rapidly sinking particles, primarily of marine snow and fecal pellets (Fowler and Knauer, 1986; Alldredge and Silver, 1988). These larger particle classes mediate the exchange of POM between the surface and the deep

ocean while the smaller, suspended size classes dominate the standing stock of particulate matter in the water column. The downward vertical flux of particulate matter decreases exponentially with depth below the mixed layer (see Berger et al., 1988). Greater than 75% of the net loss of POM occurs in the upper 500 m of the water column (Martin et al., 1987). This decrease indicates that large, rapidly sinking particles must be converted either small suspended particles or to dissolved constitutes as they descend.

Abiotic fragmentation due to fluid shear is one possible mechanism by which large particles may be converted to small, suspended forms (Karl et al., 1988). However, our data indicate that this process is unlikely to be significant in the upper ocean at most times. Physical disaggregation may affect the particle size spectra only episodically during storm events, and then only if the particles present are of algal origin and in the upper most surface layers. The size to strength relationships measured here suggest that aggregates smaller than marine snow would be even less likely to disaggregate. Moreover, large disaggregating flocs produce fragments which, because of their relatively small size, are sufficiently strong to withstand further disaggregation. However, although smaller than their parent flocs, such fragments would still be sufficiently large to sink relatively rapidly and potentially contribute significantly to the vertical flux of POM.

The strength of aggregates reaching the deep sea remains unknown. Although aggregate strength increases with short term aging, aggregates sinking on the order of 100 m d^{-1}, might require a month or more to transverse the ocean interior. During this time microbial exudates and binding material may decompose sufficiently to weaken the attraction

between attached clusters within the aggregate. Further research on affects of long term aging on the strength of marine snow is required before its disaggregation behavior in the deep sea can be predicted.

Several other alternative processes may explain the reduction in POM flux with depth. Microbial decomposition by abundant and metabolically active microorganisms attached to sinking particles has been suggested as one pathway, although large, rapidly sinking particles appear to be relatively poor habitats for bacterial growth and are unlikely sites for active remineralization of organic matter (Karl et al., 1988). The conversion of sinking particles to dissolved constituents via bacterial solubilization may also control the net loss of particulate organic matter from the upper regions of the ocean. POM soluabilized by bacteria attached to rapidly sinking particles is converted into biomass by growth of free-living bacteria around the particles and by the budding off of offspring into the water column by the attached forms. This results in production of fine suspended particles at the expense of the large, rapidly sinking ones (Cho and Azam, 1988). A third alternative is that large particles are consumed by animal grazers, both vertically migrating and nonmigrating forms, and converted into smaller fecal particles, animal biomass, CO_2 and dissolved excretory products. Our results suggest that these biological processes are far more likely to mediate the size spectrum of aggregated particulate matter in the ocean than physical processes of particle disaggregation due to fluid motion.

References

ALLDREDGE, A. L., and C. C. GOTSCHALK. 1989. The relative contribution of marine snow of different origins to biological processes in coastal waters. Cont. Shelf. Res. In Press.

ALLDREDGE, A. L., and M. W. SILVER. 1988. Characteristics, dynamics and significance of marine snow. Prog. Oceanogr. 20: 41-82.

ARGAMAN, Y., and W. J. KAUFMAN. 1970. Turbulence and flocculation. J. San. Eng. Div. Am. Soc. Civ. Engrs. 96: 233-241.

BERGER, W. H., K. FISCHER, C. LAI, and G. WU. 1988. Ocean carbon flux: Global maps of primary production and export production. p. 131-176. In C. R. Agegian [ed.], Biogeochemical cycling and fluxes between the deep euphotic zone and other oceanic realms. NOAA National Undersea Research Program, Res. Rpt. 88-1.

CAMP, T. R. 1968. Floc volume concentration. J. Am. Wat. Wks. Assn. 60: 656-673.

CRAWFORD, W. R., and T. R. OSBORN. 1979. Energetics of the Atlantic Equatorial Undercurrent. Deep-Sea Res. 26(Suppl. II.): 309-323.

CHO, B. C., and F. AZAM. 1988. Major role of bacteria in biogeochemical fluxes in the ocean's interior. Nature 332: 441-443.

DAVOLL, P. J., and M. W. SILVER. 1986. Marine snow aggregates: life history sequence and microbial community of abandoned larvacean houses from Monterey Bay, California. Mar. Ecol. Prog. Ser. 33: 111-120.

DEWEY, R. K., and W. R. CRAWFORD. 1988. J. Phys. Oceanogr. 18: 1167-1176.

T.-?. DICKEY 1975.

DILLON, T. M., and D. R. CALDWELL. 1980. The Batchelor spectrum and dissipation in the upper ocean. J. Geophys. Res. 85: 1910-1916.

FOWLER, S. W., and G. A. KNAUER. 1986. Role of large particles in the transport of elements and organic compounds through the oceanic water column. Prog. Oceanogr. 16: 141-156.

FRANCOIS, R. J. 1987. Strength of aluminum hydroxide flocs. Water Res. 21: 1023-1030.

FRANCOIS, R. J., and A. A. VAN HAUTE. 1985. Structure of hydroxide flocs. Water Res. 19: 1249-1254.

GARGETT, A. E., T. B. SANFORD, and T. R. OSBORN. 1979. Surface mixing layers in the Sargasso Sea. J. Phys. Oceanogr. 9: 1090-1110.

GLASGOW, L. A., and J. P. HSU. 1982. An experimental study of floc strength. J. Am. Inst. Chem. Engrs. 28: 779-785.

GLASGOW, L. A., and R. H. LUECKE. 1980. Mechanisms of degradation for clay-polymer flocs in turbulent systems. Ind. Engng. Chem. Fundam. 19: 148-156.

GLASGOW, L. A., R. J. POLLOCK, and W. A. BARKLEY. 1983. Particle size reduction by breakage in biological wastewater treatment. Biotech. Bioeng. 15: 901-918.

GOTSCHALK, C.C. and A.L. ALLDREDGE. 1989. Enhanced primary production and nutrient regeneration within aggregated marine diatoms. Mar. Biol. 103: 119-129.

GRANT, H. L., R. W. STEWART, and A. MOILLIET. 1962. Turbulence spectra from a tidal channel. J. Fluid Mech. 2: 241-268.

GROSS, T. F., and A. R. M. NOWELL. 1985. Spectral scaling in a tidal boundary layer. J. Phys. Oceanogr. 15: 496-508.

Tim? HARTMAN 1983.

HOPPE, V. H., W. TROGER, and F. WINKLER. 1977. Das kinetische modell der orthokinetischen phase der flockung am beispiel einer flockulierten kaolinsuspension. Wiss. Z. TH Leuna-Meresburg. 19: 399-408.

HUNTER, K. A., and P. S. LISS. 1982. Organic matter and the surface charge of suspended particles in estuarine waters. Limnol. Oceanogr. 27: 322-335.

ISENOGLE, S. S. 1985. A laboratory study of gas trasfer across an air-water interface. Masters Thesis. Univ. of Southern Calif.

KARL, D. M., G. A. KNAUER, and J. H. MARTIN. 1988. Downward flux of particulate organic matter in the ocean: a particle decomposition paradox. Nature 332: 438-441.

KORNER, W. F. 1952. Untersuchungen uber die gehausebilbung bei appendicularien (*Oikopleura dioica* Fol). Z. Morphol. Oekol. Tiere. 41: 1-53.

LAGVANKAR, A. L., and R. S. GEMMELL. 1968. A size density relationship for flocs. J. Am. Wat. Wks. Assn. 60: 1040-1046.

LEENTVAAR, J., and M. REBHUN. 1983. Strength of ferric hydroxide flocs. Water Res. 8: 895-902.

LEVICH, V. G. 1962. Physico-chemical hydrodynamics. Prentice Hall, Inc., Englewood Cliffs, NJ. pp. ???

LOGAN, B.E., and D. B. WILKINSON. 1989. Fractal geometry of marine snow and other biological aggregates. Limnol. Oceanogr. In Press.

LUECK, R. and R. REID. 1984. On the production and dissipation of mechanical energy in the ocean. J. Geophys. Res. 89: 3439-3445.

MAGARA, Y., S. NAMBU, and K. UTOSAWA. 1976. Biochemical and physical properties of activated sludge on settling characteristics. Water Res. 10: 71-77.

MARTIN, J. H., G. A. KNAUER, D. M. KARL, and W. W. BROENKOW. 1987. Vertex: Carbon cycling in the North East Pacific. Deep-sea Res. 34: 267-286.

MEAKIN, P. 1988. Fractal aggregates. Adv. Col. Int. Sci. 28: 249-331.

MUHLE, K., A. IVANAUSKAS, and T. NEESSE. 1982. A model of stability on the basis of adhesive forces acting between particles. Proc. VII Eropean Conference "Chemistry of Interfaces", Siofak, Hungary.

OAKEY, N. S., and J. A. ELLIOTT. 1982. Dissipation within the surface mixed layer. J. Phys. Oceanogr. 12: 171-185.

PAERL, H. W. 1973. Detritus in Lake Tahoe: Structural modification by attached microflora. Science 180: 496-498.

PANDYA, J. D., and L. A. SPIELMAN. 1982. Floc breakage in agitated suspensions: Theory and data processing strategy. J. Col. Int. Sci. 90: 517-531.

PARKER, D. S., W. J. KAUFMAN, and D. JENKINS. 1972. Floc breakup in turbulent flocculation processes. J. San. Eng. Div. 98(SA1): 79-99.

PETERS, H., M. C. GREGG, and J. M. TOOLE. 1988. On the parameterization of equatorial turbulence. J. Geophys. Res. 93: 1199-1218.

POMEROY, L.R., R. B. HANSON, P. A. MCGILLIVARY, B. F. SHERR, D. KIRCHMAN, and D. DEIBEL. 1984. Microbiology and chemistry of fecal products of pelagic tunicates: rates and fates. Bull. Mar. Sci. 35: 426-439.

REICH, I., and R. D. VOLD. 1959. Flocculation-deflocculation in agitated suspensions. I. Carbon and ferric oxide in water. J. Phys. Chem. 63: 1497-1501.

SHAY, T. J., and M. C. GREGG. 1986. Convection driven turbulent mixing in the upper ocean. J. Phys. Oceanogr. 16: 1777-1798.

SMITH, D. K. W., and J. A. KITCHENER. 1978. The strength of aggregates formed in flocculation. Chem. Eng. Sci. 33: 1631-1636.

SOKAL R. R., and F. J. ROHLF. 1969. Biometry. W. H. Freeman and Company, San Francisco, 776 pp.

STEVENSON, D. G. 1972. Flocculation and floc behaviour. Water Eng. J. 3: 155-169.

TAMBO, N., and H. HOZUMI. 1979. Physical characteristics of flocs. II. Strength of floc. Water Res. 13: 421-427.

THOMAS, D. G. 1964. Turbulent disruption of flocs in small particle size suspensions. J. Amer. Inst. Chem. Eng. 10: 517-523.

TOMI, D. T. and D. F. BAGSTER. 1978a. The behaviour of aggregates in stirred vessels. Part I-Theoretical considerations on the effects of agitation. Trans. Instn. Chem. Eng. 56: 1-8.

TOMI, D. T., and D. F. BAGSTER. 1978b. The behaviour of aggregates in stirred vessels. Part II-An experimental study of the flocculation of *Galena* in a stirred tank. Trans. Instn. Chem. Engrs. 56: 9-17.

TRENT, J. D., A. L. SHANKS, and M. W. SILVER. 1978. *In situ* and laboratory measurements on macroscopic aggregates in Monterey Bay, California. Limnol. Oceanogr. 23: 626-635.

YAMAZAKI, H., and R. LUECK. 1987. Turbulence in the California undercurrent. J. Phys. Oceanogr. 17: 1378-1396.

FIGURE LEGENDS

Figure 1: Diagram of the oscillating grid system used to produced a gradient of turbulent kinetic energy in the laboratory. x=62 cm; y=62 cm; z=76 cm. Aggregates were magnified by a 55 mm macrolens so as to fill approximately 5 to 10% of each frame and tracked as they moved throughout the viewing area. A second camera remained focused on a ruler yielding vertical distance above the top stroke of the grid.

Figure 2: Example of the energy spectrum produced by the grid while oscillating at ? Hz.

Figure 3: The rate of energy dissipation required to disaggregate marine snow composed predominantly of aggregated *Chaetoceros spp.* as a function of maximum aggregate diameter. Dashed line = Kolmogoroff microscale A. Size at disaggregation of individual aggregates collected on 3 sampling dates. B. Mean rate of energy dissipation required to fragment the aggregates in panel (A) grouped by ascending size into 24 bins each containing 5 aggregates. Correlation coefficient (CC) = 0.81; $P<0.001$.

Figure 4: The rate of energy dissipation required to disaggregate marine snow composed predominantly of aggregated *Nitzschia* spp. as a function of maximum aggregate diameter. A. Size at disaggregation of individual aggregates collected on May 19. B. Mean rate of energy dissipation required to fragment the aggregates in panel (A) grouped by ascending size into 10 bins each containing 3 aggregates. CC = 0.66; $P<0.05$.

Figure 5: Comparison of the mean energy dissipation required to disaggregate 1 day (June 9) and 5 day old *Chaetoceros* aggregates (June 13) as a function of size. Points represent data from Fig. 3A grouped by aggregate size.

Figure 6: Frequency distribution of the number of fragments produced in all trials resulting in disaggregation.

Figure 7: Number of fragments produced by all trials resulting in disaggregation A. Numberof fragments versus parent aggregate size. B. Number of aggregates versus the energy dissipation rate required to fragment parent floc. Closed circles represent mean maximum diameter; lines equal ± 1 standard deviation.

Figure 8: Mean volume of fragments produced on disaggregation. All data binned by fragment size (A) Fragment volume as a function of parent floc size. CC =.81; $P<0.001$ (B) Fragment volume as a function of the energy dissipation rate required to disaggregate the parent floc CC= 0.71; $P<0.01$.

Figure 9: The relative volume of fragments produced by those trials resulting in 2 fragments as a function of parent floc size. RFV = volume of smaller fragment/ volume of larger fragment. RFV of 1 means fragments were of equal size. RFV of 0.1 means larger fragment was 10 times the volume of the smaller. CC = 0.28: $P < 0.01$.

Table 1: The value of the stable floc size exponent as predicted by theory for various mechanisms of aggregate breakup.

BREAKUP MECHANISM	PREDICTED γ_ϵ			SOURCE
	inertial range	intermed-iate range	viscous range	
Erosion	1		0.5	Parker et al.(1972)
Filament fracture	0.25		0.25	Parker et.al (1972)
Pressure fluctuations	2.5		0.5	Thomas (1964)
	>0.5	0.25-0.5	<0.5	Tomi and Bagster (1978a)
	0.4-0.5		0.33-0.38	Tambo and Hozumi (1979)

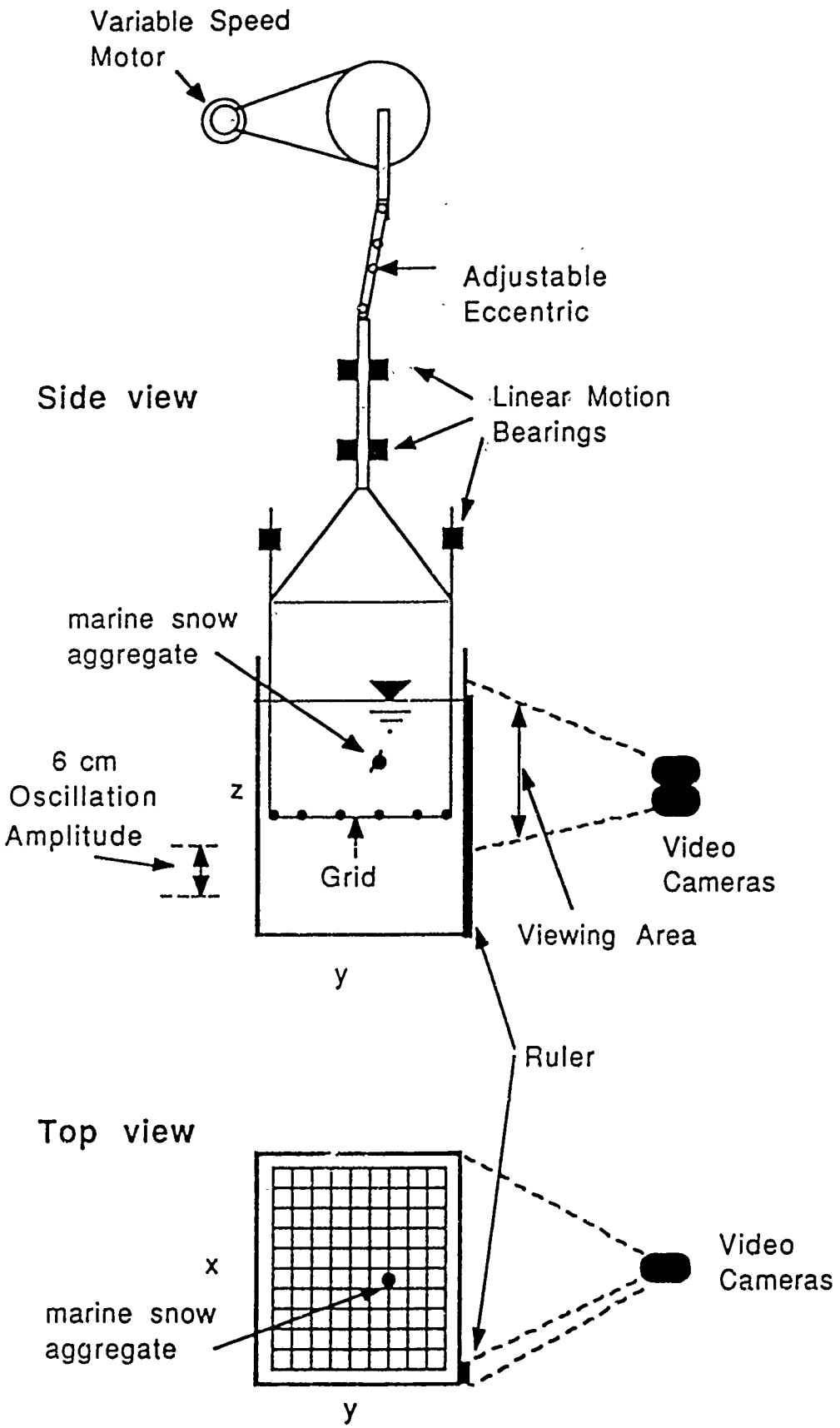
Snow Type	Date	*n*	% Disagg. at $\varepsilon<1$	% through grid	Maximum Diameter (mm)		Volume (mm^3)	
					$\varepsilon<1$	$\varepsilon>1$	$\varepsilon<1$	$\varepsilon>1$
Diatoms								
Chaetoceros	16 March	91	50	25	5.7 ± 2.2	3.9 ± 2.4	11.4 ± 10.0	8.0 ± 6.2
	9 June	75	84	7	7.4 ± 3.5	4.6 ± 2.3	36.7 ± 35.1	23.6 ± 40.9
	13 June	62	53	44	7.3 ± 3.5	4.8 ± 1.8	24.8 ± 27.4	19.5 ± 19.9
Nitzschia	19 May	65	86	3	7.6 ± 5.6	3.0 ± 0.1	4.4 ± 2.4	2.7 ± 0.1
Misc. Debris	3 Nov.	30	0	100	-	1.6 ± 0.7	-	0.5 ± 0.3
Larvacean Houses	7 Feb.	14	0	100	-	2.7 ± 0.6	-	4.8 ± 1.9
Zooglea Flocs	7 Feb.	10	0	100	-	3.5 ± 1.0	-	7.1 ± 5.6

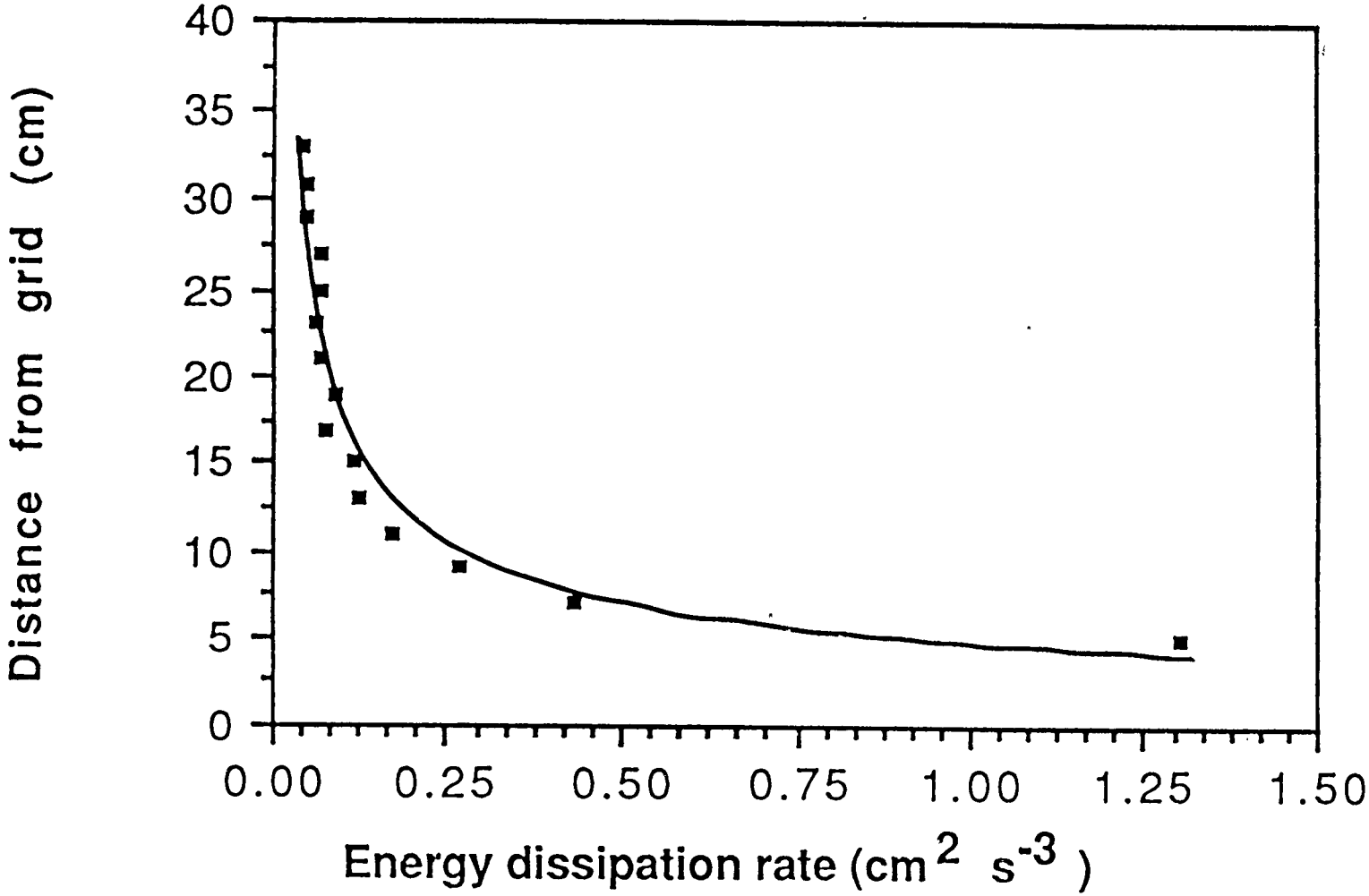
Table 3: Experimentally obtained values of the stable floc size exponent (γ) of aggregates of various compositions.

TYPE OF AGGREGATE	$^{*}\gamma$		SOURCE
Aluminum hydroxide flocs	0.5		Argaman and Kaufman (1970)
+ kaolinite	0.37		Camp (1968)
	0.33 - 0.38		Tambo and Hozumi (1979)
	0.35 - 0.75		Francois (1987)
Iron hydroxide flocs	0.34		Lagvankaar and Gemmel (1968)
	0.51		Leentvaar and Rebhun (1983)
	0.40		Stevenson (1972)
Polyacrylamide flocs + kaolinite	0.59		Hoppe et al. (1977)
Ballotini pearls + anionic flocculant	0.10		Smith and Kitchener (1978)
Latex beads + organic polymers	0.21		Hunter (1982)
Activated sludge	0.18		Parker et al. (1972)
	0.11	**	Magara et al. (1976)
	0.29		Leentvaar and Rebhun (1983)
	0.03 - 0.09		Glasgow et al. (1983)
Natural marine snow			
Chaetoceros aggregates	0.30		This study
Nitzschia aggregates	0 62		This study

*Many of the above studies determined aggregate size as a function of shear (G) rather than ϵ. We have converted their stable floc size exponents with the relationship $\gamma_\epsilon = 1/2\gamma_G$ based on equation (2) in the text.

**calculated from their Fig 4


Variable Speed
Motor
Adjustable
Eccentric
Side view
Linear Motion
Bearings
marine snow
aggregate
6 cm
Oscillation
Amplitude
z
Grid
Video
Cameras
Viewing Area
y
Ruler
Top view
x
marine snow
aggregate
Video
Cameras
y


Distance from grid (cm)
40
35
30
25
20
15
10
5
0
0.00
0.25
0.50
0.75
1.00
1.25
1.50
Energy dissipation rate (cm 2 s-3)

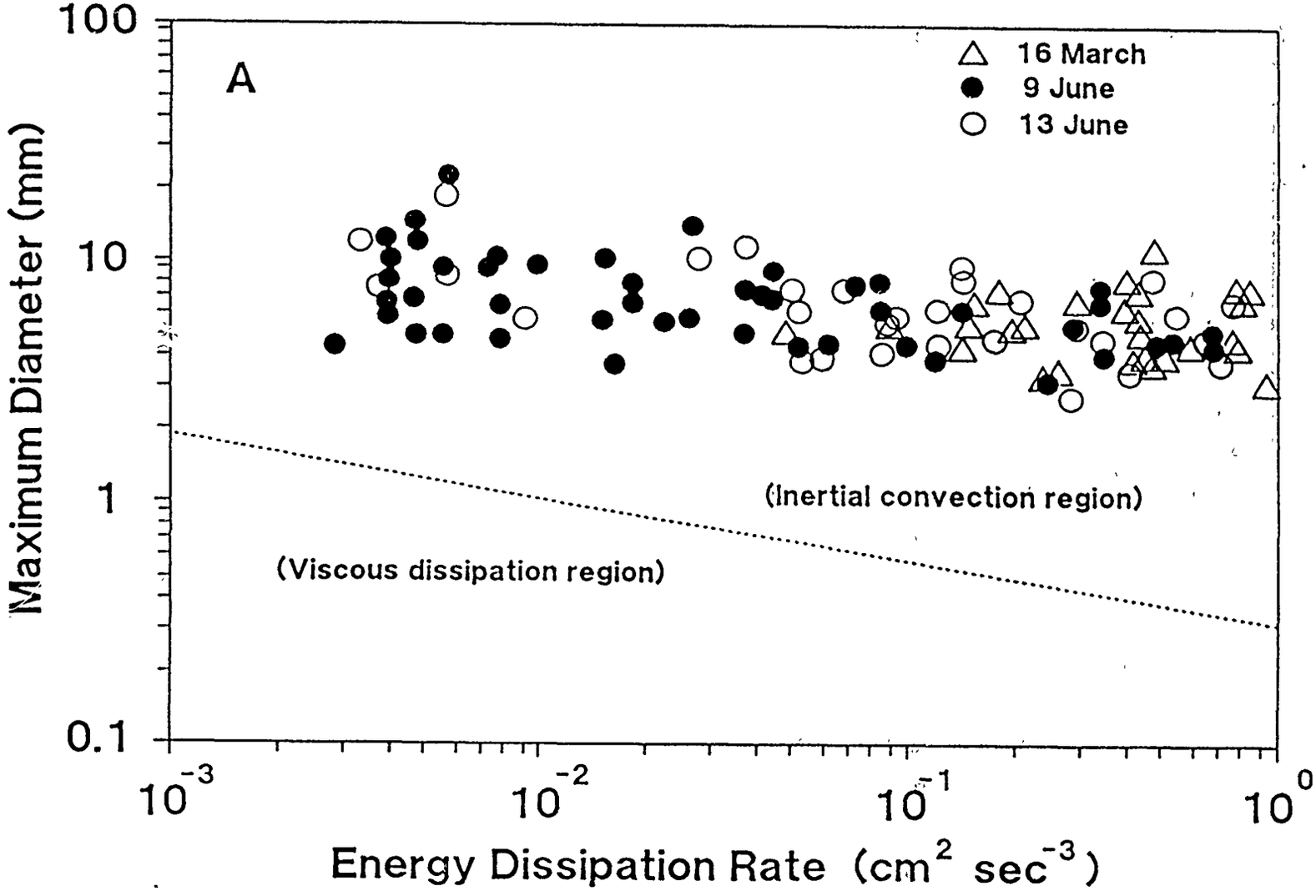
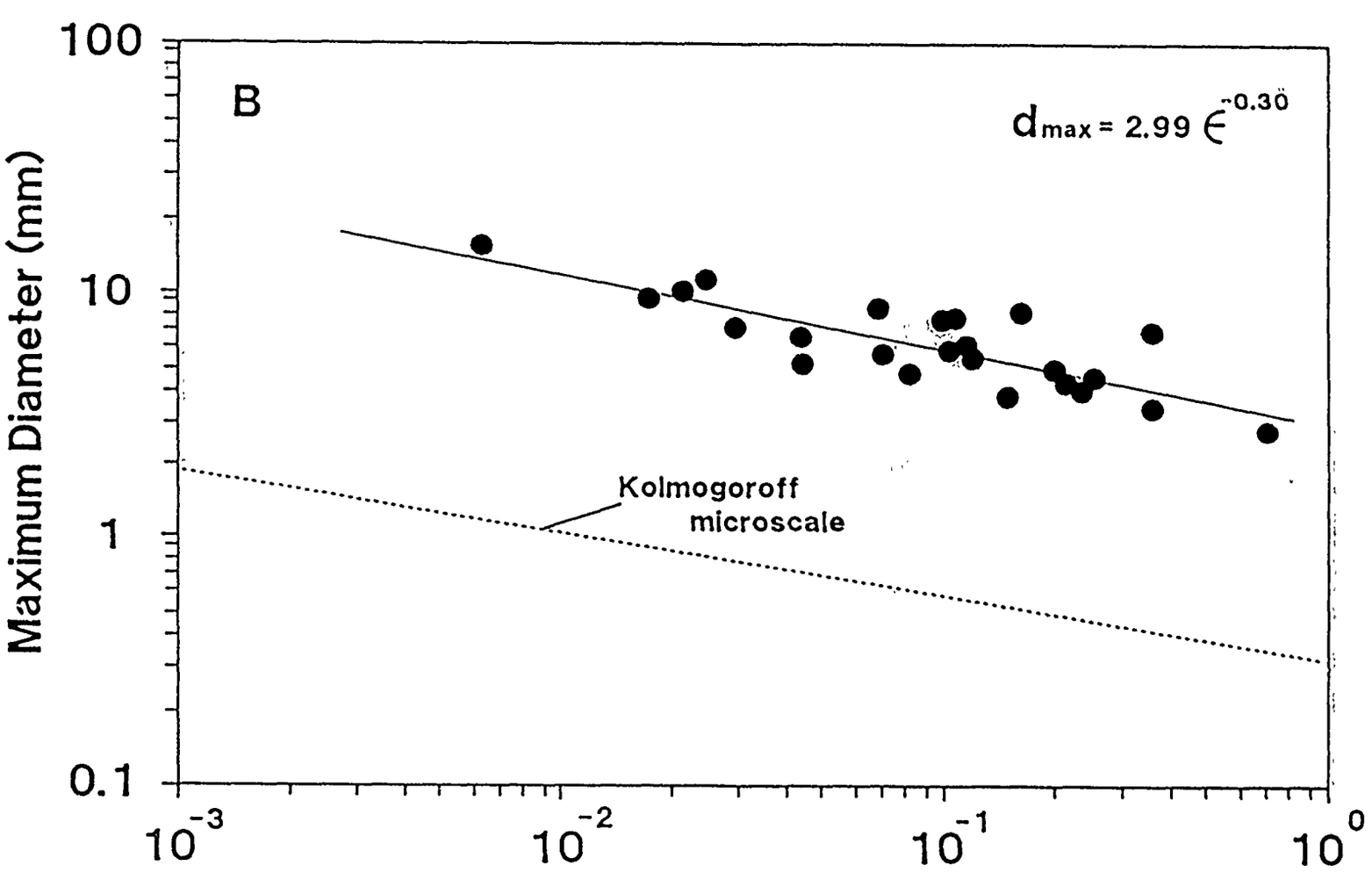
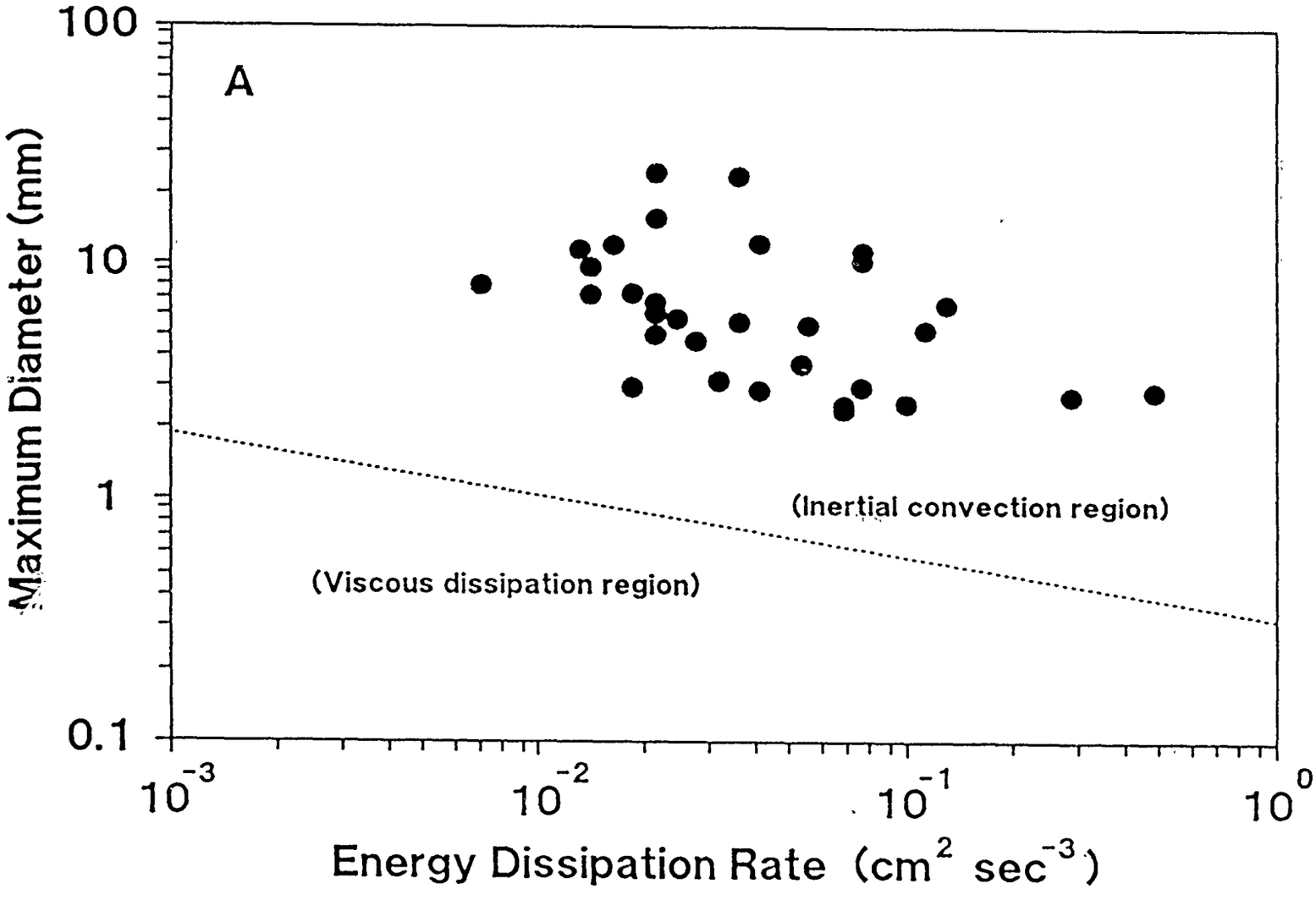

A
16 March
9 June
13 June
(Inertial convection region)
(Viscous dissipation region)
Maximum Diameter (mm)
100
10
1
0.1
10^{-3}
10^{-2}
10^{-1}
10^{0}
Energy Dissipation Rate (cm^2 sec^{-3})

Fig 3B


B
$d_{max} = 2.99\,\epsilon^{-0.30}$
Kolmogoroff microscale
Maximum Diameter (mm)
100
10
1
0.1
10^{-3}
10^{-2}
10^{-1}
10^{0}
Energy Dissipation Rate ($cm^2\ sec^{-3}$)


A
100
10
1
0.1
Maximum Diameter (mm)
(Inertial convection region)
(Viscous dissipation region)
10^{-3}
10^{-2}
10^{-1}
10^{0}
Energy Dissipation Rate (cm^2 sec^{-3})

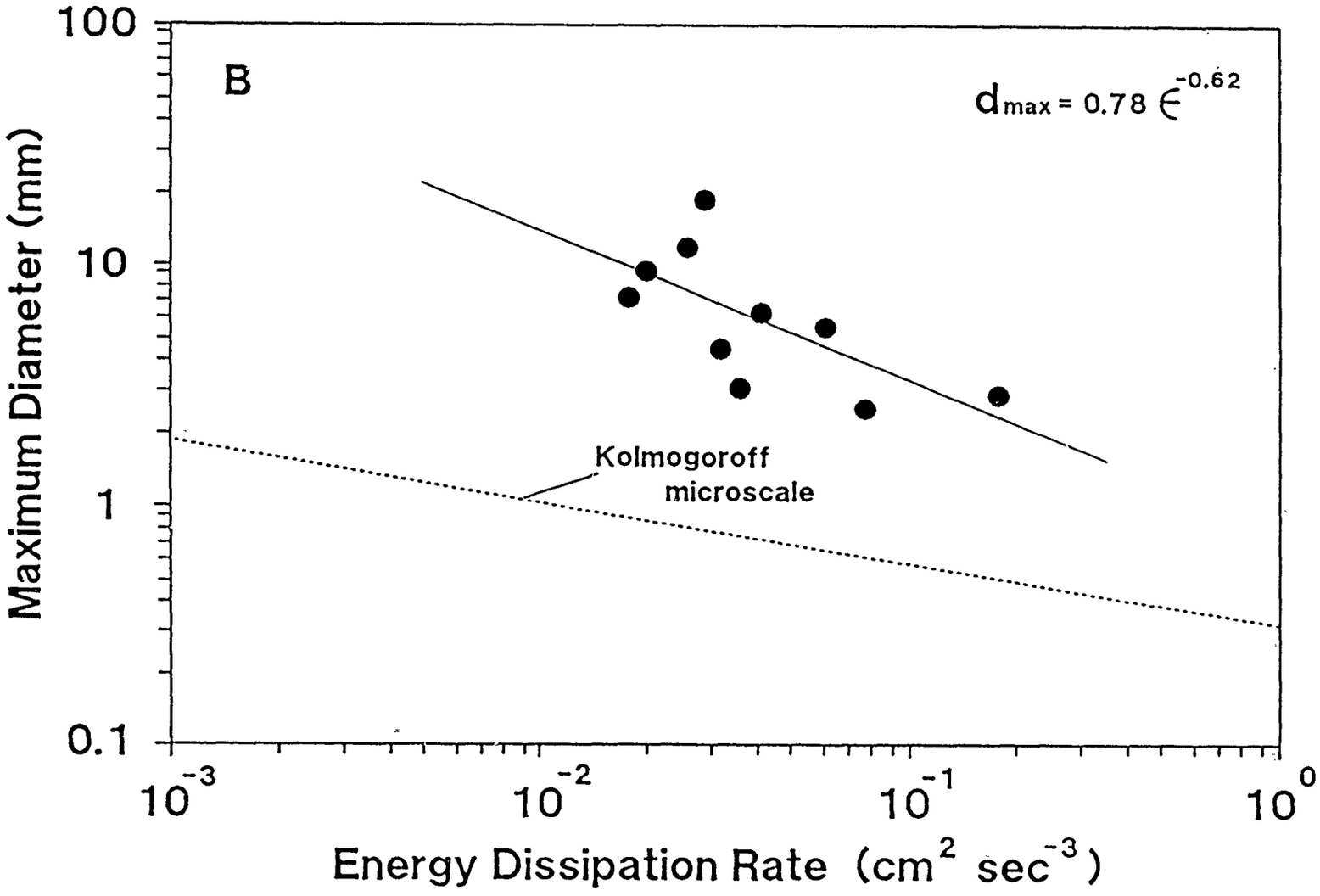

B
$d_{max} = 0.78\,\epsilon^{-0.62}$
Kolmogoroff
microscale
Maximum Diameter (mm)
100
10
1
0.1
10^{-3}
10^{-2}
10^{-1}
10^{0}
Energy Dissipation Rate ($cm^2\ sec^{-3}$)

Fig 5

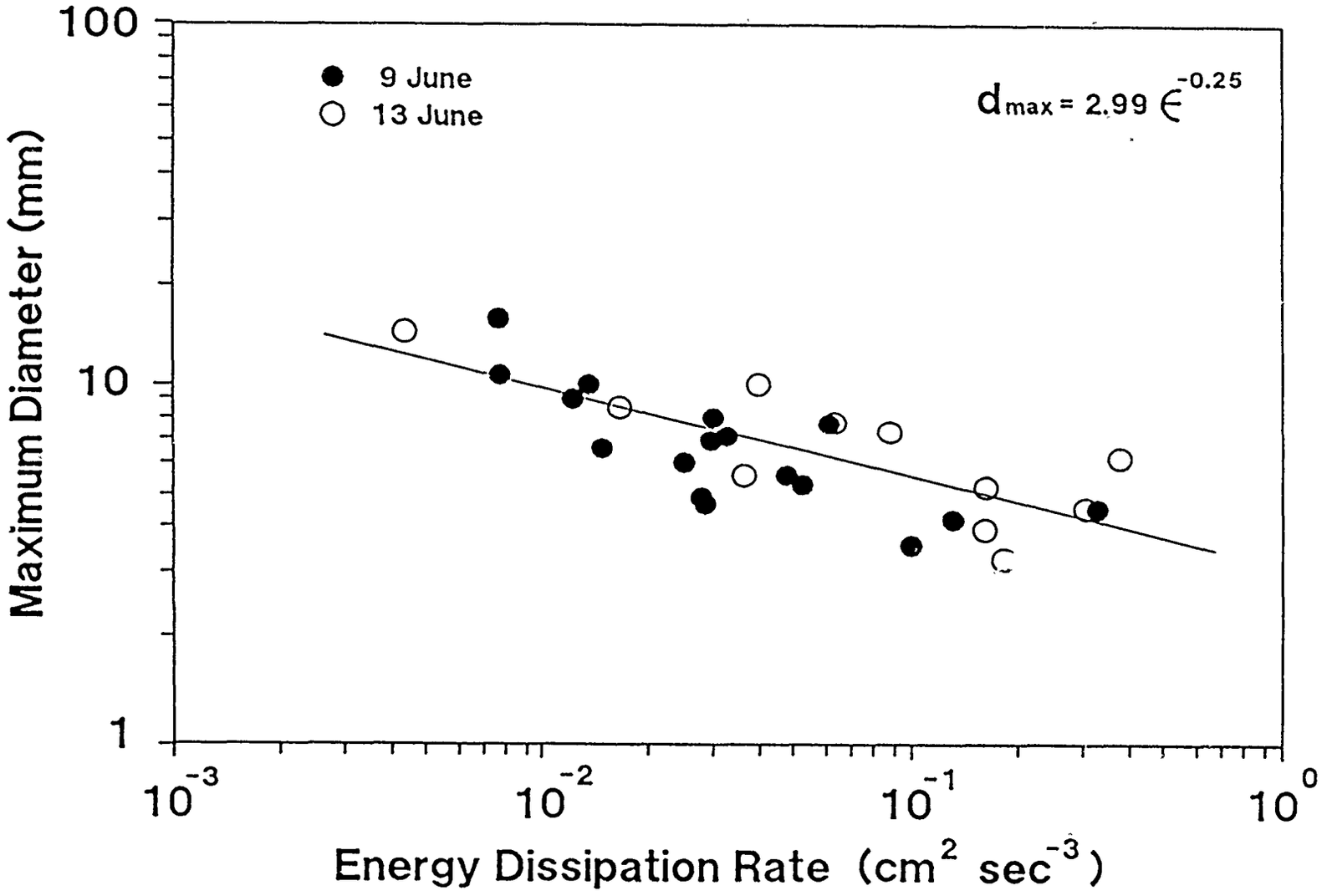
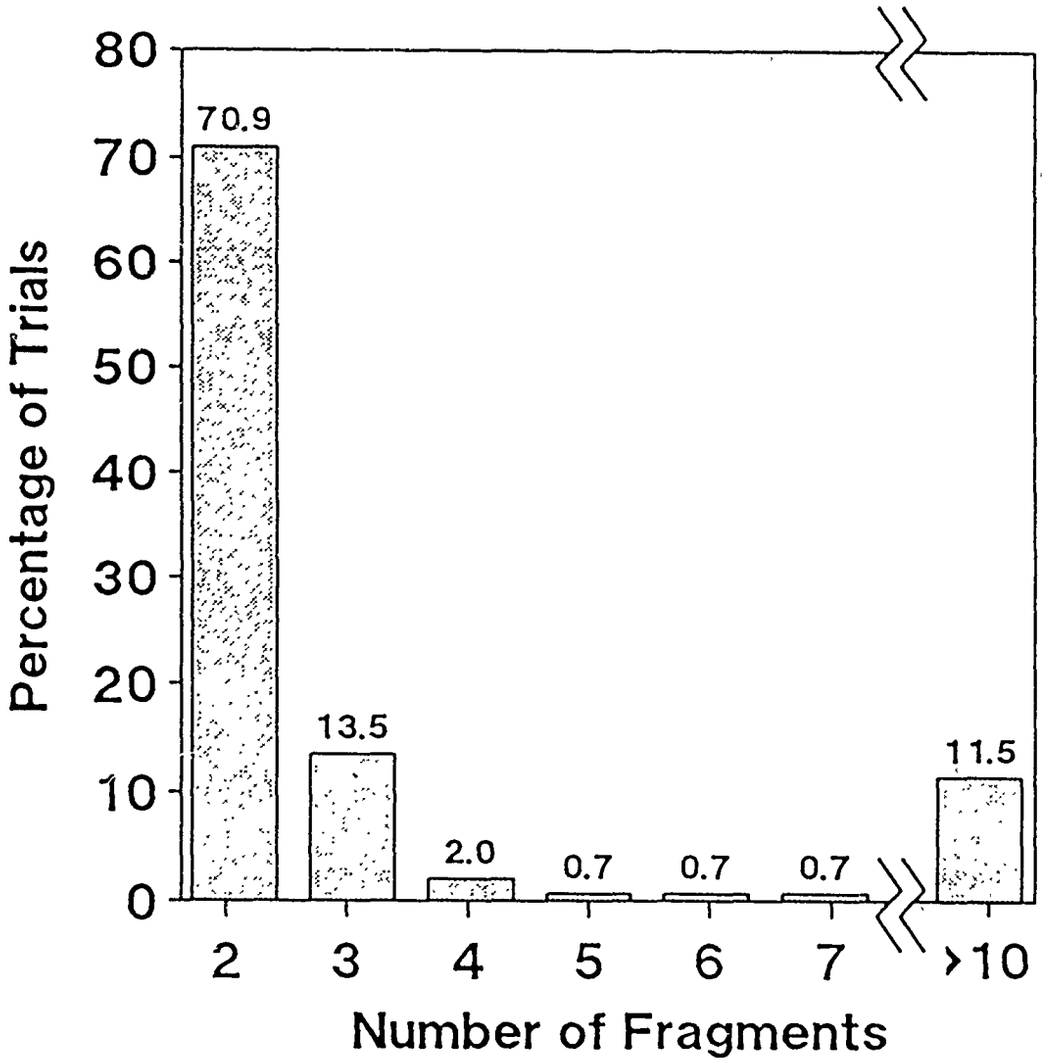
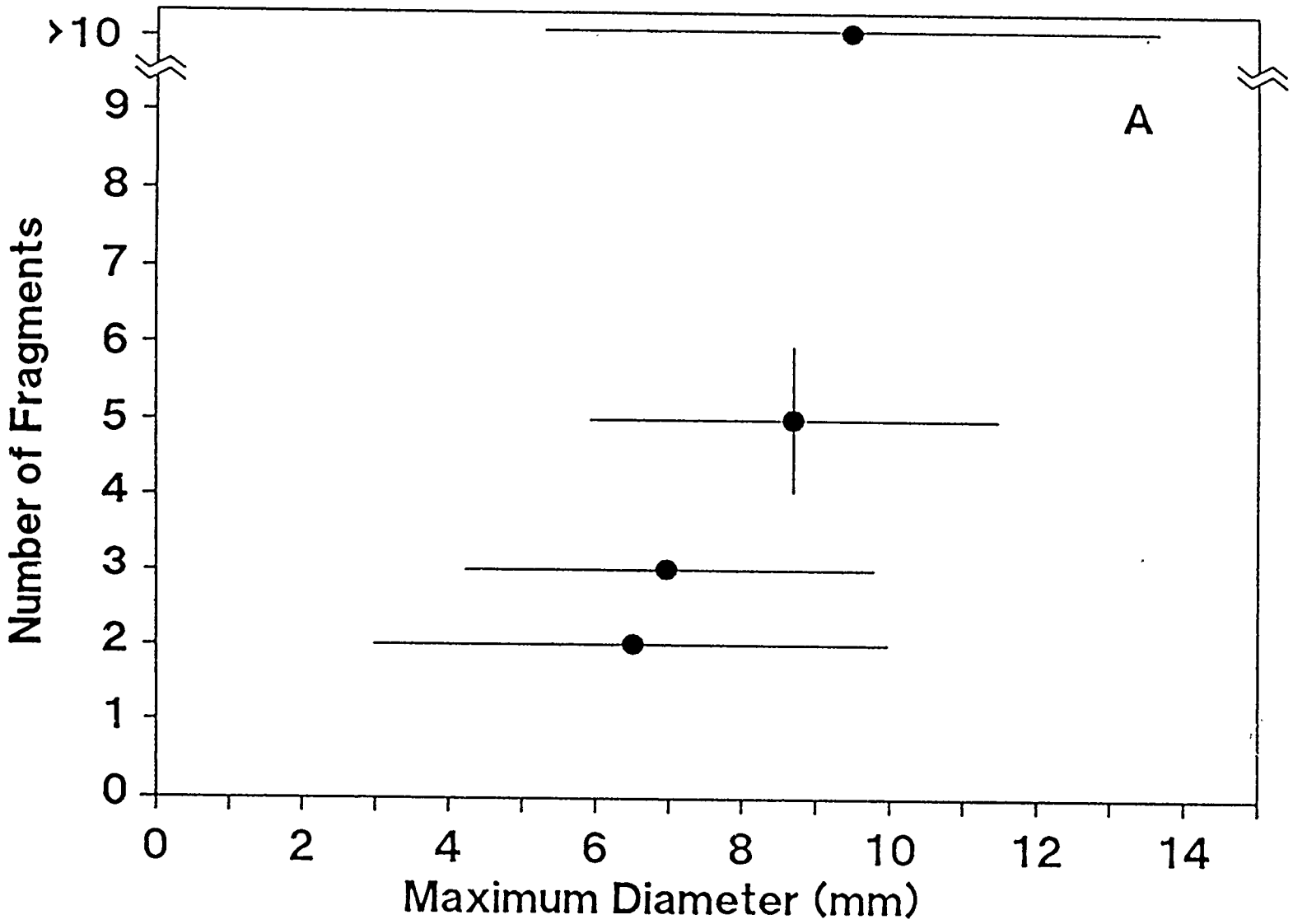
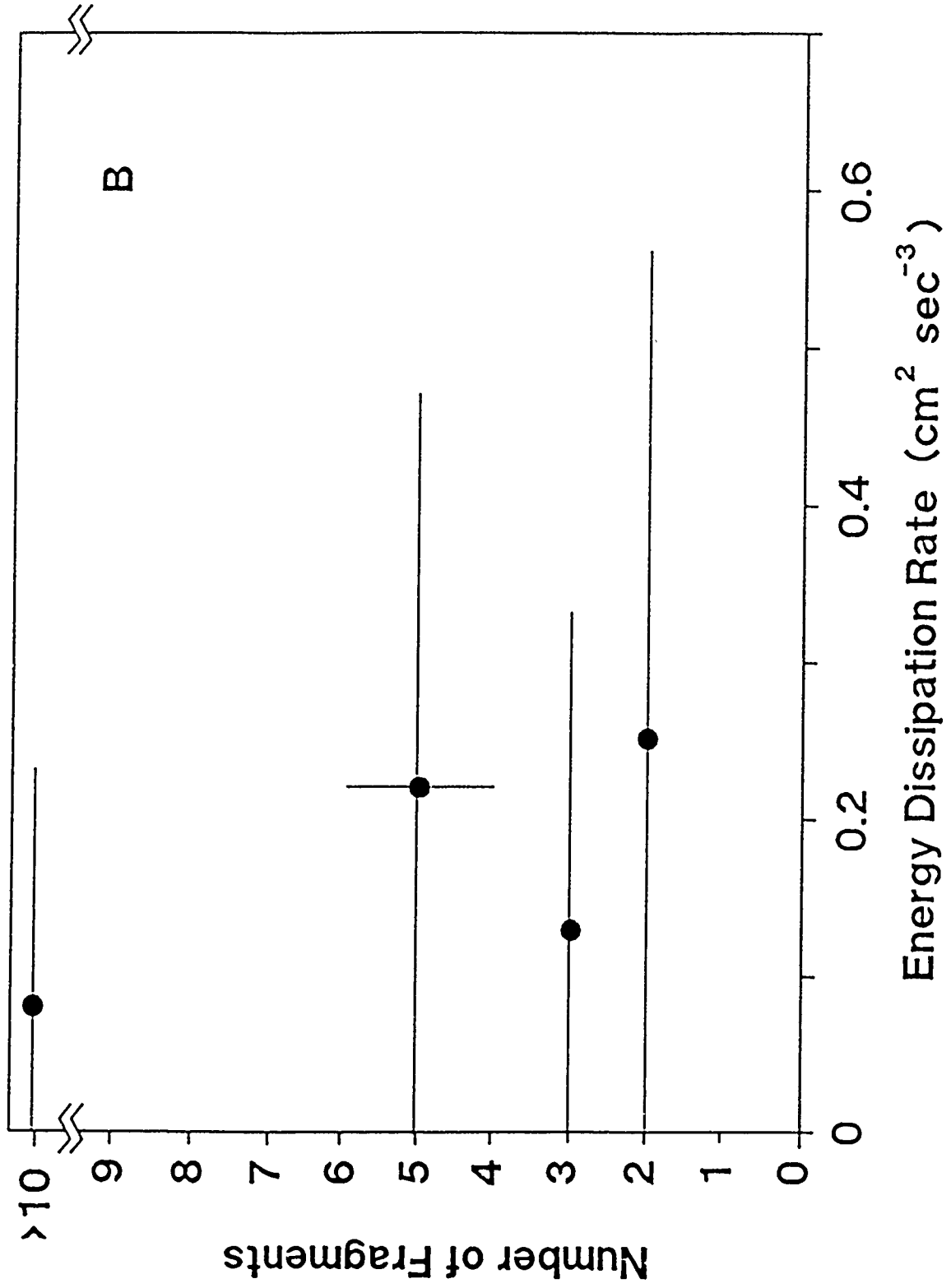
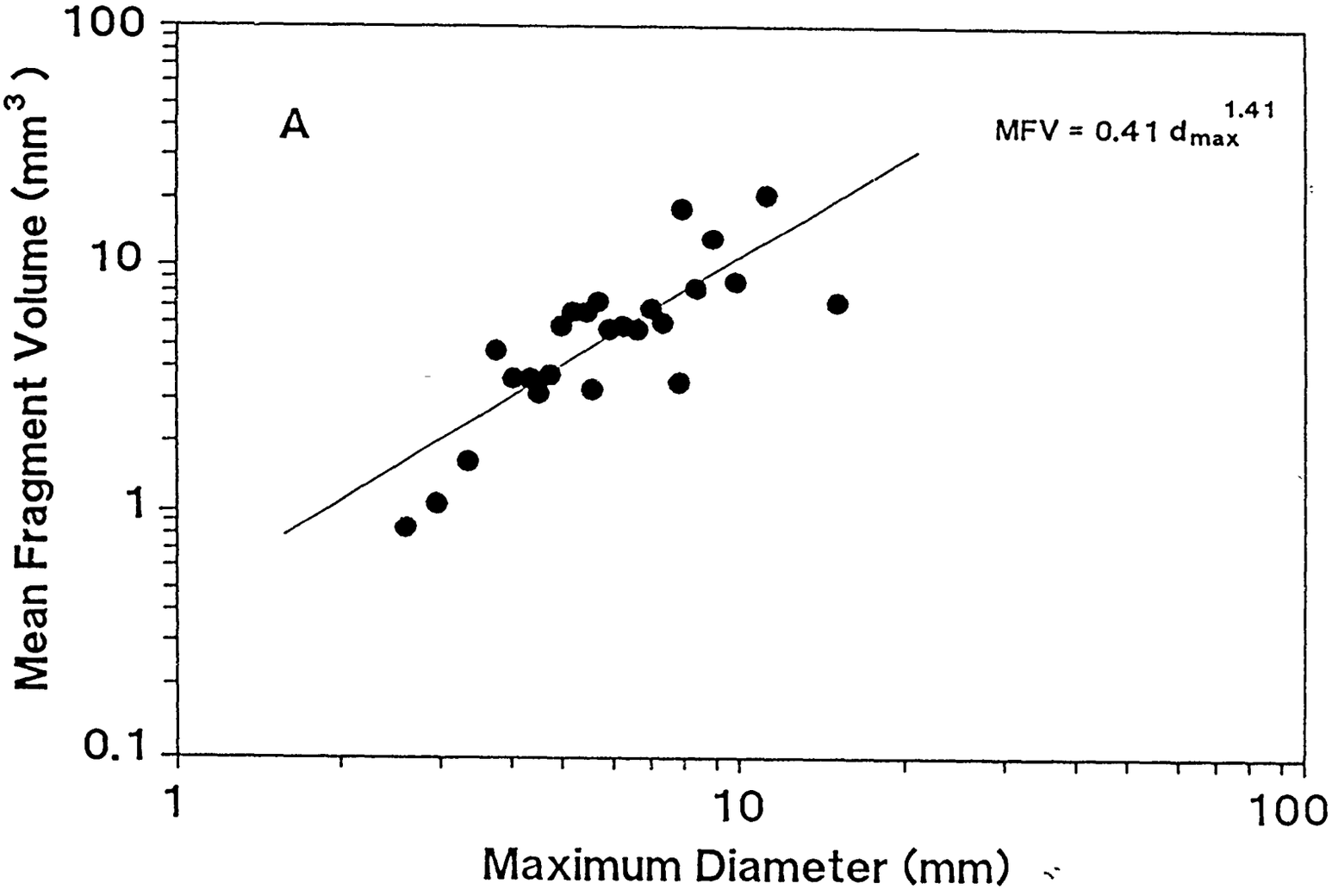

100
10
1
Maximum Diameter (mm)
9 June
13 June
$d_{max} = 2.99\,\epsilon^{-0.25}$
10^{-3}
10^{-2}
10^{-1}
10^{0}
Energy Dissipation Rate ($cm^2\ sec^{-3}$)

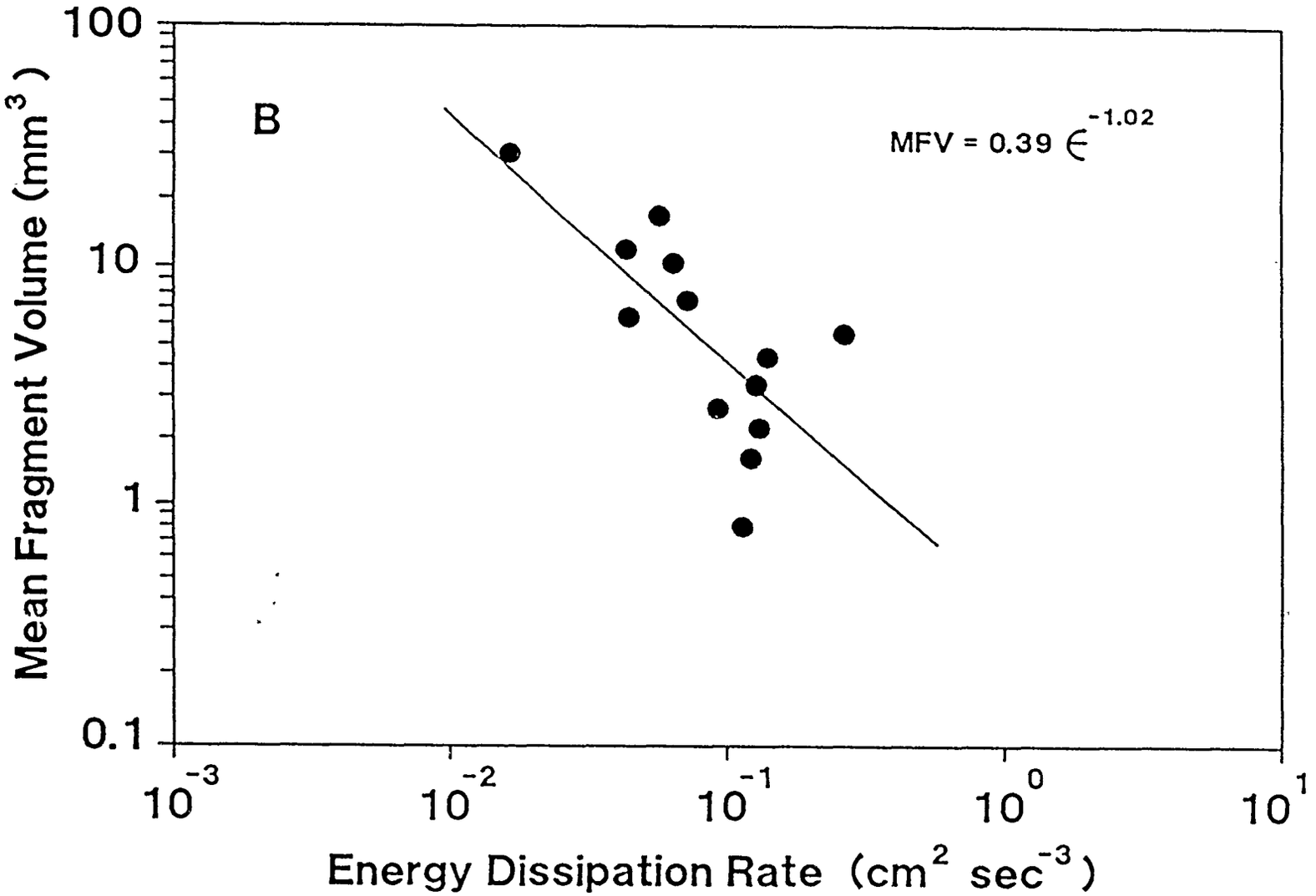
Figure 6

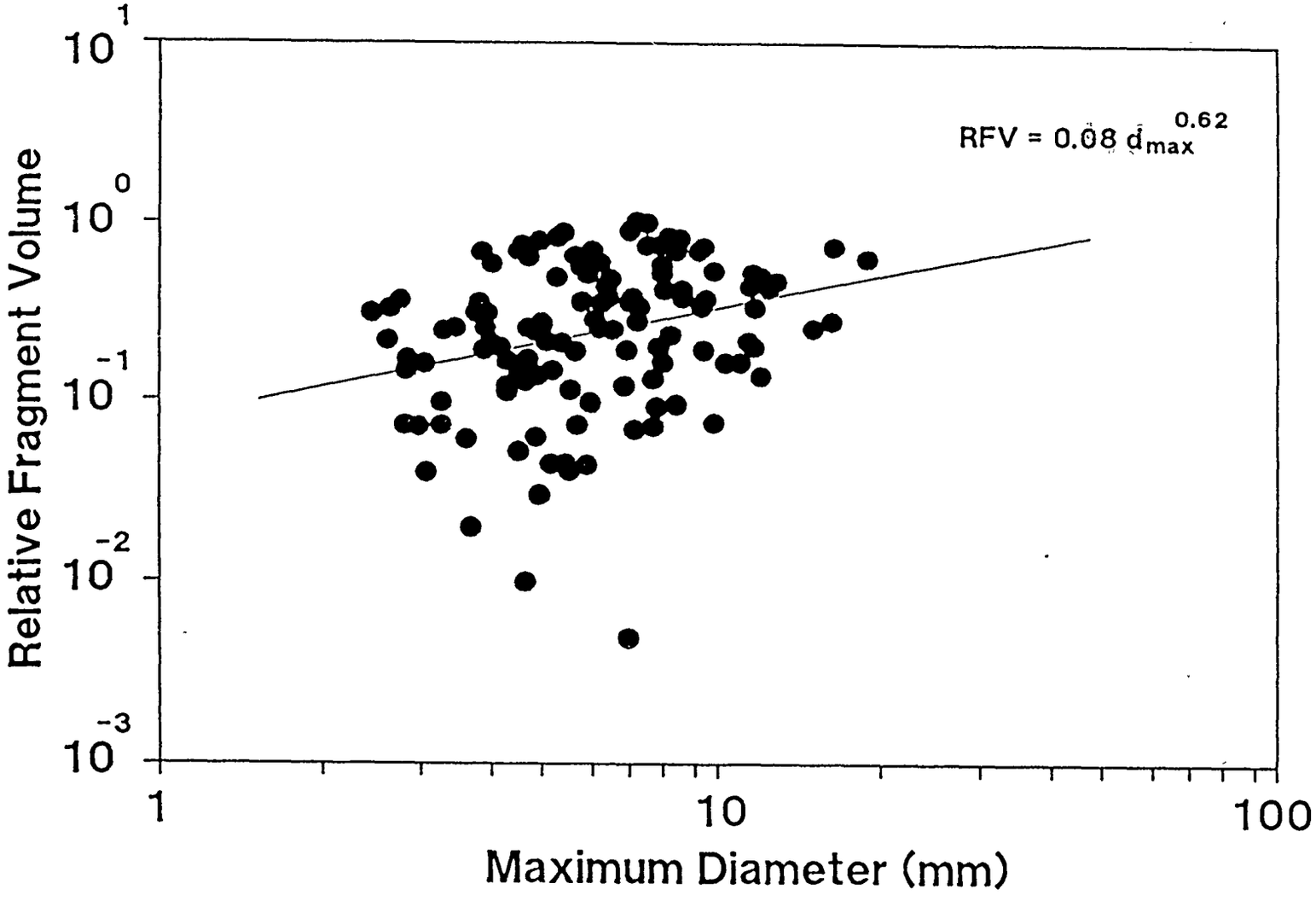

80
70
60
50
40
30
20
10
0
Percentage of Trials
70.9
13.5
2.0
0.7
0.7
0.7
11.5
2
3
4
5
6
7
>10
Number of Fragments


>10
9
8
7
6
5
4
3
2
1
0
Number of Fragments
A
0
2
4
6
8
10
12
14
Maximum Diameter (mm)


B
Number of Fragments
>10
9
8
7
6
5
4
3
2
1
0
0
0.2
0.4
0.6
Energy Dissipation Rate (cm^2 sec^{-3})


A
MFV = 0.41 $d_{max}^{1.41}$
Mean Fragment Volume (mm^3)
100
10
1
0.1
1
10
100
Maximum Diameter (mm)


B
MFV = 0.39 ∈^-1.02
Mean Fragment Volume (mm^3)
100
10
1
0.1
10^-3
10^-2
10^-1
10^0
10^1
Energy Dissipation Rate (cm^2 sec^-3)


RFV = 0.08 $d_{max}^{0.62}$
Relative Fragment Volume
10^{1}
10^{0}
10^{-1}
10^{-2}
10^{-3}
1
10
100
Maximum Diameter (mm)

OFFICE OF NAVAL RESEARCH AGGREGATE DYNAMICS IN THE SEA WORKSHOP REPORT



Asilomar Conference Center
Pacific Grove, California
September 22-24, 1986

OFFICE OF NAVAL RESEARCH

AGGREGATE DYNAMICS IN THE SEA

WORKSHOP REPORT

ALICE L. ALLDREDGE

ERIC O. HARTWIG

Asilomar Conference Center
Pacific Grove, California
September 22-24, 1986

American Institute of Biological Sciences

Cover: Aggregate of marine snow approximately 5 mm in diameter produced as a mucus feeding structure by the planktonic larvacean genus, *Oikopleura*. Photographer, James M. King, Marine Science Institute, University of California, Santa Barbara, photographed this aggregate and surrounding natural particles in situ with a macro lens and Nikon in an underwater housing.

TABLE OF CONTENTS

	Page
SUMMARY	1
PARTICIPANTS	7
WORKING GROUP REPORTS	
Aggregate Dynamics	10
In Situ Exploitable Properties of Aggregates: Optics	29
In Situ Exploitable Properties of Aggregates: Other Properties	42
INVITED TALKS	
Characteristics and Distributions of Marine Aggregates, M. W. Silver	60
Particle Size Spectra and Aggregation In, and Removal From, the Oceans, I. N. McCave	90
Aggregate Dynamics: Biological Processes Which Form, Alter and Destroy Aggregates in the Ocean, A. L. Alldredge	109
State-of-the-Art Instrumentation for Measuring Ocean Aggregates, K. L. Carder, D. Costello and R. G. Steward	131
CONTRIBUTED TALKS	
Measuring the Abundance and Flux of Marine Snow Aggregates, V. L. Asper	186
Submersible-based Measurements of the Sources, Densities, Distributions and Sinking Rates of Marine Snow Aggregates and Euphausiid Fecal Pellets, M. J. Youngbluth, T. G. Bailey, C. A. Jacoby, P. J. Davoll and P. I. Blades-Eckelbarger	191
Large Aggregate Distributions in the North Atlantic, J. Bishop	193
Bioluminescence of Marine Snow, O. Orzech and K. H. Nealson	194

Page

Acoustical Techniques for Remotely Detecting and Classifying Particles in the Ocean, T. Stanton 195

Flow Cytometric Tracing of Fluorescent Particles, K. Stolzenbach, K. Newmann, F. M. Morel and S. W. Chisholm 199

Particle Aggregation Kinetics and Ocean Energetics of Gulf Stream Boundaries, P. McGillivary 201

Observation of Marine Particles with a Laser Technique, R. Strickler 202

In Situ Measurements of Single Particle Optical Observables, P. J. Wyatt 204

In Situ Particle Diagnostics, George Gal 206

Geometry and Scaling of Hydrosol Encounter Mechanisms in Suspension Feeding, P. Jumars and A. R. M. Nowell 209

Mechanisms of Bio-Particle Interactions as Suggested by Chemotactic Models, G. Jackson 211

WORKSHOP ON AGGREGATE DYNAMICS IN THE SEA

SUMMARY

INTRODUCTION

Much of the suspended matter in the ocean exists as aggregates of organic detritus, living microorganisms and clay minerals. Historically, these aggregates have been categorized into the following two size classes: 1) marine snow, a general term describing amorphous suspended aggregates in the ocean larger than 500 μm in size; and 2) microaggregates which range from a few microns up to 500 μm in diameter. Both are primarily products of biological activity including mucus production, grazing, excretion, etc. In the open ocean, even those particles produced by physical/chemical coagulation processes (precipitation, particle collision, etc.) originate from largely biogenically derived component particles. Local loss terms include sinking, advection and decomposition which generally occur simultaneously with redistribution processes such as disaggregation, reingestion and defecation. Therefore, the dynamics of marine snow and microaggregates are functions of the actual aggregate properties, the biological processes and mechanisms which produce/redistribute them and physical/chemical processes.

Since aggregate production is largely a function of biological activity, aggregates are ubiquitous in the ocean, albeit at unknown abundances and presently with distributional statistics that are not yet quantified. Quantification of distributional patterns relies on obtaining <u>in situ</u> observations. To date, these have been accomplished by divers, submersibles and photography, all of which suffer from a small sampling base. The

properties and characteristics inherent to microaggregates and marine snow are also determined by those processes which form them. These properties and characteristics include shape, size, porosity, particle strength and rigidity, surface characteristics, chemical and biological composition, sinking rate, bioluminescence, and optical and chemical properties. However, none of these properties has been quantified either singly or in concert as unique identifiers of aggregated matter in a background environment of organisms and ocean water. A rapid advance in understanding in situ dynamics of marine snow and microaggregates, therefore, requires an advance in observational capability beyond present diver/submersible/photography technology.

PURPOSE

The purpose of the workshop was to specify and quantify, to the extent possible, the properties of marine snow and microaggregates which could be exploited to understand the abundance, distribution, dynamics and in situ characteristics and state (e.g., intact, dispersed, sinking rate, age, size, shape, source, etc.) of aggregated particles in the ocean.

The workshop participants were divided into 3 working groups: Aggregate Dynamics, In Situ Exploitable Optical Properties of Aggregates, and In Situ Exploitable Non-Optical Properties of Aggregates. The Aggregate Dynamics Working Group constructed a model of aggregate dynamics in the sea and prioritized its components as to which were most critical toward advancing our understanding. The In Situ Exploitable Properties working groups each identified crucial properties needed to understand aggregate dynamics and outlined existing or needed technologies necessary to quantify those properties.

The workshop took place in a very constructive and stimulating atmosphere which resulted from the cooperative spirit of the participants. We thank all of the attendees for their participation and input. Special thanks go to the working group rapporteurs, Nick McCave, Dave Mackas, Tim Stanton, Ken Carder, and Dick Eppley. Most of all, we thank Chris Lowe and Carol Loughney of the American Institute of Biological Sciences for organizing a most enjoyable and productive meeting.

MODEL OF AGGREGATE DYNAMICS

The building blocks of marine aggregates consist of four general classes of component particles: 1) microorganisms, especially phytoplankton and bacteria; 2) products of dissolved organic matter (DOM) to particulate organic matter (POM) conversions such as collapsed bubble coating; 3) inorganic particles of lithogenic (quartz, feldspar, clays) and biogenic (calcite, aragonite, opal, etc.) origin; and 4) the mucus produced by zooplankton as feeding structures. The model outlines the dynamics of aggregation/disaggregation of these component particles rather than their origin. The origins of these component particles are well studied in some cases (phytoplankton, bacteria, lithogenic) but are poorly known for others (DOM-POM conversions, zooplankton mucus).

For each of these classes of component particles we need to know size distribution, abundance, sinking rate, particle strength, and chemical and biological properties. We also need to know the numbers, sizes, locations, feeding and defecation rates, and feeding preferences of the major particle consumers in the sea. These data are needed so that we may make well informed estimates of the relative importance of particle aggregation mechanisms.

The major mechanisms bringing particles together are animal feeding and physical coagulation via Brownian, shear, and differential settling routes. These two mechanisms are sufficient to bring particles together, but not sufficient to make them stick. Different classes of particles have different sticking efficiencies which must be determined empirically. Fecal pellet formation may be the dominant mechamism by which particles are stuck together in some parts of the ocean. Once stuck together aggregates may be transported by mixing, sinking or lateral advection. They may be lost by deposition or mineralized via metabolic activities or they may be disaggregated by shear or animal feeding activities.

Certain portions of the model were singled out as being most important in advancing our knowledge of aggregate dynamics in the sea. These were:

- mechanisms which bring particles together (especially feeding and physical encounter mechanisms);
- mechanisms which stick particles together (especially defecation and the factors determining the sticking efficiency of various classes of aggregates);
- the abundances, properties and rates of formation of component particles.

RECOMMENDATIONS

The following recommendations were made by the three working groups with the goal of achieving a predictive understanding of aggregate dynamics in the sea.

1. Understanding of aggregate dynamics requires that we know the number concentration and size distribution of aggregates and component particles by class in situ, preferably in real time.

- develop an *in situ*, optical rapid survey instrument

- develop an accessory survey platform for assisting the optical survey instrument in providing unambiguous identification of aggregates even where plankton is abundant

- develop remote particle classification instruments

- develop an *in situ* flow-through particle counter to characterize aggregates 0.5 mm in diameter

2. Investigation of aggregate properties requires the capture of aggregates *in situ* in a gentle, selective and non-disruptive manner.

   - expand and improve existing *in situ* filtration systems, traps and water samplers

   - develop selective capture devices which can be effectively deployed by free-vehicles and submersibles

   - develop a sampler to collect aggregates at the water-sediment interface

   - refine present acoustic and optical instruments to guide efforts of *in situ* collection

3. In order to understand the relative importance of the various mechanisms which cause particles to bind together, to sink and to disaggregate we need information on the following particle properties:

   a. Settling velocity distribution as a function of particle class, size, shape

   - Conduct laboratory and field experiments to test theoretical/empirical relationships between settling speed, and aggregate size, shape, orientation, density, porosity and permeability etc.

   b. Aggregate strength, rigidity, permeability

   - measure aggregate fracture strength, deformation and rates of break-up in the laboratory and on board ship

   - develop an *in situ* method to test laboratory data on deformation and settling behavior *in situ*

   c. Surface and chemical characteristics

   - determine surface and chemical properties of each class of aggregates and component particles with laboratory/shipboard studies of freshly collected particles

   - determine how surface properties affect aggregation rates *in situ*

d. Attractiveness to consumers

- conduct lab/shipboard experiments to quantify how consumers detect and discriminate particles

- Test concepts of particle selection <u>in situ</u> using instruments developed in recommendation #1.

e. Age and origin

- identify specific organisms (types of bacteria, protozoans, etc.), chemicals (pigments, organic compounds) or isotopic tracers (stable isotopes, radioisotopes, inorganic molecules) which are specific for particles of certain ages or sources.

- Develop methods to use these markers on captured aggregates in conjunction with optical data.

4. Determine encounter rates in nature under various environmental conditions for various particle classes.

   - extend present efforts to model physical aggregation and natural encounter rates to include empirically determined sticking efficiencies and the physical complexities of a real ocean.

   - test these ideas in nature with a system for studying particle-particle interactions

5. Determine the numbers, sizes, locations, feeding and defecation rates, and particle preferences of major particle consumers.

6. Determine the rates and mechanisms of component particle formation, particularly DOM-POM conversions under varying environmental regimes. Develop models to predict the abundances of all component particles.

7. Accompany all field efforts to investigate aggregate dynamics with appropriate environmental data including physical, chemical and biological variables.

Alice L. Alldredge
Department of Biological Sciences
University of California, Santa Barbara

Eric O. Hartwig
Oceanic Biology Program
Office of Naval Research

PARTICIPANTS

ALICE ALLDREDGE
Department of Biological Sciences
University of California
Santa Barbara, CA 93106

VERNON ASPER
Center for Marine Science
University of Southern Mississippi
NSTL, MS 39529

FAROOQ AZAM
Institute of Marine Resources
A-018
Scripps Institution of Oceanography
University of California
La Jolla, CA 92093

ROBERT R. BIDIGARE
Department of Oceanography
Texas A&M University
College Station, TX 77843

JAMES BISHOP
LaMont-Doherty Geological Observatory
Palisades, NY 10964

MARVIN A. BLIZARD
Office of Naval Research
Code 1125
800 North Quincy Street
Arlington, VA 22217-5000

JAMES M. BROOKS
Department of Oceanography
Texas A&M University
College Station, TX 77843

KEN BRULAND
Institute of Marine Sciences
University of California
Santa Cruz, CA 95064

KENDALL L. CARDER
140 7th Avenue S.
St. Petersburg, FL 33701

THOMAS B. CURTIN
Office of Naval Research
Code 1122PO
800 North Quincy Street
Arlington, VA 22217-5000

RICHARD W. EPPLEY
Institute of Marine Resources
A-018
Scripps Institution of Oceanography
University of California
La Jolla, CA 92093

GEORGE GAL
Lockheed Missiles and Space Company
Department 9701, Building 201
3251 Hanover Street
Palo Alto, CA 94304-1187

ROBERT GRAN
Dynamics Technology, Inc.
21311 Hawthorne Boulevard
Suite 300
Torrance, CA 90503-5602

ERIC O. HARTWIG
Office of Naval Research
Code 1122B
800 North Quincy Street
Arlington, VA 22217-5000

RICHARD C. HONEY
SRI International
333 Ravenswood Avenue
Menlo Park, CA 94025

GEORGE A. JACKSON
Institute of Marine Resources
A-018
Scripps Institution of Oceanography
University of California
La Jolla, CA 92093

PETE JUMARS
School of Oceanography
WB-10
University of Washington
Seattle, WA 98195

JOSEPH H. KRAVITZ
Office of Naval Research
Code 1125GG
800 North Quincy Street
Arlington, VA 22217-5000

DENNIS LAVOY
NORDA
Code 331
NSTL, MS 39529-5004

CINDY LEE
Marine Science Research Center
SUNY at Stony Brook
Stony Brook, NY 11794

I. NICK McCAVE
Department of Earth Sciences
University of Cambridge
Downing Street
Cambridge CB2 3EQ
United Kingdom

PHILIP McGILLIVARY
Skidaway Institution of Oceanography
P. O. Box 13687
Savannah, GA 31416

DAVID MACKAS
Institute of Ocean Sciences
P. O. Box 6000
Sidney, British Columbia
Canada V8L 4B2

CHARLES R. O'MELIA
Department of Geography and
Environmental Engineering
The Johns Hopkins University
Baltimore, MD 21218

J. K. OTTO ORZECH
Scripps Institution of Oceanography
Marine Biology Research Division
(A-002)
La Jolla, CA 92093

ALAN SHANKS
Institute of Marine Sciences
The University of North Carolina
3407 Arendell Street
Morehead City, NC 28557

MARY SILVER
Marine Sciences 34-95
University of California
Santa Cruz, CA 95064

RICHARD W. SPINRAD
Sea Tech, Inc.
P. O. Box 779
Corvallis, OR 97339

WILLIAM STACHNIK
Naval Undersea Systems Center
Code 3422
New London, CT 06320

TIMOTHY K. STANTON
1215 W. Dayton Street
Department of Geology
and Geophysics
University of Wisconsin
Madison, WI 53706

KEITH D. STOLZENBACH
Ralph M. Parsons Laboratory
Department of Civil Engineering
48-321
Massachusetts Institute of
Technology
Cambridge, MA 02139

RUDI STRICKLER
Alan Hancock Foundation
University of Southern California
Los Angeles, CA 90089

PHILLIP R. TAYLOR
Biological Ocenography Program
National Science Foundation
Washington, DC 20550

MARY TYLER
Martin-Marietta
Environmental Systems
9200 Rumsey Road
Columbia, MD 21045

KENNETH VOSS
Visibility Laboratory
Scripps Institution of Oceanography
University of California
San Diego, P-003
La Jolla, CA 92093

NICK WELSCHMEYER
The Biological Laboratories
Harvard University
Cambridge, MA 02138

RICHARD D. WHITING
Office of Naval Research
Code 123
800 North Quincy Street
Arlington, VA 22217-5000

PHILIP J. WYATT
Wyatt Technology Corporation
820 East Haley Street
P. O. Box 3003
Santa Barbara, CA 93130-3003

MARSH J. YOUNGBLUTH
Harbor Branch Foundation
Route 1, Box 196
Fort Pierce, FL 33450

WORKING GROUP I: AGGREGATE DYNAMICS

Rapporteurs: A. Alldredge, I. N. McCave

Members: F. Azam, R. Gran, G. Jackson, P. Jumars, F. McGillivary, C. O'Melia, A. Shanks, M. Silver

INTRODUCTION

Working Group I was concerned with the processes by which changes in the sizes, abundances and characteristics of aggregates are brought about in the ocean. Our charge was two fold: first, to construct a model of the dynamics of aggregate formation, breakdown and loss in situ, and second, to prioritize the components of the model as to their importance in understanding aggregate dynamics. Our goal was to determine which avenues of research were most important in moving us toward a predictive, quantitative understanding of the spatial and temporal variations of marine snow and microaggregates in the sea.

Two major issues were identified as critical to understanding aggregate dynamics: production and fate. Quantitative knowledge of the mechanisms of aggregation, disaggregation and aggregate loss, the rates at which these processes occur, the factors governing those rates, and the properties of both aggregates and their component particles would allow prediction of the distribution, abundance, sizes and dynamics of marine aggregates. Additional information on processes of physical transport (lateral advection, mixing, etc.) would allow fine tuning of those predictions.

MODEL OF AGGREGATE DYNAMICS IN THE SEA

A conceptual model of aggregate dynamics in the ocean is presented in Figure 1. Aggregates are formed by the adhesion of smaller, component particles including living organisms, inorganic and organic particles and

zooplankton mucus. Aggregation involves two essential stages. Particles must be brought close enough together to interact and then they must stick. The two actions are unrelated in that sticking does not necessarily follow from close approach. Once formed, aggregates may undergo a variety of internal transformations which alter their size, composition and characteristics. Aggregates are typically broken apart by turbulent shear or by the activities of organisms. They may be transported by settling or lateral advection, and finally they are lost from the pelagic zone through deposition and remineralization. We will examine each of these steps in detail.

A. Origin of component particles

Marine aggregates arise from a diverse array of component particles. These particles fall into the following general classes:

(1) Microorganisms: The most abundant living particles in the sea are microorganisms, predominantly bacteria (10^6/ml) and phytoplankton (10^2-10^4/ml). They are common components of naturally occurring particles. Factors controlling the distribution, growth rates, and abundance of phytoplankton and bacteria have been extensively studied by biological oceanographers and good predictions can be made regarding their availability for aggregation. Phytoplankton growth is usually controlled by light and nutrients. Bacterial growth is controlled by dissolved organic matter composition and supply and is generally correlated with phytoplankton standing stocks (chl *a*) and primary production. Phytoplankton production is (obviously) limited to the photic zone, while bacterial production occurs throughout the water column and in the sediments.

Of great importance to the aggregation potential of plankton are their

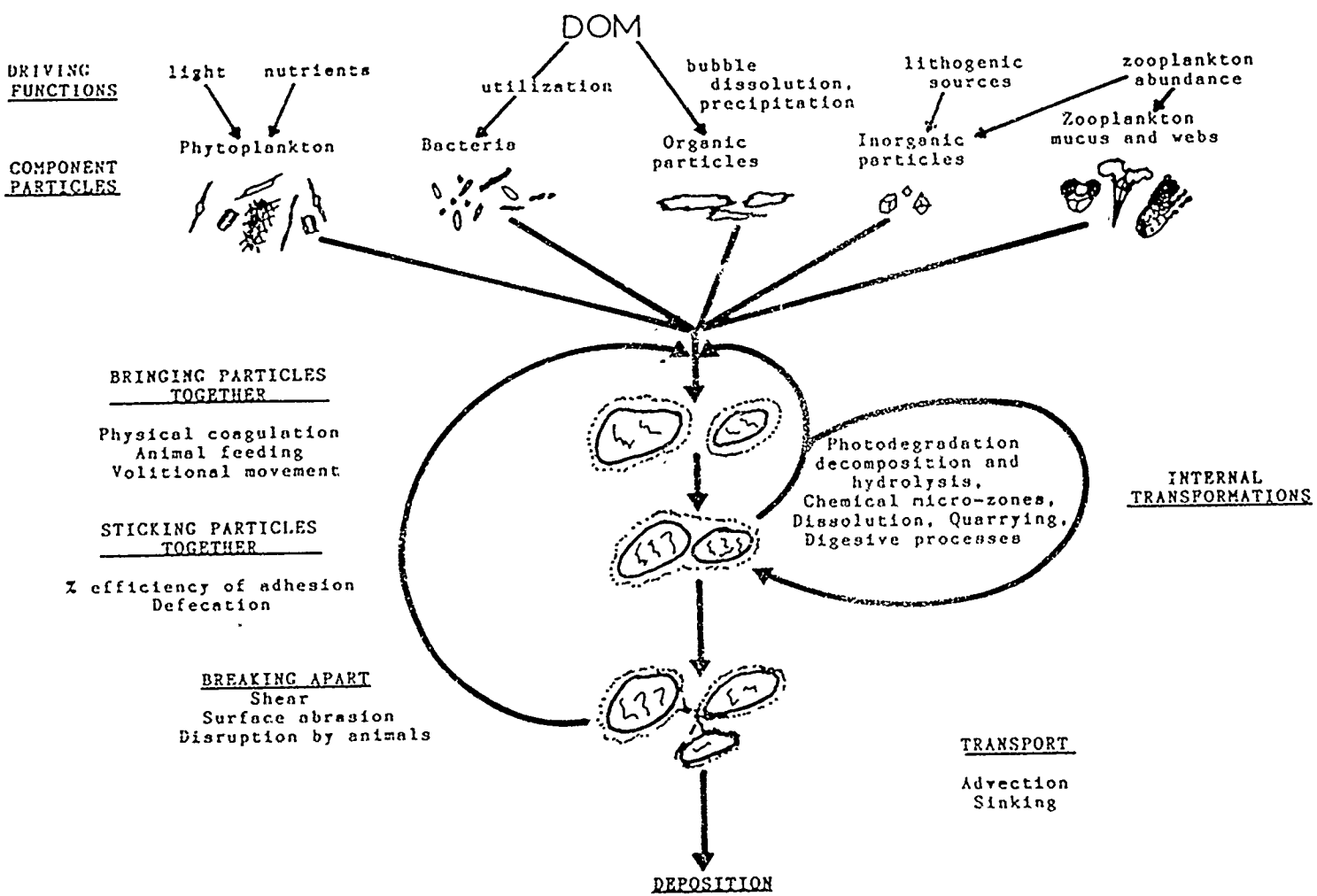


FIGURE 1: MODEL OUTLINING THE MAJOR PROCESSES DETERMINING THE PRODUCTION AND FATE OF AGGREGATES IN THE SEA

cell surface properties. These properties have been relatively little studied by ocean scientists, but it is likely that cell surfaces change with the physiological condition of the cell. Nutrient limitation leads to the production of sticky material by phytoplankton, while the production of capsular polysaccharides by bacteria may enhance aggregation. Models of aggregation thus require information regarding the physiological state, cell surface properties and exudate production rates of these microorganisms.

(2) Organic particles: Organic detrital particles are very abundant in all ocean regions, but their origins are still speculative. Various mechanisms have been suggested to account for their origins. One mechanism involves dissolved organic matter (DOM) to particulate organic matter (POM) conversions. Mechanisms of this conversion include adsorption to dissolving bubbles, de novo formation of particles via precipitation of organic and inorganic molecules, and utilization of DOM by bacteria. The rates of these processes are governed by: a) size and composition of the DOM and inorganic pools; b) abundance of bacteria; and c) sea-surface mixing. While considerable information exists regarding the rates at which bacteria in the sea convert DOM to POM, almost no quantitative information exists on the importance of bubble dissolution or precipitation (see Alldredge overview in this volume for detailed discussion). Other organic particles include crustacean moults, body parts, and carcasses which are relatively rare and are probably not major contributors to the particle pool.

(3) Inorganic particles: Inorganic particles are derived from external sources, primarily rivers and atmospheric inputs, and from the shells and tests of organisms. The importance of these non-living sources to bulk

particulate concentrations in surface ocean waters is probably relatively small, with the important exception of coastal ocean regions. The lower 500 to 1000 m of the water column in ocean basins is dominated by resuspended terrigenous particles comprising the bottom nepheloid layer.

(4) Mucus: Mucus produced by pelagic plants and animals is a significant nucleus for particle formation. Important animal sources include the filtering structures of larvaceans (houses) and pteropods (webs), and slimes produced by a variety of gelatinous zooplankton (ctenophores, salps, siphonophores). Likewise, phytoplankton produce mucus to form colonies (some *Thalassiosira, Phaeocystis*, etc.) and when they senesce or prepare for resting stages during poor growth conditions. Depending on its source, mucus likely differs chemically as does its ease of degradation, and physical properties (stickiness, rheological properties). The production rates of mucus by these sources are best known for larvaceans, where a typical individual produces 4-6 houses per day. The production rates for other zooplankton and phytoplankton sources are not so well known and require further study before models can quantitatively assess the importance of these materials for the aggregation process. Mucus production is primarily a function of producer abundance but may also be affected by the producing organism's physiological state and the quality and quantity of food available.

While models exist for the origin of many classes of these component particles, i.e., primary production models, the characteristics, abundances and sources of others are poorly understood quantitatively (e.g., bubble dissolution, chemical precipitation, etc.). Furthermore, while quantities of component particles may be a major factor governing aggregation rates physical coagulation or by feeding, particle qualities such as the sticking efficiency,

nutritional value, chemical composition, and tastiness may be more significant in certain environments. For instance, particles may be so rare in the oligotrophic ocean that biological mechanisms of aggregation substantially dominate over physical processes. In the open ocean, particle quality may thus be much more important than particle quantity in determining aggregation rates. In coastal oceans where particles including senescent diatoms and lithogenic material can be very abundant, physical aggregation processes may dominate. These hypotheses require testing.

B. Bringing particles together

In order for particles to aggregate, the component parts must first be brought together. This is accomplished by two major mechanisms.

(1) Physical coagulation: Physical aggregation occurs a) through Brownian action mainly involving small ($d<5$ μm) particles because the Brownian diffusivity ($D = kT/3\pi \mu d$) is large for small particles; b) through turbulent shear at a rate related to the shear rate and the cube of the collision radius given by the sum of the radii of the two colliding particles; and c) due to the differential movement of particles, often vertically under gravitational settling but also along other trajectories in the case of self-propelled or turbulently mixed particles. The removal rate of particles is proportional to the square of the number concentration of particles and is also affected by the fraction of particle collisions that result in coalescence. Clearly, to make a start on predictions of aggregation rates we need to know the volume (or size) distribution function, $n(v) = dN/dv$, of component particles and aggregates for different locations and depths in the ocean, the settling velocity distribution of particles, and the shear rate. Some of these data are available for a few ocean areas, but the data are very fragmentary and limited to a narrow particle size range.

At present, our knowledge of the relative importance of particle aggregation rates due to physical mechanisms is rudimentary. Calculations suggest that Brownian motion is most important for particles smaller than about 5 μm. However, only simple models which do not take retardation into account have been used for Brownian and shear coagulation and it is not clear whether shear or differential settling is more important for large particles. Certainly McCave's (1984) calculations, which suggest extremely low particle scavenging rates by aggregates, run counter to Honjo's (1982) observations in the Panama Basin which suggest appreciable removal of fine lithogenic particles by sinking palmelloid coccoliths. In fact, the models of collision efficiency for sinking particles have not been tested experimentally.

Estimates of coagulation rate have been based on monodisperse or two-component size distributions. A modelling effort involving realistic size distributions and the full range of oceanic turbulence needs to be undertaken. Only in that way can we properly examine the capacity of physical mechanisms to produce aggregates at the rates which are known to exist in nature. Labortory experiments to test differential settling and particle coagulation mechanisms should be conducted as well.

(2) Feeding: McCave (1984) concluded that physical aggregation mechanisms were inadequate to explain aggregation rates in the ocean. Aggregation rates of particles above submicron sizes appear to be biologically determined. Consumption by animals is the major biological pathway by which particles are brought together in the open ocean and is probably the best studied and

understood. Dispersed particles including phytoplankton, bacteria, and aggregates are consumed by animals and repackaged into larger, aggregated particles as fecal pellets. The rate at which food particles are brought together is a function of the concentration of the food particles, the abundance of the consumers, and the types of consumers present. Consumer species composition is critical to both the rate of production and to the characteristics of the pellets produced. Large-bodied, gelatinous zooplankton such as salps, larvaceans and doliolids are capable of consuming particles at rates an order of magnitude higher than copepods.

In general, rates of particle aggregation by zooplankton feeding are a linear function of food concentration up to a species-dependent particle concentration threshold. Beyond this threshold, feeding rates level off and aggregation is determined by the rate of digestive processes. Additional factors which affect feeding include temperature, time of day (many organisms feed in surface waters at night), size, taste, shape, species composition of food particles, and the size and age of the consumers.

Although aggregation of particles by consumption occurs in the deep sea, most of the animal biomass occurs in the upper 1,000 meters and a substantial proportion of those animals migrate into surface waters and feed at night. Phytoplankton concentrations are also highest in the euphotic zone. Thus, particle aggregation via consumption is likely to be most significant in the upper layers of the ocean. At great depths both the numbers of consumers and the concentration of particles is much lower indicating much slower particle aggregation rates. We do not know whether feeding activity dominates over physical coagulation in the production of aggregates at these depths.

(3) Active movement by organisms: Many marine organisms, including sub-micron-sized bacteria and micro-flagellates, heterotrophs, and still larger dinoflagellates and metazoans, have the capacity for active movement. Colonization of particles by organisms is one mechanism bringing particles together. However, due to the size of the organisms, relatively little biomass is involved in this process of aggregation and it is likely to be relatively insignificant in comparison with the other processes.

C. Sticking Particles Together

Once particles have been brought together, two major mechanisms cause them to stick together.

(1) Adhesion: Sticking efficiency or attachment probability is an essential component of all coagulation processes. Some determinations of sticking efficiencies have been made for clays and sediment particles, involving measurement of the rate of change in particle number in a suspension and comparison with theoretical predictions. Results indicate sticking efficiencies of 10 to 20%, but these are based on theoretical contact modes that do not include hydrodynamic retardation and therefore overestimate probable contact rates. It is possible that the sticking probability of particles in sea water is 100%. Mucus produced by phytoplankton may enhance sticking efficiency and bacterial mucus is known to greatly enhance aggregation rate. Moreover, organisms produce spines and colloidal projections which may increase the effective particle size and tendency to entangle. The role of cellular excretions and biogenic "glue" needs much further investigation.

When particles are not "sticky" in sea water, their stability may be ascribed to electrostatic and steric effects. Diffuse layers in sea water are small, on the order of angstroms in thickness, and electrostatic stabilization may be unimportant in the ocean. It is possible that oceanic particles are sterically stabilized by natural organic agents, possibly of low molecular weight. Larger organic molecules can destabilize particles. The role of organic matter on the stability and instability of particles in the ocean should be examined.

Present methods of measuring sticking efficiency should be extended to living particles and related to the physiological state of the organisms. The possibility of making optical experimental measurements of contact rates, thus eliminating the dependency of attachment probabilities on contact models should be pursued.

(2) Defecation: Feeding animals collect particles and stick them together through the process of fecal pellet formation and defecation. In parts of the ocean where component particles are scarce (such as the oligotrophic ocean) defecation may be the major mechanism by which particles are aggregated. Fecal pellet production depends primarily on animal population concentrations, on feeding rates, on ambient particle concentration and size spectra, and on digestion efficiencies. Digestion efficiencies are about 70%, and if we assume that all new production is consumed, then as much as 30% of primary production can become aggregated in fecal pellets. Digestion efficiencies decrease with increasing food concentration and thus more feces will be produced where both food and consumer populations are high.

Fecal pellet formation and repackaging appears quantitatively most important in the upper water column organisms typically

produce 10-100 pellets/day over a broad range of sizes and densities. Despite the broad range of settling velocities measured for many species, it appears that even large, relatively dense feces may remain in the upper water column for periods of at least days, allowing for interactions with other particles, and chemical and biological diagenesis. For many feces coprophagy is a common fate, indicating that component particles in feces may be stuck together several times via defecation processes before they are lost from the pelagic system. During settling, larger feces are believed to adsorb luminescent bacteria which may render them more visible to coprophagous organisms, and thus enhance their rate of reingestion.

The production of feces by many marine zooplankton groups (pteropods, amphipods, pelagic polychaetes, ctenophores, siphonophores) is poorly known. Variations in fecal composition and production rates with organism age, size and food supply, the role of coprophagous organisms and the importance of fecal pellet bioluminescence have also received very little study.

D. Internal Transformations

Once formed, particle sizes and properties may be altered by internal transformations. These include:

(1) Aggregate food webs: The size and characteristics of aggregates as well as the nature and extent of the biological glue helping hold them together will be altered by the growth, feeding, and interactions of the complex detrital communities which inhabit them. These activities will result in utilization of much of the labile organic matter and conversion of the particles to a more refractory state.

(2) Chemical microzones: Because of their high concentrations of organisms and their semienclosed physical structure, macroaggregates may serve as chemically altered microenvironments. The high metabolic activity of microorganisms leads to high concentrations of metabolic end products and inorganic molecules. These unique microzones may enhance particle degradation or colonization.

(3) Alteration of aggregate quality by microbial colonization: Aggregates, particularly those of low nutrient value (and poor "taste"), may become more attractive to animal consumers if the aggregate becomes colonized by bacteria (and protozoa). This paradigm is well established in trophic interactions in detrital food webs, microbial growth being responsible for enriching detritus with respect to N and P. Aggregate disruption (breakup) could be increased by increased attractiveness of colonized aggregates to animals.

(4) Photodegredation: DOM, primarily fulvic and humic acids, is important in coating particles and determining their surface characteristics. Photochemical transformation of marine fulvic acids has recently been shown to occur and to closely resemble photo-induced cross-linking of polyunsaturated fatty acids, which are important components of phytoplankton, especially diatoms. Such photochemical transformations would enhance particle aggregation. By contrast, polysaccharide linkages are expected to photodegrade and particle disaggregation may occur if polysaccharides are important in aggregate binding. Photodegradation is poorly understood and its impact on particle dynamics needs investigation.

E. Aggregate Breakup

Aggregates may be broken apart into smaller aggregates or into their component particles via shear or the activities of organisms.

(1) Shear breaking: Aggregates can break up in a shear field. Important factors include turbulence intensity and scale, particle size and strength, breakup mode (surface erosion or aggregate splitting) and the time of exposure of the particle to the turbulent shear.

Perhaps the largest fluid shears in the ocean interior (away from surfaces) occur in turbulent regions which result from breaking internal waves, or in the wake of larger passing bodies (fish or zooplankton) or along the boundary between differentially moving stratified layers. The parameter which characterizes the shear forces within the turbulence is the turbulent energy dissipation rate, commonly denoted as ε. Typical oceanic values of ε are 10^{-5} to 10^{-3} cm^2/sec^3. The larger values are typically found in isolated "patches". Still larger values of ε can be found in the ocean's upper mixed layer and in the benthic boundary layer. Different relationships for floc disaggregation have been proposed which depend on the floc composition and the floc size relative to the smallest turbulent scale, l_k. l_k = 5 mm at $\varepsilon = 10^{-5}$ cm^2/sec^3 and l_k = 1 mm at $\varepsilon = 10^{-3}$ cm^2/sec^3. If floc fracture does occur, such as for clay-aluminum flocs, the maximum remaining size is very nearly equal to l_k using the numbers from McCave (1984). Basically, particles larger than l_k can be broken whereas those smaller than l_k live in a "laminar world". Such calculations do not account for the strength of the aggregated material, information which is presently unavailable.

It is useful to develop models for the breakup of oceanic aggregates by turbulence, but the development of a useful theory can be expected to be

difficult and so requires some time. In the meantime, experiments to measure breakup of a variety of types of aggregates under turbulent conditions of interest in the ocean (e.g. mid-depth, the benthic boundary layer, breaking internal waves) should be made.

(2) Activities of organisms: Animals break apart aggregates during feeding. Many zooplankton are highly selective feeders capable of grasping, tasting, shredding and discarding unsatisfactory food particles. Some quarry or scrape away the aggregate surface, others consume entire particles. Bacterial decomposition on the particle surfaces may also weaken aggregates structually, potentially leading to particle fragmentation. The role of animals in breaking apart particles is poorly understood.

F. Aggregate Transport

Both aggregates and component particles may be transported either vertically via sinking and mixing or laterally via advection.

(1) Sinking: Measured or calculated sinking rates for marine snow range from 1 to 150 m/day. The rate at which an aggregate settles through the water column is dependent on the density difference between the floc and the surrounding water, and the drag on the particle. Drag is strongly dependent on shape. Marine snow comes in a large variety of complex shapes. Due to this complexity, drag will have to be determined empirically.

(2) Mixing: Various researchers have speculated on the importance of turbulence and mixing in retarding the sinking of aggregates. This has not as yet been adequately demonstrated, but it may occur in situations where sinking rates are slow relative to mixing rates.

(3) Lateral advection: The abundance of marine snow within a water parcel is dependent on the rates of aggregate formation

and destruction, the vertical flux of aggregates through the water parcel, and the exchange of aggregate populations with adjacent water parcels. However, the distribution of marine snow within a water column may also be affected by lateral advection of parcels of water bearing flocs from distant sources. The amount of horizontal advection is probably dependent on sinking rate of the aggregates (greater for slower sinking flocs), the current velocity (greater at higher current speeds), and the vertical extent of the current (greater for thicker currents). Situations where advection may be particularly important are near the continental slope, around submarine ridges, and where aggregates are "trapped" on density interfaces (i.e., aggregates which have become neutrally buoyant or nearly so at a density interface).

G. Aggregate Loss

Aggregates are ultimately lost from the pelagic zone through deposition to the sea floor, by conversion to DOM or by mineralization (conversion to CO_2, NO_2, PO_4 etc.) through the metabolic activities of organisms.

(1) Deposition: Part of the rain of aggregates survives as the sediment of the sea bed. The behavior of particles in the benthic boundary layer is principally controlled by the boundary shear stress. Deposition of most classes of suspended particles can occur when the shear velocity (U) is less than 0.5 cm/sec. However, close to the bed, in the lowermost centimeter or so, the shear may be intermittently very high, at least two orders of magnitude higher than that found above a meter away from the bed. This is likely to prove highly disruptive to some classes of aggregates. The resuspension of material may inject it back into the water column in a more finely divided form than that in which it arrived. As a part of the bottom

layer this material may be transported for long distances while reaggregating. Many cycles of deposition, breakup, resuspension and reaggregation during transport may occur.

(2) Metabolism by organisms: Bacteria and protozoa may play a major role in the degradation of aggregates. Only limited information is available regarding microbial colonization, hydrolysis, and metabolism of the organic components of macroaggregates. Microbial activity can cause rapid degradation of POM, some of which is remineralized via respiration and some of which re-enters the DOM pool. Aggregates consumed by animals are partially mineralized via metabolism and respiration, producing an as yet poorly quantified loss of particulate matter with each reconsumption.

APPLICATION OF THE MODEL TO THE OCEAN

We may think of the open ocean as comprising three zones, the upper mixed layer (UML), <200 m deep, the interior down to about 500 m above the sea floor and the bottom nephloid layer (BNL) in the lowermost 500 m. Different proportions of primary components and filter feeding animals are expected in each zone.

The UML contains the region of production of the majority of new material entering the ocean. It also has the highest concentration of biological particles. Some fraction of the aggregates produced in this region pass out of it by sinking into the interior, where concentrations of all particle classes are much lower. Physical coagulation rates will also be lower. It is not clear for any of these regions whether physical or biological aggregation is dominant, though the latter seems most likely in the interior and any which

form anew sink into the BNL. The BNL is a region of higher physical stress and the active supply of lithogenic material from resuspension may produce dominance of physical mechanisms.

A fourth zone is the continental shelf region. Both lithogenic and biogenic particles are abundant here and the relative significance of biological and physical aggregation processes is unclear. This case is particularly important for understanding the fate of particulate matter in the coastal zone.

PRIORITIZATION OF MODEL COMPONENTS

Certain portions of the model were singled out as being especially important for our understanding of aggregate dynamics in the sea.

Top Priority

- Mechanisms of particle aggregation: Both physical aggregation and feeding are of central importance to particle dynamics.
- Mechanisms of particle sticking: Understanding the % sticking efficiency of various classes of particles and the defecation and reconsumption rates of organisms are central to understanding particle dynamics.
- Abundance, properties, and rates of formation of component particles: While the rates of formation for some component particles are well known (phytoplankton), others have not been quantified. Abundances and properties are largely unknown for several classes of component particles.

Lesser Priority

- Internal transformations: Although important, these processes were considered less important in explaining particle sizes and abundances.

- Breakup: Particles appear to be lost primarily through sinking and reconsumption. Particles may not break up, once formed, in any significant quantities.

- Transport and loss: Deposition and sinking have been the subject of numerous large-scale studies which have already provided considerable information. The significance of transport processes can only be evaluated with information on formation processes.

RECOMMENDATIONS

Our goal is to achieve a predictive understanding of aggregate dynamics in the sea. Although not an exclusive list, the working group identified the following recommendations as top priorities toward achieving that goal.

(1) Understanding of aggregate dynamics requires that we know the number, concentration and size distribution of aggregates and component particles, where possible, by particle class. We recommend development of instrumentation which could provide this information, preferably in real time, over a variety of temporal and spatial scales.

(2) In order to understand the relative importance of the mechanisms which bring and stick particles together we need additional information for each class of aggregates or component particles on the following properties:

a. settling velocity distribution as a function of size, shape, source, porosity, etc;

b. strength or rigidity;

c. surface characteristics, % sticking efficiency, and significance of biogenic "glues";

d. attractiveness to consumers, including nutritional value, tastiness, bioluminescence, age.

(3) We need to determine the numbers, sizes, locations, feeding and defecation rates, and the particle size and composition preferences of major particle consumers. The prevalence of coprophagous species and rates of fecal pellet consumption require particular attention.

(4) We need to determine the encounter rates of particles in nature and the effects of physical processes, particularly short duration, high energy events such as internal waves, storms, etc., and biological factors such as phytoplankton buoyancy changes on those rates. A theoretical modeling approach taking these kinds of factors into account might be an appropriate first step toward predicting if and when physical coagulation mechanisms are significant in particle formation.

(5) The rates and mechanisms of component particle formation, particularly DOM-POM conversions, must be determined under varying environmental regimes. The factors driving production of component particles must be quantified in order to predict abundances of component particles.

(6) The abundances, aggregate class composition, and the rates of aggregation and disaggregation for each class of aggregates needs to be determined for contrasting oceanic environments in order to quantify the relative significance of the various mechanisms of aggregate formation and loss in these systems. A good start would be a comparison of the oligotrophic open ocean with a coastal or upwelling zone.

WORKING GROUP II: IN SITU EXPLOITABLE PROPERTIES OF AGGREGATES: OPTICS

Rapporteurs: K. Carder, R. Eppley

Members: V. Asper, G. Gal, R. Honey, D. Lavoy, O. Orzech, R. Spinrad, W. Stachnik, R. Strickler, K. Voss, P. Wyatt

A. Introduction

There is little information on the large scale distributions of marine aggregates; automatic aggregate identification and classification methodologies remain to be developed. Present optical classification schemes for aggregates require human attention: an objective observer to view high resolution particle images.

Acquiring particle size frequency data is feasible in the survey mode at present, and we propose the development of a Marine Aggregate Survey Camera (MASC) designed to collect size frequency data for particles from about 25 μm to 5 cm diameter as an important first step for quantifying marine aggregates.

Concurrent with the MASC development and deployment, we need to acquire improved optical methods to discriminate aggregates from living organisms by laboratory and shipboard methods. The knowledge gained can then be exploited either to improve the discrimination of MASC or to develop an additional survey instrument suite to identify, size and enumerate aggregates in the euphotic zone.

B. Aggregate Classification Methods

In order to understand the optical characteristics of marine particles well enough to develop an automatic method to accurately classify them as aggregates, an extensive suite of laboratory measurements on fresh and aged aggregates is required. Biologists typically classify aggregates microscopically. Instrumental image analysis of aggregate shape, size and texture (e.g. heterogeneity and patchiness of scattering centers) should accompany other optical measurements of aggregates until a classification scheme is fully verified.

An example of a classification strategy is to discriminate marine snow from zooplankton by the forward volume scattering function. Aggregates are clusters of smaller scattering centers, and small scatterers do not scatter light as predominantly in the forward direction as do large particles of low refractive index such as zooplankton or phytoplankton. The near-forward rate of change in scattering with angle should provide a much larger negative value for zooplankton than for marine snow of the same cross-sectional area. Tests of other hypotheses for automatic aggregate identification should be part of this laboratory effort.

Some of the optical measurements to be considered are volume scattering functions, absorbance, index of refraction, polarization, fluorescent properties, luminescent characteristics, and heterogeneous or amorphous qualities of aggregates.

Four of these exploitable optical properties of aggregates, refractive index, absorbance, bioluminescence and fluorescence, may provide aggregate age discrimination. For aggregates containing significant polysaccharide exudates which may serve as a cohesion mechanism, the exudate can be easily observed due to phase lag in light passing through it. This is due to a slight

slight increase in its refractive index relative to seawater. Schlieren or holographic interferometric techniques can be used to visualize such aggregates. If these exudates are degraded over time, the phase contrast may disappear, providing a possible aggregate age discriminator.

Marine snow may emit bioluminescent light. The characteristics of that light are indicative of its component organisms, and therefore, may be an exploitable optical property in determining the life histories and ages of the macroaggregates.

Eukaryotic luminous organisms such as dinoflagellates and radiolarians emit pulses of light which are mechanically (or acoustically) stimulable. Luminous bacteria, however, emit only a steady glow. Since the presence of bacteria in concentrations high enough to luminesce can occur only on older aggregates, the properties of emitted light may be an indication of age.

As aggregates age, they are degraded by marine bacteria. This process changes the color and chemical composition of the marine snow. Some of the constituent chemicals such as fulvic and humic acids may fluoresce. These properties, too, might be exploited in determining the age of marine snow by optical observations.

Spectral absorbance, while admittedly a formidable measurement on single particles, could provide extremely valuable data. The opacity of fecal pellets is quite high relative to that of phytoplankton and zooplankton, and its spectral character probably includes effects of degradation products. Ratios of the beam attenuation coefficient to near-forward, scattered light will increase with absorption and are easily measurable on an individual particle basis. Thus indirect methods of observing opacity effects are available for possible use as fecal pellet discriminators. Also, fluorescent

properties of fecal pellets may be useful as they should contain more products of pigment degradation such as phaeophytin, than do those of phytoplankton. This additional measurable should be considered for pellet discrimination.

C. Devices and Studies

C1. Marine Aggregate Survey Camera (MASC)

The abundance and size frequency distribution of aggregates may be determined by analyzing in situ video images of an illuminated volume of water. This volume is defined by a linear collimated light "slice" extending normal to the axis of a video camera. In the interests of great economies in costs, development time, and other resources, it is proposed that the instrument initially utilize commercially available TV cameras, recorders, and displays, with currently available resolutions and TV formats. As higher resolution systems reach the commercial market, it would be a simple matter to upgrade the cameras without altering the rest of the system.

The low resolution of commercially available TV systems, compared to either the highest pixel count charge-coupled detector (CCD) arrays of photographic systems, and the need to count and/or size aggregates over very large size ranges requires that more than one camera should be used, each with a different focal length and field-of-view.

As the system is towed through the water, aggregates entering the illuminated volume scatter light into the camera. The images produced represent the integral of all illumination received at each pixel so that a continuous volume of water is imaged as the system moves through the water. The dimensions of the illumination and imaging system are determined by the expected sizes of the aggregates and the resolution of currently available CCD imaging chips. For example, a 400 x 300 pixel chip yields an ultimate

resolution of 500 µm per pixel for a 20 x 15 cm illuminated area in the water. This primary image is designed to assess the abundance of macro-aggregates and is supplemented by a second camera with a 2 cm field width and 50 µm resolution, aimed at assessing the abundance of micro-aggregates. A photographic camera in this mode would provide resolution to less than 10 µm if needed.

The system is mounted on a towed fish configured to cycle between the surface and the maximum depth of interest at speeds up to 5 knots. Data are transmitted up the tow cable for realtime viewing and storage on a magnetic medium. Alternatively, the images could be analyzed in real time and the numbers and size frequency distributions of aggregates determined by pattern recognition algorithms. Displays could include size histograms or continuous two-dimensional contour plots of abundance.

Important surveying parameters for the MASC involve sample volume and volume sampling rate, both of which are simple to calculate. The sample volume, VS, interrogated by each frame is simply:

$$VS = \frac{h \times w \times (\text{ship velocity})}{\text{sampling rate}}$$

h = 15 cm

w = 20 cm

sampling rate = 30 Hz

A ship speed of 1 knot results in a sample volume of 0.5 liters per frame. The flow-through rate, RV, of this surveying instrument is the above

volume times the sampling rate and is 15 liters/second or 54,000 liters/hour. For 5 knot ship speed this became 2.5 liters for VS and 270,000 liters/hour for RV. Towing speed would be determined by the maximum speed of the towed fish and the sample concentration.

For the design suggested, in which the high-resolution camera has 10 times the resolution of the other, the higher resolution camera would experience a flow rate and sample volume 1/100 of the above.

Background light may be a problem in surface waters during daylight if the radiance of the particles in the sample sheet beam is less than the radiance of the background as seen by the camera. This problem can be minimized if the camera is stopped down until it barely sees the background illumination (correspondingly increasing the depth-of-focus), and if the aggregates still scatter enough light to be seen against the dark background. Correspondingly, the effects of any bioluminescence stimulated by the aggregate's passage through the sheet can be minimized if the intensity of the sheet beam can be made as bright as possible.

It is clear that the effective depth-of-field of such a camera system will be determined either by the thickness of the sheet beams, or the optical depth-of-focus of the camera system, whichever is less. The narrow field-of-view camera may require a correspondingly narrow sheet-beam thickness to reach the maximum achievable resolution. These trade-offs must be studied during early engineering design studies.

C2. Laboratory Studies of Optical Properties of Aggregates

It is recommended that a variety of optical measurements of aggregates be

made based upon a generalized multiangle configuration. This structure could be comprised of a laser source, an array of detector positions from very small scattering angles (<10°) to large angles (<170°). Near-forward scattering can be measured by focusing a collimated laser beam onto a small stop (<10 μm diameter) on an area array detector. Non-parallel scattered light will fall beyond the stops and can be measured in great detail. Measurement of scattering at larger angles is straightforward.

Although extant instruments have most of these features, the measurement of scattering at very small angles, together with larger angle scattering in the same instrument must be achieved. While such design modifications are being pursued, a variety of preliminary measurements using separate, existing small-angle and large-angle devices should be undertaken. In this manner, aggregates of various compositions may be examined for the purpose of characterizing optical observables. Integrating these scattering data over all scattering angles, realistic extinction coefficients for aggregates of various classes could be estimated for those structures whose theoretical values cannot be calculated.

Among the types of light scattering measurements that may yield meaningful observables are:

1) Intensity values versus angle: These measurements could form the basis for comparison of the measured values of the extinction and volume scattering coefficients with those theoretically derived or predicted.

2) Fluorescent properties: Laser stimulation with this device will also permit spectral observations of fluorescence for discrimination of many pigments and their degradation products.

3). Depolarization measurements as a function of $\bar{0}$ and 0: The degree of depolarization of scattered light for a fixed incident polarization state provides an excellent measure of the scatterer's asphericity, birefringence, optical activity, refractility, and/or intrinsic multiple-scattering properties. Aggregates of particulates having any of these properties will produce varying degrees of depolarization whose measurement may prove a particularly attractive means for classification.

4) Settling and dynamic measurements: Settling rates and tumbling characteristics for selected structures may be measured based on the temporal recording of their light scattering properties during their motion through an inhomogeneous laser source. Simultaneous sequential images will provide particle size, shape, dynamics and identification. Such measurements will provide important information concerning aggregate density and mass distributions that could aid further in their classification.

The light absorption characteristics of marine snow and aggregates are important for the classification of these particles. Specifically, through the use of either a reflecting tube, or integrating sphere-based absorption meter the quantitative measurement of the absorption coefficient can be made on a "per aggregate" basis. By performing these measurements for visible wavelengths the absorption of the particulate components, including photosynthetic pigments will be determined. Because of the potential significance of non-particulate exudates and pigment degradation products in the composition of aggregates, it would be of value to measure total absorption at shorter wavelengths as well, perhaps even in the ultraviolet.

Fluorometry is an essential technique for laboratory-based aggregate particle classification. An effort should be made to define the optimal excitation and emission bandwidths for aggregate analysis. Spectrofluorometric techniques should be used to assess the chlorophyll and pheopigment composition of the aggregates. Additionally, an emphasis on ultraviolet excitation may be important for measurement of pore water-dissolved organic matter. Lab measurements must be intensive enough to define the optimal wavelengths for eventual use of *in situ* fluorometry in aggregate classification. The use of fluorometry is also suggested as a means of assessing internal aggregate flushing or perfusion rates. The fluorescence history of an aggregate as it falls through (and past) a discrete layer of fluorescent dye should provide some measure of the rate of exchange of water in the aggregate in a quiescent environment.

During the course of this program, large numbers of images of various types will be collected for subsequent analysis and as permanent records. These images can be manipulated to recover information not readily apparent, to increase signal-to-noise rates, to increase contrast, etc. Image analysis can be used to recover information on aggregates such as size, shape, orientation, area, circumference and texture or homogeneity. A search for image characteristics unique to certain classes of aggregates is a very high priority in order to automate the identification and analysis of aggregates from imagery.

C3. Holographic/Photographic Camera System for Use in Sediment Traps

Aggregate fall velocity can be determined *in situ* in damped sediment traps by acquiring sequential holograms (Carder *et al*, 1982) or photographs. The

advantage of holography is magnification without loss of depth of field. Other settling techniques, such as time of flight of particles settling through narrow light beams, can also be exploited.

The porosity and permeability of aggregates affect their fall velocity and dynamic density (inversion of Stokes' equation). Methods for assessing these characteristics can be determined holographically by observing aggregates settling through density interfaces and measuring the volume of low density, low refractive index fluid flushed from the aggregate pores into the denser, more refractive layer (Carder, Steward, and Costello, this report). Organic-rich aggregates in a density gradient will continue to settle to a depth with density equal to that of the average of the non-fluid structural components of the aggregate. This structural density value together with the dynamic density of the aggregate provides a measure of its porosity.

Isotonic solutions as dense as 1.4 g/ml can be developed using heavy water-saline metrizamide solutions. Denser, inorganic-rich aggregates may be buoyed by denser solutions such as Maxidens (density = 1.9 g/ml).

C4. In situ, Lagrangian Observations of Particle Interactions

To observe the fate over prolonged time of marine snow particles which are suspended in the water column we propose the following system:

1) an optical system, called a Spatially Filtered Camera (SFC), similar to the one used in Strickler (1977, 1982, 1985) which will allow the observation of suspended particles in situ and in real time in a sample volume of typically 2 ml with a resolution of better than 10 μm.

2) an interface between the optical system and its transport system, e.g. videocable if the transport system is a submarine, targeting sights and in situ TV monitors for divers. With such an SFC it will be possible to observe:

a) the formation and "life" of a particle over a time period of up to 5 hours;

b) any interaction this particle may have with other particles and/or live animals during the observation time;

c) the desirability of capturing the particle for subsequent in vitro analyses.

The SFC would consist of two units, the laser and collimating unit and the imaging unit with the imaging lens and the TV camera. The second unit would contain also a mini-VCR and a mini-TV monitor if the transport system is a diver.

A first prototype of a SFC with divers as transport system is at the moment under construction and the first results have shown that it will produce data which are comparable in resolution and information content to results from laboratory experiments. The interface between the SFC and a submarine (e.g. Sea-Link of the Harbor Branch Oceanographic Institution) may include a digital transmitter of the video signals to facilitate using light fibers as a link.

Using manned submarines as transport systems will limit the range for deployment. In a later stage, it may become mandatory to observe the fate of particles over longer time periods and/or in greater depths. Unmanned remote controlled vehicles could then be used to transport the SFC, especially when the interface facilitates a real time link between the SFC/vehicle and the observer/driver of the vehicle.

D. Recommendations: Optics Working Group

1. Develop a marine aggregate survey instrument, MASC;
2. Develop laboratory instruments for shipboard use to determine the optical characteristics of aggregates and living organisms in order to develop aggregate discrimination strategies;
3. Use and improve existing sediment trap mounted holographic and photographic systems to measure aggregate size, shape, orientation, settling speed, density, porosity, and permeability;
4. Develop *in situ* Schlieren camera (the SFC) for studying particle interactions over time (hours).
5. Develop accessory instruments, based upon studies under 2 (above), to provide certain identification of aggregates, even in waters high in plankton. This approach should provide accurate size frequency information for aggregates even in waters of complex particle characterization.

Rationale for the Recommendations

There is an immediate need for survey instruments for assessing aggregate size-frequency distributions and for studies of the distribution and abundance of these ubiquitous marine particles.

The MASC instrument will be most effective below the surface waters where aggregates dominate the particle field. Optical studies of aggregates are needed to determine how best to discriminate between aggregates and plankton in surface waters. While these problems are being solved, work should proceed with available instruments in order to characterize aggregate dynamics,

including animal-particle interactions. The instruments that can do this are 1) the holographic/photographic camera system for use in sediment traps (see section C.3) and 2) the Spatially Filtered Camera (C.4), respectively.

Developing instruments that can remotely identify, size and enumerate aggregates is an important goal of this program. Laboratory studies are expected to lead to design criteria for robust aggregate discrimination.

WORKING GROUP III: IN SITU EXPLOITABLE PROPERTIES OF AGGREGATES: OTHER PROPERTIES

Rapporteurs: D. L. Mackas, T. K. Stanton

Members: R. Bidigare, J. Bishop, J. Brooks, K. Bruland, C. Lee, K. Stolzenbach, M. Tyler, N. Welschmeyer, M. Youngbluth

1. Introduction

Our working group was asked to evaluate the methods (other than optical) which would be most useful for improving understanding of non-living organic particles in the ocean. We identified three major categories of desirable observations and techniques. The first includes measurements relating to the distribution and classification of aggregate populations in the ocean. These provide information on the demography of the particle population. What kinds of particles are present? What is the size spectrum of each class? What are their spatial and temporal concentration fields? We also included under this heading methods for collection of samples from natural particle populations.

A second group of observations relate to the production, persistence and eventual fate of the particles in each class identified above. These measurements should describe and quantify the expected "life history" of particles. They provide information on the type and rate of the dynamic processes that create and modify the observed demographic distributions.

A third group of observations is needed to characterize the local oceanographic environment in which the particles reside. Both the distribution and dynamics of non-living aggregates are likely to vary with spatial and temporal changes in environmental properties and conditions, especially those affecting the frequency and effectiveness of encounters between particles (both living and non-living).

We recommend application and (where necessary) development of the instruments and analytical methods described in the remainder of the report. For logical convenience, we consider the methods and approaches in the sequential order listed above. Our ratings of relative importance and feasibility are given in the body of the text.

2. Detection, Classification, Census, and Capture Methods.

Detection and location may involve the optical techniques discussed by the optics working group, or the sonar, particle counting, and visual observation techniques outlined in this section. Because the occurence of marine snow is so wide-spread in the ocean, it is important that the detection and location techniques be rapid enough that the temporal and spatial variability may be measured. The measurements may often give some information on particle properties. For example, visual detection (by divers or camera) could describe size and shape of at least the larger particles. However, measurements of most important particle characteristics (e.g., their chemical and biotic composition) will require prior concentration and separation steps to allow collection of sufficient material and analysis by sophisticated laboratory techniques. Because details of the concentration field will often be of interest, it is essential that sampling methods be able to resolve local patches and layers. Because not all of the desired measurements can be made in situ, samples of the aggregate population will need to be captured for laboratory analysis and experimentation. Some aggregates are very fragile and porous, hence the capture methods should be gentle and non-disruptive to avoid altering important particle properties. Because the size, composition and origin of the aggregates are so diversified (even at a single location), the capture techniques must be selective so that analyses may be performed on targeted subsets of the total particle population.

Because of the large volumes of water that sonar systems can scan in a short period of time (order 10^7 m^3 $hour^{-1}$), it would probably be desirable to employ this technique in at least a preliminary survey mode. Acoustics could be used in two ways. The first is direct detection of the marine snow to determine its location and perhaps abundance. Marine snow aggregates may have such a small scattering cross section that they are not detectable on an individual basis. However, when occuring at sufficiently high densities it is possible that they can be "seen" acoustically when their collective echo is received. A second approach involves indirectly locating the snow by directly detecting other scatterers such as marine biota. Many organisms will have a scattering cross section much larger than that of marine snow and hence will be more readily detectable. However, their distribution may be linked to that of the non-living aggregates. Thus, scanning a large area and locating these detectable objects may give a clue as to the location of the marine snow.

Flow-through particle counters (optical and resistive) may also be useful as survey tools. A major limitation for these is the probability of particle breakup when larger aggregates are drawn through the sensor orifice. For porous aggregates, the two particle sensing methods will give very different estimates of particle size. Optical counters detect a cross-sectional area (the size of the "shaded" area as the particle passes through the sensor). Interstitial pore space will typically be included in this estimate. Resistive counters record the volume of the non-conductive particle. The interstitial water in a porous aggregate will be conductive, hence the volume estimate will be of only the particulate phase. If problems with particle breakup can be minimized, it may be possible to combine these different types of data in a useful way. By knowing the "shadow" area, the total occupied volume (including interstitial water) can be estimated for

simple external particle geometries. The ratio of particulate volume to the total volume would then provide an estimate of aggregate porosity.

Aggregates have been physically collected with bottles, *in situ* pumping systems, and traps. These devices can be tethered on wires, deployed on free vehicles, operated by divers, and attached to submersibles. Future use of these collectors to sample aggregates (such as marine snow particles and fecal material) should incorporate video (or photographic) and environmental data logging (depth, temperature, conductivity, fluorescence and transmittance) instruments into a sampling package in order to provide useful information about the natural state of the aggregates and the conditions under which aggregates were collected.

The selection of a particular sampler for aggregates should take into account: (1) the degree to which aggregates are likely to be physically altered, (2) the sample size and replication required for analysis, (3) the scales of sampling needed (spatial, temporal, and regional), and (4) the need to separate aggregates into different type classes and from organisms not associated with the aggregates. Present collection methods, when used in conjunction with visual observation by divers or from submersibles, allow both gentle and selective sampling of the larger aggregates (roughly 1 mm and larger). The smaller aggregates are probably less vulnerable to mechanical disruption, but non-selectivity of sampling is a major limitation.

Two modes of particle collection are envisioned: (1) profile studies of the water column over large spatial scales (km to 100's of km) and (2) localized studies of aggregates over scales of tens of meters. The profile studies provide information on large scale patchiness and the relationship between aggregate distributions and the physical and biotic characteristics of the water column. Local sampling can be guided by the aggregate and environmental profiles and by visual observations to give an expanded view of

particular areas of interest. For example, scientists could use a submersible or oceanographic information such as pycnocline depth to select a target area for study. An in situ filtration system fitted with several filter channels, each permitting the collection of several mgs of materials, could be activated to sample specific classes of aggregates as determined by high resolution video information. The filtration rate should be both high enough to capture the desired aggregate, and low enough to minimize the disruption of the collected materials.

Profile sampling with a multiple unit large volume in situ filtration system can collect milligram quantities of size-fractionated samples of aggregates from the water column. The slow filtration rate of the system (approximately 1 cm sec^{-1}) enables the collection of aggregates ranging from delicate gelatinous diatom colonies to robust fecal pellets. More fragile aggregates can be sampled by reducing the filtration rates.

At least two new capture devices should be developed: (1) a sampler to collect fluff at the water/sediment interface and (2) an in situ flow cytometer to characterize small (<0.5 mm) aggregates.

3. Measurement of Particle Properties Relating to Source, Persistence, and Fate

3.1 Mechanical Properties

3.1.1 Size and Shape

Because of their flexibility and fragility, the size and shape of marine snow aggregates should, if possible, be determined in situ using non-intrusive techniques. A combination of different optical methods (imaging, shadowgraphs, etc.) is the most likely method for this determination.

Specifications of size and shape for a complex form such as a marine snow aggregate must be done jointly and in terms appropriate for the process of interest. For example, the size measure (cross-sectional area) most

related to interception of smaller particles is not the same as the size measure (surface area) determining viscous drag (and thus velocity). If the aggregate is porous, in the sense of having an appreciable exchange of the internal fluid, the internal structure will be an important component of the shape and size parameterization.

3.1.2 Fragility and Flexibility

Marine snow aggregates are complex materials being at the same time viscous, elastic and compressible. The flexibility of the aggregates may be a factor in determining changes in the physical structure over time (e.g., compaction leading to higher densities) and in mediating biological and chemical interactions within the aggregate (how "well-stirred" is an aggregate?). Fragility will be important if it sets an upper limit on the size and thus the "age" of the aggregate and if aggregate breakup is a significant source of smaller particles in the water column. It is crucial to know if the physical process of aggregate breakup is a significant source of smaller particles in the water column (of comparable magnitude to chemical and biological degradation).

Marine snow aggregates may be deformed and possibly broken up by the action of local fluid motion. In the interior of the oceanic water column, marine snow particles are smaller than the turbulent microscale and will thus experience a viscous shearing regime. However, within bottom boundary layers, at pycnoclines in the presence of internal waves, and at the water surface, marine snow may be exposed to more complex turbulent fluid motions.

No generally applicable model exists for either the rate of deformation or the fracture strength of composite materials such as marine snow. Thus, aggregate behavior in the presence of fluid shear must be determined empirically by experiments on actual aggregates and the results correlated with other observable properties to the extent possible. These experiments

should provide a fluid environment with a controlled rate of shear and should enable observations of threshold shear for breakup and the rate and mode of breakup (surface erosion vs. ripping in half vs. shattering into many pieces).

3.1.3 Settling Velocity

The settling of aggregates promotes collisions with smaller particles and may determine the residence time of the aggregates in the water column. Settling velocity is determined by the aggregate size, shape, and density. Of these, the effective density is the most difficult to determine because of the complexity and fragility of the aggregates. Thus, it is likely that settling velocity will have to be determined directly by observation, and correlated with size and shape (including perhaps porosity). Settling velocity determinations are probably best done in situ using optical (unaided or otherwise) methods.

3.1.4 Permeability

Many aggregates are known to be structurally "open"; they contain interstitial water that can exchange with the surrounding fluid. The rate of this exchange is important to many aspects of particle dynamics. Flow at and near the particle "boundary" will vary with the extent to which streamlines can intersect this boundary. The extent to which the particle interior represents a chemical environment different from the outside world depends on the balance between chemical reaction rates and the rate of diffusion of dissolved reactants and products into and out of the particle. The rate of leakage of chemical attractants (and their stability in the outside environment) will determine their concentration field in the vicinity of aggregates and will thus strongly affect the rates of "volitional" encounters with living particles that use these chemical cues to guide their swimming pattern. For a permeable particle, the time history of internal concentrations of natural or artifical dissolved tracers will tend to follow

(with bond smoothing and time lag) the history of concentration in the surrounding fluid; the extent of smoothing and the length of the lag will covary inversely with the permeability of the particle. Laboratory measurements of the rate of gain or loss of dissolved tracers from particles sinking through a tracer gradient or "spike" thus provide one possible methodological approach for measurement of permeability.

3.1.5 Acoustic Estimation of Density

The density (mass per unit volume) of the marine snow is an important quantity as it dictates in part the settling rate of the particles and also gives an indication of its origin and composition. There are many techniques to measure the density of objects; however, they typically require removing the object from its natural environment. Because marine aggregates are fragile and porous, measurements of density outside the natural environment may not be representative of the true in situ value. An in situ non-invasive technique would therefore be desirable. In general, acoustic techniques are attractive both because they are non-destructive and because they can be applied in situ at many or all of the depths at which marine snow is found.

The acoustical scattering cross section depends on the size, shape, and specific density and compressibility of the scattering particle. It is possible under appropriate experimental conditions that the specific density of the scatterer can be isolated, hence allowing in situ measurement of density. Many or all of the aggregates of interest may have very small acoustic cross sections (they may be nearly "transparent" to sound). If this is the case, the result of the measurement would not be specific density, but rather an upper bound on density. Either way, the acoustically derived information is useful, especially if interpreted in conjunction with density measurements by other techniques.

3.2 Glue, Stickiness and Charge

Very little is known about the forces which cause marine aggregates to coalesce. The "stickiness" of a particle or the likelihood of aggregation is dependent on factors like electrostatic charge and the rate and strength of covalent bond formation. Charge is dependent upon the particular organic or inorganic functional groups present in the aggregate. For example, clay minerals are charged bodies whose natural repulsion can be reduced by organic coatings. We recommend laboratory and field studies of the relationship between coagulation efficiency (fraction of particle collisions which result in aggregation) and chemical composition of the colliding particles. Chemical composition of the dissolved organic matter in the surrounding fluid may also need to be considered.

3.3 Compositional Tracers of Age and Origin

The working group was very enthusiastic about the potential interpretive value of measurements describing the age and source of particles at different places in the water column. A number of investigators have used microscopy to examine the compositional makeup of organic aggregates; our present understanding of particle origin is based largely on these measurements. Chemical, biochemical, and isotopic tracers offer additional opportunities to study aggregates. So far, their use has been restricted to suspended and sediment trap particles. There is enough known at this time to strongly suggest their usefulness to studies on marine aggregates; however, this application will require rigorous evaluation of each approach. Studies of natural environments in which the aggregate population is transient (for example inlets from which the ambient population is removed by episodic flushing events) may be of particular value in developing and evaluating these tracer methods.

3.3.1 Microscopic Identification of Aggregate Components

There are a number of properties of marine aggregates that can be identified by means of microscopic techniques which may provide information as to the origin and age of the particle. Most of the existing classification of aggregates is based on this type of information. In many cases observation of bulk structures may give information as to its origin, i.e., intact larvacean houses, zooplankton feeding webs. In other cases, direct microscopic observation can define the nucleus of the particle, i.e., dinoflagellate cyst, diatom spore, fecal pellet. If the snow is degraded, chemical means of identification may be employed as well. Classification of organisms inhabiting (consuming) the particle is possible. Techniques such as fluorescence microscopy can easily distinguish non-pigmented from pigment containing organisms. Techniques such as Nomarski interference microscopy can give information about mucilage structure. Polarization microscopy can use birefringent characteristics to classify mineral matter. Vital cellular stains can distinguish living from non-living components. SEM and TEM may provide information as to the origin of broken or degraded attached particles (i.e., diatom frustule, coccolith) as well as indicate internal structure related to the "health" of intact particles. Epifluorescence microscopy is capable of enumerating and distinguishing bacteria from eukaryotes. Immunofluorescent properties can measure the activity of living components of the aggregate as well as provide a tag for origins o. individual subparticles.

Once the components are identified, diversity of the biotic community present on and within the particle might be used to indicate age. For example, newly formed aggregates may be inhabited only by a few bacteria. Their number and activity may help define the length of time the particle has been in the water column. As the particle becomes bacteria laden, it provides prime feeding sites for higher tropic level consumers such as heterotrophic

flagellates and ciliates. The types of organisms inhabiting the particle may give clues to the site of particle formation. For example, some species are indicators of shallow water or benthic environment. Their presence in the snow would indicate that the particle reached its present location by resuspension from the seabed and subsequent lateral transport rather than by vertical flux from pelagic surface waters.

3.3.2 Specific Organic Compounds

Organic compounds in particle aggregates reflect the age and source of those particles. By measuring the composition and quantities of certain individual compounds, we can estimate the age and source of an aggregate. Age can be determined by taking advantage of the basic kinetic properties of chemical reactions of biogenic organic compounds. Compounds have given stabilities on particles and are decomposed or transformed at rates which depend on the nature of the compound and on the environment in which it exists. The compounds decompose or are transformed according to the following simplified scheme:

$$R \xrightarrow{k} P$$

where R is the reactant,

P is the product, and

k is the assumed first-order rate constant

By measuring concentrations of R and P in a particle, and using an experimentally determined k, we can calculate the length of time R has been present on a particle. If we calculate ages for several classes of compounds produced during formation of the particles, we can estimate an average age for

the aggregate. Choosing compounds which react at different rates, e.g., minutes versus days, we can estimate ages for particles with different life spans.

As an example, the dating technique which has been used most frequently by organic geochemists exploits a chemical reaction, the racemization of amino acids. With time, the L-enantiomers racemize, eventually reaching equilibrium with the corresponding D-amino acids. The ratio of D/L amino acid and the racemization rate constant, k, can be used to calculate the time elapsed since all the amino acids were in the L-form. Theoretically, any organic compound which undergoes a decomposition or transformation reaction can be used in this manner. For dating particles, compounds which are chemically unstable on a time scale of hours to days may be most useful, e.g., carotenoids and other pigments. For example, diadinoxanthin, a carotenoid found in diatoms, dinoflagellates and prymnesiophytes, quickly undergoes a light-induced, reversible de-epoxidation reaction to form diatoxanthin. It also may be possible to determine k values for biological consumption of organic compounds on particles and use biological rate constants in a similar way.

In addition to the kinetic approach, organic biomarkers can be used to estimate particle history. For example, an aggregate that is composed of senescent diatoms would have significant concentrations of chlorophyllide _a_ (chlorophyll minus the phytol side chain) as a result of the chlorophyllase that is released when cells lyse. However, an aggregate composed of diatoms that have been grazed would be composed predominantly of phaeophorbide _a_ (chlorophyll minus phytol and Mg) due to the chemical environment in a zooplankton gut. This type of marker provides important information on the history of a particle to supplement the kinetic approach to aggregate dating.

Individual organic compounds reflect the source as well as the age of a particle. Certain compounds are found only in a taxonomically restricted set of organisms. This specificity can be used to determine the source of particles within an aggregate. For example, chlorophyll a can be used as a general index of phytoplankton biomass, while specific accessory pigments can be used as diagnostic tags for identifying the source of the algal material. Chlorophyll b, fucoxanthin, peridinin, phycoerythrin, and hexanoyloxyfucoxanthin are characteristic biomarkers of green algae, diatoms, dinoflagellates, cyanobacteria, and prymnesiophytes, respectively. Fucoxanthinol and fucoxanthin 6'-dehydrate are specifically produced as the result of heterotrophic and microbial metabolism, respectively. Steroidal alcohols such as dinosterol, diatomsterol, brassicasterol, etc. are specific source indicators. There are potentially hundreds of organic molecules that may be specific to particular taxonomic groups.

Molecular markers have been used to differentiate more broadly between terrestrial and marine organic matter. Such markers include sterols (terrestrial sterols are enriched in B-sitosterol), hydrocarbons (terrestrial hydrocarbons are enriched in odd number n-alkanes between C_{23} and C_{31}), lignins, fatty acids, selected polynuclear aromatic hydrocarbons, etc. These terrestrial/marine source markers could be used to determine whether the source of organic matter in an aggregate was from water column primary production or from material transported from a terrestrial source.

3.3.3 Isotopic and Inorganic Tracers of Source and Age

Isotopic and inorganic tracers provide powerful constraints for determining both the source and age of marine aggregates. These tracers can be used on either the bulk aggregates or on particular components of the aggregates and so provide information of very different kinds. Stable isotopic composition can yield information on environments of formation and

transformation pathways. Radioactive isotopes serve as time clocks for transport and reaction, yielding information unavailable from other techniques. Further information on the source and age of aggregates may be determined from other inorganic compositional information such as the clay mineral composition.

The fractionation between the stable isotopes of carbon, nitrogen, oxygen, hydrogen and sulfur is determined by the source of material in the aggregates and by the transformation pathways of this material. For example, oxygen isotopic measurements of material (in particular, foraminifera) reaching deep moored sediment traps have monitored seasonal events in the upper water column as reflected in sinking particulate matter reaching the traps. The depths and time of origin of material can be estimated from its isotopic composition. The offset between the times of origin and arrival in the sediment traps gives an unambiguous determination of settling rates.

Radioisotopes such as carbon-14, beryllium-7, and isotopes of the uranium- and thorium-decay series are natural chronometers of events because their decay occurs at a fixed rate for each isotope (generally expressed as a half-life for decay). The isotopes of thorium have proven particularly useful for studies of transformation and aging. Thorium has strong hydrolysis characteristics and thus rapidly absorbs to solids. The decay rates of the various thorium isotopes range over six orders of magnitude, from thorium-234 (half-life of 24 days) to thorium-230 (half-life of eighty thousand years). Studies of thorium-234, 228 and 230, each with identical chemical behavior but differing decay rates, have yielded important information on particle residence times and transformation rates in both the deep sea and in surface waters. Another promising measure of particle residence times in the water column involves the use of beryllium-7, produced in the stratosphere and with a short (53 day) half-life. It is delivered to the surface waters from the

atmosphere and its presence in particles in the deep sea is indicative of relatively rapid vertical transport from the surface layers.

Inorganic tags such as clay mineral assemblages have proven to be extremely useful in tracing both the source and movement of particulates in the ocean. Clay minerals may be particularly useful for distinguishing sediment resuspension and lateral transport from atmospheric input to the surface layers coupled with vertical transport.

The condition of the biogenic hard parts (opal, calcite and aragonite, and celestite) is indicative of the environments to which they have been exposed and the duration of exposure. For example, the extent of dissolution and fragmentation provides information on the age of these components and the physical and chemical processes to which they have been exposed.

Isotopic and inorganic tracers, in conjunction with the specific organic and microscopic approaches, can add valuable source and age information to studies of the distribution and dynamics of marine aggregates.

4. Supporting Oceanographic Measurements

Field measurements of aggregate distribution and dynamics will need to be supported by a suite of oceanographic measurements. Information about the local physical environment is needed to interpret aggregate movement and dispersal as well as the physical controlled subset of aggregate formation and disruption mechanisms. Chemical information is needed to interpret rates of dissolution and decomposition, and to describe ambient concentrations of selected isotopic and chemical tracers. Biological measurements are needed to estimate the importance of organisms producing or repackaging non-living organic matter, to establish local biotic tracers, and to establish correlations (or lack of correlation) with the amount and seasonality of biological productivity. The potential shopping list is very long; we have tried to highlight some of the most important variables.

4.1 Physical Measurements

These should at minimum include the following:

Vertical profiles of temperature and salinity allow calculation of density and viscosity profiles of prediction of settling velocities. It is possible, however, that in some environments the viscosity may be modified by the amount and composition of dissolved organic matter. The density field also largely controls the vertical distribution of velocity shear (discussed next).

Small scale shear (over scales of a few mm to cm, typically measured as the rate of kinetic energy dissipation) affects the encounter rates of particles (production of larger particles by accretion), and will also determine the importance of mechanical disruption as a loss mechanism for portions of the overall size spectrum (by conversion of large particles into smaller units).

Kinetic energy inputs at seabed and sea-surface interfaces control the rates of resuspension of bottom sediment and bubble injection. They will also (over greater time and space scales) control the amount and distribution of velocity shear within the water column, e.g., by determining the sharpness of internal density gradients.

Mean velocity profiles and sections are valuable for estimating the rate of lateral transport of slowly sinking particulates. This may not be needed for all studies; however, it will be extremely important where inputs are spatially localized, e.g., resuspension of sediment from continental margins by high energy boundary currents and subsequent transport into the deep sea.

Incident light and water-column attenuation properties determine the potential for photochemical transformation processes.

4.2 Biological and Chemical Environmental Variables

The formation and fate of marine micro-aggregates is closely related to the composition and activity of planktonic organisms (auto- and heterotrophs), and to non-living substances that serve as nuclei and agglutinizing agents. The latter include both particulate and dissolved substances. In order to develop an understanding of micro-aggregate dynamics, the biological and chemical characteristics of the water column must obviously be known. These characteristics can be broadly divided into three groups: 1) standing stocks; 2) activities; and 3) food web structure. Appropriate variables within these groups are listed below:

1. Standing stocks
   a. nutrients
   b. dissolved organic matter
   c. non-living particulate matter (other than aggregates)
   d. algal crop
   e. bacterial crop
   f. microheterotrophs
   g. zooplankton

2. Biological activity
   a. primary production, including DOC leakage
   b. heterotrophic bacterial production
   c. zooplankton grazing (micro- and macro-) and rate of fecal pellet production

3. Food Web Structure
   a. phytoplankton composition (algal groups; or species in those cases where aggregate-formers are obvious, i.e., *Phaeocystis* sp.)
   b. relative abundances of micro- and macro-zooplankton
   c. relative abundances of crustaceans and gelatinous zooplankton, and absolute abundance of known aggregate producers such as larvaceans and pteropods.

Aggregate formation is expected to be related strongly to biological/chemical conditions in the upper ocean (euphotic zone), but repackaging and transformations will continue throughout the water column. For these reasons, chemical and biological measurements must be made over relatively large space scales, especially in those cases where migrating organisms could influence formation or loss of aggregates. Some of the

variables listed above are of major importance, but are problematic from a methodological standpoint (especially for large scale survey sampling). Dissolved organic matter, for example, is difficult to characterize and quantify, due to its complex chemical nature. Many of the gelatinous zooplankton, although major mucus producers, are fragile and difficult to census by standard methods. New methodologies may be appropriate here.

CHARACTERISTICS AND DISTRIBUTIONS OF MARINE AGGREGATES

Mary Wilcox Silver
Institute of Marine Sciences
University of California, Santa Cruz, Ca 95064

> "When I think of the floor of the deep sea, the single, overwhelming fact that possesses my imagination is the accumulation of sediments. I see always the steady, unremitting, downward drift of materials from above, flake upon flake, layer upon layer - a drift that has continued for hundreds of millions of years, that will go on as long as there are seas and continents. . . . For the sediments are the materials of the most stupendous snowfall the earth has ever seen. . . " Rachael Carson, The Sea Around Us

INTRODUCTION

Early interest in non-living particulates was stirred by direct observations of large, amorphous flocs in coastal and deep waters. Most of the subsequent oceanographic research on particles, however, concerned itself with smaller, more numerically abundant and generally refractive particles. Only recently has attention returned to the visible, rarer flocs of detritus. The purpose of this brief review is to summarize discoveries regarding some of the biologically significant features and behavior of these large suspended flocs. The review will highlight discoveries about the particles that have been called marine snow, because these are hypothesized to be particularly important as centers of microbial activity in the water and to play central roles in geochemical cycles as they settle into the deep sea.

CHARACTERISTICS OF PARTICLES

Aggregates and Marine Snow

Historically, studies on naturally occurring particulates in seawater developed simultaneously in two distinctive schools. One is based on a tradition of *in situ* observations of particles, and was exemplified by the reports of a number of Japanese researchers. Early in the 1940s and 1950s these workers called attention to the large, fragile, readily visible flocs of material that occurred particularly in shallow coastal seas but also in deeper waters. Japanese researchers named these "marine snow" (Suzuki and Kato, 1953) after the "long snowfall" of sedimentary material described by Rachael Carson (1951). Particles were photographed underwater (Suzuki and Kato, 1953; Nishizawa et al., 1954), gently collected by hand and good descriptions of them published, including information on the associated organisms and detritus (Tsujita, 1952). Even sinking rates of submersible collected flocs were measured (Kajihara, 1971) and their origins and importance discussed as unique microenvironments in the pelagic zone (Suzuki and Kato, 1953; Nishizawa, 1966: see review in Trent, 1985).

The second tradition of studies on particulates, carried out primarily by North American scientists, studied particles obtained from water bottles. These researchers examined cleared filter preparations, which were dominated by the small, refractory, and numerically abundant size classes. Careful study of these preparations in the 1960s and 1970s led to descriptions of at least three particle classes: "organic aggregates", flakes,

and debris from organisms (Riley, 1963; Riley 1970; Gordon, 1970; Wiebe and Pomeroy, 1972). The term "organic aggregate" was chosen by Riley (1963) to describe a variable class of flocculant, often fragile-appearing conglomerates of smaller particles, materials whose origin was unknown. The aggregates commonly fell in the size range of 25-50 um (though they exhibited a large size spectrum), stained dominantly with carbohydrate reagents, were occasionally organism-rich, reached sizes up to a mm or more, and were common only in near surface waters. Some of these aggregates may have included remnants of the larger, fragile marine snow, likely broken apart during bottle collection and sample preparation. Flake-like particles were more abundant than aggregates, but were so transparent they were easily missed, unless stained. Flakes tended to be more uniform in size, small (rarely >50 um), thin and scale-like, stained mostly with protein stains, and their abundances changed little with depth. The third class of particles consisted of the fragments or remains of once living organisms, including animal and plant residues.

In the late 1970s and 1980s the two traditions of studying particulates were combined in a series of investigations on the large flocs known to divers and submersible users. Researchers made in situ observations on particle abundances in shallow water, hand-collected the fragile particles, and made quantitative measurements on their contents, extrapolating these observations to indicate the importance of the large particles to the total suspended pool (e.g. Trent et al., 1978; Silver et al., 1978). They retained the term "marine snow", using it to

describe the >0.5 mm particles, which were clearly aggregates of many different types of materials. These studies also were augmented by observations using other methods, including work on particles obtained from large-volume pumps and sediment traps, which collect large aggregates or disrupted fragments of them (Bishop et al., 1977; Honjo et al., 1982).

Abundance of marine snow

Most of the records of marine snow abundance have been obtained by divers using a now-standard approach (Trent et al., 1978): divers count the number of particles passing through a hand-held ring, as they swim a horizontal transect whose length is recorded by an attached current meter. With such counting methods, some variability in counts can be expected depending on the ability of the diver to see the particles (related to ambient light, diver's visual acuity, size and color of the aggregates, etc.). Furthermore, there will be some error in sizing the particles, and divers may differ in ability to correctly assess particles as >0.5 mm. Alternative methods of *in situ* counting involve the monitoring of fragile, larger particles by cameras (Carder et al. 1982; Honjo et al. 1984), with such methods allowing both sizing and counting of particles.

Measurements of marine snow are now available from a variety of near-surface locations, usually in neritic environments. Numbers of particles per liter vary from none to a maximum of 35, with common neritic values being 1-10/l (Table 1) within the normal SCUBA diver range of 0-30m. Even at one site, there is considerable variability in the numbers and sizes of marine snow

over time (e.g. Monterey Bay values, Table 1). Volumes of individual snow aggregates in surface waters have been shown to range between .001 ml and 1 ml with the particles occupying between .006 and .3% of the total water volume (Table 2). Larger mucus flocs are known to occur (Johannes, 1967; Alldredge et al., 1986), though they are probably uncommon. The measurements of marine snow abundances in surface waters, it should be remembered, are usually made at sites known to be good study areas for marine snow (e.g. Monterey Bay), and thus may not be representative of the range of neritic, and certainly not of oceanic, environments.

TABLE 1

Abundances of Flocculent Marine Snow

#S/liter	location	reference
Nearsurface (upper 30 m)		
1.9-2.8	Monterey Bay, Calif.	Trent et al. 1978
0-8.0	Santa Barbara, Calif.	Alldredge, 1979
0-3.7	Gulf of California	"
0.7-14	Monterey Bay, Calif.	Shanks and Trent 1980
1.0-7.0	N.E. Atlantic	"
6.6-12	Monterey Bay, Calif.	Knauer et al. 1982
35	"	Hebel, 1983
9.4-12	Pt. Sur, Calif.	"
1-79	Santa Barbara, Calif	Prezelin and Alldredge 1983
2.8-5.6	So. Calif. Bight	Beers et al. 1986
0.1-1.0	N.E. Atlantic	Alldredge et al. 1986
1.9-4.0	So. California	"
Deeper Waters		
.001-5.0	Sargasso Sea	Honjo and Asper 1982
0.2-7.5	California Current (off Monterey)	"
0.2-0.6	So. California (60 m depth)	Orzeck and Nielsen 1984
0.0005-.004	Subtropical NW Atlantic (30-650 m)	Alldredge and Youngbluth 1985
0.016-.038	Central Mexico Slope waters (80-900 m)	Alldredge and Silver unpub.
0 13-.005	Central Mexico, oceanic waters 0-400 m	"
0.014-.001	400-3000 m	"
0.5-2.5	Panama Basin (100-3000 m)	Asper, 1986
.0005-.01	NE Atlantic, warm core ring, 100-1000 m	Bishop et al. 1980

TABLE 2

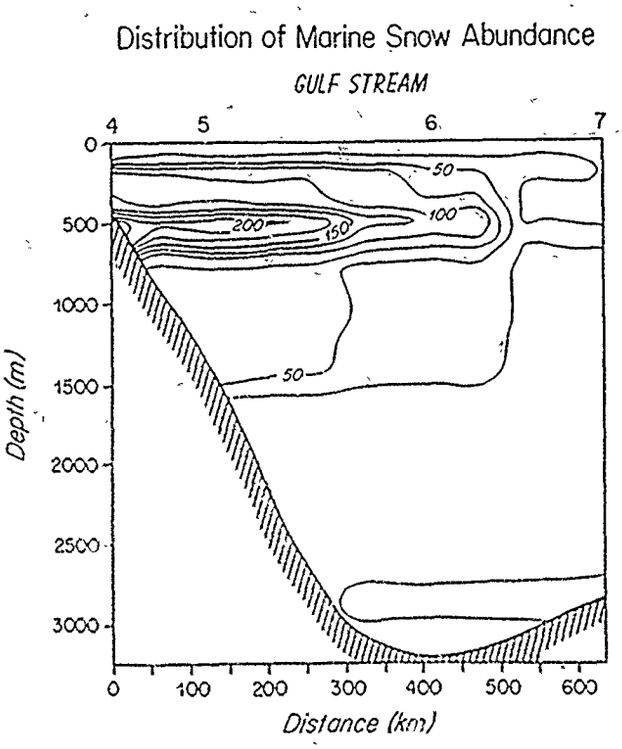
VOLUME OF FLOCCULENT MARINE SNOW FROM SURFACE WATERS

Month	Location	Volume ml/agg.	% of water column	Reference
June	Point Sur	0.025-0.08	<0.1	Hebel, 1983
June	Monterey Bay	0.15	<0.1	Hebel, 1983
July-Sept	Monterey Bay	0.003-2.24	0.01-0.67	Trent et al., 1978
April	Santa Barbara	0.034-1.0	0.1-0.27	Prezelin and Alldredge, 1983
June-Aug	Monterey Bay	0.01-0.29	0.006-0.33	Silver et al., 1978
Feb	So. Calif. Bight	0.08-0.2	0.02-0.04	Beers et al., 1986
March	"	0.01-0.05	0.002-0.009	Beers et al., 1986
Aug	"	0.092-0.2	0.001-0.1	Beers et al., 1986
Apr-June	Monterey Bay	0.0012-0.015	-	Davoll and Silver, 1986

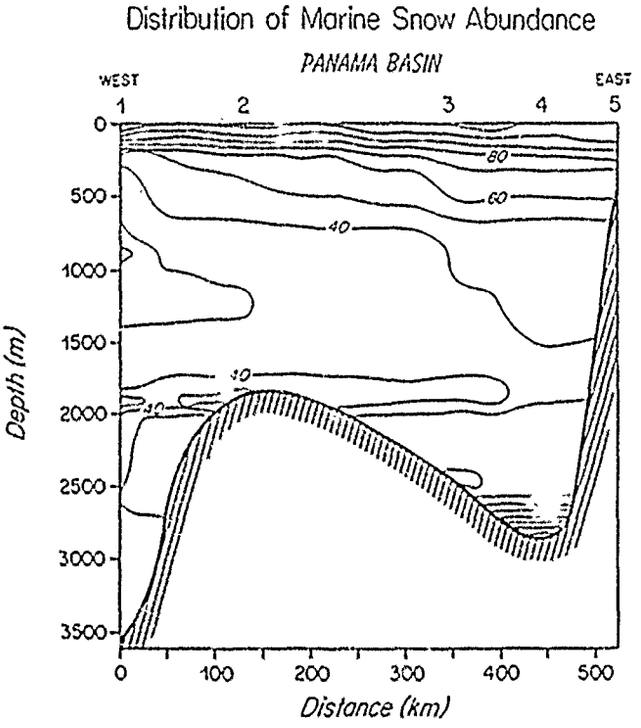
Marine snow is not only a prominent feature of near-surface waters, but has long been noted in deeper environments as well. Methods to quantitatively determine particle concentrations of the fragile aggregates in deep water have included a variety of approaches: techniques almost exactly analogous to the standard SCUBA approach, but with the observer inside a submersible (Silver and Alldredge, 1981); deep saturation divers in the lower euphotic and upper mesopelagic zone (Trent and Orzeck, 1984); in situ, large-volume pumps (Bishop et al., 1977); and remote cameras (Honjo et al., 1984). Observations on marine snow occurrence, using these various methods, are shown in Table 1. Marine snow abundances in the deep sea are considerably lower than in the surface waters, on the average. One important exception is the productive nearshore environment of Monterey Bay, in which the aggregate concentrations remained fairly high, like those of the overlying waters, to the sea floor (Honjo and Asper, 1982).

FIGURE 1. Vertical section showing marine snow volume concentrations (abundance in mm^{3-1}), from Asper (1986)

a. North west Atlantic



b. Panama Basin



In the most extensive deep-water study to date, Asper (1986) presented vertical oceanographic sections of particles >1 mm in the Panama Basin and the North Atlantic, using the Honjo et al. (1984) camera system. These data, presented mostly as total aggregate volumes (sum of particle volumes for all size classes - in mm^3) show midwater maxima likely due to shelf resuspension in the Atlantic (Fig 1a) and resuspension from the basin sides in the Panama case (Fig 1b). Repeated sampling at the same site showed horizontal patchiness of aggregates on scales of 100s of m, otherwise profiles of abundance appeared relatively stable over the time scales of sampling.

Organic content of marine snow

Various authors have measured the organic contribution of larger aggregates to total suspended material in near-surface water. Such measures indicate marine snow contributions in neritic waters can range from 0 to 63% of the total particulate organic carbon, with these showing C:N ratios like those expected

TABLE 3

CARBON:NITROGEN RATIOS OF MARINE SNOW FROM SURFACE WATERS

Month	Location	% of total POC on snow	C:N	References
June	Pt Sur	5	7.1:1	Hebel, 1983
June	Monterey Bay	9	6.2:1	Hebel, 1983
July-Aug	Gulf of California	0-63	11.3:1	Alldredge, 1979
Oct-March	Santa Barbara Channel	0-20	9.4:1	Alldredge, 1979
April	Santa Barbara Channel	07	2.8:1	Prezelin & Alldredge 1983
June-July	Monterey Bay	-	7 5:1	Shanks & Trent, 1980
Various	No. Atlantic	-	8.9:1	Caron et al , 1986

of microorganisms (i.e. about 3:1) to the more detrital-like ratios of 11:1 (see Table 3). On an individual particle basis, organic carbon and nitrogen can range from .1-4 ug C and .03-.5 ug N (Table 4).

TABLE 4

POC AND PON CONTENT OF MARINE SNOW FROM SURFACE WATERS

Month	Location	mean ug C/agg	mean ug N/agg	References
June	Pt Sur	3.21	0.48	Hebel, 1983
June	Monterey Bay	1.23	0.24	Hebel, 1983
July-Aug	Gulf of California	3.37	0.29	Alldredge, 1979
Oct March	Santa Barbara Channel	4.32	0.46	Alldredge, 1979
April	Santa Barbara Channel	0.1	0.03	Prezelin/Alldredge, 1983
June-July	Monterey Bay	1.36	0.33	Shanks/Trent, 1980
July	N.E. Atlantic	0.71	0.10	

Photosynthesis on marine snow

One of the most conspicuous features of near surface particles are their accompanying algal cells, noted by the earliest observers (Tsujita, 1952; Riley, 1963). Such photoautotrophs can be assessed by measuring the chlorophyll a content of snow, found to range between .002 and 3 ug Chl a per aggregate from collections by divers in neritic waters (Table 5). Individual particles have been found to show 3-750 fold enrichments of this photosynthetic pigment over equal volumes of water at the same site and depth (Table 5). The cumulative contribution of chlorophyll on snow particles to the total suspended population has been shown to range between 0.1 and 34% (Table 5). Likewise, these algal cells are known to be actively

fixing carbon, as shown by carbon-14 incubations (Alldredge and Cox, 1982; Knauer et al., 1982; Prezelin and Alldredge, 1983) and oxygen electrode data (Alldredge, pers. commun.,). Contributions of marine snow to total production range from negligible to 58%, depending on the numbers and sizes of the snow particles, and the physiological conditions of the associated algal populations (see discussion in Prezelin and Alldredge, 1983). In general, the role of marine snow as a center for photosynthetic activity reflects its importance as a center for chlorophyll, but relative production rates (i.e. production per unit chlorophyll a) can be lower on snow than in the surrounding water on occasion (Alldredge and Cox, 1982; Prezelin and Alldredge, 1983).

TABLE 5

CHL A CONTENT OF MARINE SNOW

Month	Location	µg Chl a/agg	% of total on snow	Enrichment factor	Reference
July - Aug	Monterey Bay	0.0023-0.59	0.1-7.2	4-750	Trent et al., 1978
March-April	Southern California Bight	0.04-3.41	0.6-34	67-442	Alledredge and Cox, 1982
April	Santa Barbara Channel	0.02-0.2	0.3-20	3-74	Prezelin and Alldredge, 1983
March	Southern California Bight	.0002-.009	0.1-1.0	27-540	Beers et al., 1986
August	Southern California Bight	.0004-.003	1.3-1.6	15-72	Beers et al., 1986

Organisms associated with marine snow

The presence of high concentrations of microorganisms on near surface marine snow likely reflects its origins, coagulation efficiency, and status as a habitat. As discussed elsewhere in this workshop (see article by Alldredge), snow can originate from

algal agglomerates, mucus food collection devices, fecal pellets and other processes that give rise to organism-rich particles at their time of formation or release. Likewise the sticky, surface-rich snow can capture additional particles, including organisms, as it moves through the water (McCave, 1984; McCave, this volume). These benthic-like midwater surfaces likely attract organisms seeking refuges, possibly ones that orient to the chemical gradients provided by the chemically enriched microenvironments (Goldman 1984; Mitchell et al. 1985).

Hard collections by SCUBA divers have allowed measurements of the colonizers on marine snow. Data from various sites for different groups of microorganisms associated with the aggregates are shown Table 6. These data show highly variable concentration factors (i.e. organismal concentration on snow/organismal concentration in an equal volume of surrounding water) for microorganisms on marine snow, with concentrations of organisms commonly ranging from 1 to 3 orders of magnitude higher in marine snow than in equal volumes of surrounding water. These observations indicate that marine snow is a microbial center in the water column and that it concentrates some classes of microorganisms more than others.

Most studies on the populations associated with marine snow have been made on aggregates collected in surface water. A few collections have been made using submersibles, allowing studies on the microorganisms associated with single aggregates in deep water, and these are shown in Table 6. Recently, however, extensive saturation, deep-diver experiments have obtained many

TABLE 6

Marine Snow Content - Intact Cells

I. Algae (photosynthetrophs)

Near Surface (0-35 m)

Organism	Environment	#/Aggregate	% total suspended population	Enrichment over surrounding water	Reference
Phytoplankton >2 µm	So. Calif.	1.0×10^4	–	3.2×2	Trent 1985
"	So. Calif. Bight	$6\text{-}1.3 \times 10^3$	0.2-2.5	$6.7 \times 10^2\text{-}3.0 \times 10^5$	Beers et al. 1986
phytoplankton <5 µm	Monterey Bay, CA	$8.0 \times 10^2\text{-}2.2 \times 10^4$	–	$1.0 \times 10^2\text{-}1.8 \times 10^2$	Davoll & Silver, 1986
phytoplankton >5 µm	Monterey Bay, CA	$6.3 \times 10^1\text{-}4.1 \times 10^3$	–	$7.5 \times 10^1\text{-}1.1 \times 10^3$	"
phytoplankton <2 µm	NW Atl-shelf&slope	–	–	$1.9 \times 10^1\text{-}4.3 \times 10^1$	Caron et al., 1986
	" warm core ring	–	–	1.9×10^1	"
	Gulf Stream	–	–	4.2×10^1	"
	Sargasso Sea	–	–	4.2×10^1	"
phytoplankton 2-20 µm	NW Atl-shelf&slope	–	–	$7\text{-}2.3 \times 10^1$	"
	NW Atl-warm core ring	–	–	2.4×10^1	"
	Gulf Stream	–	–	6.7×10^1	"
	Sargasso Sea	–	–	5.8×10^1	"
phytoplankton >20 µm	NW Atl-shelf&slope	–	–	$2.4 \times 10^2\text{-}2.7 \times 10^2$	Caron et al. 1986
	NW Atl-warm core ring	–	–	2.0×10^1	"
	Gulf Stream	–	–	1.3×10^3	"
	Sargasso Sea	–	–	7.0×10^2	"
monads & flagellates	So. C[illegible]	5.0×10^3	–	–	Trent 1985
	So Calif Bight	$5.5 \times 10^2\text{-}4.7 \times 10^3$	–	$5.5 \times 10^2\text{-}4.7 \times 10^3$	Beers et al. 1986
diatoms	Monterey Bay, CA	$0\text{-}5.2 \times 1^3$	0-16	$0\text{-}2.7 \times 10^1$	Silver et al. 1978
	So. Calif.	$2.4 \times 10^3\text{-}3.1 \times 10^4$	11-14	$5.9 \times 10^1\text{-}1.1 \times 10^2$	Prezelin & Alldridge 1983
diatoms-pennate	So. Calif.	2.4×10^3	–	–	Trent 1985
diatoms-centric	So. Calif.	2.3×10^3	–	–	Trent 1985
diatoms-pennate	So. Calif.	$2.7 \times 10^1\text{-}4.1 \times 10^3$	–	$2.8 \times 10^1\text{-}6.0 \times 10^3$	Beers et al. 1986
diatoms-centric	So. Calif.	$1.4 \times 10^1\text{-}7.9 \times 10^2$	–	$3.9 \times 10^1\text{-}4.2 \times 10^3$	Beers et al. 1986
dinoflagellates	Monterey Bay, CA	$0\text{-}1.2 \times 10^3$	0-100	$0 \text{ to } >2.1 \times 10^3$	Silver et al., 1978
	So. Calif.	1.3×10^2	25	1.2×10^3	Prezelin & Alldredge 1983
dinoflagellates-thecate	So. Calif.	3.7×10^1	–	–	Trent 1985
dinoflagellates-athecate	"	2.6×10^2	–	–	Trent 1985
dinoflagellates-thecate	"	$4\text{-}1.2 \times 10^2$	–	$4.5\text{-}8.0 \times 10^2$	Beers et al. 1986
dinoflagellates-athecate	"	$1.8 \times 10^1\text{-}2.0 \times 10^2$	–	$3.6\text{-}1.4 \times 10^2$	Beers et al., 1986
coccolithophores	So. Calif.	9.8×10^1	–	–	Trent 1985
	So. Calif.	$1.8 \times 10^1\text{-}8.7 \times 10^2$	–	$9.1\text{-}1 \times 10^3$	Beers et al. 1[illegible]
Deep Water					
cyanobacteria	(100-1650 m)			–	"
algae 1-2 µm	"	$2.3 \times 10^3\text{-}3.8 \times 10^5$	–	–	"
diatoms	"	$2 \times 10^3\text{-}1 \times 10^5$	–	$3.3 \times 10^2\text{-}7.2 \times 10^3$	
flagellates & monads	So. Calif.	$1.2 \times 10^3\text{-}4.0 \times 10^4$	–	–	Trent 1985
	(75-260 m)				
diatoms-pennate	"	7.9×10^2	–		"
diatoms-centric	"	$1.6 \times 10^2\text{-}4.6 \times 10^3$			"
dinoflagellates-thecate	"	$1.7 \times 10^1\text{-}2.8 \times 10^2$			"
dinoflagellates-athecate	"	$2.3 \times 10^2\text{-}6.8 \times 10^2$	–		"
coccolithophores	"	$1.1 \times 10^2\text{-}3.4 \times 10^3$			"

dinoflagellates-athecate — 1.1 x 10^2-3.4 x 10^3 — —

TABLE 6 (cont.)

Marine Snow Content = Intact Cells

II Bacteria

Near Surface (0-25 m)

Organism	Environment	#S/aggregate	% total suspended population	Enrichment over surrounding water	Reference
	Sargasso Sea	6.6 x 10^5-3.3 x 10^2	–	2-1 x 10^2 (or more)	Caron et al. 1982
	So. Calif.	1.2 x 10^7-2.5 x 10^7	7-78	6.7 x 10^1-1.2 x 10^3	Prezelin & Alldredge 1983
	So. Calif.	1.3 x 10^6-1.7 x 10^6	0.9-3.0	3.0 x 10^1-3.7 x 10^1	Alldredge et al. 1986
	NW Atl (oceanic)	1.8 x 10^6-2.8 x 10^6	0.2-4.4	2-5.5 x 10^1	"
	Monterey Bay, CA	4.2 x 10^5-6.7 x 10^6	–	8.3 x 10^1-3.0 x 10^2	Davoll & Silver 1986
Deep Water					
	So. Calif. (1000-1650 m)	1.0 x 10^5-1.7 x 10^5	–	—	Silver & Alldredge, 1981
	NW Atlantic (oceanic) (30-650 m)	3 x 10^6-[illegible] 10^7	<.05	up to 10^2	Alldredge & Youngbluth 1985

III. Protozoa

Near Surface (0-35 m)

Organism	Environment	#S/aggregate	% total suspended population	Enrichment over surrounding water	Reference
ciliates	Monterey Bay, CA	0-1.3 x 10^2	0-100	5.9 6 x 10^3	Silver et al. 1978
2-20 µm cells mostly flagellate	NW Atl-self&slope	–	–	or more 1.7 x 10^1-2.7 x 10^1	Caron et al. 1986
	NW Atl-warm core ring	–	–	3.1 x 10^1	"
	Gulf Stream	–	–	1.1 x 10^2	"
	Sargasso Sea	–	–	5.2 x 10^2	"
bactivorus flagellates	NW Atl-shelf&slope	–	–	4.8 x 10^2-5.1 x 10^2	"
	NW Atl-warm core ring	–	–	2.7 x 10^2	"
	Gulf Stream	–	–	7.6 x 10^4	"
bactivorous amoeba	No. Atlantic	–	–	4.1 x 10^2-6.2 x 10^3	"
ciliates	Monterey Bay, Ca	6-7.4 x 10^1	–	1.1 x 10^2-2.1 x 10^3	Davoll & Silver 1986
microflagellates	"	1.8 x 10^2-5.5 x 10^3	–	1.1 x 10^2-9.9 x 10^2	"

specimens of marine snow to nearly 300 m (Trent and Orzeck, 1984). Additional collections of snow specimens are also possible in deep water using sediment traps supplied with fixatives, devices that obtain particles that settle through the water. Microscopic observations of trap samples show mixtures of marine snow-like aggregates, fecal pellets, and a wide range of biogenic and lithogenic debris and large quantities of living organisms being transported into deep water (Fellows et al., 1981). Populations on aggregates in traps, like those on surface marine snow, contains high concentrations of intact bacteria (Karl and Knauer, 1984; Taylor et al., 1986) 6) algae (Silver et al., 1986), protozoa (Silver et al., 1984; Taylor et al., 1986) fecal pellets (Honjo, 1980; Urerre and Knauer, 1981) and a wide variety of other materials. Likewise, measurements of metabolic activity on trap collected particles suggest these are centers of microbial activity (Karl and Knauer, 1984; Karl et al., 1984). Comparisons of snow populations with those in surrounding waters are not yet possible, because sizes and contents of individual snow particles are not known from trap collections, which may either fragment large aggregates or coagulate finer materials during deployment. However, the sinking particles captured by traps appear to support highly enriched and active communities as compared with resident suspended communities through which they pass.

Successional Patterns on Marine Snow

Like other natural ecosystems, marine snow microenvironments experience predictable changes from their time of formation to

their final disruption or destruction. These changes occur in their associated populations and the chemical and physical characteristics of the habitat. Such changes are documented in a variety of detrital communities (see summary by Newell, 1984) and are now suggested for marine snow systems. For example, Pomeroy and Deibel (1980) and Pomeroy et al. (1984) describe the microbial succession on fecal aggregates, showing a rapid burst of bacterial growth upon release of the pellets, followed by increases in populations of protozoans that graze the growing bacteria, later decline of the bacterial populations after a few days, and final communities of sparse microorganisms on fragmenting remnants of the fecal material. Davoll and Silver (1986) describe the sequence of colonization on larvacean houses, a common near-surface form of marine snow. They note 3 phases: an innoculation phase when the larvacean pumps water and microorganisms through the house filter system; a second stage after house abandonment, when resident populations multiply and mobile immigrants enter, thereby changing the relative abundances of different trophic groups; and a final phase on the fragmenting house, during which trophic interactions in the house and exhaustion of the house matrix bring about a typical succession.

Successional changes in populations on marine snow and consequent alterations in the chemistry of the colonized aggregates can be expected both in particles that remain in surface waters and in those that settle to depth. Changes in the chemistry of settling materials are the subject of considerable interest and presently are being studied using sediment traps (Fowler and Knauer, 1986). Unfortunately the organisms and the

biological processes causing many of the alterations are still relatively poorly known. However, evidence clearly indicates that microbial destruction and substrate decomposition occurs as detritus settles through the water (Iturriaga, 1979; Gardner et al., 1983; Lorenzen et al., 1983; Ducklow et al., 1985; see also discussion below).

The nutrient status of marine snow

The abundance of microorganisms on marine snow would suggest that concentrations of metabolically active substances, both those produced and those consumed, would be altered in aggregates. A major difficulty in measuring these concentrations, however, is the practical one of sampling just the particle and its associated water volume: collections always simultaneously remove an unknown quantity of the surrounding water. A correction for this "contamination" from the surrounding water can be applied by measuring the bulk concentration of the desired property in a water sample nearby, and then subtracting the quantity of the test substance expected to occur in the sample volume in which the aggregate was collected. (Aggregates usually are ul in vol [see above] and commonly are collected in samples of ml size, thus occupying a small proportion of the total sample volume.) Especially for substances whose concentrations are elevated in marine snow, such measurements provide a reasonable measure of the marine snow contribution. However, estimates of concentration factors inside marine snow are more subject to error, since the true volume of water associated with the individually variable

aggregates usually is known only approximately. Thus measurements of nutrient levels associated with particles are better known than are the in situ concentrations, which are nevertheless the more important parameter for organisms inhabiting the aggregate.

Measurements of nutrient levels found in marine snow have been made by Shanks and Trent (1979). They found ammonia to be the most concentrated of the measured dissolved nutrients. Values as high as .5 mM were observed (Shanks and Trent, 1979), and these well may be underestimates because of dilution; such high values may even approach inhibitory levels for some phytoplankters, which can occur at 1 mM (Syrett, 1962). Prezelin and Alldredge (1983), who found snow particles to contain all the measurable ammonia in seawater at one of their study sites, suggest that chemoautotrophs, possibly nitrifiers, utilize these nutrients in the aggregate microenvironment. They provide evidence for substantive dark fixation of carbon that would be expected of nitrification in the ammonia-enriched aggregates. The same process is thought to occur in deep waters for the organically enriched, sinking particulates collected by traps (Karl et al., 1984). Very recently Alldredge (pers. commun.) found that persistent oxygen and pH gradients can occur out to 1 mm around marine snow particles 1-4 mm in diameter. These microzones apparently are maintained against diffusion and advection, suggesting marine snow represents a semi-isolated and chemically unique habitat in midwater.

The true nutrient concentrations associated with marine snow

and other aggregates are a subject of considerable importance. McCarthy and Goldman (1979) have stressed the possibility that nutrient enriched microenvironments occur in pelagic near surface habits, systems that otherwise usually support vanishing small concentrations of biolimiting nutrients. Predictions of nutrient concentrations rely on appropriate models of the diffusive regime of the aggregate. Jackson (1980) suggested that nutrient pulses introduced by single releases from zooplankters would quickly diffuse to background levels and Mitchell et al. (1985) calculated um zones of enrichment around phytoplankton cells excreting dissolved materials. However, as Goldman (1984) and Paerl (1984) argue, the internal regime of an aggregate, especially the large marine snow particles, may be considerably different from the environment surrounding a small, solid particle and molecular diffusion may be constrained within the aggregate microenvironment.

Marine snow aggregates, as we presently understand them, are loosely organized, physically semi-enclosed structures consisting of clusters of individual particles. The physical processes that give rise to the clusters and the importance of biological aggregating processes have been described by McCave (1984). Such aggregates may physically correspond to fractals, including soot and snowflakes - structures that are presently of considerable interest to chemists and physicists (Witten and Cates, 1986). Such fractals or aggregates can develop as random aggregates of individual particles or clusters of particles, have loose and semi-open structures, are individually unpredictable in their shapes, but can be described surprisingly effectively in their

average properties. Such particles act as traps for dissolved molecules that adsorb on their surfaces: with their extensive though open structures, the Brownian motion paths of diffusing substances are so long that molecules rarely escape to the outside of the lattice before contacting an internal surface (Witten and Cates, 1986). Such trapping characteristics would apply to both substances (e.g. the ammonium ion) that could bond with the many charged organic molecules present in the matrix (see Goldman's 1984 discussion) or to the dissolved gases that could be utilized and removed by organisms in the aggregate. Such considerations would also suggest that molecules diffusing into the aggregate would likely be trapped well before then reached the aggregate's core, producing gradients and greatly slowing diffusive process between the inside and outside of the aggregate.

Sinking Rates of Marine Snow

Major interest in marine snow has focused on the role these particles may play in carrying adsorbed and associated materials into the deep sea. Considerable theoretical (McCave, 1975; McCave 1984) and empirical evidence shows that major flux of materials often occur via marine snow or "fecal matter", as it is sometimes called (Bishop et al., 1977, 1978 and 1980). However, ability to predict the behavior of marine snow is still limited because its sinking characteristics are poorly known (particles are not within the Stoke's regime) and their shapes and physical characteristics are still not well defined. Efforts have been made to measure the settling rates of naturally

occurring snow particles, and they are described below. However, such measurements are subject to many errors: the fragile particles may be altered (likely collapsed, to some extent) when collected; the container sizes may have been too limited or physical environment inside the experimental chamber altered so that accelerations in them not typical of those of unconfined particles; some "true" results discarded such as the occurrences of particles that rise rather than sink (Riley 1970, Shanks and Trent, 1980) and so on.

Numerous measurements of the sinking rates of marine snow have been made and are shown in Table 7. These range from 1-368 m/day and have been obtained for a variety of types of aggregates, using a number of different methods. Most recently,

TABLE 7

MARINE SNOW--SINKING RATES

Type Material	Method of Measurement	Sinking Rate	Site	Reference
Reaggregated field collected marine snow from submersible	laboratory settling chamber	17-260 m/day	Japan nerine	Kajihara 1971
Field collected marine snow (3mm, spherical)	calculated	91 m/day	California, nerine	Alldredge 1979
Field collected larvacean houses	laboratory settling chamber	57-64 m/day	California nerine	Silver and Alldredge 1981
Field collected larvacean houses	laboratory settling chamber	103-368 m/day	neritic, Hawaii	Taguchi, 1982
aggregates of phytoplankton detritus from sea floor (2600 m)	calculated from time lapse *in situ* photography	100-150 m/day	north east Atlantic	Billet et al, 1983
larvacean houses from lab cultured larvaceans	laboratory settling chamber	26-157 m/day	Monaco	Gorsky et al, 1983
aggregates of phytoplankton detritus from sea floor	calculated from time lapse *in situ* photography	100-150 m/day	north east Atlantic	Lampitt, 1985
sediment trap samples from deep water (to 3560 m)	indirect calculation using *in situ* flux (trap) data and particle concentration data (*in situ* camera)	1 m/day and 36 m/day	Panama Basin	Asper, 1986
Sediment trap samples from deep water (to 3500 m)	calculated time lag from trap collections at different depths	175 m/day	North Pacific (Sta Papa)	Asper, 1986

Asper (1986) estimated snow sinking rates from in situ measurements of both flux and snow concentrations, (sinking rates are the quotient of flux and concentration), with time-series flux measurements made photographically of marine snow accumulating in a sediment trap. His results suggest that there are several kinds of snow, with some settling more rapidly than others. He suggests there are fresh, rapidly sinking particles that descend from the surface, accreting the slower particles at depth, and older, more refractory and lighter aggregates derived from resuspension at continental margins and advected at middepths to more oceanic environments. In his Panama Basin observations, the former would be smaller aggregat s (1-2.5 mm) that sink more rapidly (36m/day) than the larger (4-5 mm) particles that sink slowly (1m/day). Asper's suggestion of slow settling for the marine snow in the Panama Basin is at variance with the prediction of Lal (1977) that only very small particles (ones <5um) are transported significant differences from nearshore environments to oceanic regions.

Considerable field evidence exists to show that marine snow, or large particulates, are sinking rapidly in the sea. Evidence comes from accounts describing the rapid sedimentation of phytoplankton blooms in some near-shore environments (e.g. van Bodungen et al., 1981; Smetacek, 1985; Skjoldal and Wasserman, 1986). Many of these blooms appear to settle when the populations become senescent, and researchers have suggested that mucus production by the cells aids in their aggregation and rapid descent (reviewed in Smetacek, 1985). Fresh aggregates of surface material have also been found in sediments in deep ocean basins,

as evidenced from *in situ* photographs showing the arrival of large, phytoplankton rich aggregates at the sediment-water interface (Billet et al., 1983; Lampitt 1985) and from collections with deep-water sediment traps (Honjo, 1982). Further evidence that near-surface material settles rapidly into deep water deep-water is provided by the strongly seasonal inputs found in bathypelagic environments, inputs that reflect the production and populations of overlying waters (Deuser et al., 1981; Honjo, 1982).

DISCUSSION AND CONCLUSIONS

This brief review on larger aggregates has emphasized their biological enrichment and the consequences of these enrichments. Primary producers are usually greatly concentrated here, as evidenced by chlorophyll analyses, cell counts, and primary production measurements. These primary producers can cause large diel oscillations in photosynthesis-related phenomena: oxygen concentrations (possibly even bubble formation), exudations of dissolved organics from algae during photosynthesis, pH changes related to dissolved carbon dioxide uptake, and so on. The presence of such photosynthetic centers could be detected *in situ* by local peaks in chlorophyll absorption and fluorescence, and by bioluminescence of some of the associated microorganisms (Orzeck and Nielsen, 1984).

Not only photosynthetic related processes and metabolites are enhanced on the macroaggregates, but also those related to the catabolic activities of the associated food webs. As shown in the review, bacteria are often concentrated here, as well as

protozoans of various trophic positions. These consumers likely cause the elevated concentrations of ammonia as by-products of ingestion and excretion and they also utilize oxygen and produce carbon dioxide, likely producing redox gradients in larger aggregates, especially at night or at aphotic depths. These conditions could affect the redox chemistry of many substances (Paerl, 1984) and may account for observations of diagenesis (Lee and Cronin, 1982) and dramatic changes in the composition of organic matter in particles sinking through deep water (Wakeham et al., 1980)

One of the themes reoccurring in the marine snow literature is the variability of naturally occurring marine snow particles. The literature on microbial succession indicates that enriched particles change very rapidly - on time scales of days - and such changes are beginning to be documented for marine snow. Associated events would include the leaching and rapid utilization by microbes of labile materials, the subsequent development of microbial populations which initially may help to stabilize the substrate, the consequent grazing and reduction of the bacterial populations by invasion and growth of mobile grazers, and the final substrate collapse or decline of populations following the loss of readily usable detritus within the habitat (Newell, 1984). Such "older" aggregates are indicated to occur in surface waters (Prezelin and Alldredge, 1983; Davoll and Silver, 1986) and now evidence (Asper 1986) suggests these may also exist in deep water. The older aggregates should be chemically more refractory, less populated,

and could make the properties of aggregates difficult to predict unless their sources or ages were known. Thus the marine snow systems should share the features expected from ecological studies of other communities, namely that variability and change are troublesome but entirely expected attributes of such complex natural detrital microcosms.

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REFERENCES

Alldredge, A. L. 1979. The chemical composition of macroscopic aggregates in two neretic seas. Limnol. Oceanogr. 24:855-866.

Alldredge, A. L., and M. J. Youngbluth. 1985. The significance of macroscopic aggregates (marine snow) as sites for heterotrophic bacterial production in the mesopelagic zone of the subtropical Atlantic. Deep-Sea Res. 32:1445-1456.

Alldredge, A. L., and J. L. Cox. 1982. Primary productivity and chemical composition of marine snow in surface waters of the Southern California Bight. J. Mar. Res. 40:517-527.

Alldredge, A. L., J. J. Cole, and D. A.Caron. 1986. Production of heterotrophic bacteria inhabiting macroscopic organic aggregates (marine snow) from surface waters. Limnol. Oceanogr. 31:68-78.

Asper, V. L. 1986. Accelerated settling of marine particulate matter by "marine snow" aggregates. Ph.D. Thesis, MIT/WHOI, WHOI-96-12., 189 pp.

Beers, J. R., J. D. Trent, F. M. H. Reid, and A. L. Shanks. 1986. Macroaggregates and their phytoplanktonic components in the Southern California Bight. J. Plank. Res. 8:475-487.

Billet, D. S. M., R. S. Lampitt, A. L. Rice and R. F. C. Mantoura. 1983. Seasonal sedimentation of phytoplankton to the deep-sea benthos. Nature 302:520-522.

Bishop, J. K. B., R. W. Collier, D. R. Ketten, and J. M. Edmond. 1980. The chemistry, biology and vertical flux of particulate matter from the upper 400 m of the Panama Basin. Deep-Sea Res. 27:615-640.

Bishop, J. K. B., J. M. Edmond, D. R. Ketten, M. P. Bacon and W. B. Silker. 1977. The chemistry, biology and vertical flux of particulate matter from the upper 400 m of the equatorial Atlantic Ocean. Deep-Sea Res. 24:511-548.

Bishop, J. K. B., D. R. Ketten and J. M. Edmond. 1978. The chemistry, biology and vertical flux of particulate matter from the upper 400 m of the Cape Basin in the Southeast Atlantic Ocean. Deep-Sea Res. 25:1121-1161.

Bishop, J. K. B., M. Conte, P. H. Wiebe, M. R. Roman, and C. Langdon. 1986. Particulate matter production and consumption in deep mixed layers: observations in a warm-core ring. Deep-Sea Res., in press.

Carder, K. L., R. G. Steward, and P. R. Betzer. 1982. In situholographic measurements of the sizes and settling rates of oceanic particulates. J. Geophys. Res. 87:5681-5685.

Carson, R. 1951. The sea around us. Oxford Univ. Press, New York 230 p.

Caron, D. A., P. G. Davis, L. P. Madin, and J. McN. Sieburth. 1986. Enrichment of microbial populations in macroaggregates (marine snow) from surface waters of the North Atlantic. J. Mar. Res (in press).

Caron, D. A., P. G. Davis, L. P. Madin and J. McN. Sieburth. 1982. Heterotrophic bacteria and bacterivorous protozoa in oceanic macroaggregates. Science [illegible]:795-797.

Davoll, P. J., and M. W. Silver. 1986. Marine snow aggregates: life history sequence and microbial community of abandoned larvacean houses from Monterey Bay, California. Mar. Ecol. Prog. Ser. (in press).

Deuser, W. G., E. H. Ross., and R. F. Anderson. 1981. Seasonality in the supply of sediment to the deep Sargasso Sea and implications for the rapid transport of matter to the deep ocean. Deep-Sea Res. 28:495-505.

Ducklow, H. W., S. M. Hill, and W. D. Gardner. 1985. Bacterial growth and the decomposition of particulate organic carbon collected in sediment traps. Cont. Shelf Sci. 4:445-464.

Fellows, D. A., D. M. Karl, and G. A. Knauer. 1981. Large particle fluxes and the vertical transport of living carbon in the upper 1500 m of the northeast Pacific Ocean. Deep-Sea Res. 28A:921-936.

Fowler, S. W., and G. A. Knauer. 1986. Role of large particles in the transport of elements and organic compounds through the oceanic water column. Prog. Oceanogr. 16:147-194.

Gardner, W. D., K. R. Hinga, and J. Marra. 1983. Observations on the degradation of biogenic material in the deep ocean with implications on the accuracy of sediment trap fluxes. J. Mar. Res. 41:195-214.

Goldman, J. C. 1984. Conceptual role for microaggregates in pelagic waters. Bull. Mar. Sci. 35:462-476.

Gordon, D. C. 1970. A microscopic study of organic particles in the North Atlantic Ocean. Deep-Sea Res. 17:175-185.

Gorsky, G., N. S. Fisher, and S. W. Fowler. 1984. Biogenic debris from the pelagic tunicate, Oikopleura dioica, and its role in the vertical transport of a transuranium element. Est. Coast. Shelf Sci. 18:13-23.

Hebel, D.. V. W. 1983. Concentration and flux of trace metals, carbon-nitrogen, and particulate matter in marine snow. Master's Thesis, San Francisco State Univ., pp. 69.

Honjo, S. 1980. Material fluxes and modes of sedimentation in the mesopelagic and bathypelagic zones. J. Mar. Res. 38:53-97.

Honjo, S. 1982. Seasonality and interaction of biogenic and lithogenic particulate flux at the Panama Basin. Science 218:883-884

Honjo, S., and V. L. Asper. 1982. Deep water marine snow concentrations in two oceans. EOS, Trans. Amer. Geophys. Union 63:1016 (Abst.)

Honjo, S., K. W. Doherty, Y. C. Agrawal and V. Asper. 1984. Direct optical assessment of large amorphous aggregates (marine snow) in the deep ocean. Deep-Sea Res. 31:67-76.

Honjo, S., S. J. Manganini, and J. J. Cole. 1982. Sedimentation of biogenic matter in the deep ocean. Deep-Sea Res. 29:609-625.

Iturriaga, R. 1979. Bacterial activity related to sedimenting particulate matter. Mar. Biol. 55:157-169.

Jackson, G. A. 1980. Phytoplankton growth and zooplankton grazing in oligotrophic oceans. Nature 284:439-441.

Johannes, R. E. 1967. Ecology of organic aggregates in the vicinity of a coral reef. Limnol. Oceanogr., 12:189-195.

Kajihara, M. 1971. Settling velocity and porosity of large suspended particles. J. Oceanogr. Soc. Japan 22:158-161.

Karl, D. M., and G. A. Knauer. 1984. Vertical distribution, transport, and exchange of carbon in the northeast Pacific Ocean: evidence for multiple zones of biological activity. Deep-Sea Res. 31:221-243.

Karl, D. M., G. A. Knauer, J. H. Martin, and B. B. Ward. 1984. Bacterial chemolithotrophy in association with sinking particles. Nature 309:54-56.

Knauer, G. A., D. Hebel, and F. Cipriano. 1982. Marine snow: major site of primary production in coastal waters. Nature 300:630-631.

Lal, D. 1977. The oceanic microcosm of particles. Science 198:997-1009.

Lampitt, R. S. 1985. Evidence for the seasonal deposition of detritus to the deep-sea floor and its subsequent resuspension. Deep-Sea Res. 28:19-37.

Lee, C., and C. Cronin. 1982. The vertical flux of particulate organic nitrogen in the sea: decomposition of amino acids in the Peru upwelling area and the equatorial Atlantic. J. Mar. Res. 40:227-251.

Lorenzen, C. J., N. A. Welschmeyer, and A. E. Copping. 1983. Particulate organic carbon flux in the subarctic Pacific. Deep-Sea Res. 30:639-643.

McCarthy, J. J., and J. C. Goldman. Nitrogenous nutrition of marine phytoplankton in nutrient depleted waters. Science 203:670-672.

McCave, I. N. 1975. Vertical flux of particl s in the ocean. Deep-Sea Res. 22:491-502.

McCave, I. N. Size spectra and aggregation of suspended particles in the deep ocean. Deep-Sea Res., 31:329-352.

Mitchell, J. G., A. Okubo, and J. A. Fuhrman. 1985. Microzones surrounding phytoplankton form the basis for a stratified marine microbial ecosystem. Nature. 316:58-59.

Newell, R. C. 1984. The biological role of detritus in the marine environment. In: Flows of energy and materials in marine ecosystems, theory and practice, M. J. R. Fasham (ed), Plenum Press, New York, 317-343.

Nishizawa, S. 1966. Suspended material in the sea: from detritus to symbiotic microcosmos. Bull. Plank. Soc. Japan 13:1-33.

Nishizawa, S., M. Fukuda, and N. Inoue. 1954. Photographic study of suspended matter and plankton in the sea. Bull. Fac. Fish. Hokkaido Univ. 5:36-40.

Orzech, J. K., and K. H. Nealson. 1984. Bioluminescence of marine snow: its effect on the optical properties of the sea. In: Ocean optics VII, M. A. Blizard, Ed, Proc. of the SPIE, Vol. 489, SPIE, Bellingham, pp. 100-106.

Paerl, H. W. 1984. Alteration of microbial metabolic activities in association with detritus. Bull. Mar. Sci. 35:393-408.

Pomeroy, L. R., and D. Deibel. 1980. Aggregation of organic matter by pelagic tunicates. Limnol. Oceanogr. 25:643-652.

Pomeroy, L. R., R. B. Hanson, P. A. McGillivary, B. F. Sherr, D. Kirchman and D. Deibel. 1984. Microbiology and chemistry of fecal products of pelgic tunicates: Rates and fates. Bull. Mar. Sci. 35:426-439.

Prezelin, B. B. and A. L. Alldredge. 1983. Primary production of marine snow during and after an upwelling event. Limnol. Oceanogr. 28:1156-167.

Riley, G. A. 1963. Organic aggregates in seawater and the Dynamics of their formation and utilization. Limnol. Oceanogr. 8:372-381,

Riley, G. A. 1970. Particulate matter in seawater. Adv. Mar. Biol. 8:1-118.

Shanks, A. L., and J. D. Trent. 1979. Marine snow: microscale nutrient patches. Limnol. Oceanogr. 24:850-854.

Silver, M. W., and A. L. Alldredge. 1981. Bathypelagic marine snow: deep-sea algal and detrital community. J. Mar. Res. 39:501-530.

Silver, M. W., M. M. Gowing, and P. J. Davoll. 1986. The association of photosynthetic picoplankton and ultraplankton with pelagic detritus through the water column (0-2000 m). Canad. Bull. Fish. Aquat. Sci., 24: in press.

Silver, M. W., M. M. Gowing, D. C. Brownlee, and J. O. Corliss. 1984. Ciliated protozoa associated with oceanic sinking detritus. Nature 309:246-248.

Silver, M. W., A. L. Shanks, and J. D. Trent. 1978. Marine snow: microplankton habitat and source of small-scale patchiness in pelagic populations. Science 201: 371-373.

Skjoldal, H, R., and P. Wassmann. 1986. Sedimentation of particulate organic matter and silicium during spring and summer in Lindaspollene, Western Norway. Mar. Ecol. Prog. Ser. 30:49-63.

Smetacek, V. S. 1985. Role of sinking in diatom life-history cycles: ecological, evolutionary and geological significance. Mar. Biol. 84:239-251

Suzuki, N., and K. Kato. 1953. Studies on suspended materials. Marine snow in the sea. I. Sources of marine snow. Bull. Fac. Fish. Hokkaido Unov. 4:132-135.

Syrett, P. J. 1962. Nitrogen assimilation. In: R. A. Lewin (ed), Physiology and biochemistry of algae, Academic Press, New York, p 171-188. 1962.

Taguchi, S. 1982. Seasonal study of fecal pellets and discarded houses of appendicularia in a subtropical inlet, Kaneoha Bay, Hawaii. Est. Coast. Shelf Sci. 14:545-555.

Taylor G. T., D. M. Karl, and M. L. Pace. Impact of bacteria and zooflagellates on the composition of sinking particles: an in situ experiment. Mar. Ecol. Prog. Ser. 29:141-155.

Trent, J. D. 1985. A study of macroaggregates in the Marine Environment. Ph.D. thesis, Scripps Institution of Oceanography, Univ. Calif., San Diego,, 254 pp.

Trent, J. D., A. L. Shanks, and M. W. Silver. 1978. In situ and laboratory measurements on macroscopic aggregates in Monterey Bay, California. Limnol. Oceanogr. 23:626-635.

Trent, J. D., and J. K. Orzeck. 1984. The use of a U. S. Navy Deep-Diving System for marine biological research,. In: N. C. Flemming (ed), Divers, submersibles and marine science. Mem. Univ. Newfoundland, Occas. Papers Biol. 9:35-43.

Tsujita, T. 1952. A preliminary study on naturally occuring suspended organic matter in water adjacent to Japan. J. Oceanogr. Soc. Japan 8:3-4.

Urerre, M. A., and G. A. Knauer. 1981. Zooplankton fecal pellet fluxes and vertical transport of particulate organic material in the pelagic environment. J. Plank. Res. 3:369-387.

Van Bodungen B. v., K. v. Brockel, V. Smetacek and B. Zeitzschel. 1981. Growth and sedimentation of the phytoplankton spring bloom in the Bornholm Sea (Baltic Sea). Kieler Meeresforsch., Sonderh. 5:49-60.

Wakeham, S. G., J. W. Farrington, R. B. Gagosian, C. Lee, H. DeBarr, G.E. Nigrelli, B. W. Tripp, S. O. Smith and N. M. Frew. 1980. Organic matter fluxes from sediment traps in the equatorial Atlantic Ocean. Nature 286:798-800.

Wiebe, W. J., and L. R. Pomeroy. 1972. Microorganisms and their association with aggregates and detritus in the sea: a microscopic study. Mem. Ist. Ital. Idrobiol., 29 Suppl.:325-352.

Witten, T. A., and M. E. Cates. 1986. Tenuous structures from disorderly growth processes. Science 232:1607-1611.

PARTICLE SIZE SPECTRA AND AGGREGATION IN, AND REMOVAL FROM, THE OCEANS

I.N. McCave

Department of Earth Sciences, University of Cambridge, U.K.

INTRODUCTION

The removal of particles from surface and mid-water depths in the ocean normally requires their aggregation into larger units having a settling speed greatly in excess of the original particles. The argument has been presented and corroborated by several authors including Rex and Goldberg (1958), Schrader (1971), McCave (1975), Honjo (1976), and in many papers based on sediment-trap data. The size distribution of suspended particles is a function of several variables including source and nature of the particles, physical or biological processes of aggregation and 'age' of the suspension.

There are few measurements of particle size spectra from the ocean. Particle number data can, in nearly all cases, be fitted by a power-law distribution over some part of the measured range. Expressed as cumulative number N as a function of particle diameter d this is $N = kd^{-\beta}$. A value of $\beta = 3$ signifies equal particle volumes in logarithmically increasing size grades. This was found by Brun Cottan (1971), Sheldon et al. (1972), McCave (1975), Lerman et al. (1977), and Pak et al. (1980) in regions well away from the bed or, if close to the bed (Lerman et al.), regions of very low concentration. In more concentrated nepheloid layers near the bed the sizes show a volume peak around 4 to 8μm and the number distribution cannot be fitted by a straight line (McCave, 1983; Richardson and Gardner, 1985). Lambert et al. (1981) also maintained that the distributions of individual components (e.g.,

aggregates, goethite, aluminosilicate) they observed are not of power-law type but are log-normal by number. They found a distinct fall-off at the finest end of the distribution whereas Harris (1977) counted the finest particles down to 0.1μm and showed a power-law distribution with ß = 1.62 in the region d<1μm. Wellershaus et al. (1973) also found a decrease in numbers of fine particles but said that it was an artifact of the counting method. This is a well known artifact shown by comparisons of optical counting with other methods of size analysis (ASTM, 1983; McCave, 1979). The sum total of the components shown by Lambert et al. (1981) however, seems to be fitted by a straight line with ß ~ 3 over a good part of the measured range. The only results from the Pacific (Baker et al., 1979) are fitted by a somewhat higher value of ß = .29 for 3<d<8μm from mid-water samples.

The fine end (<1μm) of the spectrum is a particular problem. In my 1984 paper I assumed that, in contrast with the atmosphere, there was no source of fine particles analogous to condensation nuclei other than from erosion of the sea bed, and thus that old suspensions in the ocean interior would not have a Brownian spectrum. However, there are at least two sources of submicron particles in the ocean. The abundant reservoir of dissolved organic carbon (DOC) yields some of the ocean's particulate organic carbon (POC) by condensation reactions (Parsons, 1975; Degens and Mopper, 1976). This is estimated to be about 1.5% of the phytoplankton production, or ~1.5 g C m^{-2} $year^{-1}$ (Mopper and Degens, 1979). This would provide about 10^7 particles $m\ell^{-1}$ of 0.05μm diameter. Sharp (1973) estimates that up to 15% of the material reported as DOC (i.e. passing a 0.45μm filter) may in fact be colloidal, a potential 100μg C ℓ^{-1} (assuming with Mopper and Degens (1979), 700μg C ℓ^{-1} for the DOC reservoir). The second source liesin bacterial production. Azam et al. (1983) summarise the importance of microbes in the size range 0.3

to 1μm in consumption of DOM released from phytoplankton. The bacteria are fed on by flagellates and so on up the food chain. Deep water bacterial numbers are $\sim 10^6 m\ell^{-1}$.

In summary, most workers show data implying ß~3 in the size range 1 to 100μm in clear water. There is no consensus as to what is the size distribution of submicron particles. Their composition is also obscure. Relatively young (i.e., freshly eroded) suspensions in nepheloid layers have peaked volume size distributions, but old ones are flat (i.e., ß~3) according to McCave (1983) One view is that the overall distribution, whatever it may be, is made up of log-normal number distributions of several different components. The flat ß~3 distribution may extend to sizes > 1 l beyond 100μm shown by Sheldon et al. (1972).

PARTICLE DENSITY AND SETTLING VELOCITY

For model calculations some assumptions about density are necessary to obtain settling velocity. It is clear that density decreases with increasing aggregate size and there is a wide spread of values for any given size, partly because of the diversity of particle types. My best guess, justified in McCave (1984) is given below in Table 1.

PARTICLE INTERACTIONS

Although the interaction of particles must play an important role in controlling oceanic particle size spectra, there has been little work on the subject. There is every reason to believe that physically controlled particle aggregation occurs in the deep ocean, albeit slowly because of the low concentration. Within the water column and on the sea floor there are several types of organic-inorganic aggregates including those known as 'marine snow' and faecal pellets. Some such organic aggregates result from an organism actively

*Table 1. Model particle parameters**

d (μm)	$\Delta\rho$† (g cm^{-3})	w_s (cm s^{-1})	Re‡
0.1	1	3.63×10^{-7}	2.54×10^{-10}
0.2	1	1.45×10^{-6}	2.03×10^{-9}
0.5	1	9.08×10^{-6}	3.18×10^{-8}
1	1	3.63×10^{-5}	2.54×10^{-7}
2	0.746	1.08×10^{-4}	1.51×10^{-6}
5	0.506	4.60×10^{-4}	1.61×10^{-5}
10	0.378	1.37×10^{-3}	9.59×10^{-5}
20	0.282	4.09×10^{-3}	5.73×10^{-4}
50	0.191	0.0174	6.09×10^{-3}
100	0.0776	0.0282	0.0197
200	0.0315	0.0458	0.0641
500	9.58×10^{-3}	0.0870	0.305
1000	3.89×10^{-3}	0.1410	0.98
2000	3×10^{-3}	0.1447	2.03
5000	3×10^{-3}	0.1563	5.47
10^4	3×10^{-3}	0.1736	12.2

* Compared with Table 2 of McCave (1975) w_s is greater.

† $\Delta\rho = (\rho_s - \rho)$, where ρ_s is particle *in situ* bulk density and ρ is fluid density (here taken as 1.05 g cm^{-3}).

‡ $Re = w_s d/\nu$ with $\nu = 0.0143$ Stokes.

gathering and consolidating sediment plus organic matter (e.g., faecal pellets), whereas others result from the passive collision of particles, whether organic or inorganic. In the latter case an organic component may simply provide a sticky substrate for particle accumulation. It may increase the coalescence efficiency (i.e., the fraction of collisions that result in particle sticking) but the organic matter does not play any active role in increasing the frequency of collisions. The principal control on aggregation is the frequency with which particles come into contact, which is controlled by physical and biological mechanisms.

The probability that a particle of volume v_j will encounter a particle of volume v_i is proportional to the number of v_i particles and is given by $K(v_j, v_i)\, n(v_i)\, dv_i$ (Twomey, 1977, p. 123), where $K(v_j, v_i)$ is the coagulation kernel with $n(v_i) = dn/dv$ at $v = v_i$. Coagulation mechanisms are ways of bringing particles together. The principal five mechanisms are:

1. Brownian motion. Spherical particles undergoing Brownian diffusion have a probability of colliding given by the kernel $K_{B\,i,j}$ times the number of particles.

$$K_{B\,i,j} = 2\pi\, D_{i,j} d_{i,j} = \frac{2kT}{3\mu} \frac{d_{i,j}^2}{d_i d_j} \qquad (1)$$

where $D_{i,j} = (D_i + D_j)$, the sum of the diffusion coefficients ($D_j = kT/3\pi\mu d_j$), and $d_{i,j} = (d_i + d_j)$ the sum of the diameters of particles of size d_i and d_j. If all the particles are the same size at the beginning of coagulation (a monodisperse suspension) then the coagulation time t_c, the time to reduce the initial number N_o of particles per unit volume by a half, is $t_c = 3\mu/4kTN_oE$. Using appropriate values for deep ocean nepheloid layers, $\mu = 0.017$ poise, $T = 275°K$, $N_o = 4.10^5$ particles cm^{-3} in the size range 0.5 to 1μm, then $t_c \sim 8.6$ days assuming efficiency (E) of unity. With more realistic efficiency $E = 0.10$ from Edzwald et al. (1974), $t_c \sim$

3 months, which could be reduced to about 10 days for concentrated suspensions. The recent experimental results of Gibbs (1983) indicate coagulation efficiencies nearly double those of Edzwald et al. The effect of natural coatings has not yet been evaluated in this way but is clearly a necessity. Thus we expect appreciable Brownian pumping of particles from submicron size into aggregates a few μm in diameter on time scales of a few days to a few months to occur initially after introduction of suspended material into the water column. A similar situation should prevail in surface waters where concentrations are higher due to organic productivity. However, well away from the boundaries where the number of small particles is about 100 times less, the coagulation time is 20 years. Thus at mid-water depths, Brownian coagulation of small particles is very slow.

2. Laminar and turbulent shear. The laminar and turbulent shear kernels are similar:

$$K_{LSij} = \Gamma \frac{d_{ij}^3}{6} \tag{2}$$

for laminar shear with $\Gamma = dU/dz$ and

$$K_{TSij} = 0.163\, d_{ij}^3\, (\varepsilon/\nu)^{1/2} \tag{3}$$

for turbulent shear with the shear rate Γ given in the terms of the turbulent dissipation rate ε and kinematic viscosity ν (Saffman and Turner, 1956). the coagulation time corresponding to equation 3 for a monodisperse suspension ($d_i = d_j$) is $t_c = 0.693\ \pi/4V\Gamma$, where $V = \pi l^3 N_o/6$. The relative importance of Brownian and shear coagulation is approximately given by K_{Bij}/K_{LSij} or $2kT/\mu d^3\Gamma$, and so for equal importance with shear rate $\Gamma = 0.0084\ s^{-1}$ in a mono-disperse suspension $d \sim 8\mu m$, but with $\Gamma = 1.0\ s^{-1}$ ($\varepsilon = 1.4 \times 10^{-2} cm^2 s^{-3}$), $d = 1.7\mu m$. So Brownian coagulation dominates over shear in suspensions with low turbulence intensity for particles of diameter <8μm, but in more turbulent suspensions shear dominates down to

about 2μm. With variable stresses the grain size region 2 to 8μm marks the transition from Brownian to shear-dominated behaviour of particles relative to their near neighbours in size. It appears that Brownian coagulation will create aggregates of a few μm diameter faster than shear coagulation will remove them to larger sizes. Subsequently, as the number of submicron particles becomes relatively depleted, the 'bump' in the size distribution at values of a few μm will be dissipated by transfer of particles to larger sizes.

3. Turbulent inertial coagulation. In turbulent flow local turbulent accelerations produce relative particle velocities for particles of unequal mass (Pruppacher and Klett, 1978, p. 375). This process is relatively unimportant. It is normally only significant when particles differ in diameter by more than about 1 cm.

4. Differential settling. The faster settling of larger particles through a suspension leads to collisions with slower settling particles and their capture to form aggregates. The kernel is given simply by the area swept out times the relative velocity, the collision efficiency E_{cij}, and the efficiency of diffusive collection E_{bij}

$$K_{Gij} = \frac{\pi d_{ij}^2}{4} (w_{sj} - w_{si}) (E_{cij} + E_{bij})$$

The collision efficiency is the ratio of the number of particles with which the settling particle makes contact to the number in the volume it sweeps out as it sinks. Small particles are also transferred by Brownian diffusion to the surface of the larger settling particle. For 5μm particles, most of the range of interest is dominated by collision save for particles <1μm, where diffusion is most important. Inertial capture of small particles by 'marine snow' is most inefficient and may not be important, but diffusive capture is relatively efficient (see Table 2). Settling through mid-water where there are

perhaps 3×10^5 particles cm^{-3} of size 0.35 to 0.7μm, a piece of 'marine snow' of diameter 5mm and cross-sectional area 0.2 cm^2 sinking through 1000 m would collect 1700 particles in that size range assuming 10% coalescence efficiency. This may be important for the individual aggregate, but to sweep the water column clean of such particles would require about 35,000 more particles following the path of the first!

This view is based on the assumption of spherical particles. However, some components of 'marine snow' are discarded mucus webs whose shape is anything but spherical. It may well be that these irregular, deformable, porous, gelatinous particles have a much higher collision capture efficiency than a rigid sphere. At any event the behaviour of such particles should be examined theoretically.

Table 2. Settling capture efficiencies

	Catcher			
Caught	5 mm snow		50μm aggregate	
(μm.)	E_D	E_C	E_D	E_C
50	1.43×10^{-6}	$\underline{1.47 \times 10^{-4}}$	---	---
5	$\underline{6.16 \times 10^{-6}}$	1.5×10^{-6}	5.8×10^{-4}	$\underline{1.2 \times 10^{-2}}$
0.5	$\underline{2.85 \times 10^{-5}}$	1.5×10^{-8}	2.66×10^{-3}	1.47×10^{-4}

Underlined values are the most efficient for interactions of that pair of particles. E_D = diffusive capture, E_C = collision capture.

5. Biological aggregation processes. It is possible to write down a coagulation kernel for active particle catching and aggregate production by animals. Basically they sweep or filter a certain volume of water each second, $V = AU$, where A is the area of water column swept at speed U, and catch particles with an efficiency E_{Bijf}, which depends on the type of organism j, the size di of the particle, and its perceived food value f. The kernel would have the

form $K_{Bij} = AUE_{Bijf}$. Animals are likely to have the major impact on particle spectra in the upper layers of the ocean where there is most food. It is not clear what the effects will be at great depths in mid-water and in the bottom nepheloid layer, where even the population densities are not well known (Wishner, 1980).

Coagulation Rates

The regions dominated by the different coagulation mechanisms are shown in fig. 1 in a form based on the original suggestions by Friedlander (1965). the coagulation rate constants from the kernels are plotted for interactions with particles of size d_i = 5μm. The conditions assumed are those of low shear, Γ = 0.084 to 0.0084s^{-1}, and deep-sea density and viscosity mentioned above with McCave's (1984) model particle properties. The 'giant' particles represented by marine snow appear to be dominated by shear in their interactions because of the d_{ij}^3 term in the shear kernel. In particle collisions with near neighbours (in size) where small aggregates join to make bigger ones, and so on up to large sizes, the time scales calculated are very long (assuming 10% efficiency). Brownian coagulation times for 0.5μm particles are 3 months to 20 years for nepheloid layer and mid-water concentrations, respectively, and corresponding shear-coagulation times for 5μm particles are from 7 months to 7000 years! This makes it unlikely that small particles can aggregate progressively up the size spectrum to become big ones other than through biological intervention yielding faecal pellets. 'Apparently the mill grinds very slowly by physical means.

But does it? A feature of the turbulent shear kernel is that it attains high values for interactions involving large particles. One way of examining the effect of this is to calculate particle removal rate as suggested by Lerman (1979, pp. 288-299) [cf. Hidy's (1973) Tables 4 to 6 for aerosols]. This is

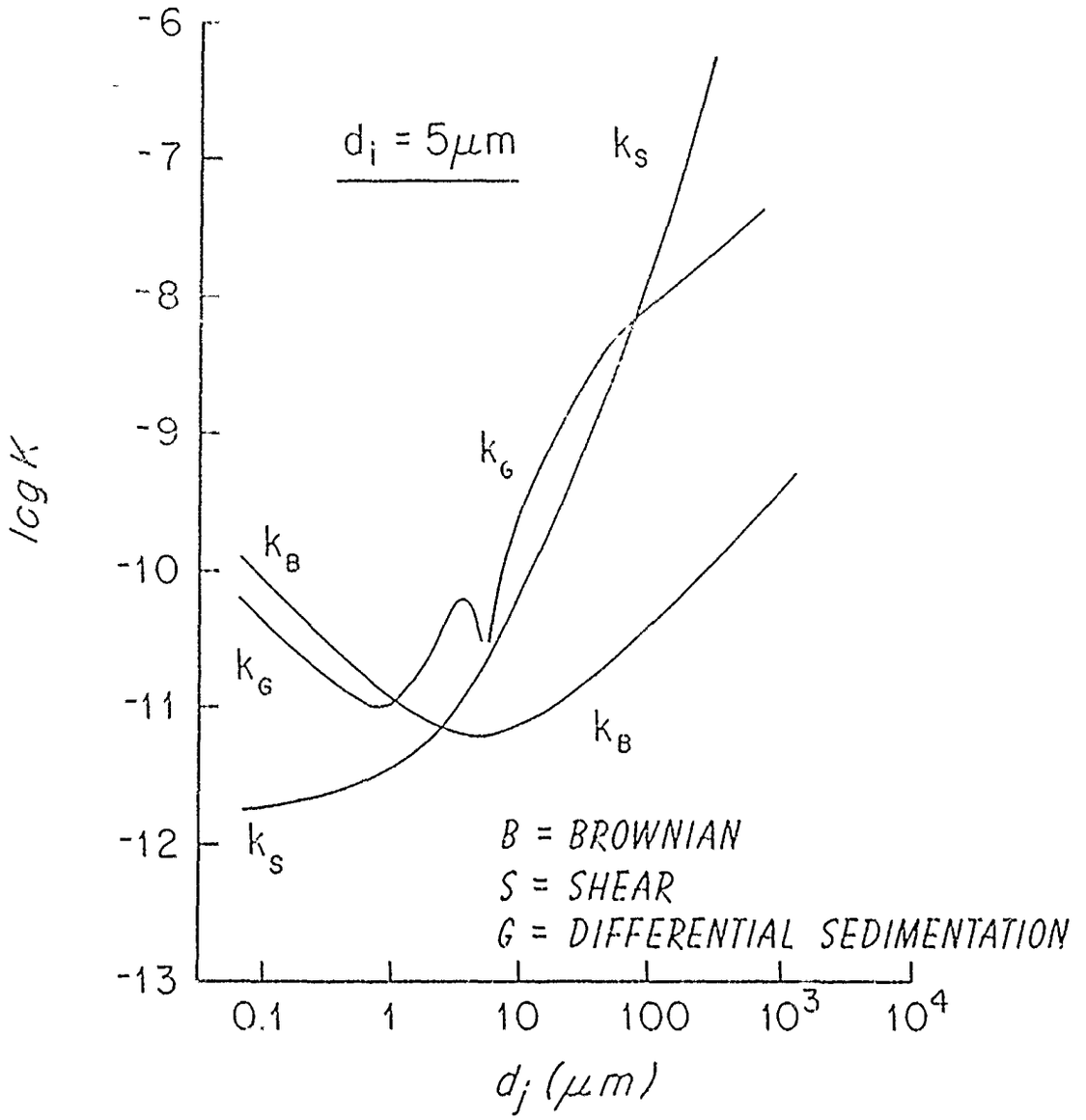


Fig. 1. Coagulation kernels K for collection of 5um particles plotted for $\varepsilon = 10^{-1}$ $cm^2 s^{-3}$ and oceanic conditions. Subscripts are B for Brownian, G for differential settling and S for shear.

given by the kernel times the numbers of interacting particles $K\ n(v_i)n(v_j)$ with units $cm^{-3}s^{-1}$. Table 3 shows the results of calculations for nepheloid layer and mid-water concentrations. The most important feature of Table 3 is that many of the collision frequencies are $<3.17 \times 10^{-8}\ cm^{-3}s^{-1}$, or less than one collision per year per cm^3.

The enhanced coagulation rates for small particles with large particles in nepheloid layers suggests that this will be a highly significant mechanism in surface waters too, where turbulence levels expressed as a shear rate may be an order of magnitude greater. In addition, the concentrations of marine snow may be two orders of magnitude greater than the figure given here [i.e. $5 \times 10^{-3}cm^{-3}$ from Shanks and Trent (1980) and $10^{-3}cm^{-3}$ from Honjo et al. (1984). Thus, in surface water the smallest particles are aggregated by Brownian motion. Such aggregates are lost by colliding with one another in motion controlled by differential settling, but they are scavenged even more rapidly by large particles with turbulent shear controlling the relative motion. They are probably collected by biological means even faster than both those physical mechanisms.

The above discussion has considered physical factors involved in aggregation. It must be tempered by the fact outlined above that some filter-feeding organisms can process the upper water column in a day. Brownian aggregation is likely to put small particles into sizes 1 to 8μm, where they stand a good chance of being filtered by larger zooplankton if they have not already been collected by microzooplankton. More data on filtration rates and population densities of suspension feeders, particularly below the surface layers, will be essential in elucidating deep-sea particle dynamics. Animals may dominate at depth as it seems probable that they do in the surface.

Table 3. Particle removal rates: $-dn/dt$ ($cm^{-3}\ s^{-1}$)*

	Nepheloid layer ($\Gamma = 0.084\ s^{-1}$)			Mid water ($\Gamma = 0.0084\ s^{-1}$)		
$d_i =$	0.5 μm	5 μm	50 μm	0.5 μm	5 μm	50 μm
L_B	6.74	6.07×10^{-5}	2.43×10^{-12}	6.74×10^{-4}	6.07×10^{-9}	1.22×10^{-14}
L_S	1.37×10^{-2}	1.23×10^{-4}	4.93×10^{-9}	1.37×10^{-7}	1.23×10^{-9}	1.23×10^{-12}
$L_S(2–4)$	1.86×10^{-2}	5.61×10^{-5}	1.18×10^{-8}	6.20×10^{-6}	1.87×10^{-8}	1.97×10^{-11}
$L_G(50)$	5.68×10^{-4}	8.33×10^{-6}	—	2.84×10^{-7}	4.44×10^{-9}	—
$L_G(2–4)$	2.42×10^{-3}	2.34×10^{-6}	1.35×10^{-8}	8.06×10^{-6}	7.80×10^{-9}	2.24×10^{-10}
$N_i(cm^{-3})$	10^6	3×10^3	0.6	10^4	30	0.03
$N_{2-4}(cm^{-3})$		6×10^{-5}			2×10^{-5}	

* Assuming 100% efficiency.
N_i is the number concentration of particles of diameter d_i.
$N_{2\text{ to }4}$ is the number concentration of 'snow' particles in the size range 2 to 4 mm.
Subscripts for loss rates L are B = Brownian, S = shear, G = differential sedimentation, (2 to 4) mm and 50 μm.
Frequencies $< 3.17 \times 10^{-8}\ cm^{-3}\ s^{-1}$ represent less than one collision per year.

Removal of Particles from Mid Water Depths

The distribution of turbidity at mid-water depths shows that there is more material present under mid-ocean high productivity areas (Eittreim et al., 1976; Biscaye and Eittreim, 1977), than under gyres. Thus the flux of large particles from the surface may reasonably be inferred to supply more material to mid-water depths than it removes, presumably by break-up of large aggregates. If the larger than average flux of large marine snow particles from high productivity results in net supply rather than removal of particles then there is reason to believe that under normal conditions in the open ocean the flux of large particles also performs no net scavenging function. However, this conflicts with the data of Honjo (1982) and Honjo et al. (1982) who show that vertical flux of aluminosilicate increases with depth and that the maximum flux of aluminosilicate coincides with a temporal maximum in surface organic carbon productivity and flux (and resulting carbonate flux). A similar, seasonally tied, result is given by Deuser et al. (1983) in the Atlantic. Do the sinking particles perform the scavenging of clays or does the presence of the organic-rich particles stimulate a scavenger (biological) to remove material indiscriminately? We must also consider the extent to which the downwards increase in flux reflects an increase in the particle concentration surrounding the trap.

Thus there seems to be no quick way of removing fine particles from mid-water depths via physical means and they must have a removal rate principally controlled by Brownian coagulation up to a size (about 5μm) where settling removal speeds up (~140m/year). This will take many years. It would explain why long residence times and slow sinking rates are inferred from analysis of radionuclides inasmuch as these are scavenged by the fine particles which are preferentially sampled by water bottles.

If there is some quicker way of removing particles from mid-waters then it must be biologically controlled.

THE RATE DETERMINING PROCESS FOR DEPOSITION

In a turbulent suspension, particles are brought into contact by several mechanisms and frequently stick, forming aggregates with a settling velocity greater than that of the individual particles. This raises the question of whether the rate of deposition to the bed is controlled by the rate at which larger aggregates are formed. If aggregates were not formed, would the rate of deposition be much slower?

One way of comparing rates due to these processes is to consider their respective half lives, that is to say, the half-residence time of the number of particles in suspension. (Aggregation reduces the effective number of particles in suspension.) For deposition, this is $t_D = 0.693/(w_s/H)(1-\tau_0/\tau_s)_1)$. For aggregation by Brownian motion, and turbulent shear, the coagulation times were given earlier. Let us assume deposition from a uniformly mixed nepheloid layer 50 m thick (H), with 100µg/litre of each size class (1, 5, and 20µm), and constant shear velocity $u_* = 0.1 cms^{-1}$. For the 1µm material, t_D = 6.1 years, but t_{cB} = 1.24 years. Thus, it appears that clay (<2µm) will be moved up the size spectrum faster than it is deposited. For 5µm material, t_D = 117 days, but t_{cB} is 30 times as long at about 10 years.

One other case to consider is whether small particles will be scavenged out by large fast-settling ones and carried to the bottom faster than they would otherwise settle. McCave (1984) showed that the most effective means of scavenging is in the turbulent agitation of large particles among smaller ones. The collection rate is $K_{s_{ij}} n_i n_j$, where $k_{s_{ij}} = 0.163\ d_{ij}^3$ in which d_{ij} is the sum of the diameters of the colliding particles and n_i and n_j

are the number of i and j particles, respectively. For large "marine snow" particles of 2 to 4 mm diameter, we assume $n_j = 6 \times 10^{-5} cm^{-3}$ and for 1μm particles, $n_i = 10^5 cm^{-3}$. With other parameters as before and 10% efficiency, the scavenging rate is $1.82 \times 10^{-4} cm^{-3} sec^{-1}$ or, in a layer 50-m thick, 0.91 particles/cm^2/sec. The rate of deposition particle-by-particle is 1.8 particles/cm^2/sec. Thus, scavenging of clay is not negligible, but neither is it dominant. In any event, it is less important than aggregation of small particles. For larger particles, scavenging becomes less important relative to their rate of deposition.

What is not at all clear is how important is the role of the benthopelagic plankton in aggregating sediment. Is it as important as the zooplankton of the upper 200 m? Good biological data are needed from great depths.

CONCLUDING QUESTIONS

I have raised a few questions, some implicit in assumptions one is forced to make, in this account. Important ones are: 1. What is the size distribution of submicron particles in the oceans? 2. What is the origin and composition of these submicron particles? (Chemists will doubtless wish to enquire into their scavenging capabilities for dissolved substances.) 3. What is the coagulation efficiency for different classes (size, composition) of oceanic particles? 4. What is the dynamical behaviour of sinking blobs, sheets and webs of mucus? 5. What are the biological scavengers of particles in the mid-water and bottom nepheloid layer regions? 6. What particle removal rates are associated with their activities?

REFERENCES

AZAM, F., T. FENCHEL, J.G. FIELD, J.S. GRAY, L.A. MEYER-REIL and F. THINGSTAD (1983). The ecological role of water-column microbes in the sea. Marine Ecology-Progress Series, 10, 257-263.

BAKER, E.T., R.A. FEELY and K. TAKAHASHI (1979). Chemical composition, size distribution and particle morphology of suspended particulate matter at DOMES sites A, B, and C: relationships with local sediment composition. In: Marine Geology and Oceanography of the Pacific Manganese Nodule Province, J.L. Bischoff and D.Z. Piper, editors, Plenum Press, New York, pp. 163-201.

BISCAYE, P.E. and S.L. EITTREIM (1977). Suspended particulate loads and transports in the nepheloid layer of the abyssal Atlantic. Marine Geology, 23, 155-172.

BRUN-COTTAN, J.C. (1971). Etude de la granulometrie des particules, measures effectuees avec un compteur Coulter. Cahiers Oceanographiques, 23, 193-205.

DEGENS, E.T. and K. MOPPER (1976). Factors controlling the distribution and early diagenesis of organic material in marine sediments. In: Chemical Oceanography (2nd ed), S.P. Riley and R. Chester, editors, Academic Press, London, vol. 6, p. 59-113.

DEUSER, W.G., P.G. BREWER, T.D. JICKELLS and R.F. COMMEAU (1983). Biological control of the removal of abiogenic particles from the surface ocean. Science, 219, 388-391.

EDZWALD, J.K., J.B. UPCHURCH and C.R. O'MELIA (1974). Coagulation in estuaries. Environmental Science and Technology, 8, 58-63.

EITTREIM, S.L., E.M. THORNDIKE and L. SULLIVAN (1976). Turbidity distribution in the Atlantic Ocean. Deep-Sea Research, 23, 1115-1127.

FRIEDLANDER, S.K. (1965). The similarity theory of the particle-size distribution of the atmospheric aerosol. In: Aerosols, physical chemistry and applications. K. Spurny, editor, Czechoslovakian Academy of Science, Prague, pp. 115-130.

GIBBS, R.J. (1983). Coagulation rates of clay minerals and natural sediments. Journal of Sedimentary Petrology, 53, 1193-1203.

HARRIS, J.E. (1977). Characterization of suspended matter in the Gulf of Mexico - II. Particle size analysis of suspended matter from deep water. Deep-Sea Research, 24, 1055-1061.

HIDY, G.M. (1973). Removal processes of gaseous and particulate pollutants. In: Chemistry of the lower atmosphere, S.I Rasool, editor, Academic Press London, pp. 121-176.

HONJO, S. (1976). Coccoliths: production, transportation and sedimentation, Marine Micropalaeontology, 1, 65-79.

HONJO, S., K.W. DOHERTY, Y.C. AGRAWAL and V.L. ASPER (1984). Direct optical measurement of large amorphous aggregates (marine snow) in the deep ocean. Deep-Sea Research, 31, 67-76.

HONJO, S. (1982). Seasonality and interaction of biogenic and lithogenic particulate flux at the Panama Basin. Science, 218, 883-884.

HONJO, S., D.W. SPENCER and J.W. FARRINGTON (1982). Deep advective transport of lithogenic particles in Panama Basin. Science, 216, 516-518.

LAMBERT, C.E., C. JEHANNO, N. SILVERBERG, J.C. BRUN-COTTAN and R. CHESSELET (1981). Log-normal distributions of suspended particles in the open ocean. Journal of Marine Research, 39, 77-98.

LERMAN, A. (1979). Geochemical processes: water and sediment environments. Wiley, New York, 481 pp.

LERMAN, A., K.L. CARDER and P.R. BETZER (1977). Elimination of fine suspensoids in the oceanic water column. Earth and Planetary Science Letters, 37, 61-70.

McCAVE, I.N. (1975). Vertical flux of particles in the ocean. Deep-Sea Research, 22, 491-502.

McCAVE, I.N.(1983). Particulate size spectra, behaviour and origin of nepheloid layers over the Nova Scotian Continental Rise. Journal of Geophysical Research, 88, 7647-7666.

McCAVE, I.N. (1984). Size spectra and aggregation of suspended particles in the deep ocean. Deep-Sea Research, 31, 329-352.

MOPPER, K. and E.T. DEGENS (1979). Organic carbon in the ocean: nature and cycling. In: The Global Carbon Cycle, B. Bolin, editor, Wiley, New York, p. 293-316.

PAK, H., J.R.V. ZANEVELD and J. KITCHEN (1980). Intermediate nepheloid layers observed off Oregon and Washington. Journal of Geophysical Research, 85, 6697 6708.

PARSONS, T.R. (1975). Particulate organic carbon in the sea. In: Chemical Oceanography, J.P. Riley and G. Skirrow, editors, Academic Press, London vol. 2, p. 365-383,.

PRUPPACHER, H.R. and J.D. KLETT (1978). The microphysics of clouds and precipitation. Riedel, Dordrecht, 714 pp.

REX, R.W. and E.D. GOLDBERG (1958). Quartz contents of pelagic sediments of the Pacific Ocean. Tellus, 10, 153-159.

RICHARDSON, M.J. and W.D. GARDNER (1985). Analysis of suspended-particle-size distributions over the Nova Scotian Continental Rise. Marine Geology, 66, 189-203.

SAFFMAN, P.G. and J.S. TURNER (1956). On the collision of drops in turbulent clouds. Journal of Fluid Mechanics, 1, 16-30.

SCHRAMER, P.G. (1971). Faecal pellets: role in sedimentation of pelagic diatoms. Science, Wash., 174, 55-57.

SHANKS, A.L. and J.D. TRENT (1980). Marine snow: sinking rates and potential role in vertical flux. Deep-Sea Research, 27, 137-144.

SHARP, J.G. (1973). Size classes of organic carbon in seawater. Limnology and Oceanography, 18, 441-447.

SHELDON, R.W., A. PRAKASH and W.H. SUTCLIFFE (1972). The size distribution of particles in the ocean. Limnology and Oceanography, 17, 327-340.

TAMBO, N. and Y. WATANABE (1979). Physical characteristics of flocs -I. The floc density function and a uminium floc. Water Research, 13, 409-419.

TWOMEY, S. (1977). Atmospheric aerosols, Elsevier, Amsterdam, 302 pp.

WELLERSHAUS, S., L. GOKE and P. FRANK (1973). Size distribution of suspended particles in sea water. Meteor Forschungsergebnisse, Series D, No. 16, pp. 1-16.

WISHNER, K.M. (1980). The biomass of the deep-sea benthopelagic plankton. Deep-Sea Research, 27, 203-216.

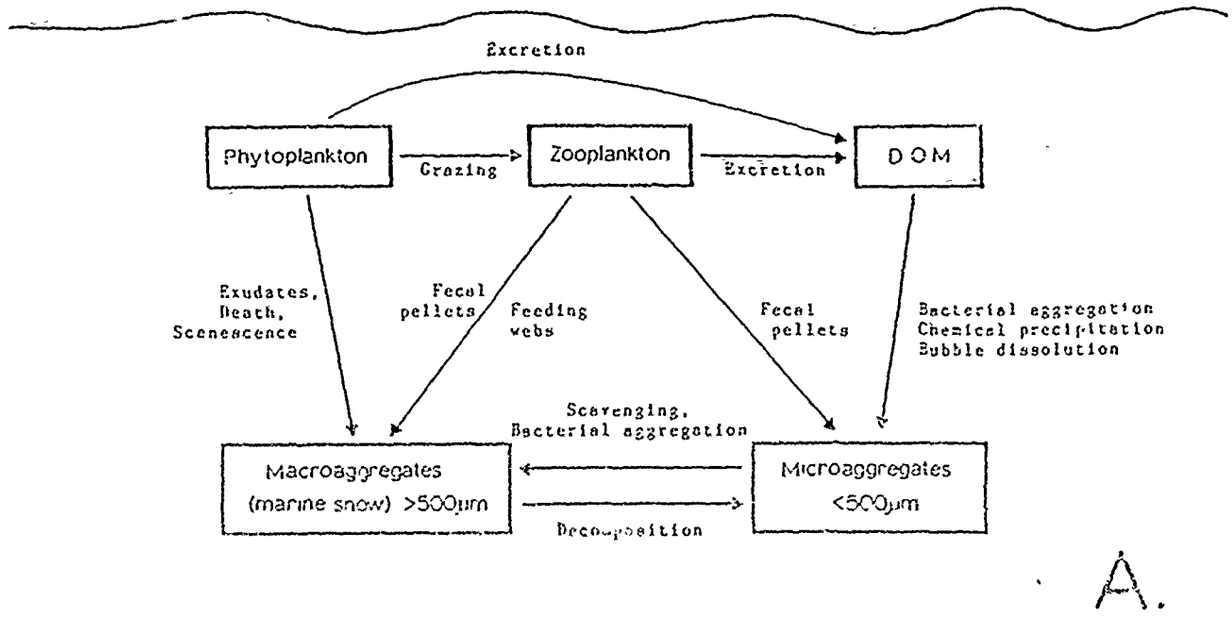
Aggregate Dynamics: Biological processes which form, alter and destroy aggregates in the ocean

Alice L. Alldredge
Department of Biological Sciences and Marine Science Institute
University of California
Santa Barbara, CA 93105

INTRODUCTION

The processes which change the abundance, size distribution and characteristics of marine aggregates in nature are complex and diverse. Many biological and physical mechanisms are involved in the dynamics of particle formation and breakdown. Biological processes may be particularly important in the formation of aggregates in the sea. McCave (1984) examined physical processes of collision and coagulation and concluded that they were inadequate to explain the high degree of aggregation seen in particulate matter in the deep sea. He concluded that the size distribution of particles above submicron sizes was largely biologically determined.

The major biological pathways by which marine aggregates are formed are illustrated in Fig. 1a. Macroaggregates, or marine snow, arise from the aggregation of senescent diatoms, from discarded zooplankton feeding webs, as flocculant fecal pellets, or from the microbial aggregation of microaggregates. Microaggregates form from bacterial aggregation and from dissolved organic



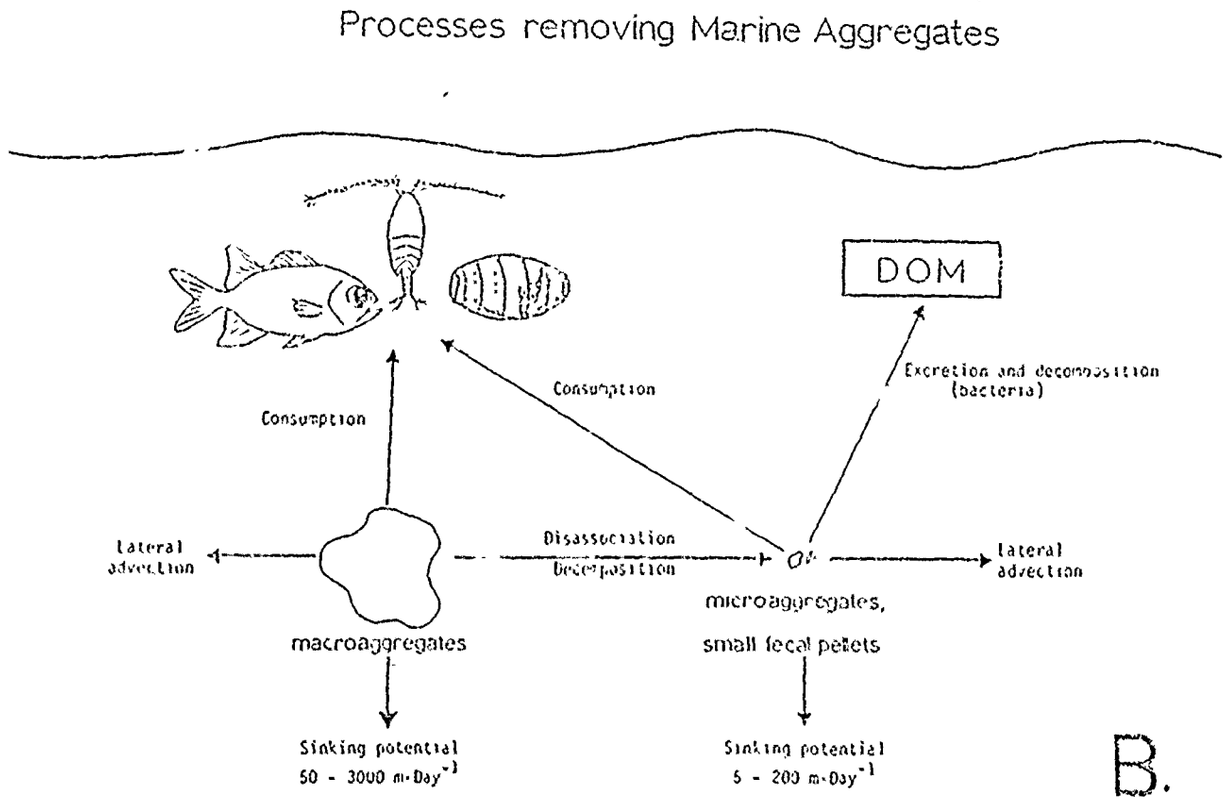


FIGURE 1: Biological processes which form, alter and breakdown marine aggregates.

matter through a variety of pathways, several of which are closely linked to physical processes as well.

The major pathways by which aggregates are destroyed or removed from the pelagic zone are illustrated in Fig. 1b. Significant biological processes of aggregate loss include consumption by zooplankton and nekton and decomposition by microorganisms. Physical processes of settlement, lateral advection, and fragmentation due to turbulence are equally important. In this review I will examine the major biological mechanisms by which aggregates are formed, altered and broken down in the ocean. Throughout I stress that many of these mechanisms can operate simultaneously to significantly change the abundance, size distribution and nature of marine aggregates.

FORMATION OF AGGREGATES

Direct production of aggregates by phytoplankton

Primary production is the ultimate source of most of the organic matter in the pelagic zone. Hence, phytoplankton contribute indirectly to most mechanisms of aggregate formation. However, phytoplankton also directly form macroaggregates through entanglement, aggregation and mass sinking following bloom conditions. Rapid mass sedimentation of phytoplankton through the water column has been documented in neritic environments (Smetacek, 1980; Wassmann, 1983), in the Baltic and North Seas (Smetacek et al., 1978; Davies and Payne, 1984), in the Panama Basin (Honjo, 1982) and in the north east Atlantic (Billet et al., 1983). Mass sinking has usually been equated with mass mortality of phytoplankton cells following bloom conditions (Walsh, 1983).

Smetacek (1985) challenges the concept of mass mortality and presents evidence that mass aggregation and sinking of certain phytoplankton groups may

be an adaptation for the transport of resting stages to the deep sea. Aggregation may insure the ultimate survival of the species via the maintenence of seed populations at depth. Diatoms, such as Thalassiosira, Skelotonema, Chaetoceros and Rhizosolenia are major genera contributing to aggregate formation. Diatom populations experiencing nutrient stress under bloom conditions produce large flocculant aggregates, identical to marine snow, which sediment at rates of 50 to 200 m day^{-1}, considerably higher than the <10 m d^{-1} expected of individual diatom chains. These sinking diatom aggregates produce, for a few days, very high abundances of marine snow which Smetacek (1985) refers to as a "marine blizzard".

Three mechanisms apparently lead to the aggregation of diatom blooms. First, as nutrients become depleted, cell buoyancy is reduced and the cells begin to sink. Protuberances and spines on the cells entangle the sinking cells together, beginning the aggregation process. Second, the production of extracellular mucus, which increases under nutrient stress (Degens and Ittekot, 1984) serves to adhere cells together as they collide. Third, although not addressed by Smetacek, some nutrient stressed cells actually die. Deterioration of the girdle upon death may split the diatom frustules apart, releasing protoplasm. This sticky gelatinous material could serve as a nucleus for the continued aggregation of particles. Although direct evidence for the aggregation of diatoms via these mechanisms has not yet been obtained directly in the sea, flocculation of diatoms in senescent cultures is commonly observed in the laboratory (Eppley et al., 1983), and considerable laboratory evidence exists to support mucus production and entanglement of nutrient stressed and negatively buoyant diatoms.

Diatom blooms usually progress from the coast toward the open sea. Strong lateral advection, such as the squirts and jets of the California coast, probably transport diatom blooms and aggregates off shore. Seasonal and regional patterns in cross-shelf transport will thus have a major impact on the distribution and abundance of diatom-generated marine aggregates. Moreover, evidence from marine sediments suggest that diatom-generated marine snow may be a widespread phenomenon throughout the world's oceans. The ditribution of silliceous ooze in the sediments of the Pacific is closely correlated with phosphate concentration and primary production (Berger, 1984, Fig. 2). Areas of high productivity are the most likely areas for the production of macroaggregates by diatom blooms and the rapid sedimentation of silica to the sea floor.

Phytoplankton also directly produce marine snow via the formation of gelatinous colonies. The coccolithophorid, Emiliania huxleyi, and some diatoms such as Thalassiosira sp. can form gelatinous colonies (Fryxell et al., 1974), which serve as nuclei for macroaggregates. Although such colonies are occasionally abundant, the quantitative significance of gelatinous colonies as sources of marine snow remains unknown.

Production of aggregates by zooplankton

Zooplankton produce aggregates through two major mechanisms. 1) Large, flocculent aggregates are produced by appendicularians and pteropods as part of their feeding biology and, 2) animals repackage small particles into larger ones via consumption of food particles and defecation of the unassimilated portion as fecal pellets.

Zooplankton feeding webs can be a major source of marine snow at certain times and locations and may be particularly important in oligotrophic waters where conditions are less favorable for aggregate formation by other mechanisms.

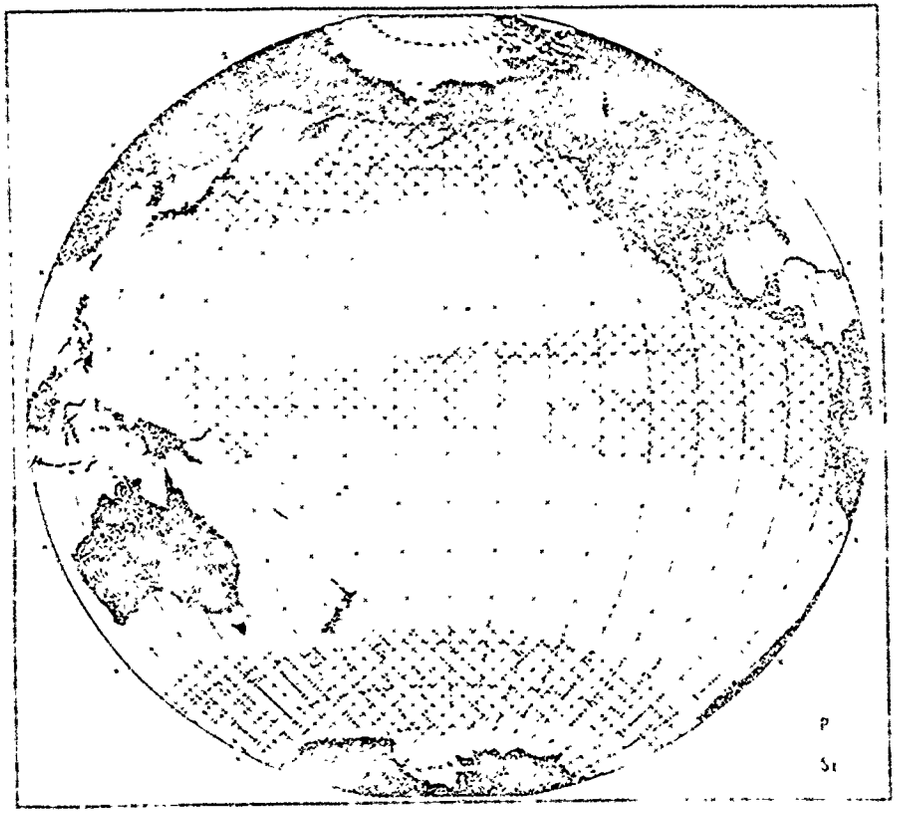


FIG. 29.25. Distribution of sediments rich in siliceous fossils ("Si") with respect to fertile areas, as indicated by the regions where $PO_4^{3-} \cdot P \cdot I\ \mu g\text{-at}\ l^{-1}$ at 100 m depth ("P"). From Berger (1970b).

Figure 2: from Berger, .984

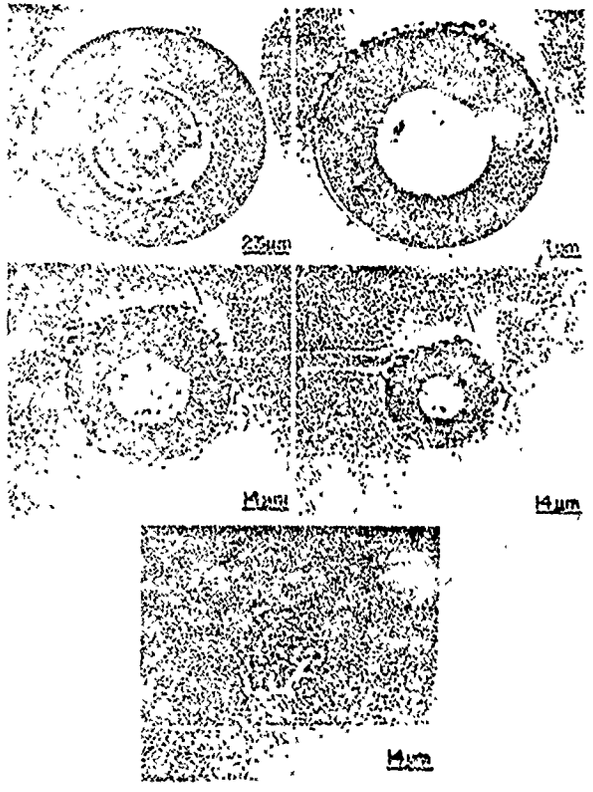


Figure 3: from Johnson and Cooke, 1980

Appendicularians, abundant planktonic tunicates, feed using a gelatinous feeding structure, the house, which contains a complex array of filters and passages. The house is composed a mucopolysaccharides and is secreted by specialized cells on the animal's trunk. The animal forces water through the filters of the house with its tail. Phytoplankton, bacteria, fecal pellets and microaggregates become concentrated, either on the external filters of the house or within the internal filter. The house is abandoned periodically and a new structure is secreted. Individual appendicularian houses may contain up to 50,000 phytoplankton cells and vary in diameter from a few hundred microns to 30 or more cms. Most are on the order of 3 to 20 mm in diameter (Alldredge and Madin, 1982).

Individual appendicularians produce and discard from 4 to 16 houses per day (Fenaux, 1985). These discarded houses become macroaggregates containing diverse detrital populations of phytoplankton, bacteria and protozoans (Alldredge, 1972). The rate of house production increases with increasing temperature and with increasing food concentration (Fenaux, 1985). Where appendicularians are abundant, houses may be the major macroaggregates in the water column. Discarded houses reach densities up to 80/l (Prezelin and Alldredge, 1983). A mean of 6% and 24% of macroscopic aggregates in the Santa Barbara Channel and the Gulf of California respectively are identifiable appendicularian houses (Alldredge, 1979).

Pteropods, gelatinous planktonic molluscs which feed with mucus sheets (Gilmer, 1972), are also sources of macroaggregates. Pteropods are ubiquitous and webs are occasionally abundant in surface waters (Caron et al., 1982), but no quantitative information exists regarding the rates of web production and the significance of pteropod webs as sources of macroaggregates in the pelagic zone.

The major impact of zooplankton on the size distribution and abundance of aggregates in the ocean is through the consumption and repackaging of food particles, primarily phytoplankton, into fecal pellets. Although a vast literature exists on the feeding rates of various zooplankton, previous research on zooplankton feeding has emphasized the impact of zooplankton on phytoplankton and other food populations or the growth rates and biological characteristics of the grazing animals themselves. Very little research has examined zooplankton feeding from the repackaging perspective.

Assimilation rates of most marine zooplankton are on the order of about 70% (Angel, 1981). If we assume that most of the primary production in surface waters is consumed by herbivores, than up to 30% of primary production eventually exists as fecal pellets. Fecal pellets form a special class of aggregates. The production of fecal pellets in the water column is controlled primarily by the abundance and feeding rate of the animals, and by their ingestion and assimilation efficiencies. Most available rates of pellet production are for crustaceans (Table 1). In copepods, the volume of fecal pellets produced per day is a linear function of animal dry weight (Paffenhofer and Knowles, 1979). Smaller individuals tend to produce more pellets per unit weight then larger individuals and small species have higher production rates than large species (Heyroud, 1979). Moreover, as assimilation efficiencies increase, pellet production decreases. Thus deep sea animals, which tend to have higher assimilation efficiencies may have lower fecal pellet production rates and we might predict that pellet production/individual would vary with depth (Angel, 1984).

Most zooplankton migrate in the top 1000 m of the water column and most micronekton in the top 1000-1500 m (Angel, 1984). Since most production of new particulate organic matter occurs in the euphotic zone, consumption and repackaging of new production is most significant in the upper 1000 m of the water

Table 1. Some observed fecal pellet production rates

From Angel, 1984

Species	Feeding Conditions	Fecal Pellets per day	Authors
Acartia tonsa	3 order of magnitude of food concentration	1-6	Reeve and Walter, 1977
Acartia clausi	$5 \times 10^5 m\ell^{-1}$ natural particles	24.5	Honjo and Roman, 1978
	$1.6 \times 10^5 m\ell^{-1}$ coccolithophores	91	
	$2.0 \times 10^4 m\ell^{-1}$ coccolithophores	8	
Temora turbinatus	Natural conditions	10-169	Paffenhofer and Knowles, 1979
Eucalanus pileatus	Natural conditions	55-160	
Oikopleura longicauda	Natural conditions	243±105	Taguchi, 1982
Cyclosalpa affinis	Excretion of animals collected by SCUBA divers and held in aquaria	9.9*	Madin, 1982
Salpa maxima		13.0*	
Pegea confoederata		17.8*	
Meganyctiphanes norvegica	25 mg animals fed on Acartia in laboratory	5.1+	Small et al., 1973
M. norvegica	" "	5.3+	Heyraud, 1979

*µg fecal C mg $C^{-1} h^{-1}$ +mg feces (mg animal dry Wt.)$^{-1}$ day^{-1}

(N.B. a Meganyctiphanes fecal pellet weighs = 17 ug, Fowler, personal communication).

column. Repackaging of aggregates, both fecal pellets and other aggregates originating in surface waters, may occur throughout the water column (Turner and Ferrante, 1979). Fecal matter appears to be efficiently cycled in the upper layers of the ocean with relatively little fecal matter fluxing to the deep sea in some areas (Hoffman et al., 1981; Bishop et al., 1977) while high numbers of fecal pellets reach the sediments in others (Dunbar and Berger, 1981).

Fecal pellets, as a class of marine aggregates may be a considerably more abundant component of the pelagic zone than previously thought. Krause (1931) noted the prolonged residence of large numbers of copepod fecal pellets (up to 100 l^{-1}) in surface water in the North Sea, suggesting that not all pellets sank or were consumed. Macrocrustacean pellets, probably of Euphausia pacific, are abundant in the Santa Barbara and Santa Cruz Basins off Southern California, ranging from 550 to 98,000 pellets m^{-3}. Studies of the aging of the peritrophic membranes of these pellets in the laboratory indicate that up to 40% of pellets at 10 meter depths may be 3 or more days old, despite sinking rates of 13 to 170 m d^{-1} (Alldredge, unpublished). Turbulent mixing and entrainment events may maintain fecal pellets in surface waters, where they remain available for further repackaging via consumption by zooplankton.

Production of aggregates from dissolved organic matter (DOM)

The quantity of dissolved organic matter in the ocean generally exceeds that of particulate phase by an order of magnitude. Of this material about half is believed to be truly dissolved while the remaining half consists of colloidal sized particles (Cauwet, 1978). This DOM is composed of many types of complex organic molecules including proteins, lipids, and carbohydrates and is biological in origin. DOM is produced by the exudation of organic molecules by phytoplankton and marine microbes. It is excreted by zooplankton and is produced by

cell death and lysis and by decomposition processes. Some arises from nearshore and terrestrial environments. The conversion of matter from the dissolved to the particulate phase may be one of the major pathways forming marine aggregates. Such conversion may take place via one of three major mechanisms. Although 2 of these mechanisms involved physiochemical aggregation, they are included here since the primary source, DOM, is biological in origin.

De nova formation of particles in seawater by physiochemical processes may be a significant source of microaggregates. Particles spontaneously form in standing seawater even after ultrafiltration to remove all particles and molecules with a molecular weight greater than 2000 (Johnson and Cooke, 1980). ^{14}C labeled extracellular products of phytoplankton immediately form particles when added to seawater. Jensen and Sondergaard (1982) attribute this phenomenon to the absorption of organic molecules to the colloidal size fraction of DOM. Flocculation of humic materials in river water commonly occurs when freshwater mixes with seawater and 3 to 11% of the DOM in rivers may become particulate in this way (Sholkovitz, 1976). Wangersky (1978) has hypothesized that DOM may coprecipitate with $CaCO_3$ in seawater as well.

Adsorption of organic molecules to existing particles in seawater is well documented. Neihof and Loeb (1974) found that all particles in seawater are coated with high molecular weight organic molecules which produce a negative surface charge. Adsoption occurs via hydrogen bonding, Van der Waal forces and electrostatic attraction depending upon the nature of the particles and the organic molecules involved. Such adsorption enlarges colloidal particles. Reduction of the electrostatic charges which normally keep particles dispersed can result in aggregation. Sewage effluents are aggregated by chemical or bacterial treatments which accomplish this purpose (Riley, 1970). However, the physical and chemical processes behind de nova particle formation in seawater

have not been thoroughly explained and quantitative data on the conditions required and the rate of de nova particle formation do not exist.

Moreover, a twenty year old controversy is still raging regarding the necessity of bacteria in the de nova formation of aggregates from seawater. Biddanda (1985) found that particle formation occurred in filtered seawater kept idle, circulated or bubbled (with or without the addition of additional DOM and POM) only in the presence of bacteria. Bacteria growing at the expense of the DOM present formed large particles >100 um by aggregation. Killed treatments did not show any particle formation of the type described by Baylor and Sutcliffe (1963), Sheldon et al. (1967) or Krank and Milligan (1980).

A second mechanism of aggregate production from DOM involves the adsorption of surface active dissolved molecules onto the surfaces of bubbles in the sea. The subsequent dissolution of the bubble results in a collapse of the surface coating forming a flake or microaggregate of particulate matter. Dissolved substances which are known to produce stable monolayers include fatty acids, proteins, sterols and fatty alcohols. The size of the aggregate produced is a function of the bubble size (Johnson and Cooke, 1980, Fig. 5), and small particles may also become incorporated into the flakes. Large bubbles appear to scavenge surface active materials less efficiently/unit surface area then smaller bubbles.

Although the qualitative process of aggregate formation from bubble dissolution is well documented, little quantitative information exists regarding its importance as a source of aggregates in nature. Dissolution rates indicate that most bubbles injected to a depth of 20 m in the ocean produce particles (Johnson and Cooke, 1980) although the surface organic coating can serve to stabalize the bubbles and prolong their life (Johnson and Cooke, 1981). While aggregate production from dissolving bubbles is clearly linked to wave action and weather

patterns at the sea surface, much additional quantitative information is needed on the rate of aggregate production in surface waters by this mechanism to assess its impact on the abundance and size distribution of aggregates in the sea.

A third mechanism by which DOM is converted to aggregated particulate matter is through the activity of marine microorganisms, primarily bacteria. Bacteria assimilate DOM and form capsular and fibriller materials outside their cell walls. This material apparently helps to glue together particles, thus enlarging aggregates (Paerl, 1974). Although Paerl (1973) observed some aggregation of dissolved and particulate matter within sterile dialysis bags, aggregates were 10 times larger in non-sterile bags containing bacteria at natural concentrations. Particles formed by bacterial aggregation are held together by web-like structures of microfibrils produced by the bacteria on the particles. Considerable quantitative information exists on the assimilation and growth rates of marine bacteria, although this information has not been directly applied to problems of bacterial aggregation in situ.

In conclusion, while the mechanisms of the biological formation of aggregated organic matter are fairly well described, little quantitative information exists on the rates at which each of these mechanisms alters the abundance and size distribution of particles in nature. With the exception of the feeding biologies of zooplankton, the environmental factors altering those rates are largely unknown. Quantitative information on the environmental constraints of aggregate formation, the rate of aggregate production under various conditions and the relative significance of each mechanism in different oceanographic regimes or seasons is required in order to make accurate quantitative predictions of the abundances and size distributions of aggregates at any particular time and place in the ocean.

PROCESSES WHICH REMOVE OR BREAKDOWN AGGREGATES

The mechanisms by which aggregates are removed from the pelagic zone has been more extensively studied than processes of formation. Two major biological processes contribute to the removal or size reduction of aggregates; consumption by zooplankton or nekton and decomposition by microorganisms. Physical processes include settling, lateral advection, and particle fragmentation via turbulence and mixing.

1. Consumption: The primary resul of consumption is to reduce the size and alter the physical and chemical characteristics of aggregates. While most zooplankton repackage small particles into larger ones, thus shifting the particle size spectrum toward the large size fractions, some zooplankton and nekton, including salps, doliolids and fish, consume large macroaggregates, repackaging them into smaller, but more compact and dense fecal pellets (Alldredge and Madin, 1982). Small copepods and euphausiid larvae also feed on the surfaces of macroaggregates and produce small fecal pellets (Alldredge, 1976). Many fecal pellets are consumed in the mixed layer. Hoffman et al. (1981) found only 0.2% of daily production reached the benthos as fecal pellets on the southeastern continental shelf. Likewise Bishop et al. (1977) found >94% of produced organic matter, much of it "fecal matter" and fecal pellets, was recycled in the upper 400 m of the North Atlantic.

Other investigations indicate that fecal pellets can be a significant component of vertical flux (Dunbar and Berger, 1981). Many are incorporated into marine snow (Turner and Ferrante, 1979), thus becoming unavailable to smaller particle feeders. Consumption of aggregates ultimately reduces their food value. Thus coprophagy may be most significant in nutritionally dilute environments where more nutritional foods are less available (Angel, 1984).

These and other studies suggest that consumption of aggregates, particularly fecal pellets, may be a significant sink for aggregated particulate matter.

2. Decomposition: The role of microorganisms as decomposers in the pelagic zone and the rates at which decomposition occurs have been the subject of considerable study. Bacterial decomposition primarily alters the chemical composition and nutritional value of aggregates. The C:N ratios and % of refractory matter in aggregates increases with depth (Riley, 1970) suggesting that aggregates become nutritionally depleted with age.

However, decomposition may not be a major pathway by which aggregates become fragmented or reduced in size in nature. Less than 10% of heterotrophic activity in seawater is associated with attached bacteria (Azam and Hodson, 1977; Ducklow and Kirchman, 1983). While the bacteria associated with aggregates are as metabolically active per cell as free-living forms, they are only rarely more active (Alldredge et al., 1986). Moreover, utilization of labile material on marine aggregates occurs very rapidly following formation. Rapid microbial growth occurs within the first 48 h and by 96 h most microbial activity had ceased (Pomeroy and Deibel, 1980). The majority of marine aggregates in nature appear to be nutritionally spent. Although some fragmentation of very flocculent particles may occur as labile matter is decomposed, microbial activity appears to aggregate rather than fragment particles (Paerl, 1973, 1974).

Fragmentation of fecal pellets may also be relatively insignificant. The peritrophic membranes of copepod fecal pellets decompose within 3 h at 20°C but 3 days at 15°C and 20 days at 5°C (Honjo and Roman, 1978). Pellets probably decompose slowly in surface waters of temperate and polar seas and experience reduced fragmentation once they sink to the thermocline in tropical seas. Much further research is needed to quantify decompositon as a process fragmenting aggregates in nature.

3. Sinking: Sinking is a major mechanism by which aggregates are removed from the pelagic zone. Dr. Silver (this publication) has described published rates of sinking for marine snow and fecal pellets. Although sedimentation is not a biological process, I wish to present some unpublished data here on sinking of marine snow which may prove relevant to later discussion.

We have determined the rate at which completely undisturbed aggregates of marine snow sink in nature by measuring the time required for particles to sink in situ relative to a stationary, neutral spot of dye placed 3 cm below them in the water column. We then photographed and collected these aggregates. Sinking rates of marine snow was a log function of particle mass and a linear function of mean particle length (Fig. 4). Sinking rates varied from 18 to 200 m d^{-1} with maximum rates observed by particles 4-8 cm maximum length. Reynolds numbers ranged from hundreds to thousands. Densities of marine snow are near that of seawater. Greater than 80% of the particles have densities of 1.025-1.030 g cm^{-3} (Fig. 4).

Rapid settling rates such as these strongly suggest that settlement is a major mechanism by which aggregates, including fecal pellets and marine snow, are removed from the pelagic zone. These particles are the most abundant components of many sediment trap collections. However, the affects of turbulent mixing, entrainment and other physical processes on the sinking behavior and loss of aggregates has received relatively little attention. Rapid sinking rates do not necessarily mean that all particles settle out immediately. Many may be retained in the mixed layer or accumulate at the thermocline. Considerably more information on the affects of physical mixing processes on aggregate abundance, depth distributions and sinking is needed before the role of sedimentation as a mechanism of aggregate loss to the water column can be adequately accessed.

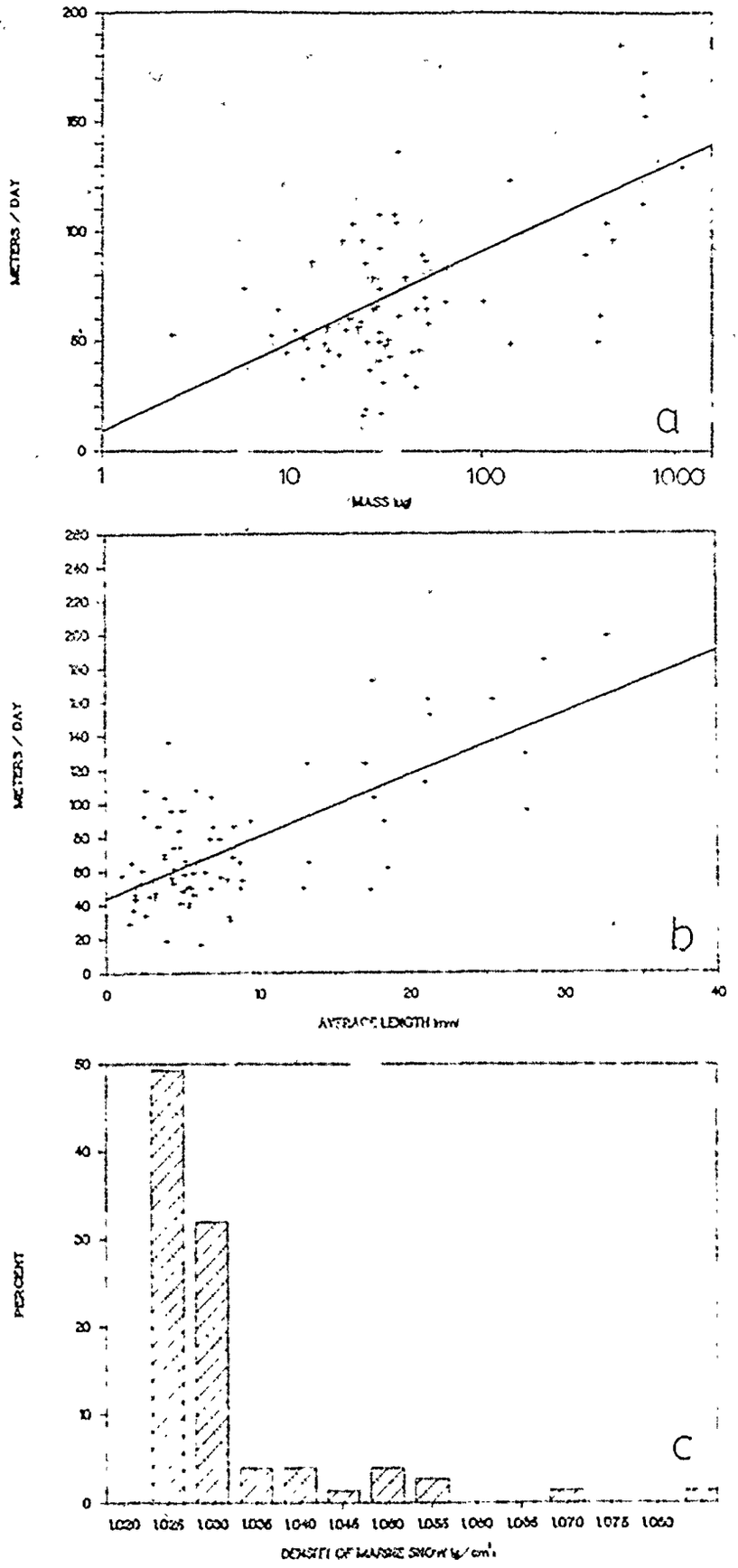


FIGURE 4: Sinking rate of marine snow measured in situ as a function of particle dry weight (A) and average length (B). C. Density of marine snow, n= 85. (A1 dredge, unpublished).

CONCLUSIONS

While the major mechanisms of aggregate formation and loss have been identified, only in a few instances does our understanding of these mechanisms extend beyond mere qualitative description. If we are to clearly understand aggregate dynamics and make meaningful predictions regarding the abundance and size distributions of aggregated particulate matter occurring in the ocean on meaningful space and time scales, considerably more quantitative information is required. Information of the following types would greatly enhance our understanding of aggregate dynamics in the sea.

1. Mechanisms of aggregate formation must be more clearly understood. While some mechanisms, including fecal pellet formation, marine snow production by mucus-producing zooplankton, and microaggregate formation by bubble dissolution have been well studied, even good qualitative information is still needed for others. The mechanisms of de nova particle formation need to be clarified and the controversy regarding the role of bacteria in this process layed to rest. Mechanisms of bacterial aggregation need clarification, as do those for aggregation of senescent diatoms.

2. Chemical, biological or physical "markers" need to be identified for each mechanism of aggregate formation in order to identify the source of various aggregates in nature.

3. Quantitative information is needed for all processes including:

   a. What conditions are necessary for each process to occur?

   b. What are the physical, chemical and biological characteristics of aggregates produced by each process?

   c. At what rate does each process occur in nature?

   d. What factors influence these rates and how?

e. What is the relative importance of each mechanism of formation and loss under various types of environmental conditions, seasons, or oceanographic regimes?

LITERATURE CITED

Alldredge, A.L. 1972. Abandoned larvacean houses: A unique food source in the pelagic environment. Science 177:885-887.

Alldredge, A.L. 1976a. Discarded appendicularian houses as sources of food, surface habitats, and particulate organic matter in planktonic environments. Limnol. Oceanogr. 21:14-23.

Alldredge, A.L. 1979. The chemical composition of macroscopic aggregates in two neritic seas. Limnol. Oceanogr. 24:865-866.

Alldredge, A.L. and L.P. Madin 1982. Pelagic tunicates: Unique herbivores in the marine plankton. Bio. Sci. 32:655-661.

Alldredge A.L., J.J. Cole and D.A. Caron 1986. Production of heterotrophic bacteria inhabiting macroscopic organic aggregates (marine snow) from surface waters. Limnol. Oceanogr. 31:68-78.

Angel, M.V. 1984. Detrital organic fluxes through pelagic ecosystems. In Flows of Energy and Materials in Marine Ecosystems, M.J.R. Fasham, ed., Plenum Publish Co., pp. 475-516.

Azam, F. and R.E. Hodson 1977. Size distribution and activity of marine microheterotrophs. Limnol. Oceanogr. 22:492-501.

Baylor, E.R. and W.H. Sutcliffe Jr. 1963. Dissolved organic matter in seawater as a source of particulate food. Limnol. Oceanogr. 4:369-371.

Berger, W.H. 1976. Biogenous deep sea sediments: Production, preservation and interpretation. In Chemical Oceanography, J.P. Riley and R. Chester, eds., Academic Press, London.

Biddanda, B.P. 1985. Microbial synthesis of macroparticulate matter. Mar. Ecol. Prog. Ser. 20:241-251.

Billet, D.S.M., R.S. Lampitt, A.L. Rice and R.F.C. Mantoura 1983. Seasonal sedimentation of phytoplankton to the deep sea benthos. Nature, Lond. 302:520-522.

Bishop, J.K.B., J.M. Edmond, D.R. Ketten, M.P. Bacon and W.B. Silker 1977. The chemistry, biology and vertical flux of particulate matter from the upper 400 m of the equatorial Atlantic Ocean. Deep Sea Res. 24:511-548.

Caron, D.A., P.G. Davis, L.P. Madin and J. McN. Sieburth 1982. Heterotrophic bacteria and bacterivorous protozoa in oceanic macroaggregates. Science 218:795-797.

Cauwet, G. 1978. Organic chemistry of sea water particulates-concepts and developments. Oceanologica Acta 1:99-105.

Davies, J.M. and R. Payne 1984. Supply of organic matter to the sediment in the northern North Sea during a spring phytoplankton bloom. Mar. Biol. 73:315-324.

Degens, E.T. and V. Ittekot 1984. A new look at clay-organic interactions. Mitt. Geol.-Palaont. Inst. Univ. Hamberg 56:229-248.

Ducklow, H.W. and D.L. Kirchman 1983. Bacterial dynamics and distribution during a diatom bloom in the Hudson River Plume, USA. J. Plank. Res. 5:333-355.

Dunbar, R.B. and W.H. Berger 1981. Fecal pellet flux to modern bottom sediment of Santa Barbara Basin (California) based on sediment trapping. Geol. Soc. Amer. Bull. 92:212-219.

Eppley, R.W., E.H. Renger and P.R. Betzer 1983. The residence time of particulate organic carbon in the surface layer of the ocean. Deep Sea Res. 30:311-323.

Fryxell, G.A., R.W. Gould Jr. and T.P. Watkins 1984. Gelatinous colonies of the diatom Thalassiosira in the Gulf Stream warm core rings, including T. fragilia, sp. nov. Jr. Phycol 19:141-156.

Gilmer, R. 1972. Free-floating mucus webs: A novel feeding adaptation for the open ocean. Science 176:1239-1240.

Heyraud, M. 1979. Food ingestion and digestive time transit times in the euphausiid Meganyctiphanes norvegica as a function of animal size. J. Plank. Res. 1:301-311.

Hoffman, E.E., J.M. Klinck and G.-A. Paffenhofer 1981. Concentrations and vertical fluxes of zooplankton fecal pellets on a continental shelf. Mar. Biol. 61:327-335.

Honjo, S. 1982. Seasonality and interaction of biogenic and lithogenic particulate flux at the Panama Basin. Science 218:883-884.

Honjo, S. and M.R. Roman 1978. Marine copepod fecal pellets: production, preservation and sedimentation. J. Mar. Res. 36:45-57.

Jensen, L.M. and Sondergaard 1982. Abiotic formation of particles from extracellular organic carbon released by phytoplankton. Microbial Ecol. 8:47-53.

Johnson, B.D. and R.C. Cooke 1980. Organic particle and aggregate formation resulting from the dissolution of bubbles in seawater. Limnol. Oceanogr. 25:653-661.

Johnson, B.D. and R.C. Cooke 1981. Generation of stabalized microbubbles in seawater. Science 213:209-211.

Krank, K. and T. Milligan 1980. Macroflocs: Production of marine snow in the laboratory. Mar. Ecol. Prog. Ser. 3:19-24.

Krause M. 1981. Vertical distribution of fecal pellets during FLEX '76'. Helgol. Meeresunter 34:313-327.

McCave, I.N. 1984. Size spectra and aggregation of suspended particles in the the deep ocean. Deep-Sea Res. 31(4):329-35.

Neihof, R.A. and G.J. Loeb 1974. Dissolved organic matter in sea water and the electric charge of immersed surfaces. J. Mar. Res. 32:5-12.

Paerl, H.W. 1973. Detritus in Lake Tahoe: Structural modification by attached microflora. Science 180:496-498.

Paerl, H. 1974. Bacterial uptake of dissolved organic matter in relation to detrital aggregation in marine and freshwater systems. Limnol. Oceanogr. 19:966-972.

Paffenhofer, G.-A. and S.C. Knowles 1979. Ecological implications of fecal pellet size, production and consumption by copepods. J. Mar. Res. 37:35-49.

Pomeroy, L.R. and D. Deibel 1980. Aggregation of organic matter by pelagic tunicates. Limnol. Oceanogr. 25:643-652.

Prezelin, B.B. and A.L. Alldredge 1983. Primary production of marine snow during and after an upwelling event. Limnol. Oceanogr. 28:1156-1167.

Riley, G.A. 1970. Particulate matter in sea water. Adv. Mar. Biol. 8:1-118.

Sheldon, R.W., T.P.T. Evelyn and T.R. Parsons 1967. On the occurrence and formation of small particles in seawater. Limnol. Oceanogr. 12:367-375.

Smetacek, V.S. 1980. Annual cycle of sedimentation in relation to plankton ecology in Western Kiel Bight. Ophelia, Suppl. 1:65-76.

Smetacek, V.S. 1985. Role of sinking diatom life-history cycles: ecological, evolutionary and geological significance. Mar. Biol. 34:239-251.

Smetacek, V.S., B.V. Bodungen, B. Zeitzchel and W. Zenk 1978. Sedimentation of particulate matter during a phytoplankton spring bloom in relation to the hydrographical regime. Mar. Biol. 47: 211-226.

Sholkovitz, E.R. 1976. Flocculation of dissolved organic and inorganic matter during the mixing of river water and seawater. Geochemica et Cosmochemica Acta 40:831-845.

Turner, J.T. and J.G. Ferrante 1979. Zooplankton fecal pellets in aquatic ecolsystems. Bioscience 29:670-677.

Walsh, J.J. 1983. Death in the sea: Enigmatic phytoplankton losses. Progr. Oceanogr. 12:1-86.

Wangersky, P.J. 1978. Production of dissolved organic matter. In Marine Ecology, O. Kinne, ed., John Wiley and Sons: New York.

Wassmann, P. 1983. Sedimentation of organic and inorganic particulate material in Lindaspollene, a stratified, land-locked fjord in western Norway. Mar. Ecol. Prog. Ser. 13:237-248.

State of the Art Instrumentation for Measuring Ocean Aggregates

by

Kendall L. Carder, David Costello, and Robert G. Steward

Introduction

Ocean aggregates, by their very nature, are more difficult to measure accurately than nonaggregated particles in a laboratory. They can be extremely friable and are easily disintegrated. Shear forces as small as 0.2 dyn cm^{-2} can break apart loosely associated, high order estuarine aggregates (Krone, 1976). Their size and shape may also change by colliding with other particles in the water column or on surfaces of vessels used in the sampling or measurement processes. Fresh biologically aggregated fecal pellets can often be handled repeatedly without disintegration. Older, biochemically altered pellicles, on the other hand may be quite friable.

Because of the susceptibility of aggregates to modifications in size, shape, and other properties prior to or during measurement, certain *in situ* techniques provide inherently less intrusive measurements of aggregates than do laboratory methods. Also, because of the heterogeneity of particle size and composition in the ocean, methods that extract individual particle characteristics or properties from the measurements are inherently superior to bulk measurements. As

a result, the major portion of this review will concentrate on in situ methods for measuring individual particles, or laboratory measurements that might be adapted to in situ applications.

Physical Structure

Perhaps the most fundamental measurement of particle size is volume, which does not require a shape discriminator. Because of this, the sphere-equivalent diameter or radius of a particle is often used as a de facto particle size standard. Thus, instruments that measure volume directly (e.g. by use of particle electrical resistivity methods) provide particle volume data unbiased by shape. Unfortunately, these methods draw particles through a small oriface in a dielectric tube, often disrupting aggregates.

On the other hand, particle shape is very important for purposes of identifying or categorizing particles, calculating their drag, surface area, settling speed, optical properties and diffusion. Mathematical relationships among size categories (e.g. major and minor axes, perimeter, cross-sectional area, surface area, volume) can be provided given a general shape category for a particle. Because of the dependence of scattering and absorption coefficients on the areal cross section of particles projected normal to the incident light, for example, the shape and orientation of a particle also have significant effects upon optical measurements of a particle. Shape and orientation are also quite important to particle settling dynamics, especially for noncompact particles (Lerman, 1979).

Internal Structure

The internal structure of a particle is also important to its settling dynamics and its microscopic identification. For solid particles such as mineral grains and most fecal pellets, the internal mass distribution or mass density directly affects settling speed. Knowledge of particle density permits the general classification of ocean particles into heavy mineral, nonheavy mineral, fecal pellet, and other categories. It also permits the calculation of mass from a measured volume. This is important since the mass of individual ocean particles is generally too small for direct measurement.

Aggregates and lysed phytoplankton cells have a somewhat open internal structure. If seawater can effectively flow through the interstices of a particle, this occluded water can be considered in somewhat the same way as are pore waters in sediment. While it reduces the apparent mean density of the particle, if water can flow through as well as around the particle, it provides complications when making particle settling velocity calculations (see Appendix 1).

The flow or diffusion rate of sediment pore waters is often described in terms of porosity and tortuosity (see Berner, 1980). The porosity is considered the ratio of the volume of the interstices to the volume of the sediment and interstices. Tortuosity is a measure of the mean path length a water parcel must travel to move a unit distance in the vertical through the sediment. These concepts may be helpful when conceptualizing the occluded water or pore water of aggregates. The simplest pore is a tube. When falling parallel to its length, it would have a tortuosity of 1. The same tube falling at a 45° angle would have a tortuosity of 1.41. However, we can show by a simple

example that the pore water flushing rate of a settling aggregate is somewhat different than that for sediment, due in part to the pressure differential across the particle induced by the balance between inertial and drag forces.

Because the water inside a cylindrical tube falling vertically is not restricted, it might appear at first to provide little of the added buoyancy to the tube that would occur if the ends were capped off. However, there is significant drag on the inside of the tube, so much of the fluid inside is not flushed when it settles a distance equal to the tube length. As the diameter is reduced to capillary dimensions under laminar flow conditions, and as the tube is lengthened, a much larger fraction of the original fluid remains after it has settled a distance equal to its length (see Fig. 1 and Appendix 1). The drag of this retained water has provided an added "buoyancy" to the pipe, even though its tortuosity is still 1.0. Adding tortuosity will increase the drag of pore waters, reduce their flushing, and increase the "buoyancy" provided by the occluded pore waters.

Since we don't know the internal structure of aggregates, we can only make some estimates of porosity based upon other measureables and some assumptions. If we consider an aggregate of diameter d consisting of a collection of solid particles of density ρ_s and occluded water of density ρ_w, the porosity of the particle or water fraction is f_w, and the solid fraction is f_s. The mean density of the particle can then be expressed as

$$\bar{\rho} = \frac{M_s + M_w}{V_s + V_w} = \rho_s f_s + \rho_w f_w = f_s(\rho_s - \rho_w) + \rho_w,$$

where M_s and V_s are mass and volume of the solid part of the aggregate,

respectively. M_w and V_w are the mass and density of the water, respectively, and $f_s + f_w = 1$. Since the water density is known, methods for determining $\bar{\rho}$ and ρ_s are required in order to determine f_s and f_w.

The density ρ_s of the solid or nonaqueous part of an aggregate can be determined by allowing it to settle to it own density level in an isotonic density gradient. Given time the original pore waters of the aggregate will be replaced by the density gradient media due to flushing and diffusion (Carder and Steward, 1984), and the density at any depth of the gradient can be determined from its index of refraction.

If one assumes that by a combination of tortuosity and high capillarity (long, narrow pores), flow through the aggregate is small compared to flow around it, the mean density of the aggregate $\bar{\rho}$ can be determined by inverting Stokes settling equation. For a sphere of diameter, d, this becomes

$$\bar{\rho} = \frac{\rho_w + 18 w_a \eta}{980\ d^2}$$

where w_a is the aggregate settling speed and η is the water viscosity. A method for measuring the flushing rate or flow through the aggregate in lieu of the above assumption is discussed in Appendix 2.

This exercise has allowed us to focus on the types of measurements required to better understand the settling dynamics of particles and aggregates, but the mechanics of aggregation and disintegration should also be mentioned. Aggregates form as a result of collisions between particles. These collisions can be caused by at least four mechanisms

(see Lerman, 1979): i) Brownian motion-induced particle diffusion; ii) water shear; iii) differential settling speeds; iv) and biological filtering or scavenging. In additon, retardation of settling and particle buildup on density interfaces enhances the probability of collisions or biological filtering and scavenging.

The first mechanism is most important in causing aggregation of colloidal or small particles under low shear conditions (e.g. $du/dz < 0.1\ sec^{-1}$), while differential settling is most effective for larger particles. Water shear is the dominant mechanism for $du/dz > 0.5\ sec^{-1}$ (Lerman, 1979). Water shear is typically most effective above the pycnocline and in the near bottom nepheloid layer. Both regions are usually regions of significant vertical shear. The sheet and layer, stepped density structure in the pycnocline provides a region where low density particles slow or accumulate at density interfaces, greatly increasing the probability of particle collisions. Here, also, there is a likelihood that detrital filter feeders would concentrate.

The primary disintegration mechanism for aggregates is high shear stress. Krone (1976) points out the shear strength of various orders of estuarine aggregates, above which disaggregation to a lower order aggregate occurs. Storms, breaking internal waves, and high bottom stress are candidate mechanisms for causing stresses exceeding ocean aggregate shear strength.

Optical Properties of Particles

The effects of particle shape and index of refraction are secondary to the effect of particle size on light scattering in the ocean (Jerlov, 1976). This property is exploited by particle sizing

instruments that measure the particle attenuation coefficient c_p or estimate the particle scattering coefficient b_p.

In general, all of the light energy impinging directly on a large particle of geometrical cross section G is scattered or absorbed, while an equal amount of light energy passing near the particle is scattered by diffraction (e.g. recall Babinet's principle, Van de Hulst, 1957). Thus the ratio of the total energy removed by a particle from a proceeding wave to the energy physically intercepted by a particle of cross sectional area G corresponds to an attenuation cross section or efficiency factor $Q_c \doteq 2 = Q_a + Q_b$. Q_a and Q_b are the absorption and scattering cross sections, respectively.

For sizing purposes, then, the attenuation coefficient for a spherical particle i is

$$c_i = G\,Q_c$$

or

$$c_i = \frac{\pi d_i^2}{4} Q_c \doteq \frac{\pi d_i^2}{4}(2) = \frac{\pi d_i^2}{2},$$

the absorption coefficient is

$$0 \leq a_i = \frac{\pi d_i^2}{4} Q_a \leq \frac{\pi d_i^2}{4}(1),$$

and the scattering coefficient is

$$1 \leq b_i = \frac{\pi d_i^2}{4} Q_b \leq \frac{\pi d_i^2}{2}\ .$$

An important question, then is "what constitutes a large particle?" For spherical particles with real refractive indices near 1.0 relative to the medium, Van de Hulst (1957) has derived

relationships among Q_a, Q_b, and Q_c, particle diameter d, and the refractive index m relative to the medium. These relationships are shown in Figure 2, where rho = $2\pi\eta_w d(m-1)/\lambda$, λ is the wavelength in vacuo, and η_w is the refractive index of water. It is clear that when rho is smaller than about 3, the particle becomes an inefficient scatterer, and when rho exceeds 8 to 10, $Q_c \doteq 2$, regardless of the absorbtion coefficients (related to the imaginary part η' of the refractive index according to $\eta' = a_p\lambda/4\pi$). Increases in η' force Q_c closer to 2 for smaller rho values, and decrease Q_b values to 1.0. Again for large rho values, Q_c is much less variable than Q_b.

For phytoplankton, the absorption coefficient a_p is less than 15% of the attenuation coefficient for much of the visible light spectrum (550-640 nm) (Bricaud et al. 1983).

Since $c_p = a_p + b_p$, then $b_p \geq 0.85\ c_p$. For quartz grain , $b_p \doteq c_p$. However, for large opaque particles such as certain fecal pellets, the absorption coefficient can equal the total scattering coefficient, or $b_p = 0.5\ c_p$. Because of the variation in a_p in the oceans, attenuation or c meters are inherently more accurate than scattering or b meters as particle sizing devices.

In order that an optical particle sizing meter measure the signal due to a single particle rather than from an ensemble of particles, the measurement or sampling volume must be very small, or the particle concentration must be very dilute. Two methods are presently in use by automatic laboratory particle sizing and counting devices to increase the odds of measuring single particles. One method used by HIAC/ROYCO draws the media fluid through a narrow flow constriction (e.g. 100 μm x 1000 μm cross section), inducing turbulence to make the particles

tumble. The largest particle cross section presented to the 100 μm x 100 μm cross section of collimated light passing across this constriction is recorded as a pulse height and counted.

A second method, used by Spectrex, focuses a scanning laser beam down to a narrow waist where an illuminated particle will intercept the greatest fraction of the incident radiant flux and provide the largest scattered or attenuated signal. Pulse length discrimination is used to reject signals that are too short (particle at the beam edge) or too long (particle not at the beam waist) to have been centered in the intensity maximum at the waist of the scanning beam. This method requires no fluid flow and thus is less destructive, but the pulse discrimination process provides about a 15% uncertainty in the projected cross sectional area of the particle. The methods also differ in that the first measures the "largest" areal dimension of a particle, while the second measures a random areal dimension. The scanning beam method in present use measures near-forward scattered light rather than light attenuation, adding an additional uncertainty if the particle absorption coefficient of particles is heterogeneous. However, the attenuation principle could be incorporated together with the scanning beam methodology to avoid the absorption uncertainty.

These automatic techniques are probably both adaptable to in situ observations, but discrimination of one particle type from another except by size would not be possible. That is the reason particle imaging and sizing systems are most commonly in use for studying marine particles and aggregates in situ.

Particle Imaging Methods

The in situ methods presently in use for imaging particles and aggregates fall into two categories: photographic and holographic. Because vidicon tubes and area array sensors for television have an order of magnitude lower resolution than photography, they can be considered for only low resolution photographic applications. For this reason, they are not considered independently in this review even though they provide real time data.

The choice of methodology used to image particles is often dependent upon the size of the particles of interest. As a rule of thumb, the number of particles of diameter d in the ocean decreases as the function d^{-k}, where k is typically between 3 and 4. For living particles Sheldon et al. (1972) found a value of about 3, while for all particles, a value near 4 may be more representative (see Lerman et al. 1977).

With a paucity of particles at larger sizes, one must either measure a given volume continuously for a long time to observe a statistically representative population of large particles, increase the volume of water imaged, or use a concentration mechanism. Because the depth of field of a photographic system is inversely proportional to its magnification, high magnification systems have very little depth of field. The odds of a free-falling or floating particle of the appropriate size occurring at the focal distance may be quite small, unless they come to rest on a fixed horizontal, optical surface such as the bottom of a sediment trap. However, photographic systems can be quite useful for the in situ imaging of large particles where magnification can be much less than 1.0, providing for adequate depths of field for large sample volumes.

The photographic methods are typically used to image large particles and aggregates with fractional magnification values to increase the depth of field. A large sample volume increases the probability that a particle of interest (e.g. marine snow) will be in the sampling volume. The cost of increasing the sample volume in this way is an image that appears to be perhaps 25% longer and wider at the near edge of the volume than it does at the far edge, even with a "perfect" pinhole camera (see Fig. 3). For an actual camera with a finite aperture, the particle images will appear to be out of focus at the near and far edges of the sample volume. Reduction in the depth of the sample volume ameliorates both the magnification and the focusing problem, but reduces the number of particles imaged. Increasing the radiant flux of the source and/or the sensitivity of the film can provide a larger f-stop for the system, improving the depth of focus by reducing the camera aperture.

At least two in situ photographic particle imaging and sizing systems are presently in use for measuring aggregates and particles. One of moderate resolution (diameter > 50 μm) measures backscattering along with photographic images with 1/4 magnification (Johnson and Wangersky, 1985). The backscattering meter is used to activate a strobe only when imaging larger particles or organisms. While the sample volume of the imaging system is not discussed, it appears to be of order 10-20 ml.

A system of lower resolution (diameter > 500 μm; 1/40 magnification) but much larger sample volume (.66 m^3) has been been described by Honjo et al. (1984) for studying large amorphous

aggregates or marine snow. A particle at the near edge of the sample volume relative to the camera would appear to be about 29% larger than would the same particle at the far edge (e.g. see Fig. 3). This ± 14.5% uncertainty in size could be easily reduced by narrowing the depth of the lighted or sample volume viewed. This modification and others will be discussed in detail by Vernon Asper in a later talk.

Methods using holographic microscopy are more useful for measurement systems requiring image magnification, since the diffraction patterns from all particles in a volume are recorded rather than the images from the particles at a given focal plane. In the image reconstruction process the diffraction patterns on the film diffract light such that images of the original particles can be formed by moving an image screen along the optical axis of the system (see Fig. 4). Transmission or Gabor holography has been the method of choice in ocean applications because of the inherent stability and low power requirements of the method.

Magnification of the diffraction patterns (already much larger than the original particle) onto the holographic film can be achieved with lenses (see Thompson et al., 1967; Carder et al., 1982), but most of the magnification is performed during the holographic reconstruction process. Total system magnification factors of more than 500 can be achieved (Costello et al., in press) with a sample depth of more than 3.5 cm. Typical sample volumes range from about 1 to 4 cm^3 (Carder et al., 1982). Adequate resolution of the reconstructed image is achieved if three or more diffraction rings are captured on the hologram and if the particle moves a distance less than 1/10 its diameter during the exposure (Thompson et al., 1967).

Holography is of additional interest in studies of aggregate behavior at density interfaces because the phase contrast due to differences in refractive index across the interface and mixing induced by settling particles can be visualized. Transmission or Gabor holography is adequate to visualize mixing between fluids of relatively high contrast in refractive index (see Appendix II), but for more sensitivity, multiple beam, multiple wavelength, multiple pass or double exposure holographic interferometry methods can be employed (Vest, 1979). Such studies are important because i) density interfaces increase the probability of aggregate formation, ii) aggregates cause mixing by flushing occluded water below the interface as low density, low viscosity cylindrical streamers, iii) these streamers provide a faster, preferred pathway for subsequent aggregates, and iv) because vertically elongated aggregates are formed when subsequent aggregates overtake slower aggregates in the streamer (see Appendix II). These density interface processes involving aggregates have ramifications on aggregate collision probabilities, size, shape, settling speed, fluid mixing, and most likely feeding behavior, and should be considered for study as the technology becomes available.

Photographic and holographic methods can both be used to measure particle settling speeds by taking sequential photographs or holograms. However, the fluid must not be moving relative to the imaging system, and gravity should be the only acceleration on the particles. Carder et al. (1982) and Costello et al. (in press) have achieved platform stability and stationary fluid conditions by holographically imaging particles inside a large sediment trap suspended from the surface by a system of damped buoys in tandem (see

Fig. 5). A constant downward particle settling velocity through multiple images confirms platform stability.

For studies of eolian mineral transport from Asia to and through the central north Pacific we have developed a multiple sample sediment trap equipped with vertical and horizontal axis holographic cameras. Figure 5 shows a 0.66 m^2 collection cone, horizontal camera and laser housings, a vertical camera housing, the sampling chamber assembly and battery pack/timer. The vertical laser is inside the collection cone. The sampling chamber has six collection cups with windows which are sealed except during sampling. The cone is deployed and retrieved open. One-way valves permit filling and flushing of the cone. A programmable delay of typically six hours is used to avoid sampling of most particles entrained in the cone during deployment. Then the first cup is pulled by a lead weight and locked into place. Burn wires are used to control the cup progression by releasing an elastic locking mechanism upon a signal from the timer.

A dense (1.11 gm/ml), viscous (0.053 poise), isotonic mixture of sugar, dextran and saltwater in the cups dramatically slows the speed of fecal pellets and minerals to permit multiple holograms of the same particles before they leave the 1 cm diameter laser beam. Typical frame rates are 1/minute to 1/15 sec. for the horizontal camera, and 1/6 minutes for the vertical camera. Each camera contains 250 exposures of 35 mm high speed holographic film (Kodak 50-253).

Reconstructed holograms of typical quartz-like particles, heavy minerals, fecal pellets, and aggregates are shown in Figure 6. The Stokes settling equation for prolate spheroids was used to calculate density values of about 2.6, 5.0, 1.136, and 1.12 gm/ml for

these classes of particles (Carder et al., in press). Fecal pellets captured at greater depth had densities as high as 1.21 gm/ml.

Other Methods

For robust particles such as some fecal pellets, laboratory measurements can be made to enhance our understanding of their nature. Light microscopy of carefully collected aggregates by SCUBA divers has been used (Alldredge, 1972). Scanning electron microscopy with individual particles electron dispersive x-ray analysis might be used on similarly collected aggregates to better determine the composition of the heavier elements of the aggregate components.

It is known that large aggregates break apart when passing through the Coulter Counter (Sheldon, 1967; Hunt, 1982), and the same fate may await aggregates passing through a flow cell cytometer, an instrument used to estimate individual particle size and fluorescent properties by light absorption, scattering and fluorescence (e.g. see Olson et al., 1985; Yentsch et al., 1983). For robust fecal pellets, it may be possible to qualitatively estimate their pigment content by fluorescence, and their degree of opacity may be a useful fecal pellet classifier. Sizing can be performed by either light attenuation or near-forward scattering techniques similar to those discussed earlier, and scattering at large angles is thought to provide a measure of internal structure and/or index of refraction (R. Spinrad, personal communication). More details about flow cell cytometry are provided later in the talk by K. Stolzenbach.

A final laboratory method useful for sizing nonodisperse distributions of very small (30 Angstroms to 3 μm) particle populations

is Photon Correlation Spectroscopy (PCS). It may be useful for studying Brownian motion induced aggregation since it provides a measure of the particle diffusion coefficient A_p. Since large particles diffuse more slowly than small ones due to the frictional drag of the water viscosity, the particle diameter can be expressed by the Stokes-Einstein equation as

$$d = \frac{kT}{3\pi A_p},$$

where k is the Boltzman constant and T is the absolute temperature (Ford, 1983). The Brownian motion of each particle imparts a small Doppler shift in the wavelength of the scattered light. This Doppler shift is too small to be effectively analyzed spectroscopically. However, interference between this doppler-shifted scattered light and that of incident light as a function of time produces a beat frequency at the receiver which increases as the Doppler-induced wavelength difference increases. Recalling that these beats are a measure of group wave or envelope frequency, the beat period γ is proportional to $\lambda/\delta\lambda$. The spectra of beat frequencies due to interference of scattered light from all particles in the sample volume are analyzed using the auto-correlation function of the scattered signal (Ford et al., 1973). The spectral distribution of the scattered intensity as a function of frequency ω is Lorentzian in shape

$$I(\omega) = \frac{(\text{constant})}{2 + (\omega-\omega_o)^2},$$

where ω_o is the incident frequency. It is centered around the

incident frequency w_o, with half-width at half-height of

$$\Gamma = A_p \frac{4\pi\eta}{V_o} \sin^2(\theta/2),$$

where A_p is the particle translational diffusion coefficient, η is the index of refraction of the medium, λ_o is incident wavelength, and θ is the scattering angle. Combination with the Stokes-Einstein expression permits determination of the effective diameter of a spherical particle.

It may be possible to use this photon correlation spectroscopy technique to observe the increase in the effective or mean diameter of a population of colloidal particles as Brownian motion induces aggregation. Instruments such as Langley Ford or the Coulter Model N4 are designed for laboratory use, and the method is vibration sensitive. Even the motility of micro-organisms affects the results, so use in a shore-based facility is probably a firm requirement for PCS applications at present. However, many colloidal particles form at the river-ocean interface, so this restriction may not be as severe as it first appears.

Summary

A number of optical methods are in use presently in laboratory instruments which may be adaptable for in situ applications. These include automatic particle sizing by light attenuation or light scattering methodologies. These methods do not provide particle shape and orientation discrimination, however.

For large particles (diameter > 50 μm) photographic techniques have been developed to measure particle size and shape, and these methods could be modified by particle measurement inside a stable sediment trap to measure particle settling speeds by taking sequential photographs of particle position. These methods sample volumes from about 10 ml to 0.6 m^3, with sizing accuracies of better than ± 15%, depending upon the magnification and sample depth.

For intermediate to small particles (nominally 5 μm to 5000 μm diameter), transmission holographic microscopy is being used to sequentially image particles in sample volumes of .5 to 4 cm^3, depending upon the application. Particle size, shape, orientation, position in three-space, and velocity in three-space are determined holographically for all particles in the sample volume. Magnification is uniform with particle distance from the camera, so size ambiguities do not result from the position of the particle in the sample. Particle size, shape and settling speed used with Stokes settling equations then provide a measure of the particle density. The flushing rate of occluded water for aggregates can be determined at density interfaces either holographically or using holographic interferometry.

A number of laboratory methods are not expected to be successfully adapted to in situ application. Flow cell cytometry equipped with

particle sizing by attenuation or scattering methodologies and fluorescence provides single particle or cell characteristics for classification and sorting. Shipboard sea trials have been successful. Photon correlation spectroscopy is not expected to be useful at sea because of effects of ship vibration on the motion of colloidal and small particle populations. For shore based facilities, experiments on the growth in size of colloidal and small aggregates due to Brownian motion induced collisions may be directly observable use photon correlation spectroscopy.

Acknowledgements

Special thanks to Richard Young for his invaluable assistance in preparing photographs of holographic reconstructions and to Carole Cunningham for her dedication in manuscript preparation. This research has been supported under NSF grant OCE-85-00739, NASA grant NAGW-465, and ONR contract N00014-75-C-0539 to the University of South Florida.

References Cited

Alldredge, A.L., 1972. Abandoned larvacean houses: a unique food source in the pelagic environment. Science 177: 885-887.

Berner, R.A., 1980. Early Diagenesis: a Theoretical Approach. Princeton Univ. Press, Princeton, N.J., 241 p.

Bricaud, A., A. Morel and L. Prieur, 1983. Optical efficiency factors of some phytoplankters. Limnol. Oceanogr. 28(5): 816-832.

Carder, K.L. and R.G. Steward, 1984. Evaluation of Stokes settling equation for variable density aggregates. Final Report, ONR Contract N000'4-83-K-0082, University of south Florida, St. Petersb :g, 14 p.

Carder, K.L., R.G. Steward, and P.R. Betzer, 1982. In situ holographic measurements of the sizes and settling rates of oceanic particulates. J. Geophys. Res. 87(C8): 5681-5685.

Carder, K.L., D. Costello, R. Young and P. Betzer, in press. Dynamics and composition of holographically recorded particles from A.IOS I. EOS, Fall AGU Meeting, Dece ber 1986.

Costello, D., R. Young, K. Carder and P. Betzer, in press. Multiple-sample sediment traps with in situ holographic imaging of p rticles. EOS, Fall AGU Meeting, December 1986.

Ford, N.C., Jr., 1983. Theory and practice of correlation spectroscopy. In B. Dahneke (ed.): Measurement of Suspended Particles by Quasi-Elastic Light Scattering, Wiley, New York.

Ford, N.C., Jr., R. Gabler and F.E. Karasz, 1973. Self-beat spectroscopy and molecular weight. Advances in Chemistry Se ies 125: 25-54.

Happel, J. and H. Brenner, 1973. Low Reynolds Number Hydrodynamics, 2n ' rev. ed., Noordhoff, Leyden.

Honjo, S., K.W. Doherty, Y.C. Agrawal and V.L Asper, 1984. Direct optical assessment of large amorphous aggregates (marine snow) in the deep ocean. Deep-Sea Research 32(1): 67-76.

Hunt, J.R., 1982. Particle dynamics in seawater: implications for predicting the fate of discharged particles. Environmental Science and Technology 16: 303-309.

Jerlov, N.G., 1976. Marine Optics, Elsevier, New York, 231 p.

Johnson, B.D. and P.J. Wangersky, 1985. A recording backward scattering meter and camera system for examination of the distribution and morphology of macroaggregates. Deep-Sea Research 32(9): 1143-1150.

Krone, R.B., 1976. Engineering interest in the benthic boundary layer. In I. McCave (ed): The Benthic Boundary Layer, Plenum, New York, 143-156.

Lamb, H., 1945. Hydrodynamics, 6th ed. Dover, New York.

Lerman, A., 1979. Geochemical processes water and sediment environments, Wiley, New York, 481 p.

Lerman, A., K.L. Carder and P.R. Betzer, 1977. Elimination of fine suspensoids in the oceanic water column. Earth Planet. Sci. Lett. 37: 61-70.

Olson, R.J., D. Vaulot and S.W. Chisholm, 1985. Marine phytoplankton distributions using shipboard flow cytometry. Deep-Sea Res. 32(10): 1273-1280.

Schlichting, H., 1955. Boundary Layer Theory. Pergamon, New York, 535 p.

Sheldon, R.W., A. Prakash and W.H. Sutcliffe, Jr., 1972. The size distribution of particles in the ocean. Limnol. Oceanogr. 17: 327-340.

Thompson, B.J., J.H. Ward and W.R. Zinley, 1967. Applications of hologram techniques for particle size analysis. Applied Optics 6(3): 519-526.

Van de Hulst, H.C., 1957. Light scattering by small particles, pp. 172-199, Wiley, New York.

Vest, C.M., 1979. Holographic Interferometry. Wiley, New York, 465 pp.

Yentsch, C.M., and others, 1983. Flow cytometry and cell sorting: A powerful technique for analysis and sorting of aquatic particles. Limnol. Oceanogr. 28: 1275-1280.

Figure Legends

Figure 1. Family of approximate settling velocity curves as a function of radius R for open (solid) and capped (open) circular tubes of varying length L, falling parallel to the long axis. The wall thickness dr is 0.1 times the radius, and the wall density is 2.65 gm/ml. Sea water density is 1.02 gm/ml and viscosity is 0.01 poise. Note that for long open tubes the settling speed approximates those of capped tubes (see Appendix 1 for details)

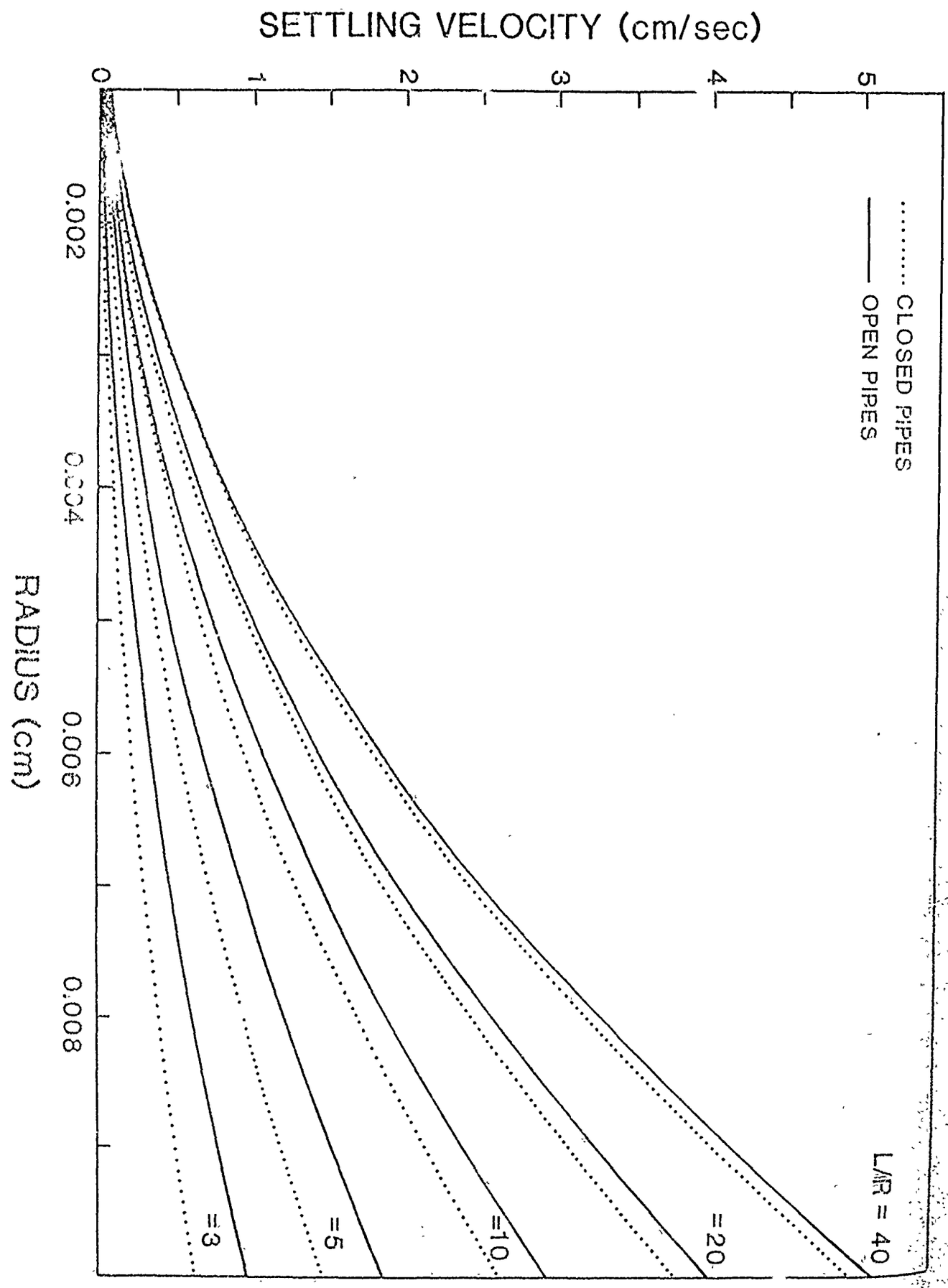
Figure 2. Families of curves for the cross sections for attenuation, total scattering and absorption as a function of rho for different values of the imaginary or absorbing part η' of the index of refraction. The parameter rho is the optical size of a particle and is defined in the text.

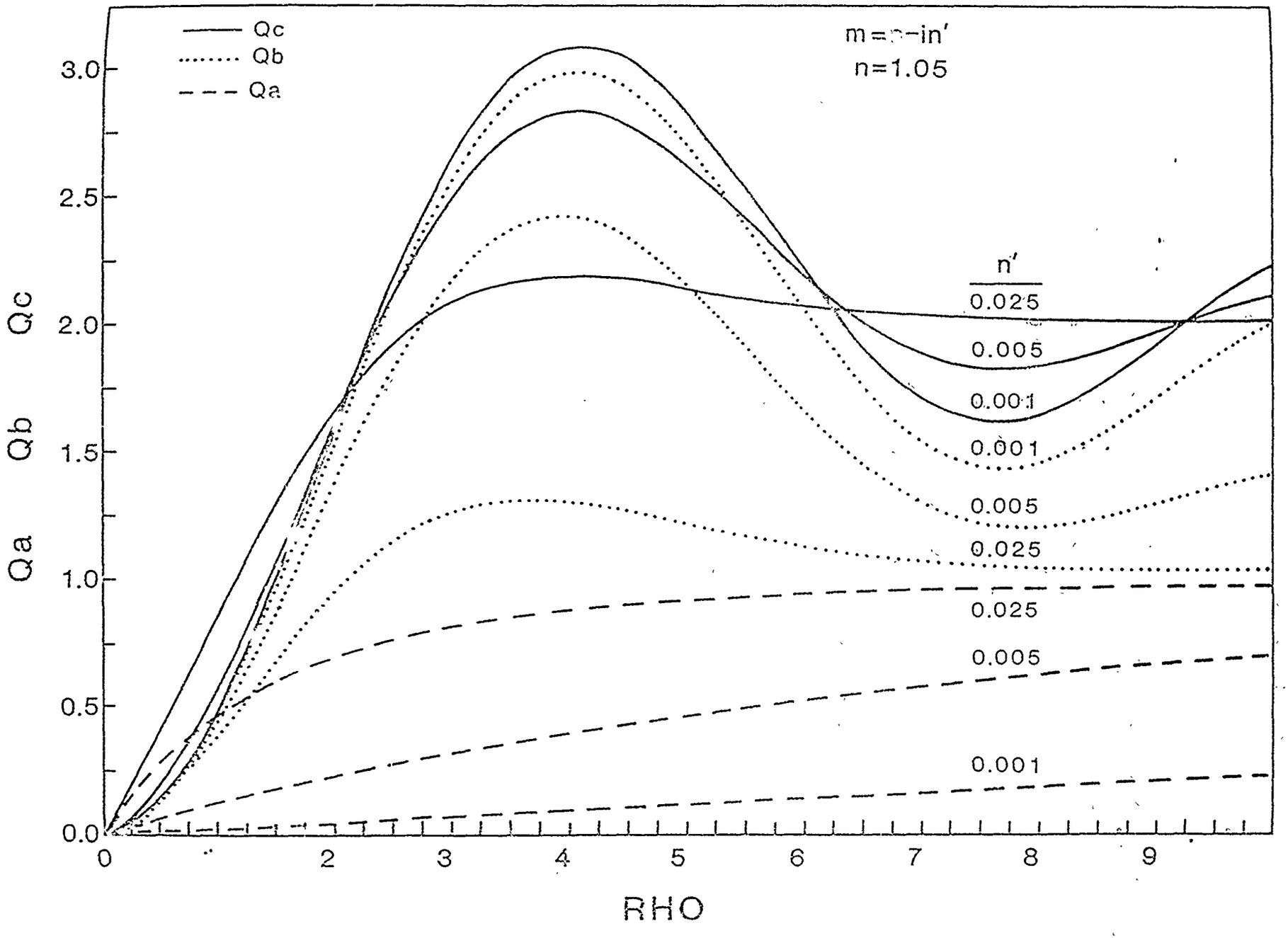
Figure 3. A schematic representation showing the ambiguity in particle size for a pinhole camera with a large depth of field. L_1 is the image on the film of either object L_1 or L_2, at the front and rear edges of the sample volume. L_2 is about 30% longer than is L_1.

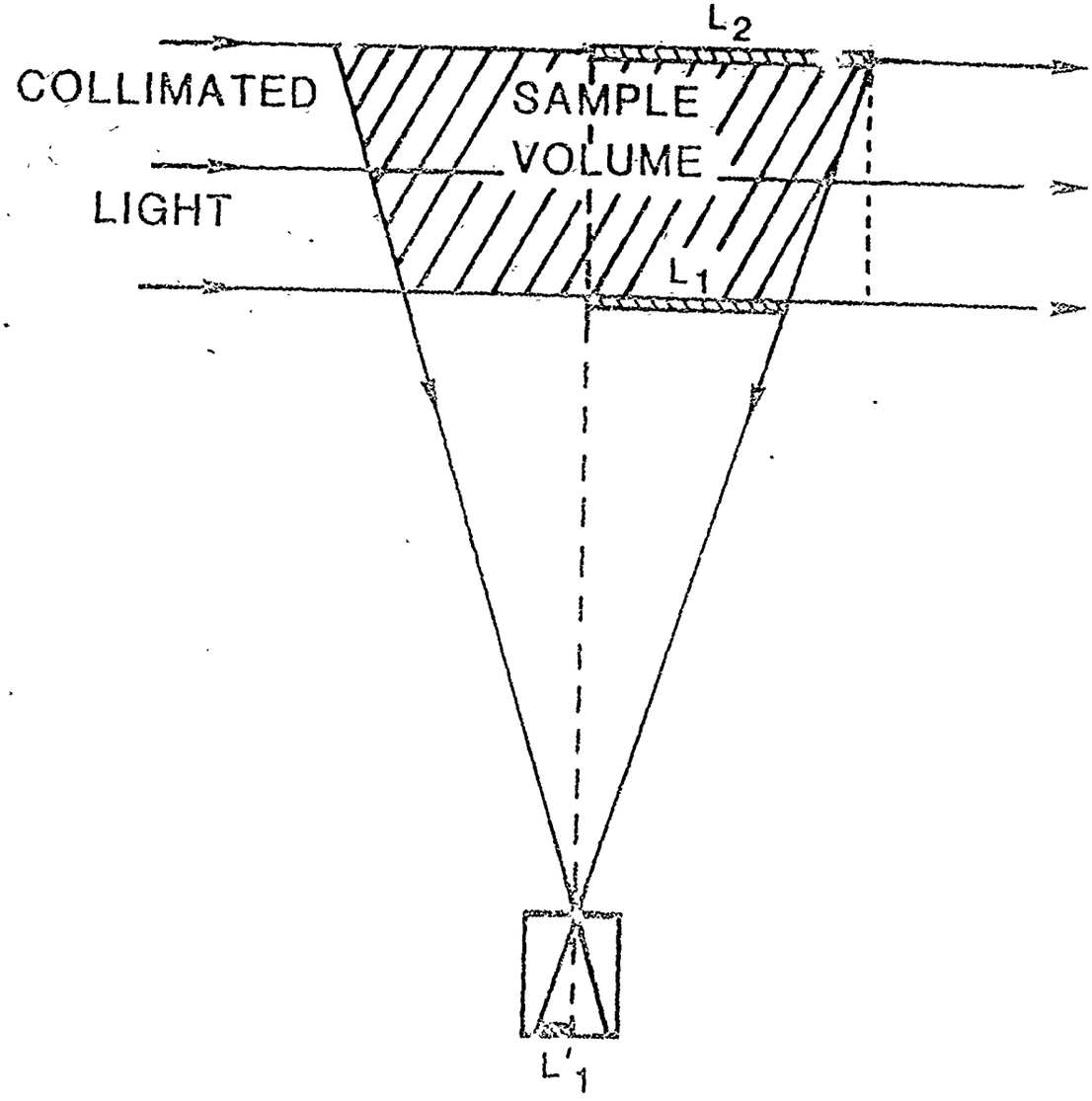
Figure 4. A schematic of Gabor or transmission holography. Planar wavefronts of a collimated laser beam are diffracted by a particle P. Diffracted light (spherical wavefronts) constructively interfere with planar wavefronts at the film plane producing high density or dark circular diffaction rings. Destructive interference occurs between the dark rings, providing low density or light rings. Placing the developed hologram back in the film plane and passing a collimated laser beam through it in the opposite direction causes light scattering off the diffraction rings themselves such that constructive interference occurs at P, creating the image of the original particle at the position P.

Figure 5. Drawing of a sediment trap equipped with horizontal and vertical axis holographic camera systems for viewing particles orthogo ally. At the apex of the inverted conical concentrator (A) is the six-cup viewing and sampling assembly (B). The timer/battery pack (horizontal cylinder at bottom) controls the timing sequence of cups (C), laser on/off cycles, and camera firing. Motive force for advancing cup assembly through sequentially fired registration pins (D) is provided by a lead weight in the long plexiglass sleeve (E) vertically attached to the trap frame. The horizontal laser housing (F), horizontal camera housing (G), and verticle camera housing (H) are shown.

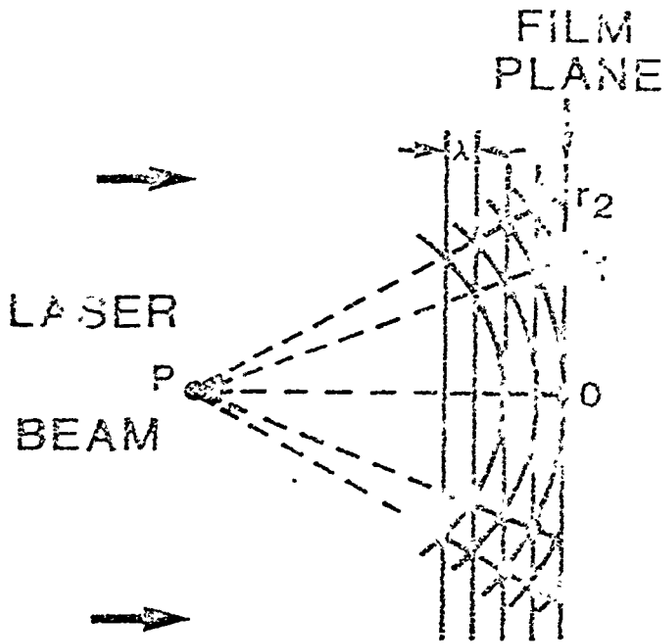
Figure 6. Photog aphs of reconstructed of in situ particles captured in the north central Pacific gyre during March/April, 1986.


SETTLING VELOCITY (cm/sec)
0
1
2
3
4
5
RADIUS (cm)
0.002
0.004
0.006
0.008
CLOSED PIPES
OPEN PIPES
L/R = 40
=20
=10
=5
=3


Qc
Qb
Qa
m=n-in'
n=1.05
n'
0.025
0.005
0.001
0.001
0.005
0.025
0.025
0.005
0.001
Qa Qb Qc
RHO
0.0
0.5
1.0
1.5
2.0
2.5
3.0
0
2
3
4
5
6
7
8
9


L_2
COLLIMATED
LIGHT
SAMPLE
VOLUME
L_1
L'_1


A
B
C
D
E
F
G
H



ROTATED VIEW OF
FILM OR HOLOGRAM

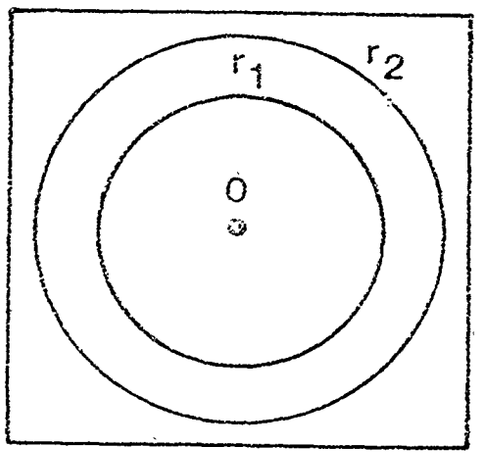


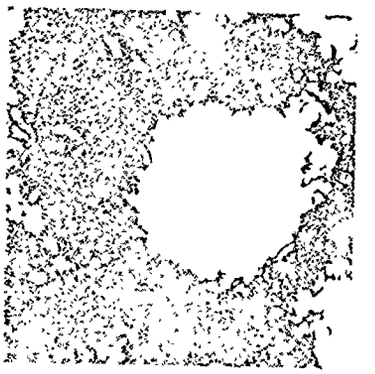
Figure 6. Holographic reconstructions of particles imaged in situ



a) Copepod: (37X)
850 um X 550um



b) Fecal pellet: (513X)
48.7um X 22.2um
1.136g/cc



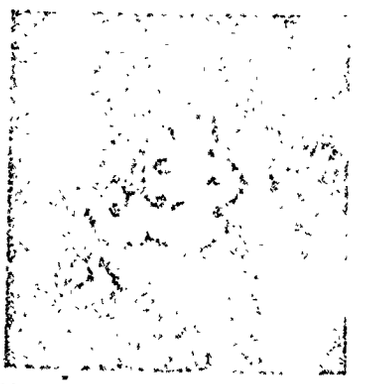
c) Fecal pellet: (258X)
90um dia., 1.137 g/cc
1.137 g/cc



d) Aggregate: (513X)
62.8um X 41.9um
1.12 g/cc



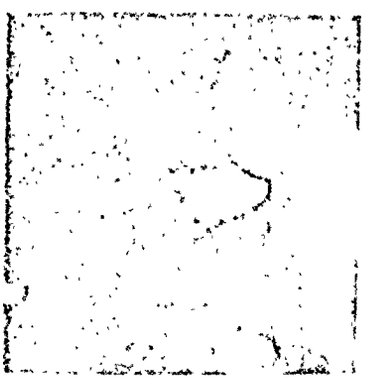
e) Aggregate: (513X)
54.2um X 52.4um
1.12 g/cc



f) Aggregate: (513X)
35.7um X 36.1um
1.12g/cc



g) Quartz: (513X)
31.6um X 21.1um
2.61g/cc



h) Heavy Minerals: (513X)
[illegible] X 15.3um
[illegible]

APPENDIX I

The flushing rate of aggregates is important to consider in terms of its effect on the buoyancy of particles. For many flocculated mineral materials, the flushing rates are of the order of minutes to tens of minutes and appear to be controlled by the rate of diffusion (Lerman, 1979; p. 311). In cases of aggregates stopping on density interfaces, the flushing time is of the order $t = L^2/D$, where L is the particle length and D is the molecular diffusion coefficient for salt or temperature. Except at density interfaces, the time it takes such aggregates to settle a distance L is typically short compared to the diffusional flushing rate, and flushing has little effect on the Stokes settling rate calculations.

For aggregates with larger structural components and pores, the effect of flushing rate on Stokes settling calculations and particle buoyancy may need to be considered. As a simple illustration, suppose a pore is modelled as a long, hollow tube of radius R and length L. If it settles parallel to L, a first order estimate of its drag is that for a long cylinder (Happel and Brenner, 1965):

$$F_D = \frac{2\ \pi\eta U_s\ L}{\ln\ (L/R) - .72} \qquad \text{(A1}$$

where η is the fluid viscosity and U_s is the settling speed. The pressure differential dp required at low Reynolds numbers to force water through the tube at mean internal velocity U_i is (Schlicting, 1955)

$$dp = - \frac{4\eta\ L\ U_i}{R^2} . \qquad \text{(A2}$$

In order to estimate the pressure differential between the bottom and top of the tube created by a settling velocity U_s, consider the drag force F_{DD} on a disk settling face down (Lamb, 1945; Happel and Brenner, 1973) in the limit of no thickness:

$$F_{DD} = 5.1\ \pi\ \eta\ U_s R. \qquad \text{(A3}$$

This equation approximates the part of the drag on a cylinder that results from the flat end surfaces.

Combining equations A2 and A3

$$dp\ (\pi R^2) = F_{DD}$$

$$\frac{4\ \eta\ L\ U_i}{R^2}\ (\pi R^2) = 5.1\ \pi\eta\ U_s\ R$$

or

$$\frac{U_i}{U_s} = \frac{5.1\ R}{4\ L} = 1.275\ R/L. \qquad \text{(A4}$$

Thus, for L/R = 10, the pore velocity U_i is about 13% of the settling speed. This result is for a vertically oriented tubular pore of uniform cross section and no tortuosity.

To consider the settling speed of a circular, thin-walled tube, the buoyancy force on the tube must be calculated, including that of the internal pore water carried with it. The volume of pore water carried with the tube in settling a distance equal to its length L is

$$V_{pore} = \pi R^2 L\ f_{pore}, \qquad \text{(A5}$$

$$\text{where } f_{pore} = \frac{U_s - U_i}{U_s} \qquad \text{(A6}$$

is the fraction of the pore retaining unflushed water.

The volume of the tube is

$$V_c = \pi L[(R + dr)^2 - R^2] \doteq 2 \pi L R dr \qquad \text{(A7}$$

for $dr << R$. The average density of the tube and entrained pore water is

$$\bar{\rho} = \frac{V_{pore}\rho_w + V_c\rho_c}{V_{pore} + Vc}. \qquad \text{(A8}$$

Combining eqs. A4, A5, A6, and A7,

$$\bar{\rho} = \frac{(1 - 1.275\ R/L)\ \rho_w + 2dr/R\ \rho c}{(1-1.275\ R/L) + 2\ dr/R}.$$

Setting the buoyant force equal to the drag force for the open tube,

$$\pi(R + dr)^2 Lg(\bar{\rho}-\rho w) = \frac{2\pi\eta\ U_s L}{\ln\ (L/R) - .72},$$

and solving for the settling velocity provides

$$U_s = \frac{g}{2\eta}(R + dr)^2(\ln\ (L/R) - .72)(\bar{\rho}-\rho_w). \qquad \text{(A9}$$

This equation provides the family of curves shown in Fig. 1 for an open tube with $dr/R = 0.1$, $\rho_c = 2.65$, and variable values of R/L. The settling curves for capped tubes are also shown, and the fraction of pore water retained can be calculated from the curve differences.

Appendix II: Evaluation of Stokes Settling Equation for Variable Density Aggregates

by

Kendall L. Carder
and
Robert G. Steward

Department of Marine Science
University of South Florida
140 Seventh Avenue South
St. Petersburg, Florida 33701

I. Introduction

Reduction of viscous drag has been cited as a reason for the relatively faster settling speeds than expected for aggregates using Stokes settling equation with a particle packing model density (Chase, 1979; Hawley, 1982). However, the inability to measure the actual density of individual particles in these studies has made it necessary to make gross estimates of one or more of the Stokesian parameters, usually the aggregate density. If settling aggregates were assigned too small a density based upon a given density packing model, it would appear that viscous reduction had occurred in order to provide faster-than-Stokes settling speeds. Also, if aggregates settled and then broke up at depth, the smaller aggregate components observed would appear to have settled faster than Stokes equation allows. Again, viscous reduction could erroneously be used to explain this settling behavior. Our program objectives were to conduct settling-chamber/density-gradient experiments to measure aggregate particle density and viscous drag independently.

A key element of the project was the independent measurement of particle density by the use of high density fluids (isotonic with the seawater) in density gradient columns. Although the holographically-measured settling velocity and Stokes equation predicted montmorillonite aggregate densities of the order 1.05 g/ml (similar to the high-order aggregates found by Krone (1976)), none of the aggregates remained buoyant in the columns of high-density sugar solutions, which reached densities of 1.40 g/ml. This suggested that the occluded water or pore water of the aggregate was constantly being

flushed and replaced by the density of the surrounding media. This would remove the buoyancy due to lower density occluded waters of the original aggregate, and the settling aggregate would have a net negative buoyancy due to the clay (montmorillonite) component. Holographic investigation of the behavior of the aggregates as they traversed a sharp density interface has demonstrated some aspects of aggregate settling behavior which are of more importance than the objectives of the initial program. Pore water flushing has been demonstrated holographically to occur and to have significant effects on the settling behavior of aggregate particles.

As a summary of the work performed under this contract, this report will describe the behavior of inorganic aggregates encountering fluids of differing composition than those in which they were created. Holographic techniques have been used to show that the interstitial water of these aggregates is not tightly bound. In fact, it is exchanged rapidly, and suggests an initiation mechanism for the formation of vertical sediment fingers in stratified water columns.

II. Experimental Design

The settling chamber was constructed for this project with the following features: an upper cylinder to dampen injection forces and allow the settling particles to achieve terminal settling velocity, and a lower chamber equipped with dual ports for holographic velocimeters crossed at 90° to each other and the settling direction. Below the horizontal laser paths, the particles came to rest on another optical plate providing an opportunity to holographically image the particles in the vertical direction.

Three types of aggregates were prepared in filtered abiotic artificial seawater. Three standard clays, kaolinite, montmorillonite, and illite from the U. S. Geological Survey were each allowed to aggregate in 35ppt artificial seawater for about one month. Flocculated aggregates on the order of 20-300 μm were gently withdrawn and introduced both to the settling chamber and the density gradient chamber.

Two different density media were used in the gradients. In the initial setup runs and test, serum dextran was used to save the extremely expensive metrizamide for later runs. Metrizamide-heavy water solutions isotonic with 35ppt seawater were created with densities as high as 1.40 g/ml. Even at these high densities, the aggregates consistently failed to become buoyant, even those with densities determined using Stokes settling equation (with measured water viscosity) to be less than 1.05 g/ml.

III. Results

To examine the behavior of the aggregates as they settled into the higher density fluids, the holographic microvelocimeter was employed. A two-layer, isothermal, isotonic density gradient was prepared from artificial seawater (35ppt, 1.0241 g/ml, 23.5°C, 0.92 centipoise) and dextran-artificial seawater (35ppt, 23.5°C, 1.054 gm/ml, 7.45 centipoise). The 1 cm diameter laser beam crossed the settling chamber at the sharp interface. Time-sequential transmission holograms revealed why the particles were not reaching density equilibrium with the heavier medium. As the particles

encountered the interface, they slowed down. After a pause of less than a second, the larger particles punched through the interface, leaving a streamer of lower-density, extruded pore water in their wake. This streamer shows up holographically since the difference in index of refraction between the pore water streamer and medium results in interference patterns.

An example of this behavior is shown in Figure 1a-c. This was the second experiment performed with this density gradient, so the original step-like structure had broken down somewhat near the interface due to the mixing induced by the settling particles of the first experiment (some ten minutes earlier). These unreconstructed holographic images show only the diffraction fringes. An in-focus reconstruction of Figure 1b is shown in the Appendix.

The first visible particle to resume settling after hitting the interface is labelled A. This particle is 256 microns diameter and extrudes a low viscosity conduit in its wake that influences the settling of particles B and C. In addition to channelizing the subsequent particle settling paths, this conduit also tends to affect particle morphology and settling orientation. The reduced viscosity and density in the conduit and the alignment of the particle long axes with it, permits increased settling speed by the subsequent particles. This increases the likelihood that particles will collide with slower moving particles downstream, and can result in elongate aggregates with their long axis oriented vertically (shown in Figure 2). A detailed explanation of the settling behavior and flushing rate of the particles in Figure 1 is provided in the discussion.

IV. Holography of Pore Water Streamers

The tube-like conduits of flushed aggregate pore waters contain a lower density, lower viscosity, and lower refractive index media than that surrounding the conduits. The maximum refractive index contrast is $\Delta n = .0046$ that difference between that of the upper and lower layers. The streamer left by particle A stretches to about .2 cm below the original interface (about 8 diameters of particle A). If we calculate the diameter D of a cylinder .2 cm long that contained only seawater, its diameter would be on the order of .0075 cm in order that its volume match that of the volume of particle A (.0256 cm diameter).

A light ray ($\lambda = 632.8$ nm in vacuo) passing through the center of a seawater cylinder ($n = 1.3396$) of .0075 cm diameter would exit 0.54 wavelengths ahead in phase of the part of that wave front that passed just outside the cylinder. Since the index of refraction contrast is so small, very little refraction will occur ($n_{sw}/n_d - 1 \ll 1$). Rays passing just outside the cylinder diffract toward the central axis, where interference occurs with those having traversed through it. For a cylinder such that

$$\rho_c = \left| \frac{2\pi d}{\lambda} \left(\frac{n_{sw}}{n_d} - 1 \right) \right| \doteq 3.9 ,$$

the largest anomalous diffraction constructive interference peak occurs (Van de Hulst, 1957). Here d is the diameter of the cylinder, λ is the wavelength in the medium, and n_{sw} and n_d are the refractive indices of seawater (1.3396) and dextran (1.3342), respectively. For our model cylinder, the value of $\rho_c \doteq 3.41$, producing a constructive

interference peak (bright fringes) which is very close to the maximum value possible. For larger cylinders with similar refractive indices, the axial interference peaks decrease, but never by more than 50%. For cylinders with d < .0025 cm, the amplitude of the interference peak decreases rapidly toward background values. Small destructive interference fringes (dark fringes) will occur at an angle of about 0.5° off axis and downstream from the cylinders and will be most apparent for cylinders about twice (or increments thereof) the diameter of our model cylinder ($\rho \doteq 7, 14, 20, \ldots$).

In summary, maximum fringe formation will occur on our film if $\rho_c \doteq 3.9$. For lower refractive index contrast (smaller $|n_{sw}/n_d - 1|$), a larger cylinder (presumably created by a larger aggregate) is required to produce similar constructive fringes. For fresh water over salt water (e.g., $m = n_{fw}/n_{sw} \doteq \frac{1.3330}{1.3390}$), the maximum refractive contrast approaches that of our model cylinder. Only iceberg melt or river plumes over deep water scenarios (e.g., Amazon, Magdalena) might provide that much refractive contrast. However, less contrast from larger diameter cylinders (larger particles) would produce similar fringes to the ones we have viewed.

V. Particle Dynamics Model for Aggregates with Occluded Water Flushing

To understand the dynamics of porous aggregates which exchange their occluded waters at some unknown rate with that of the surrounding medium, we developed a model to estimate the density of the occluded waters as a function of a flushing factor. To begin, we require some definitions.

A wet primary particle is defined as a particle containing no voids but has water bound in the molecular matrix. The density of such a particle, ρ_p, is defined as

$$1) \quad \rho_p = \frac{M_s + M_w}{V_s + V_w}$$

where M_s and M_w are the masses of the solid material and water respectively, and V_s and V_w are volumes of the same respective materials. We have determined in previous work that the density of our samples of wet, primary montmorillonite particles is 1.77 gm/ml (Gartner and Carder, 1977).

As the material aggregates, internal voids are created, partially enclosing occluded water (ow). If this ow is tightly bound, a static density results as defined by

$$2) \quad \rho_{static} = \frac{M_s + M_w + M_{ow}}{V_s + V_w + V_{ow}} .$$

If the ow is exchanged with the surrounding medium, then a dynamic density ($\rho_{dynamic}$) results as

$$3) \quad \rho_{dynamic} = \frac{M_s + M_w + M_{ow}'}{V_s + V_w + V_{ow}} .$$

M_{ow}' is an apparent mass of ow as defined by the Stokes equation for a sphere of diameter D settling with velocity v_s in a medium of density ρ_m and viscosity η. If aggregates or phytoplankton contain the occluded water (or cytoplasm) tightly enough that there is no significant flushing or exchange of pore waters with the surrounding isotonic medium, then it follows that

4) $$\rho_{static} = \rho_{dynamic}.$$

Otherwise

$$\rho_{static} \leq \rho_{dynamic}.$$

We can describe, to the first order, the effect of the flushing of aggregate pore waters on the Stokes settling speed by developing a relationship to describe ρ_{ow}, in terms of a flushing rate for the particle. Suppose that some fraction f of the ow is flushed each time the particle settles a distance of one diameter D. Then $f/D = F$ is the flushing rate per unit distance settled. If $\rho_{ow}(Z)$ and $\rho_{ow}(Z + \Delta Z)$ are the occluded water density values at depths Z and $Z + \Delta Z$, and the density of medium ρ_m increases linearly with depth then

5) $$\rho_m(Z) = \rho_m(0) + KZ,$$

where K is a constant that describes the change in ρ with depth.

A first order approximation of the change in ρ_{ow} in settling over a short depth $\Delta Z = D$ can be expressed as

$$\frac{\Delta\rho_{ow}(Z)}{\Delta Z} \doteq \frac{\rho_{ow}(Z + \Delta Z) - \rho_{ow}(Z)}{\Delta Z}$$

$$\doteq \frac{f\rho_m(Z + D) + (1 - f)\rho_{ow}(Z) - \rho_{ow}(Z)}{D}$$

$$\doteq \frac{f[\rho_m(0) + K(Z + D)] - f\rho_{ow}(Z)}{D}, \qquad 6)$$

where the fraction f of $\rho_{ow}(Z)$ that is flushed is replaced by the denser water of the medium $\rho_m(Z + D)$ found at depth $Z + D$. Rearranging terms, we can write the quation as a differential equation

$$\rho_{ow}'(Z) + \frac{f}{D}\rho_{ow}(Z) = \frac{f}{D}KZ + \frac{f}{D}(\rho_m(0) + KD)$$

or

$$\rho_{ow}'(Z) + F\rho_{ow}(Z) = FKZ + F(\rho_m(0) + KD),$$

where $F = f/D$.

The solution to this equation is

$$7) \quad \rho_{ow}(Z) = \rho_{ow}(0)e^{-FZ} + e^{F/Z}[\rho_m(0) + K(Z + D - 1/F)]$$

$$- \rho_m(0) - K(D - 1/F).$$

To simulate our two-layer, density-gradient, particle dynamics problem, we let $\rho_{ow}(0) = \rho_m(0) = 1.024$ g/ml and the density contrast gradient, $K \doteq .12$ g/cm^4.

We chose to exercise F over a range of values in order to evaluate the effect that the density contrast of the occluded waters with the solid has on the particle settling speed for various aggregate densities. As mentioned previously, the variation in viscosity across the interface had a more significant effect on settling speed than did the change in density, and in order to arrive at a solution, we originally assumed the density contrast of the aggregate ($\rho_{dynamic} - \rho_m$) to be constant with depth. We can now estimate how much in error that assumption may have been for the various particles in this study.

Now that ρ_{ow} can be estimated as a function of flushing rate F and depth, one can solve Stokes equation for viscosity as a function of depth, given the measured settling speeds of the particles.

Since the streamer from particle A (Figure 1) affected the viscosity of the cylinder in which particles B and C traveled, it is important to analyze the viscosity encountered by particle A first. It is clear even at .2 cm below the original interface (position of particle A in Figure 1e) that a gradient in refractive index between the streamer and surrounding waters remains. Thus, we chose .25 cm

below the interface as the depth at which the density, viscosity, and refractive index gradients of the medium with depth disappeared (medium of purely layer 2 type properties). Thus,

$$K = (1.054 - 1.024)/0.25 \text{ cm} = .12 \text{ g/cm}^4.$$

$$8) \quad \eta(Z,F) = \frac{980[1.77 \text{ g/ml } VF_s + (1 - VF_s)\rho_{ow}(Z,F) - \rho_m(Z)]D^2}{18\, v_s(Z)}$$

where

$$9) \quad VF_s = \frac{\rho_{dynamic}(Z,F) - \rho_{ow}(Z,F)}{1.77 \text{ g/ml} - \rho_{ow}(Z,F)},$$

and $\rho_{ow}(Z,F)$ and $\rho_m(Z)$ are known from equations 7 and 5, respectively, and VF_s is the volume fraction of the aggregate occupied by solid matter. To solve exactly this set of equations, $\eta(Z,F)$ should be known at some point where a velocity measurement $v_s(Z)$ is known. We do know that $\eta(Z > .25 \text{ cm})$ is about .0745 poise; however, no velocity measurements were available at that depth since it was out of our field of view. We thus assumed a relatively smooth transition between the viscosity at .25 cm below the interface and the viscosity at .175 cm, our deepest particle velocity observation.

VI. Application of Model

The resulting viscosities associated with the velocities of each particle for four depth intervals and two F factors are shown in Figure 2, with the upper and lower points representative of F factors

of 0.5/cm and 0.2/cm, respectively. The flushing factor had little or no effect on particles A and C since montmorillonite made up larger fractions of their mass values than for particle A (62% and 15% versus 8.6%, respectively.

The dotted lines represent regions where two different settling transitions occurred: i) in Figure 1b and 1c particle A can be seen to be settling along or just adjacent to a streamer from an earlier particle, and ii) in Figure 1d and 1e, particle C seems to have moved out of the streamer tube of particles A and . Particle A apparently encountered a relatively constant viscosity when in the proximity of the old streamer, with the viscosity sharply increasing as it moved away from the streamer remnant. Particle C also encountered fluid of relatively constant viscosity within the streamer of particle A, with an abrupt increase occurring on passage out of it. Figure 2 reflects these facts.

Particle B settled within the streamer of particle A until Figure 1d, where it seems to have edged out of the tube. In Figure 1e it appears to be slightly behind the tube. Figure 3 also corroborates this fact, since the viscosity encountered by particle B is clearly much less (within the streamer tube) than that encountered by particle A at the same position before the streamer was extruded.

An estimate of the effective viscosity increase outside versus inside a streamer is indicated by the arrow bar of .8 centipoise on Figure 3. That represents a viscosity increase of about 25%, a significant effect.

Summary

Holography of aggregates settling through density interfaces provides a direct observation of pore-water flushing due to the contrast in refractive index between the extruded pore waters and the medium. These extruded pore-water tubes provide a pathway where subsequent particles encounter reduced viscous drag and less buoyancy than would be available outside the tube. Viscosity reductions of at least 25% were observed. This means that if two particles of similar settling speeds are following each other in a streamer tube, the second will settle faster since it encounters lower viscosity. The probability of collisions, in such a system, then, changes from one with a random or Gaussian likelihood to one that favors low density, highly porous aggregates, capable of providing a reduced viscosity, funnel-type of pathway at density interfaces for subsequent particles to traverse and within which to collide. As these aggregates build in size, they increase even more the probability of subsequent collision. Figure 2 shows several elongated aggregates apparently created by particle collisions in a streamer tube.

References Cited

Chase, R. R., 1979. Settling behaviour of natural aquatic particles. Limnology and Oceanography 24(3): 417-426.

Gartner, J. and K. Carder, 1979. A method to determine specific gravity of suspended particles using an electronic particle counter. Jour. Sed. Petr. 49(2): 631-633.

Hawley, N., 1982. Settling velocity of natural aggregates. J. Geophys. Res. 87(C12): 9489-9498.

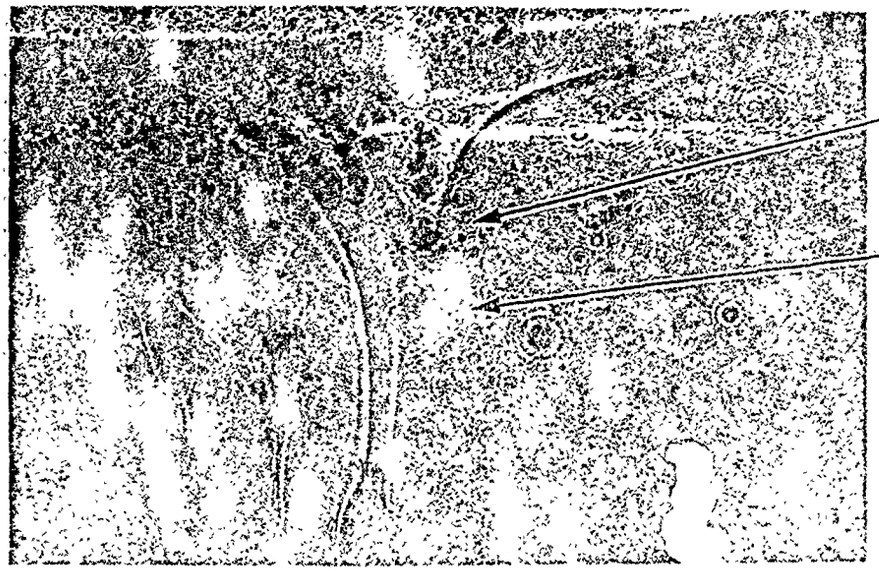
Jerlov, N. G., 1968. Optical Oceanography, Elsevier, New York, 194 p.

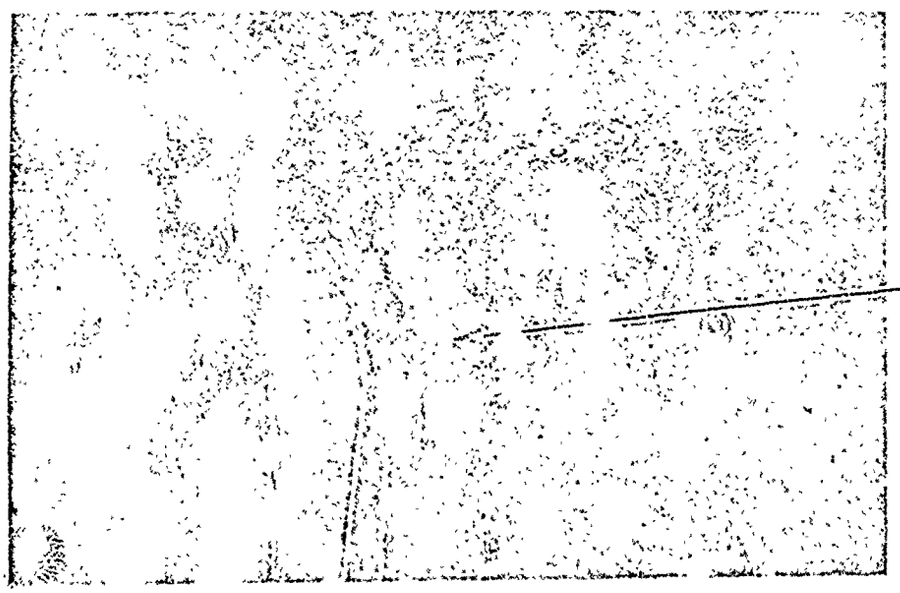
Krone, R. B., 1976. Engineering interest in the benthic boundary layer, in N. McCave (ed.), The Benthic Boundary Layer, Plenum, New York: 143-156.

Van de Hulst, H. C., 1957. Light Scattering by Small Spheres, Wiley, New York, 470 p.

Figures 1a (top), 1b (middle), 1c (bottom)

A sequence of holograms taken with 1 0 second intervals. The top hologram has an arrow on the left showing the oringinal level of the density gradient interface which represent in the reference point ($Z = \phi$). Three aggregates labelled A (246 μm diameter), B (76.5 μm diameter), and C (113 μm diameter) are settling along the same conduit which is marked by a bright pore water streamer flushed out of particle A. Note in fromation of elongate particles in the streamer above particle C.


B C
A


C

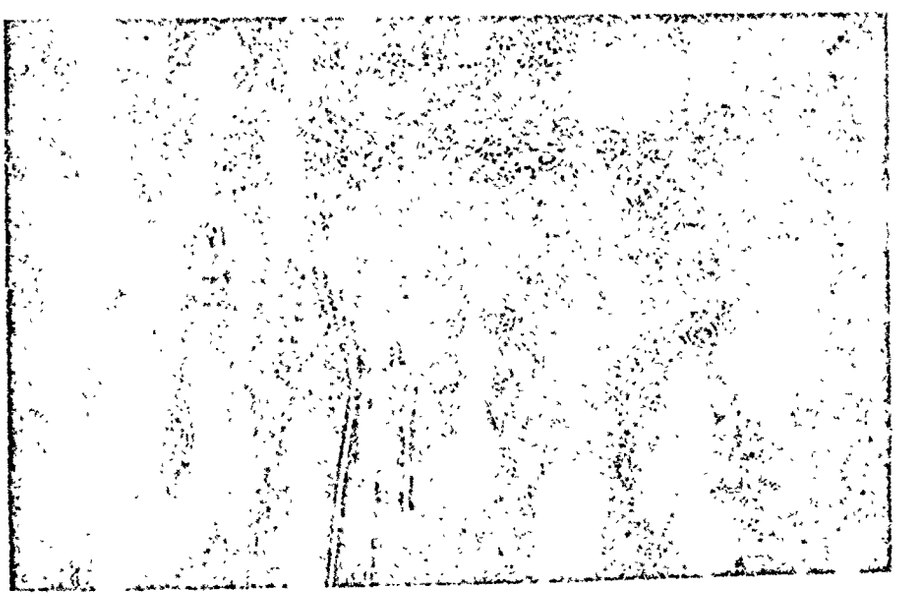


Figure 2. Hologram of several elongated aggregates found about 1 cm below the interface (note especially the lower left corner). These streamlined morphologies suggest their formation to have occurred in a streamer. Note the continued presence of low index streamers even this far below the interface, suggesting relatively slow flushing rates.

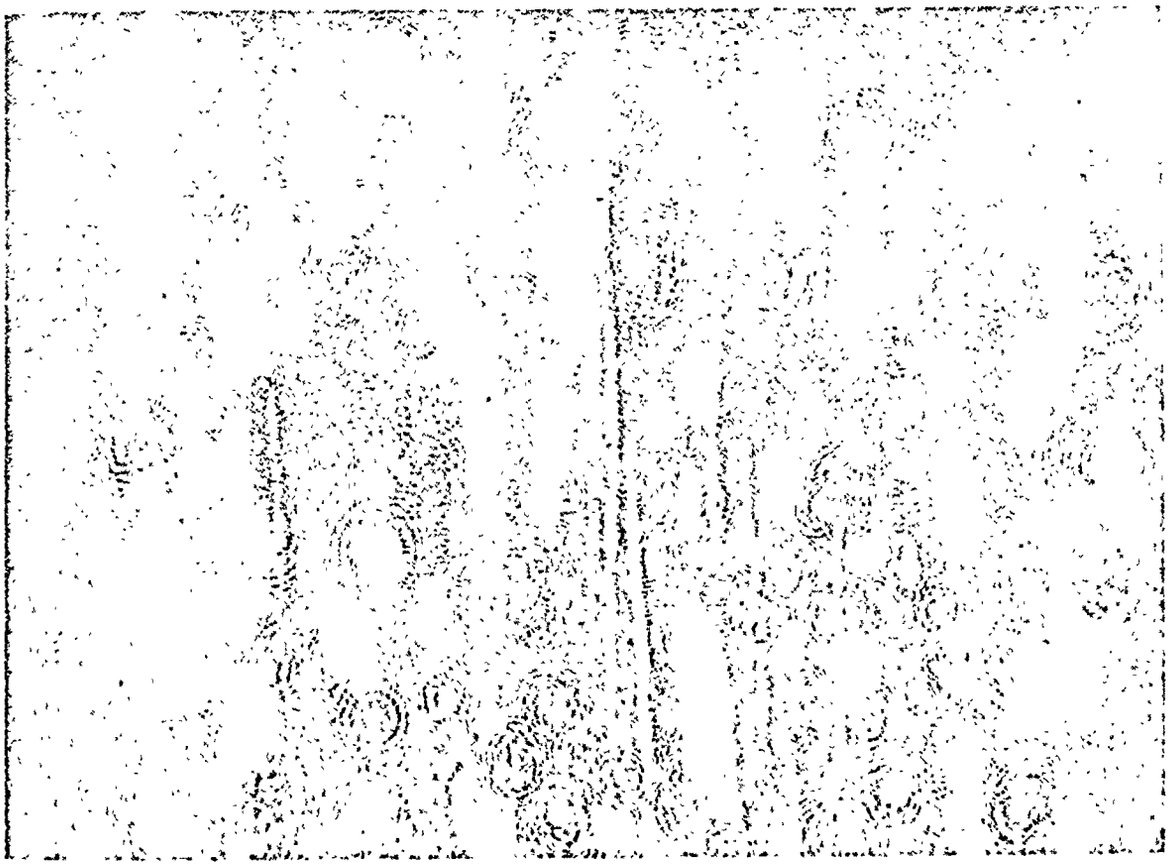
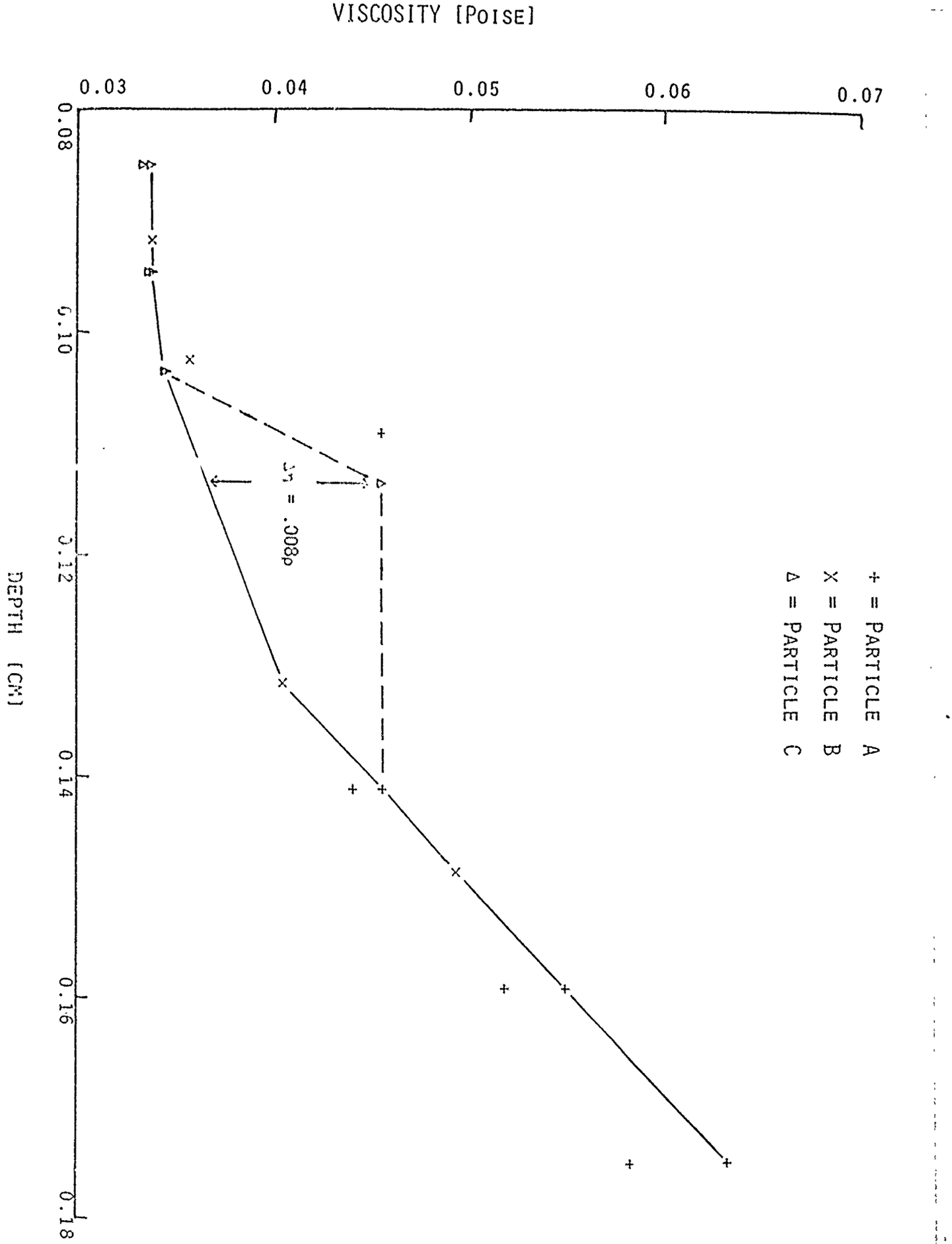


Figure 3. Viscosity profile in the density gradient traversed by and inferred from particles A, B, and C. The sudden increase in viscosity observed for particle C some .11 cm below the interface occurred when the particle left the low viscosity streamer and suddenly encountered more resistance to settling.


VISCOSITY [POISE]
0.03
0.04
0.05
0.06
0.07
0.08
0.10
0.12
0.14
0.16
0.18
DEPTH [CM]
η_n = .008p
+ = PARTICLE A
X = PARTICLE B
Δ = PARTICLE C

MEASURING THE ABUNDANCE AND FLUX OF MARINE SNOW AGGREGATES

by
Vernon L. Asper

University of Southern Mississippi
Center for Marine Science
National Space Technology Laboratory
NSTL, MS 39529 (601)-688-3178

INTRODUCTION

Marine Snow aggregates are thought to be important in the vertical and lateral transport of particulate matter in the oceanic water column (Alldredge, 1981; Asper, 1986; Asper, in press; Shanks and Trent, 1980; Silver, 1981). Their delicate nature and relative low abundance (0.1 to 1.0 aggregates liter^{-1} in deep water) have prohibited assessment of their in situ flux, abundance and sinking speeds using standard oceanographic sampling techniques. These parameters have only been measured in the uppermost water column which is accessible by SCUBA. To learn more about marine snow aggregates in the deeper water column we have developed two complimentary photographic systems; the first measures the abundance (number liter^{-1}) and the second measures the flux (number m^{-2} day^{-1}) of aggregates at any depth in the water column.

MEASURING THE ABUNDANCE OF AGGREGATES

Figure 1 shows a diagram of the Marine Snow Survey Camera (MSSC) developed by Susumu Honjo at Woods Hole (Honjo et al., 1984). This system consists of one or two deep-sea strobe lights mounted at the focal point of a compound Fresnel lens, producing a collimated 'slab' of illumination. Mounted at approximately 90° to this slab, a deep-sea camera photographs an intersecting volume of water (600 liters). The light scattered image of marine snow particles within this well-defined slab of light are photographed against a background of dark (unilluminated) water. The system is lowered slowly (10-20 m min^{-1}) through the water column on a trawl wire, exposing frames at a time interval of 7 to 20 seconds calculated to yield 800 frames between the surface and the sea floor at a distance of 1.2 to 5.6 m frame^{-1} throughout the water column. Depth is monitored and recorded using a pinger and the ship's precision depth recorder. Lowering is halted when the frame is within 2 to 10 meters of the sea floor. Film from the camera is developed as a continuous roll in order to insure consistent development. The negatives are then analyzed directly using a computer aided image digitizer and the abundance of marine snow is plotted vs. the depth at which the image was obtained.

MEASURING THE FLUX OF AGGREGATES

From a sedimentological point of view, the existence of marine snow in the water column becomes important only when it can be shown that these aggregates are settling at significant rates and contributing to the flux of material. The second photographic system (Marine Snow Flux Camera, MSFC) was constructed in order to assess the flux of these aggregates through the water column. This system (figure 2) consists of a polypropylene cylinder (0.069 m^2 opening) which

is open at the top (with a closing mechanism) and closed at the bottom by a clear plexiglass plate. Four flash tubes from Vivitar[T] strobe heads are attached to Impulse[T] connectors which are threaded into clear plexiglass rod. These pressure-tight strobe units are mounted just above the trap bottom and flush with the walls of the cylinder so as to illuminate any material lying on the clear plate. A deep-sea camera is mounted one meter beneath this apparatus, so that the bottom of the trap is in focus and only material lying on the plate is photographed. Using a 30 m roll of film, 800 frames can be exposed, each showing successive additions of material to the trap. Experimental results show that a resolution of approximately 50 um is attainable using fine grain film (Kodak[T] Panatomic-X).

This system is deployed on a mooring (either floating or bottom-tethered) and allowed to collect material for a specified time interval. After recovery of the system, negatives are developed and analyzed in the same manner as for the MSSC except that the numbers are plotted vs. time rather than depth. Sealing off the top of the trap prior to recovery allows retention of the material which settled into the trap and which was photographed by the camera system. Examination of the composition and quantity of this material provides some insight into the types and amounts of particles delivered to the sea floor by marine snow aggregates.

MEASURING THE SINKING SPEED OF MARINE SNOW AGGREGATES

Probably the most difficult to obtain measurement relating to marine snow aggregates is their sinking speed. The work by Shanks and Trent (1980) in surface water indicates the value of this number but also demonstrates the difficulties associated with obtaining it, even near the surface. Howeve , estimates of *in situ* sinking speeds are obtainable either using a combination of the MSFC and MSSC numbers or else using a proposed, but not yet developed *in situ* settling tube system.

Use of MSSC/MSFC in combination. The amount of new material added to the flux camera per area per time interval between frames in the photograph is flux of that material. When this flux value is divided by a concentration value obtained by lowering the MSSC to the depth of the MSFC, an effective *average* sinking speed of all aggregates imaged by the MSSC can be obtained:

$$\frac{\text{number}}{\text{volume}} * \frac{\text{distance}}{\text{time}} = \frac{\text{number}}{\text{area * time}}$$

This procedure can be employed over any practical time scale; temporal resolution is determined by the time interval between frames. Also, flux and abundance numbers can be obtained for several size classes of aggregates, allowing the determination of a sinking speed estimate for each size aggregate.

In addition to questions relating to the hydrodynamics of trapping particles (e.g., over/under trapping, swimmer interactions, effects of entrapment on aggregate morphology etc., which will not be addressed here), several assumptions inherent in this experimental design limit the usefulness of these sinking speed estimates. First, material falling into the MSFC must represent the same

material as that photographed by the MSSC for each size class. Any temporal or spatial variability in the input of material either vertically or horizontally will influence the results unless both instruments are deployed in close proximity along the same mooring. Second, all material of a given size is assumed to be sinking at the same speed. This assumption is problematic because particles of a given size will not necessarily be of uniform density. Even within a population of aggregates, differences in content and porosity could foreseeably result in a wide range of densities and therefore sinking speeds. The sinking speed obtained by this method represents the average sinking speed for all particles photographed by the MSSC and not the average sinking speed of particles actually entering the MSFC; some particles (aggregates) observed by the MSSC may not be sinking at all while others settle at rapid speeds, resulting in an intermediate overall value.

Direct sinking speed measurement. An average sinking speed for all aggregates obtained this way is useful for modelling "typical" water column residence times for large particles; however, measuring the actual in situ sinking speeds of individual aggregates would be of considerably more value in modelling particle transport. To this end, a new camera system capable of measuring the fall of aggregates in a quiescent volume of water is proposed (figure 3). This system would consist of dual settling tubes with a camera mounted normal to their vertical axis. Particles settling through the tubes would be photographed several times over a programmed time interval; settling speed could be determined by the distance traversed during that time interval. Ball valves mounted at the openings of the tubes could be used to open and close the trap, sealing the contents for retrieval and subsequent analysis. Duplicate tubes are used either for the collection of replicate samples or for investigating the effects of poisons, preservatives, density gradients, baffles, screens, and tube geometry (aspect ratio, etc.) on the quantity and quality of material retained. A second camera mounted beneath the trap would record material arriving on the bottom of the trap (flux estimate) and would observe any material which might settle through the tubes quickly enough to be missed by the side-looking camera. This approach is thought to be capable of yielding some extremely useful information relating to the flux and in situ sinking speeds of aggregates.

SUMMARY

In order to be important in the vertical transfer of particulate matter in the world's oceans, marine snow aggregates must be present in significant concentrations and must settle at sufficient rates to produce an appreciable mass flux. The two photographic systems which have previously been built and tested have been shown to be capable of assessing the abundance and flux of relatively undisturbed aggregates in the water column. A third system has been proposed which would also measure the in situ sinking speed of individual aggregates and thus provide even more useful information relating to the contribution of these aggregates to oceanic sediment flux.

REFERENCES

Alldredge, A.L. (1984) Macroscopic organic aggregates (marine snow). In: Global Ocean Flux Study proceedings of a workshop. National Academy of Sciences, National Research Council, Washington, D.C. 167-179.

Asper, V.L. (1986) Accelerated settling of particulate matter by 'marine snow' aggregates. Ph.D. Thesis in the joint educational program of the Woods Hole Oceanographic Institution and Massachusetts Institute of Technology, 189pp.

Asper, V.L. (in press) Measuring the flux and sinking speed of marine snow aggregates. Deep-Sea Res.

Honjo, S., K.W. Doherty, Y.C. Agrawal and V.L. Asper (1984) Direct optical assessment of large amorphous aggregates (marine snow) in the deep ocean. Deep-Sea Res. vol. 31(1), 67-76.

Shanks, A.L. and J.D. Trent (1980) Marine snow: sinking rates and potential role in vertical flux. Deep-Sea Res. vol. 27A, 137-143.

Silver, M.W. and A.L. Alldredge (1981) Bathypelagic marine snow: deep-sea algal and detrital community. J. Mar. Res. vol. 39(3), 501-530.

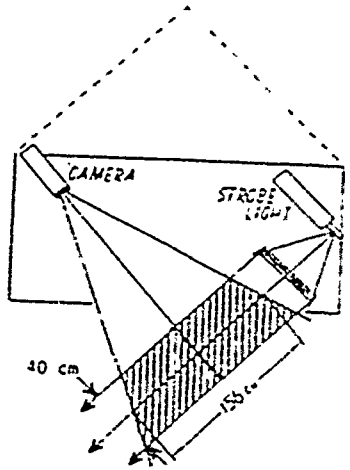


Figure 1. Diagram of Marine Snow Survey Camera (MSSC) showing dimensions of light slab. 600 liters of water are included in the photograph.

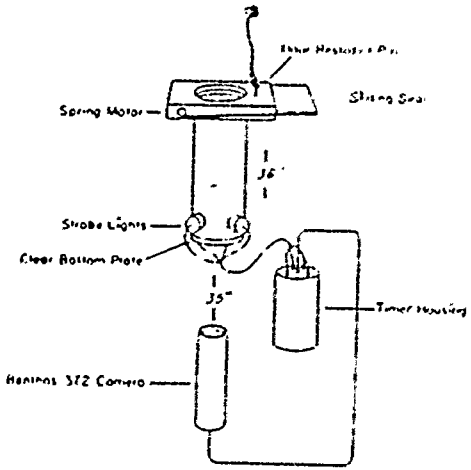


Figure 2. Schematic showing principal components of the Marine Snow Flux Camera (MSFC). Only particles lying on the clear bottom plate are photographed.

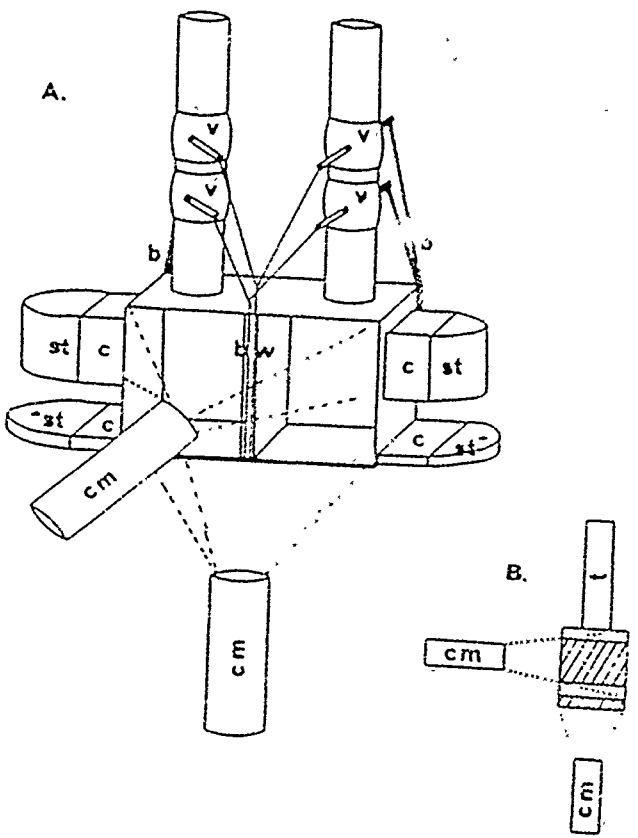


Figure 3. a) Sketch of proposed ASTAC (Aggregate Settling Tube And Collector) showing closing valves (V), burn wire (BW), light sources (ST) with collimators (C), and cameras (CM). Particles settling into the device will be photographed as they settle through a quiescent chamber (sinking speed) by the side-mounted camera and again upon their arrival on the clear bottom plate by the bottom-mounted camera (flux). The chambers can be sealed prior to deployment and prior to recovery by ball valves mounted above the settling chamber. Bungee cords (B) pull the valves closed upon release of the burn wires. Activation of the valves is confirmed photographically by observing the burn wire. Duplicate systems are used to provide replicate samples or to evaluate the effects of poisons, baffles or tube geometry, in which case one tube/chamber is used as a control. b) Diagram of the ASTAC showing illuminated areas (hatched) and geometry of the system.

Youngbluth, M.J., T.G. Bailey, C.A. Jacoby, P.J. Davoll and P.I. Blades-Eckelbarger. Submersible-based measurements of the sources, densities, distributions and sinking rates of marine snow aggregates and euphausiid fecal pellets.

Manned submersibles and the technical equipment they carry represent one kind of sampling system that has been used to define various properties and characteristics of macroscopic (> 0.5 mm) particulate matter in marine environments. Water column investigations with mobile undersea vehicles have been conducted primarily in the uppermost 1000 m. Visual observations coupled with photography (still and video), pumps and traps, and environmental data logging systems have provided new information about the diversity, distribution, abundance and behavior of marine particles on relatively small spatial scales.

Qualitative and quantitative data from over 300 dives in the uppermost 800 m of temperate and tropical seas with the JOHNSON-SEA-LINK vehicles have revealed:

(1) Most macroscopic particles are irregularly-shaped flakes and flocs (0.5-5 mm) but larger masses (5 mm-1.5 m) in globular, string and sheet forms are common.

(2) Particles are frequently concentrated at physical interfaces. For example, massive numbers (>3000 m^{-3}) of flocs (3-5 mm) have been observed repeatedly near the pycnocline (90-150 m) in the Bahamas. The origin of these particles has not been determined. A portion of this material may represent degredation products of periodically abundant organisms or the remains of mucilaginous secretions of soft-bodied zooplankton. Strings (3-100 cm long x 0.5-2 mm OD) of mucoid material formed by the foraminiferan Hastigerina pelagica, were frequently abundant (10-50 m^{-3}) throughout the uppermost 400 m and the largest aggregations of these particles often appeared in the 90-150 m interval. Sheet-like feeding webs (25 cm^2-2.3 m^2) of mucous, produced by the pteropods Gleba cordata and Cavolina tridentata, were numerous only in the pycnocline region of Exuma Sound. Neither reliable estimates of the number of webs nor the density of pteropods could be made owing to the fragile nature of the webs and the photonegative behavior of these zooplankton.

In addition to aggregate material derived from animals, tufts (clusters of strands 0.5 cm long x 0.2 mm OD) of the blue-green alga Trichodesmium sp., have appeared within the mixed layer (uppermost 40 m) in substantial numbers (400-20,000 m^{-3}).

Relatively dense aggregations (3-9 individuals m^{-3}) of the giant larvacean Bathocordaeus charon, have developed in the Gulf Stream during springtime periods and were concentrated in a narrow depth interval (45-65 m) which overlapped with the subsurface chlorophyll maximum (50-70 m). The ovoid filter-houses (30 cm OD) they produced and abandoned, constituted a major source of marine snow debris, especially along the continental shelf off eastern Florida where thick masses of this mucoid matter extended from the surface downward to the sea floor at 200 m. At midwater depths (400-750 m) in Bermuda and the Bahamas spherical filter-houses (2-5 cm OD) were common (0.1-2 m^{-3}). They were made by several

undescribed and vertically segregated (100-m intervals) species of kowalevskiid larvaceans.

High densities (100-1000 m^{-3}) of fecal pellets (2-6 mm long x 0.2 mm OD) occurred in discrete layers (7-12 m thick) coincident with the thermocline (15-30 m) throughout the Gulf of Maine and over the submarine canyons south of Georges Bank (Youngbluth et al. 1985). High standing stocks (1-100 m^{-3}) of the euphausiid Meganyctiphanes norvegica, were the source of these pellets.

(3) Large particles originate both in the epipelagic and the mesopelagic zones. As they sink from these zones of origin into deeper water and to the benthos, they transport nutritive material. Extrapolations based on the abundance of two of the particle types noted above (i.e., euphausiid fecal pellets and midwater larvacean filter-houses) and measurements of their carbon contents, daily production rates and sinking velocities suggested the potential for significant amounts of carbon export to deeper waters. For example, pellets from the single euphausiid species could supply, on the average, 50 mg C $m^{-2}d^{-1}$ to the benthos. This amount represented 29% of the daily primary production in the mixed layer and 11% of the total benthic community respiration.

Flux rates of 3-65 mg C $m^{-2}d^{-1}$ could originate from the filter-houses. If these estimates of flux are correct, the mesopelagic larvaceans may be modifying, repackaging and transporting the elevated microbial production noted in sediment trap collections from midwater regions.

(4) Individual larvacean filter-houses collected from 400-750 m in Bahamian and Bermuda seas had bacterial densities (7×10^5-3×10^6 per house) equal to marine snow aggregates from surface waters in the Atlantic and Pacific Oceans. Houses that were incubated for 4 d showed higher bacterial densities (6×10^6-1×10^7 per house). Bacterial production on houses varied widely (0.01-4 ng C ml $house^{-1}h^{-1}$) and represented substantial enrichments over equal volumes of the surrounding water (10-5000X). However, the bacterial activity on these particles was a small portion of the total bacterial production (0.01-0.4%). The midwater filter-houses and the larvacean fecal pellets they contained also were ladened with olive-green bodies (2-20 um OD), numbering 4×10^3-2×10^5 per house. Only low densities (50-130 per house) of eukaryotic photoautotrophs (2-4 um) and cyanobacteria (1 um) were attached to the houses.

(5) Most macroscopic particles appear to bioluminesce. Presumably microbial organisms attached to these particles were the sources of the bioluminescent light. The size and number of bioluminescent flashes, stimulated by turbulence from movements of the submersible or its thrusters, was usually greatest above and within the thermocline. However, on several occasions an unusual bioluminescence was induced within narrow layers at midwater depths (frequently at 250-300 m) while the submersible was stationary. Hundreds of luminescent spheres (3-6 cm OD) would glow for 5-15 s immediately after a flashlight or strobe lamp was activated. The particles responsible were almost indistinguishable under incandescent light.

Distributions of macroscopic aggregates in the Northwest Atlantic Ocean.

James K.B. Bishop
Lamont-Doherty Geological Observatory of Columbia University
Palisades, NY. 10964.

Macroscopic aggregates play an important role in the vertical transport of chemical elements in the ocean. Vertical profiles of > 1 mm sized aggregates in the "fecal matter" and "fecal pellet" categories (Bishop et al 1977) were obtained from the upper 1000 m by large volume in-situ filtration as part of the Warm Core Rings Program in 1982. Stations were occupied in the Slope Water, Warm Core Rings (WCR) 82B and 82H, the Gulf Stream and Sargasso Sea.

Greater than 1 mm sized aggregate abundances in the upper 100 m of the NW Atlantic ranged from 2 m^{-3} to 1000 m^{-3}. Abundances ranged from < 0.1 m^{-3} to 30 m^{-3} in deeper waters. The lowest levels of this material were found at stations in the Gulf Stream and Sargasso Sea. Highest abundances were found in waters of greatest primary productivity. These results indicate a correlation between aggregate abundance and water column productivity. The correlation is not linear since the dynamic range of aggregate abundance (500:1) greatly exceeds that of primary productivity (approx 10:1; Hitchcock et al, 1985).

Data also show that zooplankton are important in determining the vertical concentration gradients of large aggregate particles (Bishop, Conte, Wiebe, Boman and Langdon, 1986). For example, profiles of aggregate abundance and zooplankton biomass were obtained from the core waters of WCR 82B in April and June 1982. In April, > 333 mm zooplankton biomass ranged between 400 and 100 nmol C kg^{-1} over the depth interval 50 - 400 m. At the same time, aggregate abundances varied less than a factor of 3 over the same depth interval and averaged 10 m^{-3}. In June 1982, zooplankton biomass ranged between 2000 and 100 nmol C kg^{-1} from 25 m to 400 m. At this time, however, aggregate abundances decreased from 1000 m^{-3} at 25 m to 3 m^{-3} by 150 m. Thus, aggregate abundances in the water column appear to be governed by the activities of zooplankton. Once again, the relationship is not linear.

In spite of the large dynamic range of aggregate abundance and the importance of large aggregates to sedimentation, the above demonstrates that we have incomplete knowledge about the mechanisms of formation and destruction of these particles in the oceanic water column. More emphasis needs to be placed on understanding of the hydrographic, physical and biological factors controlling these important particles.

References:

Bishop, Collier, Ketten, and Edmond (1977). Deep-Sea Research: 27, 615-640

Hitchcock, Langdon, and Smayda (1985). Deep-Sea Research: 32, 1287-1300.

Bishop, Conte, Wiebe, Langdon, and Boman (1986). Deep-Sea Research: 33, in press.

Bioluminescence of Marine Snow

J. K. Orzech and K. H. Nealson

In this research, we employed both scuba and saturation divers to hand-collect samples of marine snow and surrounding water in separate syringes for discrete analyses. The samples were taken at depths as great as 260 m during 16 saturation dives from 1982 through 1984. Within hours of collection, the samples were brought to the surface and measured for emitted light flux (ϕ) in an integrating photometer calibrated for its response to light in the blue-green (480 nm) spectral region characteristic of bioluminescence. Of the 250 macroaggregate samples collected, 44% were luminous emitting measurable light from two to six orders-of-magnitude greater than that found in comparable volumes (0.01 ml) of the surrounding water. Many of these samples, however, were bright enough to be seen at 1p cm.

Our analyses further have shown that this light was produced by bacteria, dinoflagellates, radiolarians and/or other luminous microorganisms associated with the marine snow.

The use of saturation divers and deep-diving systems to collect samples at depths unattainable to conventional divers has been a major innovation and an integral part of this research. Operating from the Deep-Diving System Mk 2 (DDS) on board the Diver Training Vessel ELK RIVER and the U.S.S. Pigeon, U.S. Navy saturation divers have performed a variety of scientific tasks to depths between 26 and 260 m including the collection of marine snow. These extremely fragile macroaggregates are most successfully sampled by hand because of the diver's excellent manual dexterity and hand-to-eye coordination. Prior to this program, DDSs had been used only twice for marine research although they are used extensively for military and commercial diving. By working in cooperation with the U.S. Navy's Submarine Development Group ONE, and by employing the DDSs during their already scheduled certification and training dives, the substantial costs of operating a DDS were circumvented.

Using underwater video and stereo photography, we estimated the size distributions and concentrations of the macroaggregates during several dives in which light flux also was measured. A light budget was obtained for two dives one week apart in September 1982. During the first of these dives, nearly all of the ambient light (97%) emanated from the marine snow. One week later at the same location, 98% of the light flux originated in the surrounding water.

These studies have indicated that marine snow frequently is an emitter of light in the sea. As the macroaggregates form and then disintegrate, they have a significant role in defining the distribution of light-emitting organisms as well as other optical properties of the sea.
This work was funded by the Office of Naval Research.

ACOUSTICAL TECHNIQUES FOR REMOTELY DETECTING AND CLASSIFYING PARTICLES IN THE OCEAN

by

Timothy K. Stanton
Department of Geology and Geophysics
1215 West Dayton Street
University of Wisconsin
Madison, WI 53706
(608) 263-8950

Sonar systems can be used to remotely detect and classify particles (Fig. 1). These systems can provide high volume coverage in relatively short amounts of time. Furthermore, the results can be displayed in real time to allow directed sampling. For example, a system with 100 m range, 10° beamwidth and towed at 6 knots can scan about 10 million cubic meters of water per hour. While this produces large amounts of data, the scan can be qualitatively summarized in real time intensity plots or "echograms" (Fig. 2).

A common quantity used to describe each object's ability to reflect sound is the backscattering cross section σ_{bs} and the resultant target strength TS:[1,2]

$$\sigma_s \equiv R^2 I_{bs}/I_0$$

$$TS \equiv 10 \log \sigma_{bs}$$

where I_0 and I_{bs} are the incident and backscattered intensities of the sound, respectively, and R is a reference distance at which I_{bs} is evaluated. σ_{bs} is essentially the fraction of acoustical intensity reflected back toward the transmitter. Even for simple objects like a sphere, σ_{bs} is a very complicated function of size, shape, density and speed of sound contrast with respect to the surrounding water, and acoustic wavelength. In general, the larger the size, density, and/or speed of sound contrast, the greater the echo from the object. At low frequency, the size-to-wavelength ratio is especially important. Figure 3 shows that for low frequencies and/or small size (i.e. $ka \ll 1$) σ_{bs} is small but increases rapidly with ka to $ka \sim 1$ where a characteristic "wriggly" pattern develops. The $\sigma_{bs}/\pi a^2$ curve approaches a constant level for sufficiently high ka.

The effectiveness of the sonar system not only depends on each particle's target strength, but the spatial resolution of the sonar. Counting and classifying objects becomes much more straight forward when they are resolved. To obtain adequate angular resolution a sonar transducer that is large compared to a wavelength is required (i.e. higher frequencies are required). Also with higher frequencies, shorter transmission pulse durations can be achieved, providing better range resolution. However, because of absorption effects in seawater, the higher the frequency of sound, the less the penetration. Because of these factors investigators tend to use the highest frequency (shortest wavelength) possible that can penetrate to the desired range.

The ocean is composed of many objects of different sizes and composition. If the nature of the backscattering cross sections of these objects is known then one can combine data from a multiple frequency sonar with inverse analytical techniques to derive size distributions of the objects.[3,4] If it is not known, then one can use a high resolution single frequency sonar, whose frequency is chosen to detect a specific size class, to count the objects.[5-8]

Depending on the method, there are several levels of expertise, technology, and effort involved. To detect and locate objects, a simple commercial sonar can be used along with some basic knowledge of acoustics to produce data such as in Fig. 2. Counting objects may involve more specialized (and expensive) yet available equipment and much more knowledge of acoustics. Finally, determining the size distribution with a multifrequency sonar requires mostly custom technology and expert knowledge (and a great deal of effort I might add).

In summary, sound can conveniently be used to probe the ocean rapidly and versatilely. Depending on the level of technology and expertise involved, simple detection and location, counting, and even determining size distribution of the objects are possible.

REFERENCES

1. C.S. Clay and H. Medwin, Acoustical Oceanography: Principles and Applications, (Wiley Interscience, New York, 1977).

2. R.J. Urick, Principles of Underwater Sound, (McGraw Hill, Co., New York, 1983).

3. D.V. Holliday, "Extracting Bio-Physical Information from the Acoustic Signatures of Marine Organisms" in N.R. Andersen and Bernard J. Zahuranec (Ed.), Oceanic Sound Scattering Prediction, (Plenum, New York, 1977).

4. D.V. Holliday and R.E. Pieper, "Acoustic Volume Scattering: 100 kHz to 10 MHz," J. Acoust. Soc. Am., Suppl. 1, 75, no. S2, p. S29.

5. J.E. Ehrenberg, "Two Applications for a Dual-Beam Transducer in Hydroacoustic Fish Assessment Systems," in Proc. 1974 IEEE Conf. on Eng. Ocean Environment, 1, 152-155 (1974).

6. C.S. Clay, "Deconvolution of the Fish Scattering PDF from the Echo PDF for a Single Transducer Sonar," J Acoust. Soc. Am. 73, 1989-1994 (1983).

7. K.G. Foote, Asgeir Aglen and Odd Nakken, "Measurement of Fish Target Strength with a Split-Beam Echo Sounder," J. Acoust. Soc. Am, 80, 612-621 (1986).

8. Timothy K. Stanton and Clarence S. Clay, "Sonar Echo Statistics as a Remote-Sensing Tool: Volume and Seafloor," IEEE J. Ocean. Eng. OE-11, 79-96 (1986).

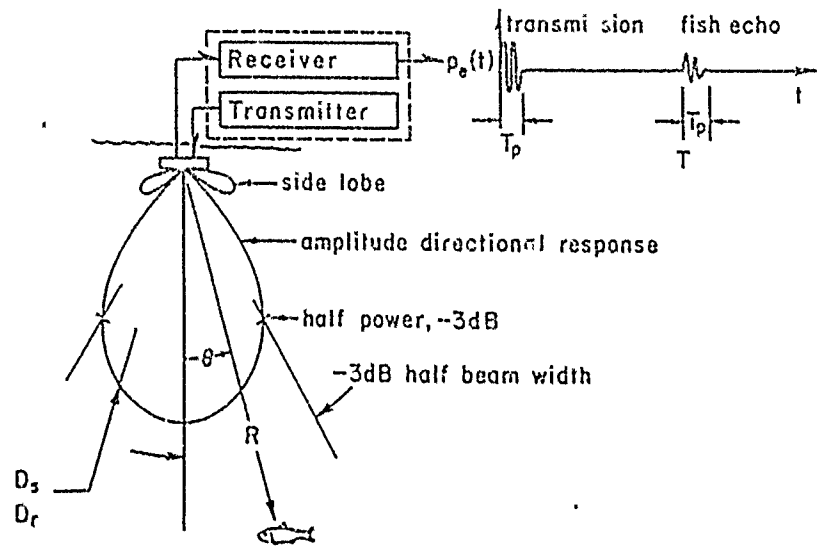


Figure 1. Sonar system that transmits pulse and receives echo from fish at a time T later.

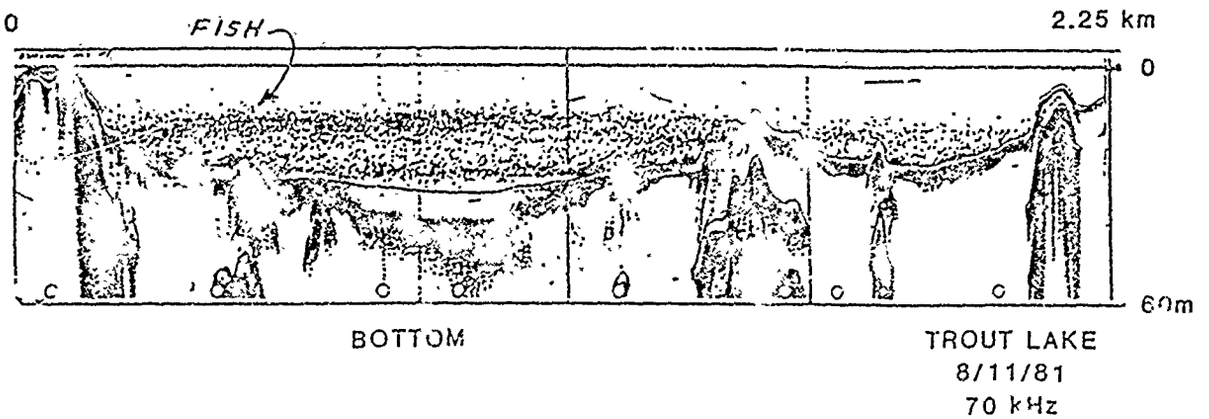


Figure 2. "Echogram" or intensity plot of sonar echoes from fish and lake bottom. Private communication, Lars Rudstam, Center for Limnology, University of Wisconsin, Madison, WI.

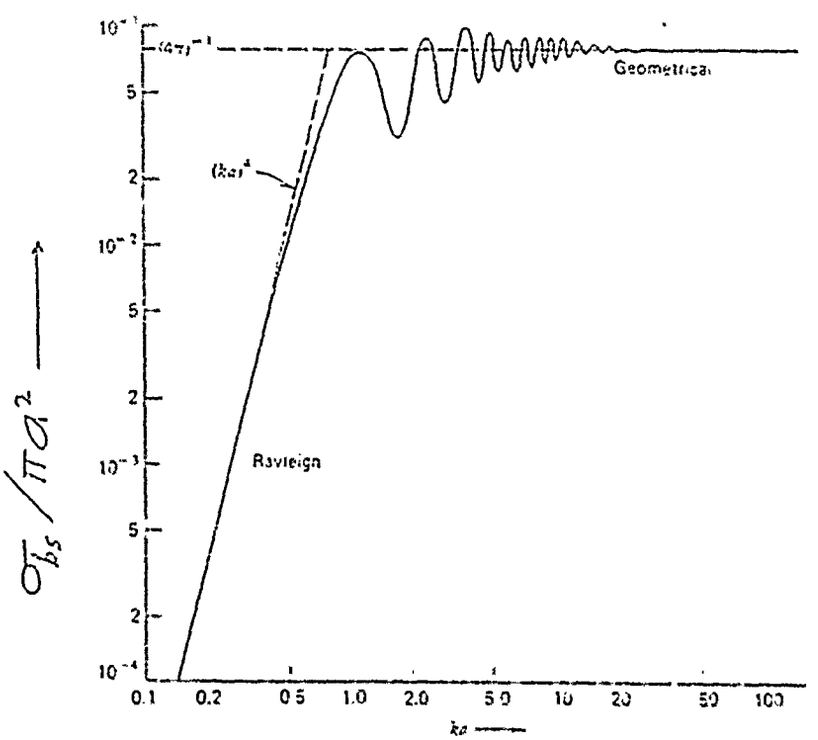


Figure 3. Backscattering cross section σ_{bs} normalized by projected area of sphere πa^2 versus ka where a is the radius of the rigid and fixed sphere and k is the acoustic wavenumber which is proportional to frequency.(1)

Flow Cytometric Tracing of Fluorescent Particles

K. D. Stolzenbach, K. A. Newman, F. M. M Morel,
S. W. Chisholm, and S. L. Frankel
R. M. Parsons Laboratory for Water Resources and Environmental Engineering
Department of Civil Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts

We have developed a new methodology for studying the transport and deposition of particles in the field using fluorescent pigment particles as a tracer and flow cytometry for their detection. Our initial interest in these studies has been the fate of particles in sewage discharged into relatively shallow coastal waters, but we believe our findings have general relevance to particle dynamics in other environments.

The pigment particles used are available commercially (DayGlo Corp.), fluoresce intensely at 600 nm, have a specific gravity of 1.4, and range in diameter from 0.1 to 10 microns. The corresponding settling velocity range is 0.0002 to 2 m/day. Laboratory sedimentation experiments with these particles show that they do not coagulate with themselves or with sewage particles at concentrations typically observed in the water column (1 to 100 mg/ℓ).

The pigment particles are detected in field samples using a flow cytometer. This instrument measures the intensity of fluorescence emission from individual particles as they flow in single file past the detection optics. Our instrument utilizes an epifluorescence microscope adapted by mounting a flow cell beneath the objective (Olson et al., 1983). The emitted light is split into two separate beams which are then filtered optically to yield sensitivity to different wavelength ranges. The tracer particles are identified among background particles by the characteristic ratio of the two signals. Particle size is calculated from the fluorescence intensity relative to that of a known standard. Tracer concentration is calculated from the number counted in a known volume. Sediment cores are prepared for analysis by suspension in water, agitation, and filtration through a 10-μm Nitex screen. Sediment trap samples are agitated and filtered. Agitation by sonification yields quantitative recovery of tracer mass from the sediment; agitation by gentle shaking leads to loss of tracer on the screen but maintains the sample's tracer particle size distribution in the filtrate.

We have applied this technique to a site in Salem Sound, Massachusetts. Two hundred kilograms of tracer slurry (50:50, wt:wt) was discharged over several hours through the sewage outfall of the South Essex Sewerage District (10 mg/ℓ at a flow rate of 23 mgd). Water and sediment samples were taken at 18 stations within 5 km of the outfall before and 1, 3, and 8 days following the tracer release. Sediment traps were set at three locations the day before and collected 9 days after the release.

Quantitative analysis of cores collected after 8 days shows that roughly 7% of the mass of released tracer particles was deposited in the study area. This value is consistent with estimated rates of particle deposition and removal by tidal flushing. Most interestingly, size distribution analysis of both core and sediment trap samples reveals that the size distribution of the sedimented particles is indistinguishable from that in the initial tracer

slurry. That is, deposition of particles is independent of their size and thus independent of their Stokes settling velocity. As the laboratory experiments rule out coagulation in the water column, we conclude that the particles are mixed down to sediment interface where they are indiscriminately removed by some mechanism. We postulate that this may be achieved by circulation through and coagulation with a high-concentration fluidized sediment layer.

Olson, R. J.; Frankel, S. L.; Chisholm, S. W. 1983. An inexpensive flow cytometer for the analysis of fluorescence signals in phytoplankton: Chlorophyll and DNA distributions. *J. Exp. Mar. Bio. Ecol.*, 68:129-144.

Particle aggregation kinetics and ocean energetics at Gulf Stream boundaries

Philip McGillivary
Skidaway Institute of Oceanography
P.O. Box 13687
Savannah, Ge 31416

Rates of particle aggregation in the ocean are determined by both environmentally dependent and particle dependent variables. Data for spatial and temporal variabilities of environmental parameters can be used in particle aggregation models to better assess hypotheses about the effects of particle dependent variables on aggregation. Energy fluxes to the density and current shear fields are known to be crucial environmental data needed for aggregation studies. A method for incorporating 1-3 dimensional oceanic mixing data (acoustic current profiles and density structure profiles) into encounter probability particle aggregation models is presented. Data are furnished for this model from the Gulf Stream western and eastern boundaries, where particle aggregation is actively ongoing. Model runs are used to predict the potential importance and effect of various particle dependent data in these environments.

Observation of marine particles with laser techniques

J. Rudi Strickler
Department of Biological Sciences
University of Southern California
University Park
Los Angeles, CA 90089

The purpose of our work is to construct an instrument which will enable us to observe in situ particles suspended in the marine water column in real time. The system is designed for a resolution better than 15 um in all three dimensions and will allow 30 observations/ second. With these specifications, the field of observation is about 15 mm wide, 15 mm long and 12 mm high. The optical pathway has been described previously (Fig. 1, Strickler 1977, 1982, 1985) and is a modification of a Schlieren optical pathway. A collimated light beam is focused by a condensing lens. At the focal point, a small black spot stops the light from reaching the image plane. Hence, there is only a dark exposure. Any light scattered by a particle within the collimated beam will miss the spot and reach the image plane, forming a light image on a dark background. Out of focus particles do not form a sharp image on the image plane, but particles up to a few centimeters out of focus can be detected. Three-dimensional information is obtained by photographing the same field of view with two cameras at 90 degrees to one another. An infrared laser, which does not disturb marine life in the dark, is used as a light source.

We have already tested and used this method in the laboratory, video taping live zooplankters interacting with each other and with algae. We have observed the behavior of sinking particles of marine snow and subjected them to shear in order to observe particle cohesiveness.

Deployment of this instrument directly in the ocean will allow investigation of many questions arising in the study of particles in marine environments. Analysis of video images taken in situ will give information of particle size distributions, abundances, and particle spacing, shape, and potential origin. Information on processes of particle fragmentation and flux may also be possible. For example, we have observed that phytoplankton become entrained around sinking copepods, particularly near their mouth parts, and thus are transported to depth more rapidly than single cells. Similarly, sinking patterns of particles, behavior of zooplankton and processes occurring at boundary layers may be

observed directly.

This system is different from most systems used for the observation of suspended particles in that 1) we videotape the temporal behavior of the particles allowing us real-time first evaluation of the observation as well as computerized image processes of the observations and 2) we observe suspended particles in a frontview-sideview fashion allowing us to use the computer assisted design (CAD) programs for the analyses.

This system can be modified to resolve particles of around 1 um in size, or to scan large volumes of water. F rther application may use the same basic optical path because it allows simultaneous observations of suspended particles in the size range of 10 um to 3 cm.

Strickler, J. R. 1977. Observations of swimming performances of planktonic copepods. Limnol. Oceanogr. 22: 165-170.

Strickler, J. R. 1982. Calanoid copepods, feeding currents, and the role of gravity. Science 218: 158-160.

Strickler, J. R. 1985. Feeding currents in calanoid copepods: two new hypotheses. pp. 459-485, In M. S. Laverack (ed.), Physiological Adaptations in Marine Animals, Symp. Soc. Exp. Biol. 39.

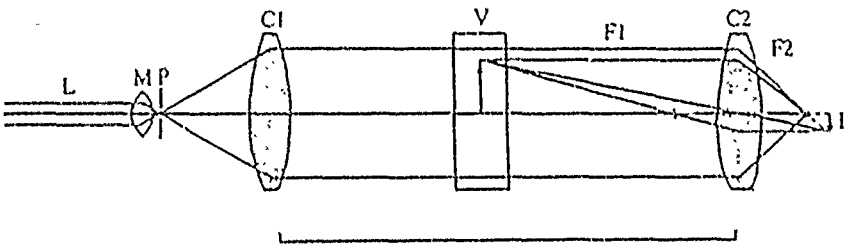


Fig. 3. Optical pathway used to obtain Fig. 1. The collimated light beam (4 cm diameter) is an enlarged laser beam (L) which passed a spatial filter (M = microscope lens, P = pinhole, C1 = collimator lens). All collimated light is focused by the condenser lens (C2) onto the black dot in the back focus (F2). The image (I) of the object in the vessel (arrow in V) is formed by diffracted light (F1 = front focal point). Bar equals ~ 100 cm.

In Situ Measurements of Single Particle Optical Observables

Philip J. Wyatt

Wyatt Technology Corporation
820 East Haley Street
Santa Barbara, CA 93130-3003

Measurement of the light scattering properties of single particles permits the development of certain sets of "optical observables" by which means such particles may be characterized, classified, and/or identified. Ideally, these particles should be measured in situ, but until this time, instrumentation to achieve this has not existed.

Under the ongoing ONR Contract N00014-85-L-0307 we have developed an instrument that may be operated at any depth and which measures the scattered light intensity at many angles from single particles entering the approximate one microliter field of view. Although the contract is devoted primarily to phytoplankta characterization and identification, its broad range of application certainly includes bacteria, bubbles, and many types of aggregates. For example, a dual read head instrument was delivered to NORDA in July for the in situ measurement and discrimination bubbles in the 2μm to 100μm range at depths down to 250m.

The typical read head structure is comprised of a polarized laser light source, a set of 16 optical collimators (optical fibers plus field of view limiting lens), 16 polarizing analysers, and a open framework to support the optical collimators at up to 72 different angular positions. The framework consists of three intersecting great circles whose common diameter is the laser beam. Small radially-aligned apertures in these circles permit the insertion and holding of the optical collimator/analyser structures at any unoccupied angular position. The optical collimator/analysers have a very restricted angular acceptance angle ($\pm 1^{\circ}$) which, in turn, limits the field of view seen to about 2mm of the laser beam ($1/e^2$ diameter = 0.8mm). This corresponds to an effective "target" volume of about 1 microliter at the center of the sphere defined by the great circle framework.

As a particle enters the target volume, it scatters light outwardly in spherical waves. Each collimator/analyser collects the light reaching it and transmits it through optical cables corresponding, remote photomultiplier detectors. The 16 PMT signals are converted by means of a 16-channel A/D multiplexer and stored in a computer memory unit for subsequent processing.

By varying the multiplexer scanning frequency, the light scattering profile of the single particle as it traverses the beam may be followed. The collection of these light scattering data is triggered by selecting a required minimum threshold signal at any one of the 16 detectors. Once the threshold signal is detected, the collection and storage of all angular scattering data proceeds until terminated.

The collected data are analysed and reduced to a set of optical observables on which basis the source particle may be characterized. Some of these observables are described that permit velocity, size, density and structural inhomogenity to be monitored. For example, measurements are presented that permit the differentiation of bubbles (spheres) from aggregates, as well as motile from immobile particles.

Finally, other applications of the optical observables are discussed. Foremost among these are the generation of bulk radiative transfer properties such as bulk scattering and absorption coefficients. Such coefficients may be synthesized by the suitable combination of optical observable catalogs corresponding to the unique particle population distributions hypothesized to exist at specific locations.

IN SITU PARTICULATE DIAGNOSTICS*

George Gal, Senior Staff Scientist

Electro-Optical Sciences
Research & Development Division
LOCKHEED MISSILES & SPACE COMPANY, INC.
3251 Hanover Street
Palo Alto, California 94304

Characteristics of the radiation scattered by a unit volume of sea water containing suspended particulates depend upon several parameters, such as the wavelength of the incident radiation and the particulate properties. In general, particulate properties can be divided into two categories: (1) properties that appear as parameters in the Mie theory of scattering which are the relative index of refraction, particle size, and size distribution. These parameters must be specified to predict laser beam propagation and light transmission through absorbing media such as atmospheric haze, clouds, and sea water; and (2) properties that involve an approximation, such as the shape of the particle, orientation relative to the scattering plane, and optical depth; i.e., single or multiple scattering. For this discussion we assumed locally homogeneous distribution with spherical particles and that the single scattering (optically thin) condition exists.

Determination of the aerosol cloud number density distribution function, which is essential to the application of the Mie computer codes, can be achieved by two methods, direct sampling and optical scattering measurement. The direct sample method involves collecting samples from the aerosol cloud and sizing the particulate individually. Various sampling techniques are available, but they are subject to calibration errors.

Optical scattering measurement provides an indirect way to determine the cloud particulate size distribution function. Optical techniques have been used for particulates with narrow size distribution functions. However, with the availability of lasers and better computational tools, these indirect diagnostic techniques can be extended to wide size distribution functions. In this technique, measurements are made of the attenuation and scattering of laser radiation from a small volume containing the particulates. By making these measurements at several wavelengths and angles, the data can be used to deduce the particle size distribution and refractive index. This is accomplished by using an accurate matrix inversion scheme and efficient Mie computational subroutines.

Based on our experience with Mie scattering and electro-optical instrumentation, we developed a diagnostic concept to obtain the aerosol size distribution function and the index of refraction. Our approach has two main features: (1) experiments that include a multiwavelength and multiangle bistatic measurements, simultaneously measured spectral extinction, and a time of flight (TOF) velocimetry correlation method, and (2) data analysis that includes the Mie scattering theory and the Backus-Gilbert data matrix inversion technique.

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To prove our diagnostic concept, we have performed a mathematical experiment utilizing atmospheric cloud models, since most of our applications are atmospheric related. However, the method may be directly applicable to underwater conditions as well. We assumed a modified gamma function for particle size distribution representing large $0.01 \leq R\ (\mu m) \leq 20$ droplets that exist as a cumulus cloud layer, or $0.01 \leq R\ (\mu m) \leq 1.0$ polydispersion that can be found under a hazy atmospheric condition. Cloud averaged angular intensity functions $\sigma(\theta)$ $[cm\text{-}sr]^{-1}$ have been obtained from Mie theory. Arbitrary error ϵ (2 to 10 percent) have been added to represent realistic measurements data set. Application of the Backus-Gilbert inversion algorithm provided "experimentally" obtained size distribution function. Careful study of our results (shown in Fig. 1) indicates that a multiwavelength bistatic data set matrix inversion yields the best fit to the originally assumed function.

Application of this method to marine aggregate in situ diagnostics is straightforward with the appropriate wavelength selection. TOF laser velocimetry technique can be applied to measure the suspended aggregates' fall velocity. Two parallel ribbon-like laser beams are transmitted into the measurement volume. When a particle crosses the first beam, it scatters light into the receiver. This light is detected and a correlator clock started. When the same particle crosses the second beam, the light is detected by a second detector and the clock is stoped. The time (t) to cross the distance (d) between the two light sheets is obtained from the correlator. Velocity components perpendicular to the two beams can be determined by $v=d/t$.

At the Lockheed Palo Alto Research & Development Division, we have built and tested a 3-dimensional TOF laser velocimeter system to measure aircraft velocity to a very high degree of accuracy. In principle, we can see no difficulty in combining a 3-dimensional TOF laser illumination system to a bidirectional nephtalometer to provide marine aggregates in situ diagnostic information.

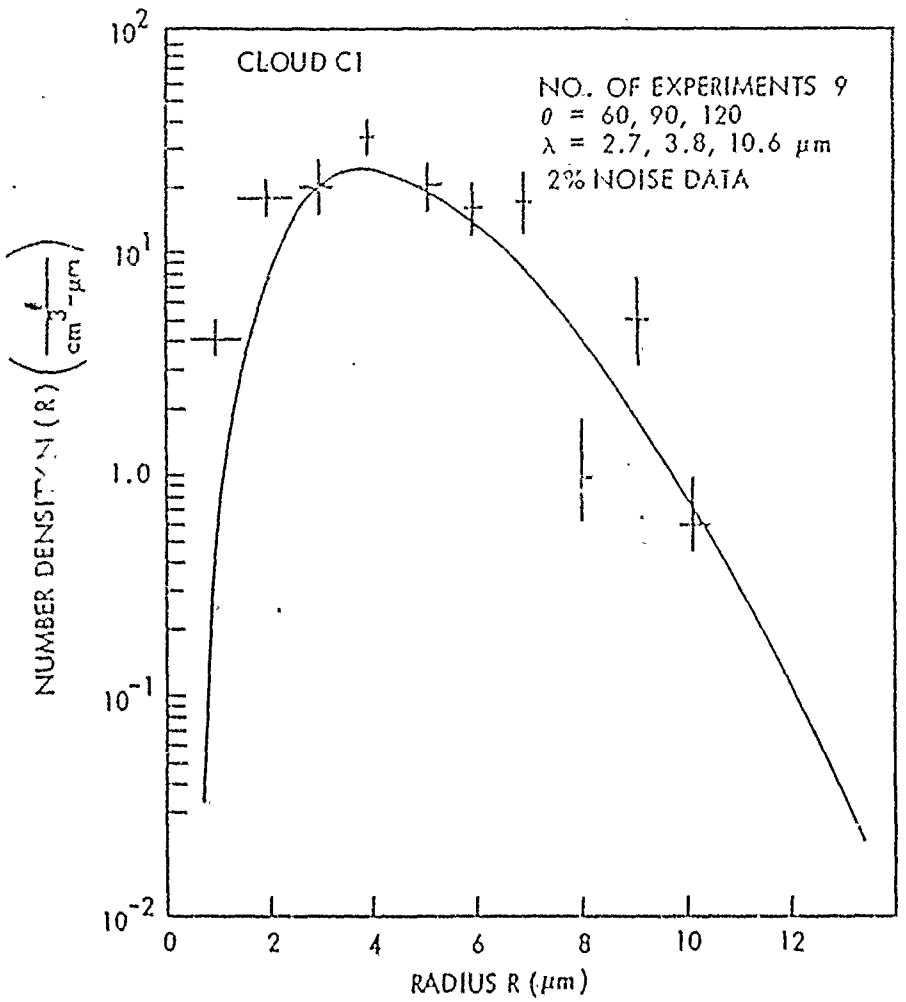


Fig. 1 Actual and Recovered Size Distribution (Mathematical Experiment)

GEOMETRY AND SCALING OF HYDROSOL ENCOUNTER MECHANISMS

Peter A. Jumars and Arthur R.M. Nowell
School of Oceanography, WB-10, University of Washington
Seattle, Washington 98195

Suspension feeding is a major removal mechanism for particles from seawater. Rubenstein and Koehl (1977) provide a listing and parameterization of mechanisms whereby the particle-collecting surfaces of suspension feeders can encounter hydrosols. Their approach is drawn directly from aerosol filtration theory. Focus in aerosol engineering is on efficiency of removal of particles, while success in suspension feeding depends on rate of particle capture. A further major difference between aerosol filtration and many kinds of suspension feeding is that flow is constrained, usually by a duct or pipe, to go through an aerosol filter. One of the consequences, since the aerosol filter occupies some volume, is that flow velocity in the filter will exceed that upstream of it. While not especially important at the single-fiber level (other than with respect to fiber orientation to the flow and gravity vectors) this difference in aerosol filtering versus feeding on hydrosols becomes extremely important when fibers or filter-feeding appendages are close enough to each other to interact. The geometry of suspension feeding resembles the constrained arrangement of aerosol filtration in bivalves, tunicates, appendicularians, and some polychaetes and crustaceans with enclosed filtering systems, resembles it less well for suspension feeders sweeping collecting appendages through open water, and resembles it very poorly for passive suspension feeders. In aerosol filtration a denser filter packing will remove particles with greater efficiency (percent of total particle number); in a passive suspension feeder denser packing of filtering structures may deflect flow around the collector and lead to capture at a lower rate (particles per time) than would a sparser array.

We choose to focus directly on incident particle flux per individual, inherently a biologically more meaningful quantity than filter efficiency. We first provide simple, dimensional parameterizations for each of the hydrosol encounter mechanisms listed by Rubenstein and Koehl (including sieving) and show how they may be generalized to capture structures of any geometry. We do not suggest ours as a replacement for that provided by Rubenstein and Koehl (1977), but rather as an alternative perspective that may be more suitable for some purposes and less suitable for others. The re-analysis we present here makes the physical homology with particle aggregation mechanisms (McCave, this symposium) and with deposition (on the seabed) more obvious.

As one example of the benefit of retaining the dimensional form of the equations or of an alternative non-dimensionalization (i.e., dividing the actual encounter flux by the the particle flux required to just prevent weight loss but not allow growth), consider encounter by gravitation. Flux [particles per time] to the collector surface is simply maximal collector area [length squared] in the plane normal to the gravity vector times particle concentration [number per length cubed] times particle settling velocity [length per time]. Intensity of capture [dimensionless] in the aerosol filtration sense of fiber efficiency is the ratio of particle settling velocity to flow velocity. The dependence on flow velocity and the independence from both particle concentration and collector size arise in the aerosol filtration-intensity term in the process of nondimensionalization. While use of the aerosol intensity-of-capture indices often leads to the conclusion that gravitational capture is unimportant in suspension feeders, consideration of the geometry and

dimensions of the gravitational flux lead to the alternative conclusion that an organism using gravitational mechanisms in particle capture would probably not use a fiber. Since the mechanism does not require a relative (to the collector) flow velocity but does benefit from a large collector area in the horizontal plane, particularly likely users are the net-spinning pteropods. The other mechanisms of capture can be analyzed similarly, retaining important information on the geometry and flow orientation of the collector.

All these equations are written for rigid particles that can be characterized by a single length scale and a single excess density with respect to seawater. It is clear that the physical dynamic properties of aggregates cannot be characterized in the same way. Therefore we are examining several alternative characterizations of particle aggregates from the dynamic perspective, with foci on relaxation times, densities (mass per unit volume), sizes, and behavior in shear flows. These dynamic properties are needed to predict suspension-feeding encounters as well as the behavior of aggregates during settling and deposition.

Reference

Rubenstein, D.I., and M.A.R. Koehl. 1977. The mechanisms of filter-feeding: some theoretical considerations. Am. Nat. 111: 981-191.

Mechanisms of bio-particle interactions as suggested by chemotactic models

George A. Jackson
Scripps Institution of Oceanography
La Jolla, CA 92093

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A potentially important mechanism for aggregation in the marine environment involves the interactions among organisms. Examples include the concentration of phytoplankton by feeding zooplankton and the chemotactic accumulation of bacteria around leaking algae. Simulations of bacterial chemotaxic behavior under a range of conditions helps to understand the potential role of chemotactic interactions in bioparticle interactions. Results show that the efficiency of chemotactic detection is a strong function of the size and chemical efflux rates. Particles smaller than 2-5 μm in diameter are undetectable by chemotactic means. Such a limitation on chemotactic behavior could explain the drop in efficiency of copeod feeding on particles less than about 5 μm. It implies that the mechanisms that organisms use to find particles, either to eat them or to colonize them, depend on the particle size and the leakage of material from the particle. This has implications for the dynamics of aggregate formation and removal.