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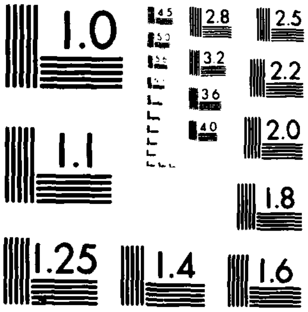

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THE MICROPHYSICS AND CHEMISTRY OF SEA SPRAY AND MARINE AEROSOLS IN THE NORTHERN GULF OF MEXICO

C.K. Akers and E.J. Mack
August 1980
Final Report
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The microphysics and chemistry of sea spray and aerosol in the lower marine boundary layer were evaluated at the NCSC "STAGE I" platform offshore from Panama City, Florida. The results of this program are presented in the form of a technical papers (one to be published and two presented at meetings).

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TABLE OF CONTENTS

SECTION I

INTRODUCTION AND SUMMARY

The understanding of the air/sea boundary requires consideration of at least three layers: the water immediately beneath the surface, the interface itself, and the atmospheric boundary layer above the water. Chemically, the interface itself is dominated by organic molecules. At substantial distances above and below the interface, chemical characteristics are dependent on extended time histories of meteorologic and oceanographic phenomena that affect the air and water respectively. Immediately above the interface, air chemistry is seriously affected by mass transfer, both gaseous and particulate, from the sea. Immediately below the interface, a microlayer exists with chemical and physical properties that are substantially different from the bulk water.

Organic surface films modify physical and chemical phenomena near the sea surface in many ways. Whether natural or synthetic, interfacial films are known to influence such important sea surface phenomena as damping of capillary waves, alterations in sea surface temperature and formation of surface convectional cells, stability of bubbles and foams at the sea surface, movement of gases through the interface, and generation of sea salt aerosols which serve as the condensation nuclei responsible for visibility restriction in the marine atmosphere. Further, concentration and/or collapse of these films, induced by bubble motion and breaking, and by actions of wind and waves, probably generates much of the abundant organic detritus in natural waters.

Microscopic physiochemical and hydrodynamic processes profoundly affect larger-scale geophysical phenomena by modifying the transfer of material from sea to air. Water borne pollutants transported to the sea surface by bubbles are subsequently introduced into the atmosphere by bubble bursting processes, and wind borne pollutants first deposited on the sea surface may be resuspended in the same manner.

Investigations of the mechanisms involved in chemical fractionation should be intensified with particular attention to transfer of matter from bulk water to the air/sea interface to the marine atmosphere as droplet aerosols. Of vital importance is a more complete understanding of the chemistry of the marine atmosphere near the sea surface. The investigation of the chemistry of individual aerosol particles as a function of size will increase our understanding of the effect that material which has been transported across the air/sea interface has to visibility modification.

Under Contract No. N00014-79-C-0033 from the Office of Naval Research, Calspan Corporation initiated an experimental investigation of the transfer of material across the air/sea interface into the marine atmosphere. The primary task was to acquire, during a limited field study, a set of data and samples with which to access the relationship of the microphysics and chemistry of marine aerosols and sea spray to the chemistry of the ocean's microlayer and bulk sea water. It was recognized at the time of the initial contract award, that funding would support only limited data analysis.

The field study was conducted during November-December 1978 in conjunction with a program supported by the Naval Air Systems Command (Contract No. N00019-79-C-0186) to study marine fog and marine boundary layer characteristics at the Naval Coastal Systems Center's offshore platform in the Gulf of Mexico. During this field study, a considerable quantity of data, including sea spray samples for size spectra analysis and samples of sea spray, ocean surface water and bulk sea water for chemical analysis were acquired. Even with the amount of data obtained, the full objective of this program was not met due to instrument failure on the platform. At the beginning of the field trip, the electronic circuit boards of the infrared spectrometer burned out and could not be repaired in time for use during this study (a probable cause of the burn-out could have been the enormous power fluctuations obtained from the platform generators). Infrared analysis of bulk sea water, surface microlayer, and marine aerosol including sea spray was the key technique to be used in correlating all chemical and microphysics data and addressing the question of the air/sea interface transfer.

Sea water samples were acquired at several depths below the air/sea interface. Bulk sea water samples were acquired at a depth of ~10 cm by "grab" sampling" techniques and by pumping water from a depth of 15 m. (The latter sampling apparatus was supported by a Calspan internal IR&D study of microfouling.) The top 125 µm of the sea surface microlayer was sampled using the plate-dipping technique, and the microlayer film at the air/sea interface was sampled using a germanium-prism-dipping technique. A total of 17 sets of samples (surface to a depth of 15 m) was acquired, and these samples were analyzed to provide vertical profiles of the ocean's chemical composition as well as to provide data for comparison with aerosol chemistry.

Marine boundary layer aerosols were sampled at several heights above the surface using a variety of impactor and lo-vol filtration techniques. Samples for size spectra analysis were acquired by impaction on gelatin-coated slides at heights ranging from 1 to 16m above the surface; a total of 41 sets of data to provide vertical profile information was obtained. Aerosol collections, via Casella cascade impactors, were acquired at heights of 3 and 16m above the surface for analysis of individual particle composition (via scanning electron microscopy) as a function of size; a total of 30 sets of Casella data was acquired. Finally, 21 hi-vol samples of the sea spray aerosols were obtained on Teflon filters for quantitative elemental analysis of the bulk aerosol. A total of 21 complete data sets were acquired with which to provide vertical (atmospheric) profile information on aerosol size and composition for comparison with measured sea water composition.

In addition to these data, a considerable quantity of additional back-up data was acquired in support of the NASC effort.

Sea water samples acquired during the field study were analyzed for chemical composition. Twelve sets of water samples were analyzed for heavy metals, and seventeen sets were analyzed for sulfate concentration, pH, conductance and liquid surface tension.

Due to the location of the STAGE I platform with respect to the Florida coastline, the aerosol data are segregated into two groups based on wind direction: Group I (continental air mass) consists of all data obtained when winds were from 300 to 135 degrees true (northerly component) and Group II (marine air mass) contains all data acquired when winds were from 150 to 270 degrees. Segregation of the data permits comparison of continental and marine aerosol characteristics.

The two types of aerosol samples (bulk filter and impactor) were analyzed for chemical composition. Forty lo-vol filter samples were analyzed by x-ray fluorescence for bulk elemental composition. Thirty-seven impactor aerosol samples were analyzed for surface active organic content using the Force-aera isotherm technique. (The aerosol force-area isotherms were compared with force-area isotherms of bulk and microlayer seawater samples.) Thirty-seven samples for sea spray size analysis were also analyzed. Approximately 8 sets (from a total of 30) of Casella impactor samples were analyzed for individual particle composition.

A technical paper summarizing results of this investigation has been submitted to the Journal of Geophysical Research for publication. A copy of the transcript of the paper is provided in Section 2.1. A portion of these data was presented at the 1979 Annual Spring Meeting of the AGU in a paper titled Microphysics and Chemistry of Sea Spray in the Marine Boundary Layer, by Akers, et. al. A copy of the transcript of this paper is provided in Section 2.2. A portion of these data was also presented at the Second Conference on Coastal Meteorological, in January 1980 at Los Angeles, California in a paper by Mack, et. al. A copy of the transcript of this paper is provided in Section 2.3.

SECTION 2

RESULTS

2.1 Technical Paper submitted to the Journal of Geophysical Research:

The Physical and Chemical Characteristics of Sea Spray and Marine Aerosols in the Northern Gulf of Mexico.

Part 2: Chemistry at the Air/Sea Interphase.

BY

AKERS, C. K. AND MACK, E. J.

TITLE: The Physical & Chemical Characteristics of Sea Spray and Marine Aerosols in the Northern Gulf of Mexico. Part 2: Chemistry at the Air/Sea Interphase.

AUTHORS: Akers, C. K. and Mack, E. J.

ACKNOWLEDGEMENT: This program was sponsored by Office of Naval Research Code 465 (Contract No. N00014-79-C-0033). The authors acknowledge the co-operation of the Naval Air Systems Command, Naval Avionics Center, the Coastal Studies Institute, and the Naval Coastal Systems Center during the Panama City II field program. The authors would also like to express their appreciation to other members of Calspan's Environmental Sciences Department who participated in the acquisition of these data and to Dr. Jack Durham (EPS's National Environmental Research Center) for the XRF analysis. Particular appreciation is expressed to Mr. R. J. Pilie for his many contributions during the conduct of this program.

I. INTRODUCTION

The understanding of transport of material across the air/sea boundary (interphase) requires consideration of at least three layers: the water immediately beneath the surface, the air/sea interface (surface microlayer), and the atmospheric boundary layer above the water. At substantial distances above and below the air/sea interface, chemical characteristics are dependent on extended time histories of meteorologic and oceanographic phenomena that affect the air and water, respectively. Immediately above the air/sea interface, air chemistry is seriously affected by mass transfer, both gaseous and particulate, from the sea. Immediately at the interface, a microlayer exists with chemical and physical properties that are substantially different from the bulk water.

Organic surface films located at the air/sea interface modify physical and chemical phenomena near the sea surface in many ways. Whether natural or synthetic, interfacial films are known to influence such important sea surface phenomona as damping of capillary waves, alterations in sea surface temperature and formation of surface convectional cells, stability of bubbles and foams at the sea surface, movement of gases through the interface, and generation of sea salt aerosols which serve as the condensation nuclei responsible for visibility restriction in the marine atmosphere. Further, concentration and/or collapse of these films, induced by bubble motion and breaking, and by actions of wind and waves, probably generates much of the abundant organic detritus in natural waters.

Microscopic physiochemical and hydrodynamic processes profoundly affect larger-scale geophysical phenomena by modifying the transfer of material from sea to air. Water-borne pollutants transported to the sea surface by bubbles are subsequently introduced into the atmosphere by bubble bursting processes, and wind-borne pollutants first deposited on the sea surface may be resuspended in the same manner. Assessment, therefore, must be made of the mass transfer of many elements at the air/sea interphase before the relative importance of oceanic and continental aerosol sources can be determined.

In collaboration with the Naval Avionics Center (NAC), the Naval Coastal Systems Center (NCSC), the Coastal Studies Institute (CSI), and the Naval Oceanographic Research and Development Activity (NORDA), Calspan participated in a study of the marine boundary layer in the Northern Gulf of Mexico. This interagency cooperative experiment has been named PANAMA CITY I and II. PANAMA CITY I was conducted during a two-week period in February 1977 (Refs. I and 2), and PANAMA CITY II was conducted during a four-week period in November and December 1978 (Refs. 3 and 4). During the experiments, Calspan obtained measurements from aboard NCSC's offshore platform (STAGE I) and initiated a limited experimental program to investigate the transfer of material across the air/sea interface. The objective of this experimental effort was to obtain measurements of the physical and chemical characteristics of sea spray with which to assess parametric dependencies of the marine aerosol on the meteorology and oceanobraphy of the air/sea interphase.

This paper is divided into two parts. Part 1 documents measurements of sea spray size spectra as functions of wave height, wind speed, relative humidity and height above wave crest, obtained primarily during the PANAMA CITY I experiment. Part 2 provides detailed data describing the composition of marine aerosols and sea spray observed primarily during PANAMA CITY II.

2. MATERIALS AND METHODS

Sampling Site: The sampling phase of this portion of the study was performed during a 26-day period from 18 November to 13 December 1978 on the Naval Coastal System Center's offshore platform, "STAGE I." The platform is situated approximately 20 km southwest of Panama City, Florida, as depicted in Figure 1. The platform is approximately 32m by 32m with the upper sampling site located on the deck of the platform approximately 16 meters above mean sea level. The lower sampling site (2 meters above mean sea level) was on a catwalk around the perimeter of the platform. All aerosol and seawater samples were taken from the windward side of the platform to minimize any platform artifact.

Due to the location of the platform with respect to the continental land mass, the data set was divided into two major groups according to wind direction. Samples designated as ",arine" were obtained when wind directions had a southerly component (from 150° to 270° True) and "Continental" samples were taken with wind directions of 300° to 130° True.

Absolute Bulk Aerosol Chemistry: Lo-vol absolute aerosol samples were obtained at the 16m level. Aerosols were collected on 47mm Fluropore Teflon membrane filters (0.5 um pore size). Samples were collected as either marine or continental air mass designates. Therefore, sampling time varied (from 3 hours to 14 hours) depending on the variability of the wind direction. Aerosol samples were taken continuously except during periods of rain or fog. Filter samples were sealed in individual petri dishes for transportation and storage until analyses could be performed. Elemental composition was determined by wavelength dispersive x-ray fluorescence (XRF).

Individual Particulate Aerosol Chemistry: The aerosol particulates greater than 0.2 um diameter were collected on cellulose acetate substrates using a 4-stage impactor (Casella, London, England). A sampling interval of five minutes was used to collect sufficient quantities of particles to permit determination of individual particle morphology and elemental chemical composition. The samples were sealed in petri dishes for storage and transportation.

The individual aerosol particles were examined by scanning electron microscopy (ETEC-Autoscan I) and energy dispersive elemental x-ray analysis (KEVEX) for elemental composition with atomic numbers greater than 10. The substrates were coated with a 20-40nm layer of cadmium to provide a conductive surface for electron microscopic analysis. The morphology and density of individual particles were observed at 50x, 500x, and 5000x magnification. The quantitative elemental composition of individual particles was obtained at 20,000x magnification for an x-ray counting time of 100 seconds. Particles were randomly examined to insure representative analysis.

Seawater: Samples of sea water were taken at three levels: subsurface (at a depth of 50 ft.), bulk (approximately 10cm below surface), and microlayer (top 150 um layer). A submersion pump was used to sample by continuously pumping sea water from 50 feet below sea surface at a rate of 25 millimeters per minute. The bulk seawater, representing the top 10-20 cm of the ocean, was collected by a grab sampling technique using a one-liter glass container. The surface microlayer was collected using the glass-plate dipping technique of Garrett (Ref. 5). The collected sea water samples were split for various analyses. One portion of the samples was analyzed on-site, and the other was returned to Calspan for analysis.

The on-site portion of the water sample was analyzed for sulfate and nitrate anions using EPA standard methods (Hack procedures). Sea water pH was measured using a combination pH electrode (Orion Model No. 407A). The conductivity of the water was measured using a Yellow Spring conductivity cell with 1.06 cell constant. Surface tension of the sea water samples was measured using a DeNouy densitometer with a flamed Pt plate.

The other water samples were sealed in pre-leached polyethylene containers for storage and transportation to Calspan where heavy metal (Zn, Cu, Mn, Fe, Mg, Ca, K, Al, Na) concentration was determined using atomic adsorption. Chloride was determined using EPA standard methods.

3. RESULTS

Aerosol-Bulk Chemistry: The elemental composition data for the bulk aerosol samples are listed in Table 1 in micrograms per cubic meter. The date and sampling time are shown along with the indicator of continental or marine air flow based on wind direction relative to the platform. The sodium ratios of the aerosol bulk chemistry data are listed in Table 2.

Individual Particle Chemistry: Aerosol samples collected with a 4-stage impactor were analyzed for the elemental composition of individual particles in the size range between 0.2 and 10 μm in diameter. The particles were grouped into five categories according to composition:

(1) Those with atomic number lower than Na
(2) NaCl only (sea salt)
(3) NaCl with minor amounts of other inorganic salts
(4) Inorganic salts without NaCl
(5) Si-containing compounds

Of the chemical species composited of elements having an atomic number lower than Na, there are 10 elements which could make up the particulates containing only those elements. However, only four of those have a high probability of being found in the atmosphere: H, N, C, O. There is a high probability that these particles were organic in nature, their sources being combustion products, photochemical processes, or natural continental material.

If the particles are inorganic, then a cation and an anion combination must be formed from those four elements. The only logical cation formed from H, N, C and O in the atmosphere as a particulate is the ammonium ion (NH_4^+). There are several combinations of C, N, O and H which may form inorganic anions, the most likely of which are NO_3^- and CO_3^{--}. It is unlikely, however, that ammonium nitrate was the primary aerosol, since it sublimes under the evacuated conditions of the SEM and would not have been detected as a particle.

The lack of available inorganic ions, therefore, leads to the conclusion that these aerosols were organic material.

The second category of the aerosols are those composed solely of NaCl. In general, these particles were cubic in shape but a few rounded particles were also observed. The source of these particles is, of course, predominantly sea water. Other major constituents of sea water are at least an order of magnitude lower in concentration and, hence, did not show up in the x-ray elemental analysis.

Marine air flow samples typically contained approximately 10 times the number of NaCl particles than did the continental air flow samples.

The third category contains particles that are predominantly NaCl with small amounts of coprecipitated inorganic salts. Based on the Cl x-ray peak, the other inorganic salts were less than 10% of the NaCl present. The data indicate that S was the most common coprecipitate and is assumed to be the $SO_4^=$ ion. S and Ca comprised the next common coprecipitate, presumed to be $CaSO_4$ (gypsum).

The fourth category of particle composition consists of inorganic salts not containing either NaCl or Si. Table 3 shows the elemental composition of particles detected more than once and the number of samples in which the particle species was detected. The majority of this category of particles was found in the continental air flow samples. The ratio of this type of particle found in continental air flow to marine air flow is 9 to 1. The predominant particle elemental composition contained S alone. This particle species was found in 58% of the samples and is assumed to be ammonium sulfate.

In the last category are particles containing Si. In all, 26 different elemental compositions containing Si were observed more than once and these are listed in Table 4. Of these, one was seen in 11 samples, 2 in 7 samples, 1 in 6 samples, 2 in 5 samples, 1 in 4 samples and 19 in either 2 or 3 samples. The predominant Si-containing particle observed in these samples contained Si only. These particles are presumed to be SiO_2 and not of marine biological source (based on particle morphology).

<u>Seawater</u>: The elemental composition and other parameters of sea water that were measured at three depths are listed in Table 5. The only element measured that showed a consistent enrichment at the surface microlayer was Zn with an enrichment at the surface microlayer was Zn with an enrichment factor of 2.3. Zn smelters along the Mississippi River may be responsible for airborne debris which deposits on the ocean surface.

DISCUSSION

Total Aerosol Bulk Chemistry

The sodium ratio vs wind direction data indicate there was constant mixing of marine and continental material (Figure 2). The sodium ratios of Si, Al, Fe, and Ti were high with large variation when the wind was from the continental direction and a minimum when the air was from the marine direction (150° - 270°). This indicates, as expected, that Al, Si, Ti, and Fe are continental in source, and the variation in the data implies a variation in the relative proportions of marine and continental air being mixed.

The Mg/Na ratio was essentially independent of wind direction, although the maximum variations in the data were observed in continental wind flows. The mean value for the Mg/Na ration was, within statistical error, close to that of sea water. Since magnesium is a predominant element in marine salts, the lack of large fluctuations in the magnesium/sodium ratio indicates that the predominant source of magnesium and sodium is from the sea. It is unlikely that the mean continental Mg/Na ratio would be similar to that of sea water.

Chloride concentration detected in the air mass was a function of wind direction with the highest concentration, as expected, from the marine wind direction. However, the sodium ratio for chlorine as a function of wind direction varied considerably, ranging from 0.1 to 2.1, illustrating that there was a constant mixing of marine and continental air at all times.

The K and Ca sodium ratios were also wind-direction-dependent. The marine air samples exhibited the lowest sodium ratios, approaching that of sea water. The continental air samples had higher sodium ratios, indicating that K and Ca were also of continental source.

Individual Particle Chemistry

The percentage of particles found in each of these five categories is illustrated in Figure 3 as function of wind direction (marine or continental) and height above the sea surface. The top set of bar graphs illustrates the total composition at both the deck sampling site (16 m above sea level) and the lower level sampling site (2 m above sea level). The data in Figure 3 clearly show that the marine air flow was dominated by NaCl particles. The continental air data also shows the presence of NaCl but shows a significant amount of the particles in the "lower than Na" and "other salts" categories.

The distribution of particles between the 16 m and 2 m sampling levels illustrates the mixing of continental and marine derived particles. The marine air flow samples are obviously dominated by NaCl particles at the 2 m level with a slightly greater proportion of continental-source particles being observed at the 16 m level. The continental air flow samples, however, are not dominated by NaCl particles at either sampling heights; the relative fraction of NaCl particles at the 16 m level being only half that observed at the 2 m level. Further, for continental air flow, particles (lower than Na, other salts, and Si-containing compounds) have the same general distribution at the 2 and 16 m sampling height suggesting that the air mass is predominantly continental with some marine input.

The morphology of the particles varied considerably between the various particle categories (Figure 4). Of the particles that were in the "lower than Na" category, the larger particles were typically amorphous in shape, and the very small particles ($<$ 0.4 um diameter range) were globular. The NaCl particles were generally, but not always, cubic in shape with well defined to rounded edges. The variation in morphology suggests that the NaCl particles with rounded edges may be due to aging in the marine boundary layer. The inorganic salt particles that did not contain NaCl were always globular in shape. The elemental composition of this category of particles suggests that coprecipitation did not allow crystallographic crystal growth. The Si-containing particles were irregular -- generally rectangular in shape. The morphology of the $(SiO_2)_x$ type of particle, which was predominantly found in the continental air flow, suggests that they were not pieces of diatoms but of continental source.

The analysis of the number of times an elemental species was detected in particles with diameters greater than 1 um and less than 1 um provides qualitative information on the source of the particles.

In the marine air flow, the dominate species is Na and Cl with about equal numbers in each particle size range. The other elements are predominantly in the less than 1 um size range as shown in Figure 5 . In the continental air flow, Na and Cl are present in significant proportions. However, there is a dominance in the larger particle size range. This could be a consequence of the surf action on shore compared to the more even distribution in the marine air mass samples caused by white cap action. The other elements are distributed approximately equally between the size ranges. The distributions between elements (excluding Na and Cl) are very similar in each size range indicating a common source.

For each element, the ratio between continental air flow and marine air flow indicates that the continental air contains more of the Al, Si, S, and Zn elements plus more of the "lower than Na" particles. The marine air flow contains more of the sea salt type of elements such as Na, Cl, Mg, K, and Ca. Also, Fe was observed more in the marine air flow than the continental air flow. This distribution of elements indicates that, in the lower marine boundary layer near a coastline, the particles in the 0.1 to 10 um size range are a result of the mixing of particles generated over both the sea and the continent.

Seawater Analysis

The elemental composition of seawater at three depths was the same for Na, Cl, Cu, Mn, Fe, Mg, Ca, K and agreed with known seawater values. However, unexpectedly high concentrations of Zn were observed (the bulk seawater contained an average of 0.04 mg/l, and the surface layer contained an average of 0.046 mg/l). This indicates an enrichment factor of 2.3 in the surface microlayer. Only aerosol samples from the continental air flow contained Zn.

The surface tension lowering of the surface microlayer seawater sample varied, indicating very little to a considerable amount of enrichment of organic material at the surface microlayer (Ref. 6). There was no correlation between surface tension lowering and Zn concentration, indicating that the process of organic enrichment from the bulk seawater is not the mechanism for Zn enrichment. Therefore, the presence of Zn suggests deposition of continental-derived material in the Gulf coastal waters.

SUMMARY AND CONCLUSION

At the "Stage I" platform off the coastline of Panama City, Florida, the aerosol samples were divided into two groups. Continental air flow consisted of aerosol samples obtained when wind directions were between 300° and 130° True. Marine air flow was designated for aerosol samples obtained when wind directions were southerly between 150° and 270° True. The data show that air coming from the continent was modified by the short 20 km fetch between the platform and the shore. Likewise the "marine" air typically originated over continental areas, subsequently experiencing substantial marine modifications. At no time was the type of air being sampled either pure marine or pure continental. Hence, at this close coastal site, pure marine and pure continental air baseline samples were not obtainable.

On the program, bulk aerosol chemistry, individual particle chemistry in the 0.2 to 10 um diameter range, and seawater chemistry was determined. Analysis of results indicates that the lower marine boundary layer is a mixing zone for particulates generated by the sea and by the continent. When the wind direction indicated a marine air flow, the presence of sea salts (i.e., NaCl) was evenly distributed between the 2 m and 16 m sampling levels, and the presence of continental material (i.e., Si, Al, Ti) was at a minimum. When the wind direction indicated a continental air flow, the presence of continental material was as expected, maximum. In some sampling cases with light continental wind, the sea salt was predominant only at the 2 m level, indicating that the 20 km fetch between the shore and the platform was not sufficient to mix sea-derived particles to the 16 m height.

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6. To be published.

Table 1
ABSOLUTE CONCENTRATION OF BULK AEROSOL

DATE (1978)	TIME ON - OFF	ELEMENTAL COMPOSITION (μg/m^3)												
		Na	Mg	Al	Si	P.	S	Cl	K	Ca	Ti	V	Fe	Ba
18/19 NOV	1735 - 0845	0.19	0.037	0.050	0.17	•	1.16	0.18	0.063	0.060	0.011	•	0.096	0.008
19 NOV	0845 - 2245	0.11	0.019	0.058	0.20	•	1.61	0.075	0.053	0.061	0.011	•	0.067	•
19/20 NOV	2250 - 1135	0.48	0.078	0.17	0.57	•	2.33	0.17	0.13	0.14	0.042	0.030	0.18	0.027
20/21 NOV	1350 - 0020	0.24	0.048	0.31	1.16	•	2.81	0.044	0.12	0.14	0.067	0.033	0.23	0.033
21 NOV	0030 - 1730	0.23	0.039	0.26	0.88	0.014	2.27	0.030	0.13	0.12	0.042	0.028	0.20	0.009
21/22 NOV	1735 - 1130	0.28	0.046	0.35	1.24	0.017	1.93	0.035	0.16	0.12	0.063	0.037	0.26	•
22/23 NOV	1230 - 0230	0.15	0.039	0.20	0.89	•	1.80	0.008	0.036	0.043	0.021	0.008	0.072	0.014
23 NOV	0245 - 1402	0.48	0.072	0.15	0.55	•	1.72	0.18	0.090	0.12	0.031	•	0.096	•
23 NOV	1410 - 2046	1.20	0.16	0.035	0.17	•	1.48	1.24	0.083	0.19	0.006	•	•	•
23/24 NOV	2050 - 1202	0.56	0.077	0.013	0.059	•	1.15	0.31	0.051	0.061	0.005	•	•	0.010
24/25 NOV	2150 - 1325	0.24	0.04	0.097	0.30	0.015	0.92	0.40	0.050	0.072	0.015	•	0.092	0.016
25/26 NOV	1330 - 0030	0.19	0.021	0.28	0.85	•	0.95	0.39	0.074	0.074	0.046	•	0.19	0.025
26 NOV	0040 - 1610	0.60	0.121	0.17	0.53	0.015	1.15	0.50	0.11	0.17	0.030	•	0.11	0.023
26/27 NOV	1615 - 0015	1.84	0.277	0.058	0.29	•	1.55	3.35	0.12	0.24	0.019	•	0.087	0.083
27 NOV	0025 - 0340	0.99	0.129	0.012	0.036	•	1.91	1.31	0.084	0.060	•	•	•	•
28 NOV	1130 - 1732	0.098	0.020	•	•	•	0.18	0.14	0.013	•	•	•	•	•
29 NOV	0015 - 1445	0.054	0.008	•	•	•	0.049	0.11	0.005	0.005	•	•	•	•
29 NOV	1500 - 1845	3.66	0.54	0.052	0.19	•	2.93	5.23	0.29	0.29	•	•	•	•
30 NOV	1350 - 2100	0.38	0.054	•	0.011	•	0.53	0.48	0.043	0.027	•	•	•	•
30/1 DEC	2105 - 1005	0.13	0.021	0.006	0.042	•	0.84	0.15	0.036	0.018	•	•	•	•
1 DEC	1040 - 1543	0.085	0.008	0.015	0.054	•	1.31	0.039	0.031	0.023	•	•	•	0.023
1/2 DEC	2000 - 1000	0.18	0.028	0.019	0.075	•	1.22	0.033	0.047	0.24	•	•	0.028	0.008
2 DEC	1023 - 1540	0.17	0.022	•	0.015	•	0.81	0.059	0.022	0.022	•	•	•	•
3 DEC	0120 - 0850	0.93	0.12	0.010	0.041	•	1.61	0.67	0.062	0.15	•	•	•	•
3 DEC	0900 - 2238	1.23	0.19	0.026	0.11	•	0.68	2.20	0.11	0.13	•	•	•	•
4 DEC	0830 - 1627	1.66	0.21	0.054	0.41	•	0.54	3.27	0.10	0.10	•	•	0.068	0.078
5 DEC	0623 - 1043	0.21	0.018	•	•	•	0.50	0.422	0.027	•	•	•	•	•
5 DEC	1550 - 1863	0.87	0.18	0.050	0.20	•	1.50	1.50	0.10	0.25	•	•	•	•
5/6 DEC	2206 - 0700	0.084	0.008	•	•	•	0.096	0.17	0.008	•	•	•	•	•
6 DEC	1028 - 1605	0.16	0.020	0.006	0.052	•	0.43	0.22	0.026	0.033	•	•	•	•
6/7 DEC	2118 - 0641	0.55	0.11	0.020	0.086	•	0.94	0.78	0.051	0.16	•	•	•	•
7 DEC	0937 - 2031	1.11	0.16	0.020	0.081	0.024	1.08	0.91	0.12	0.21	•	•	0.037	0.014
8 DEC	1144 - 1814	1.95	0.24	•	0.012	•	0.60	3.38	0.097	0.16	•	•	•	0.017
8/9 DEC	2306 - 0214	3.16	0.36	•	•	•	0.70	6.80	0.14	0.18	•	•	•	•
10 DEC	1008 - 1450	0.15	0.016	0.016	0.055	•	0.59	0.26	0.023	0.016	•	•	•	•
10/11 DEC	1600 - 0010	0.14	0.018	0.027	0.081	•	0.72	0.25	0.027	0.023	•	•	•	•
11 DEC	0015 - 0745	0.21	0.024	0.048	0.11	•	0.82	0.26	0.043	0.029	•	•	•	•
11 DEC	0750 - 1515	0.069	0.010	0.056	0.10	•	0.79	0.059	0.030	0.025	•	•	•	•
11/12 DEC	2006 - 0403	0.28	0.037	0.037	0.13	•	1.03	0.47	0.066	0.061	•	•	•	•
12 DEC	0408 - 0800	0.33	0.037	0.065	0.15	•	1.12	0.43	0.084	0.056	•	•	•	•

•NOT-DETECTABLE

Table 2
SODIUM RATIO OF BULK AEROSOL

DATE (1978)	TIME ON - OFF	SODIUM RATIO											
		Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Fe	Ba
18/19 NOV	1735 - 0835	0.19	0.26	0.88	*	5.9	1.0	0.32	0.31	0.06	*	0.48	0.04
19 NOV	0845 - 2245	0.18	0.53	1.8	*	14.6	0.88	0.48	0.58	0.10	*	0.80	*
19/20 NOV	2250 - 1135	0.17	0.36	1.2	*	4.9	0.35	0.28	0.29	0.09	0.06	0.38	0.06
20/21 NOV	1350 - 0020	0.20	1.3	4.8	*	11.9	0.10	0.50	0.61	0.28	0.14	0.98	0.14
21 NOV	0030 - 1730	0.17	1.1	3.8	0.06	9.8	0.13	0.67	0.61	0.18	0.12	0.88	0.04
21/22 NOV	1735 - 1130	0.16	1.2	4.4	0.06	8.8	0.12	0.58	0.42	0.22	0.13	0.92	*
22/23 NOV	1230 - 0230	0.25	1.3	5.8	*	11.8	0.15	0.66	0.78	0.38	0.15	1.3	0.25
23 NOV	0245 - 1402	0.15	0.30	1.1	*	3.6	0.38	0.19	0.24	0.06	*	0.20	*
23 NOV	1410 - 2045	0.13	0.03	0.13	*	1.2	1.0	0.06	0.15	0.01	*	*	*
23/24 NOV	2050 1202	0.14	0.02	0.10	*	2.0	0.86	0.09	0.11	0.09	*	*	0.02
24/25 NOV	2150 - 1325	0.16	0.40	1.2	0.06	3.8	1.6	0.21	0.30	0.06	*	0.34	0.07
25/26 NOV	1330 - 0030	0.11	1.5	4.4	*	4.9	0.20	0.38	0.38	0.24	*	1.0	0.13
26 NOV	0040 - 1610	0.20	0.28	0.86	0.03	1.9	8.3	0.18	0.29	0.05	*	0.10	0.04
26/27 NOV	1615 - 0015	0.14	0.03	0.16	*	0.84	1.8	0.08	0.13	0.01	*	0.06	0.04
27 NOV	0025 - 0340	0.12	0.01	0.04	*	1.9	1.3	0.08	0.06	*	*	*	*
28 NOV	1130 - 1732	0.20	*	*	*	1.9	1.4	1.3	*	*	*	*	*
29 NOV	0015 - 1445	0.15	*	*	*	0.90	1.4	0.10	0.10	*	*	*	*
29 NOV	1500 - 1845	0.15	0.01	0.05	*	0.80	1.4	0.08	0.08	*	*	*	*
30 NOV	1350 - 2100	0.14	*	0.03	*	1.4	1.3	0.11	0.07	*	*	*	*
30/1 DEC	2105 - 1005	0.17	0.06	0.33	*	6.7	1.2	0.29	0.14	*	*	*	*
1 DEC	1040 - 1543	0.09	0.18	0.64	*	16.5	0.45	0.36	0.27	*	*	*	0.27
1/2 DEC	2000 - 1000	0.15	0.11	0.41	*	6.7	0.18	0.28	1.3	*	*	0.15	0.05
2 DEC	1023 - 1540	0.13	*	0.09	*	4.8	0.35	0.13	0.13	*	*	*	*
3 DEC	0120 0850	0.13	0.01	0.04	*	1.7	0.72	0.07	0.16	*	*	*	*
3 DEC	0900 - 2236	0.15	0.02	0.09	*	0.55	1.8	0.06	0.10	*	*	*	*
4 DEC	0830 1627	0.13	0.03	0.24	*	0.32	2.0	0.06	0.06	*	*	0.04	0.06
5 DEC	0623 - 1043	0.09	*	*	*	2.4	2.0	0.13	*	*	*	*	*
5 DEC	1560 - 1863	0.20	0.06	0.23	*	1.7	1.7	0.11	0.29	*	*	*	*
5/6 DEC	2206 - 0700	0.10	*	*	*	1.2	2.1	0.10	*	*	*	*	*
6 DEC	1028 - 1606	0.13	0.04	0.33	*	2.7	1.4	1.0	0.21	*	*	*	*
6/7 DEC	2118 - 0641	0.19	0.04	4.5	*	1.7	1.4	0.09	0.29	*	*	*	*
7 DEC	0937 - 2031	0.15	0.02	0.07	0.02	0.87	0.82	0.10	0.19	*	*	0.11	0.01
8 DEC	1144 - 1814	0.12	*	0.01	*	0.31	1.7	0.06	0.08	*	*	*	0.01
8/9 DEC	2306 - 0214	0.11	*	*	*	0.22	2.1	0.04	0.08	*	*	*	*
10 DEC	1008 - 1450	0.11	0.11	0.37	*	3.9	1.7	0.16	0.11	*	*	*	*
10/11 DEC	1600 - 0010	0.13	0.19	0.68	*	6.2	1.8	0.19	0.16	*	*	*	*
11 DEC	0015 - 0745	0.11	0.23	0.60	*	3.8	1.3	0.20	0.14	*	*	*	*
11 DEC	0745 - 1515	0.14	0.78	1.4	*	11.4	0.86	0.42	0.36	*	*	*	*
11/12 DEC	2006 - 0403	0.14	0.14	0.46	*	3.7	1.7	0.24	0.19	*	*	*	*
12 DEC	0408 - 0800	0.11	0.20	0.46	*	3.4	1.3	0.28	0.17	*	*	*	*

*NON-DETECTABLE

Table 3

NON-NaCl INORGANIC SALTS

	CONTINENTAL																		MARINE							
	DATE (MO/DAY) TIME																		DATE (MO/DAY) TIME							
	12/01 1015	12/01 1140	12/01 1430	12/05 1250	12/06 0905	12/06 0650	12/06 1509	12/10 1458	12/11 1450	12/11 1428	12/12 1337	12/02 0635	12/03 0400	12/06 1509	12/07 1123	12/07 1145	12/07 1417	12/07 1725	11/29 1710	11/30 1128	12/03 1310	12/03 2236	12/04 1306	12/08 1427	TOTAL # OF PARTICLES	TOTAL # OF SAMPLES
Na, S	3	2								1	3		1			1	4	2	1	1					18	10
Cl	2								2											1				2	7	4
Na	2	2				1				1						2				1					9	6
Ca	3							2			3	1			2	6						5			19	7
Na, S, Zn	2															1									3	2
S	1	17	3	1				2		2	2	33	27			4	4	4			3	2			105	14
Cl, Ca		1							1															1	3	3
Fe		1		1							1					1					1				5	5
S, Ca		3				1				1		1				2		2			1	1			12	8
S, K			1					1					1			1	4	6							14	6
S, Mg												1				1									2	2
S, Ca, K												1	2				1	1						1	6	5
S, Al													2				2								4	2
S, Al, K													1				1	3							5	3
Cl, S, K								3					1					1							5	3
Cl, S											1					1					1			1	3	3
Na, S, Mg																1	1								2	2

Table 4
CHEMICAL COMPOSITION OF Si CONTAINING PARTICLES

	CONTINENTAL																	MARINE					
	DATE (MO/DAY) TIME																	DATE (MO/DAY) TIME					
	12/01 1015	12/01 1140	12/01 1430	12/05 1250	12/06 0905	12/06 0650	12/10 1458	12/11 1450	12/11 1428	12/12 1337	12/12 1350	12/07 1123	12/07 1145	12/07 1417	12/07 1725	12/02 0636	12/03 0400	12/08 1427	12/03 1310	12/03 2235	12/04 1306	∑	# SAMPLES DETECTED
1. Si				1		1	1	1		2	2		3		3	2			1	3		20	11
2. Na, Al	1					2			1	4	4		1							1		14	7
3. Al		1	1				1						1					1		2		7	6
4. S			1				3							2		4	5		4	1		20	7
5. S, Al			1							1						1	1			1		5	5
6. S, Ca							1							1		1				1		4	4
7. S, Na														1		2	2				1	6	3
8. S, K				1			1								1	1	2					6	5
9. Na, S, Al											1					2						3	2
10. K, Al							1												1	1		3	3
11. Na, Cl, S, K																		1	1			2	2
12. Ca, Al														1						1		2	2
13. Ca														1						3		4	2
14. Na, S, K, Al, Mg, Fe															1					1		2	2
15. Al, Mg, Fe														1	1					1		3	3
16. Na, S, Mg														1						1		2	2
17. Na, Cl, S. Al, Mg, Fe				1										1								2	2
18. Na, Mg.						1								1								2	2
19. Na, Ca, Al											1		1	1								3	3
20. Na, S, K, Mg														1	1							2	2
21. Na, S, K														2	1							3	2
22. Na, Cl							3							1								6	2
23. Na, S, Ca														1	1							2	2
24. Na, Cl, S							2											2				4	2
25. Na, Cl, S, Ca							1											1				2	2
26. Cl							2											1				3	2

Table 5

CHEMICAL COMPOSITION OF SEAWATER

**(50:15 M Below Surface, B:~10 CM Below Surface
M:Microlayer ~150 Micron Surface Layer)**

DATE	TIME hours	SITE	Zn	Cu	Mn	Fe	Mg	Ca	K	Al	Na	Cl
			mg/l									
21 NOV 78	1400	50	–	–	–	–	–	–	–	–	–	–
		B	.013	.039	.027	.100	1010	280	380	ND	11K	19K
		M	–	–	–	–	–	–	–	–	–	–
28 NOV 78	1400	50	–	–	–	–	–	–	–	–	–	–
		B	–	–	–	–	–	–	–	–	–	–
		M	.037	.038	.028	.120	1030	270	390	ND	11K	19K
1 DEC 78	1435	50	.015	.039	.036	.110	1030	280	390	ND	11K	19K
		B	.014	.038	.022	.090	1020	270	380	ND	11K	19K
		M	.022	.035	.033	.130	1030	280	400	ND	11K	20K
2 DEC 78	1700	50	.010	.039	.036	.120	1040	280	400	ND	11K	20K
		B	.014	.038	.034	.120	1060	270	410	ND	11K	20K
		M	–	–	–	–	–	–	–	–	–	–
3 DEC 78	1700	50	.010	.034	.040	.110	1060	280	400	ND	11K	20K
		B	.014	.031	.034	.130	1050	280	390	ND	11K	20K
		M	–	–	–	–	–	–	–	–	–	–
4 DEC 78	1230	50	.019	.035	.043	.110	1060	290	410	ND	11K	20K
		B	.011	.034	.036	.120	1020	280	410	ND	11K	19K
		M	–	–	–	–	–	–	–	–	–	–
6 DEC 78	1500	50	–	–	–	–	–	–	–	–	–	–
		B	–	–	–	–	–	–	–	–	–	–
		M	.042	.035	.025	.130	1020	290	400	ND	11K	20K
7 DEC 78	1110	50	–	–	–	–	–	–	–	–	–	–
		B	.012	.036	.036	.120	1030	280	410	ND	11K	20K
		M	.039	.038	.032	.110	1020	280	410	ND	11K	19K
7 DEC 78	1425	50	–	–	–	–	–	–	–	–	–	–
		B	–	–	–	–	–	–	–	–	–	–
		M	.059	.035	.023	.100	1020	280	400	ND	11K	19K
7 DEC 78	1700	50	–	–	–	–	–	–	–	–	–	–
		B	–	–	–	–	–	–	–	–	–	–
		M	.075	.036	.037	.115	1040	290	400	ND	11K	20K
10 DEC 78	1400	50	–	–	–	–	–	–	–	–	–	–
		B	.014	.037	.034	.120	1040	280	410	ND	11K	20K
		M	.051	.029	.028	.100	1040	290	400	ND	11K	20K
12 DEC 78	1300	50	–	–	–	–	–	–	–	–	–	–
		B	.014	.038	.030	.130	1050	280	400	ND	11K	19K
		M	.046	.029	.034	.110	1030	280	380	ND	11K	19K
ERROR (+ / –)			.003	.005	.005	.010	20	20	10	–	.5K	1K
AVERAGE		50	.014	.037	.039	.113	1048	283	400	–	11K	19.8K
		B	.013	.036	.032	.116	1035	276	400	–	11K	19.5K
		M	.046	.034	.033	.114	1029	282	398	–	11K	19.5K

ND: NON-DETECTED (<0.20 mg/l)

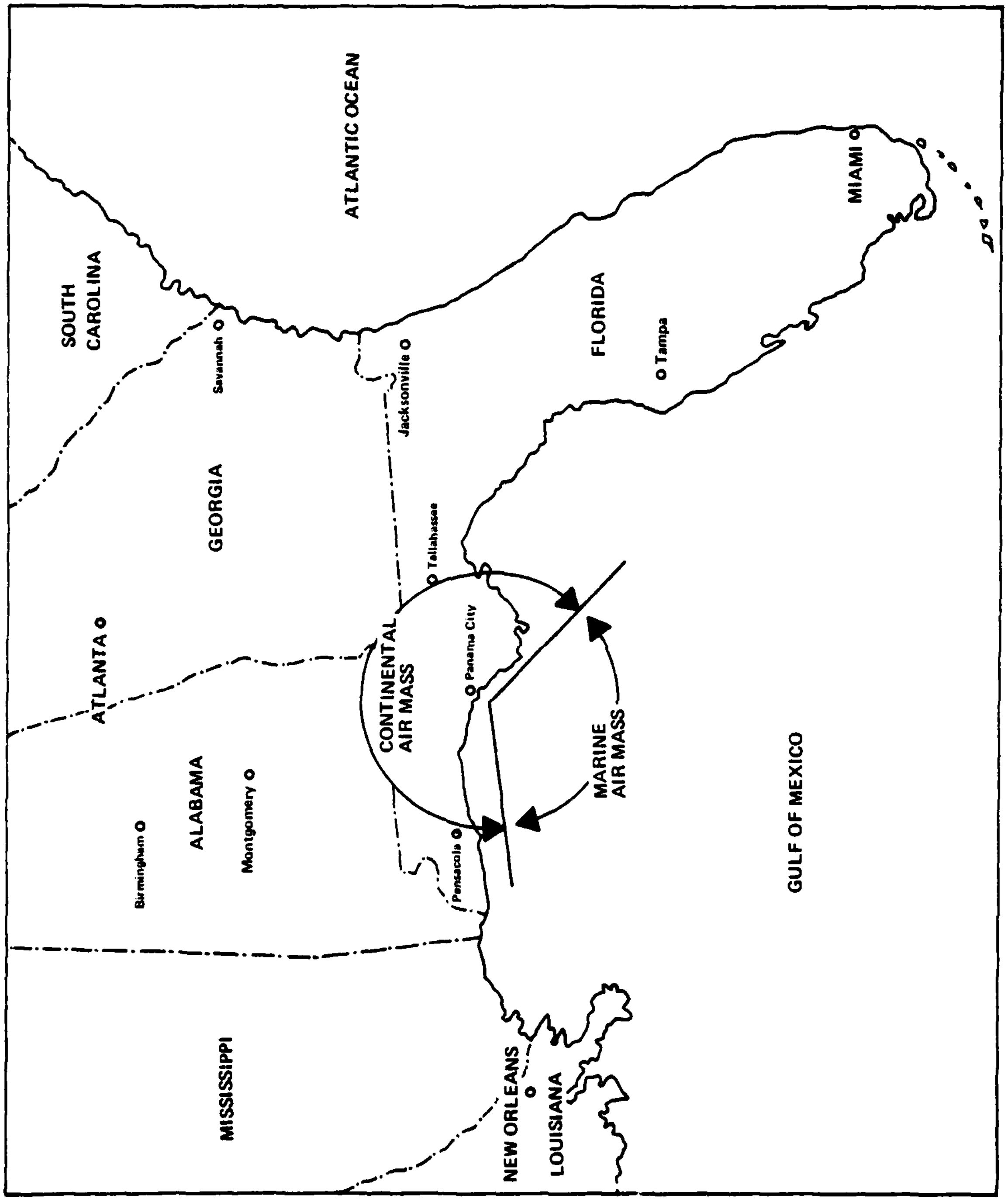


Figure 1 STAGE 1 PLATFORM LOCATION

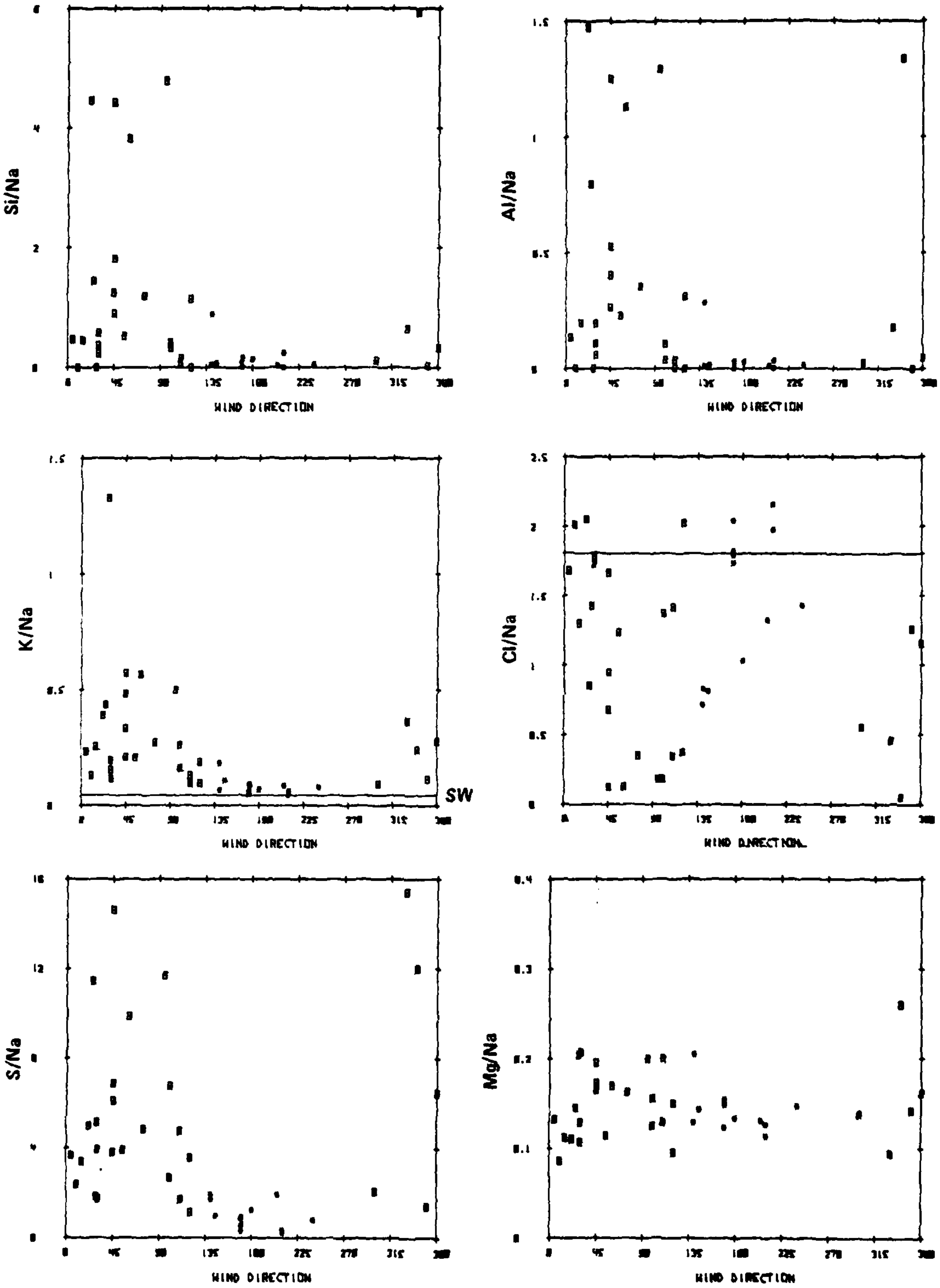


Figure 2 SODIUM RATIO AS FUNCTION OF WIND DIRECTION

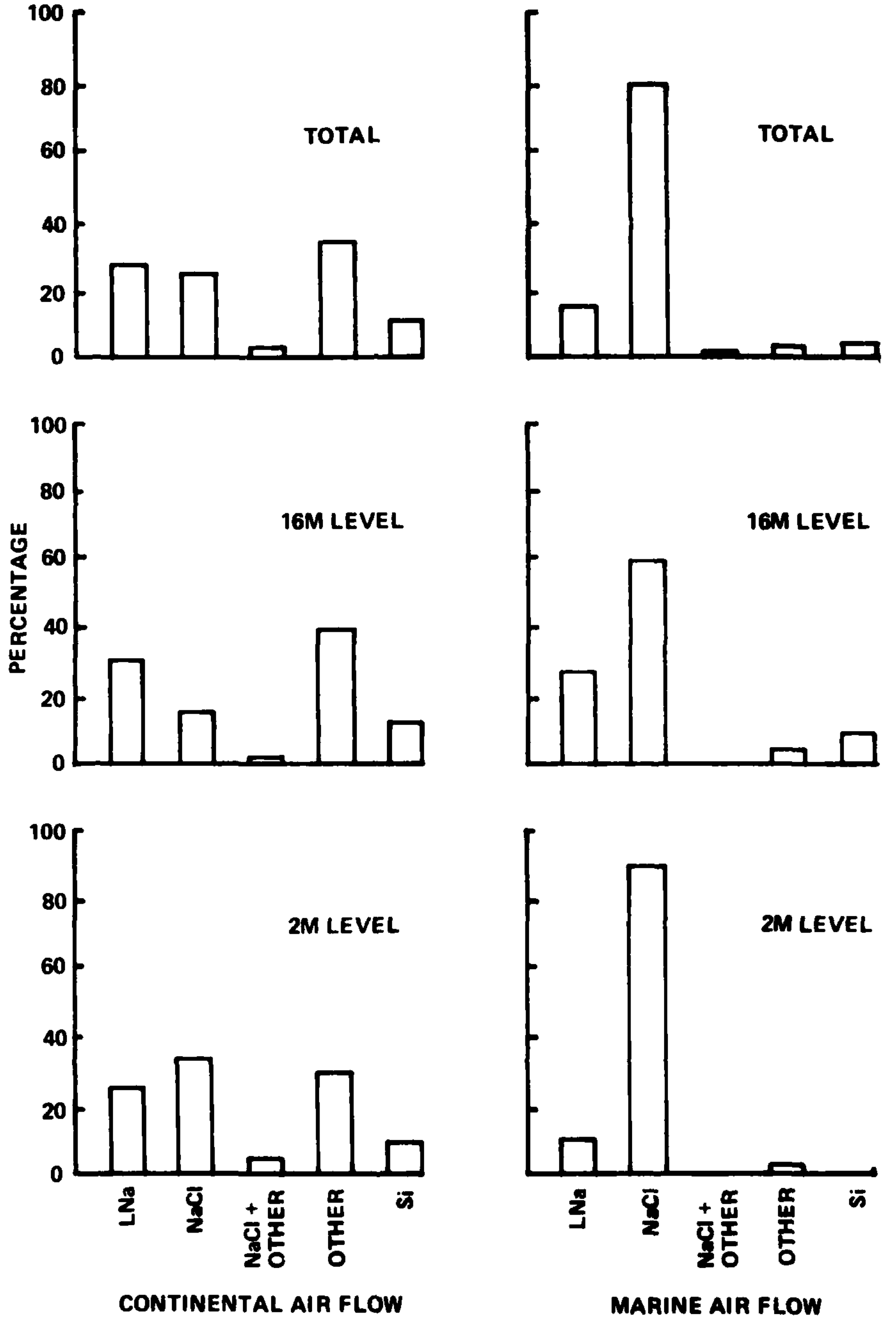
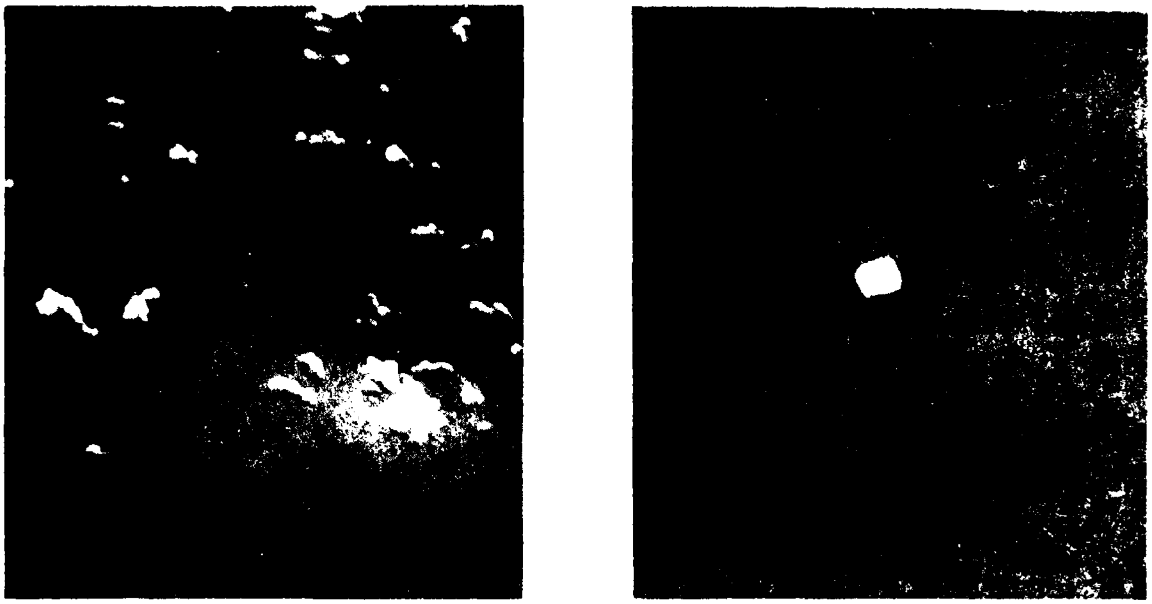
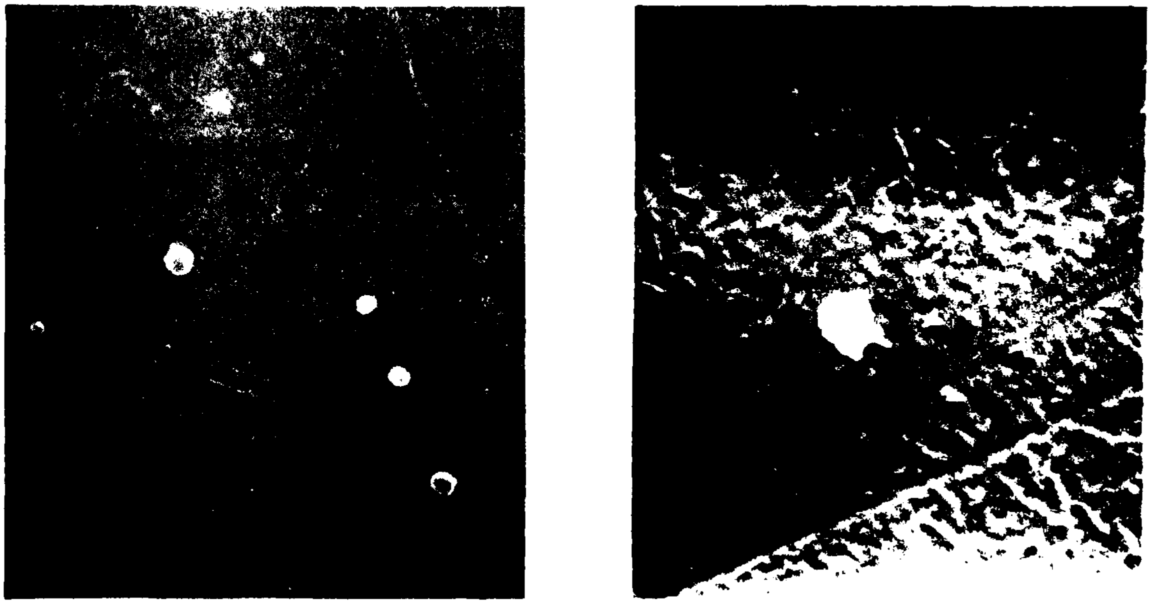


Figure 3 PERCENTAGE OF PARTICLES ACCORDING TO CATEGORY



PARTICLE CONTAINS ONLY
ELEMENTS LESS THAN Na

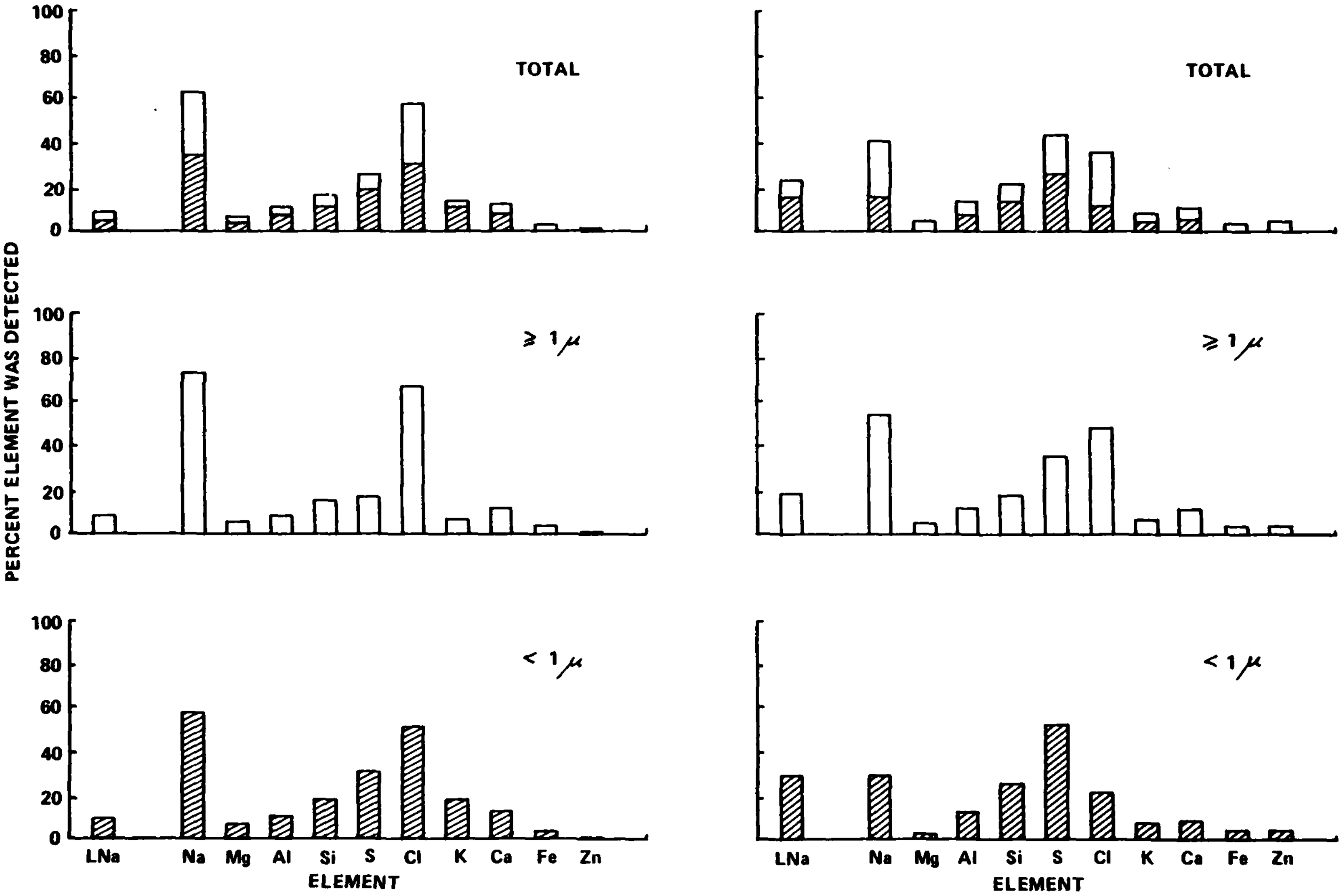
PARTICLE CONTAINS
ONLY Na, Cl



NON-NaCl SALT
(S: ONLY ELEMENT GREATER
THAN Na IN PARTICLES)

Si-COMPOUND
(PARTICLE CONTAINS
Na, Al, Si, Ca, S)

Figure 4 SCANNING ELECTRON MICROGRAPHS OF INDIVIDUAL PARTICULATES



A: MARINE AIR FLOW – WIND 135-270°

B: CONTINENTAL AIR FLOW – WIND 270-135°

Figure 5 ELEMENTAL DISTRIBUTION ACCORDING TO PARTICLE SIZE

2.2 Technical Paper presented at the 1979 Spring Meeting of the American Geophysical Union, Washington, D. C.

MICROPHYSICS AND CHEMISTRY OF SEA SPRAY IN THE MARINE BOUNDARY LAYER

BY

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Goupil, D. W., Anderson, R. J., Hanley,
J. T., and Pilie, R. J.

MICROPHYSICS AND CHEMISTRY OF SEA SPRAY IN THE MARINE BOUNDARY LAYER

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ARLINGTON, VIRGINIA 22217
CONTRACT #N00014-79-C-0033

For the past six years, under sponsorship of the Naval Air Systems Command, Calspan Corporation in cooperation with the Naval Avionics Center, the Naval Postgraduate School, and the Naval Research Laboratory has been conducting an investigation of the evolutionary processes and physical properties of marine fog and marine boundary-layer aerosols. During the first 4 years, attention was focused on determination of the formation mechanisms and physical characteristics of marine fogs occurring off the coast of California and Nova Scotia. For the past two years, the scope of Calspan's effort was expanded to include investigation of evolutionary processes which control compositional and physical characteristics of marine boundary layer aerosols, sea spray, and marine fog.

In this effort, Calspan in collaboration with Naval Avionics Center, the Naval Coastal Systems Center, and the Coastal Studies Institute participated in a study aboard the Naval Coastal System's Center off-shore platform, called STAGE I, to obtain data describing the marine boundary layer characteristics in the Northern Gulf of Mexico. This interagency cooperative experiment has been named PANAMA CITY II and was conducted during a four-week period in November-December 1978. Panama City I was conducted during February 1977.

The Stage I Platform was selected as a test site because it offers the advantage of platform stability while being far enough out to sea that surf generated-aerosols do not interfere with sea spray size spectra. The platform is located 20 km off the coast of Florida, SW of Panama City (Figure 1).

Samples were classified into two categories: marine air (wind with southerly component from 130° to 270°) and continental air (wind from 270° to 130°). This separation of samples according to wind direction is used on all data presented. According to this classification during the 4-week study, marine air was observed ∿28% of the time while, approximately 72% of the time, continental air was observed.

Through the 24-day period of observation, winds, visibility, scattering coefficient, sea surface and air temperature, dewpoint, and wave height were monitored continuously at several levels. Wet/dry bulb temperature readings, atmospheric pressure, weather and cloud cover, total particle concentration, and aerosol size spectra were recorded hourly. In addition, vertical profiles of sea spray size spectra, aerosol impactor samples, lo-vol filter samples and vertical profiles of sea water were acquired at frequent intervals.

Bulk aerosol collections were acquired with lo-vol, absolute Teflon-filter samplers on the main deck. (We gratefully acknowledge the assistance of Dr. Jack Durham and his staff of the Atmospheric Chemistry and Physics Division of the Environmental Protection Agency in providing x-ray fluorescence analysis of these aerosol samples.) Bulk aerosol chemistry was determined from 40 such lo-vol filter samples taken over the three week period. Figure 2 shows the ratio of absolute elemental composition of marine to continental air as derived from XRF analysis of these samples. As expected, the marine air masses contained more of the sea water components (Na, Cl, Mg, Ca, K), and the continental air masses contained more of the elements Si, Fe, Al, and Ti.

Casella cascade impactors were used to obtain particulate aerosol samples in the 0.5 to 5 μm size range at two levels on the platform. These impactor samples were examined using the SEM, and the composition of individual particles was determined via energy dispersion x-ray spectroscopy. From the SEM analysis, the compositions of individual particles were grouped into four classes as shown in Figure 3: (1) particles which contained only elements less than atomic number 11, that is less than <Na; (2) particles which contained only NaCl; (3) particles which were inorganic salts other than NaCl, and (4) particles which contained silicon. In the 0.5 to 5.0 micron size range the continental air contained a distribution of aerosols in the four classes of particulates with a considerable NaCl content and variation between the 4m and 16m levels. The NaCl content, particularly at the lowest level, is presumably due to the 20 km fetch between shore and the platform. With calm wind, little or no NaCl is found at the upper level but measurable concentrations are found at the lower level.

In the marine air, particles in the 0.5 to 5.0 micron size range show a predominence of NaCl particles. The composition data for the two levels illustrates that the marine air mass is essentially well-mixed up to the 16m level due to long fetch over Gulf waters.

During the experiment, more than 150 observations of giant sea spray size spectra were obtained using Calspan's droplet samplers at various heights above the sea surface. The sampler is an impaction device employing gelatin replication to obtain permanent replicas of the droplet population at sizes > 2 μm diameter. Analysis requires tedious microscopy, but the technique provides reliable data which are unavailable by other means. Three such droplet samplers were located at different levels on the platform, and complete vertical profiles of sea spray size spectra were obtained simultaneously.

Figure 4 compares aerosol size spectra for marine and continental air. These spectra were drawn using data from three different pieces of equipment: EAA, Royco, and sea spray droplet sampler. These spectra illustrate the typical differences between continental and marine aerosols, ie., continental air generally has more small particles and fewer giant particles than does marine air. This result is not unexpected since gas-to-particle conversion and combustion processes are major sources of small particles in continental air, while marine air has sea spray and bubble bursting as its major sources of giant particles.

In order to correlate sea spray size spectra with other variables, it was desirable to combine the sea spray size parameters into a single significant parameter that would take into consideration particle number and size distribution at > 2 μm diameter. For this parameter, we have chosen visibility calculated only from the particle size spectra for sizes greater than 2 micron. In this fashion, sea spray size spectra can be correlated with other observed parameters.

Figure 5 illustrates the vertical profiles of calculated visibility obtained from sea spray size spectra taken at heights of from 0.2m to 24m above wave crest. As shown by the data, the contribution to visibility restriction in the marine boundary layer by sea spray aerosols is constant up to a height of at least 24m. Further, we did not observe a droplet size or number dependence to sampling heights upto the 24m level. These observations also imply that the marine boundary layer is well mixed.

Figure 6 shows that there exists a linear relationship between relative humidity and calculated-visibility based on sea spray. However, relative humidity is not solely responsible for the change in visibility from one situation to another because the data do not follow the well known size vs RH relationship for salt solution droplets. This implies that there may be different sea spray droplet populations present at different times and at different relative humidity.

Since wind is the source of wave action and wave action via bubbles bursting phenomena and wave stripping is the main producer of sea spray droplets, it is reasonable that there is a positive relationship between calculated visibility and wind speed (Figure 7).

The relationship between calculated and measured visibility, shown in Figure 7, suggests that only when the relative humidity is high (i.e., > 85%) do the sea spray particles contribute significantly to the visibility restriction in the marine boundary-layer.

In summary, the following conclusions concerning aerosols observed at 20 km offshore in the Gulf of Mexico can be made:

1. The continental air had an observable marine influence even after only a 20 km fetch.
2. The marine air had a continental influence.
3. The sea spray number concentration is a function of wind speed and wave action.
4. But the resultant sea spray particle size distribution is a function relative humidity.
5. Sea spray is predominantly NaCl.
6. The sea spray contribution to visibility restriction seems to be important only at high relative humidity.

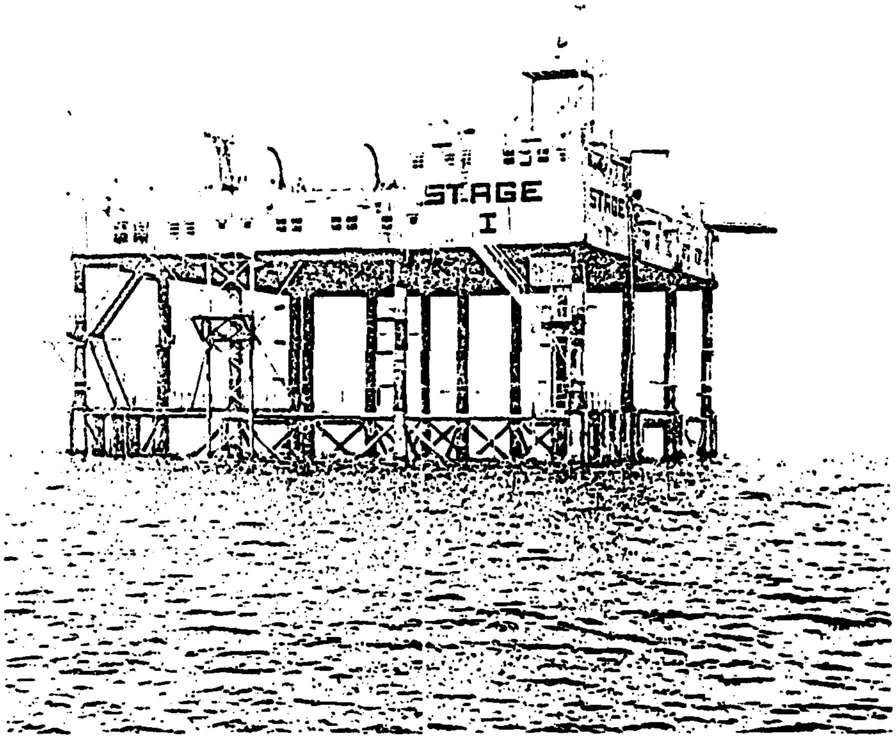

FIGURE 1: PLATFORM

FIGURE 2: RATIO OF ELEMENTAL COMPOSITION OF AEROSOL
(Lo-vol absolute filter samples at 16m level)

	Na	Cl	Mg	Ca	K	S	P	Si	Fe	Al	Ti
MARINE / CONTINENTAL	7.0	9.7	5.9	2.2	1.9	1.2	1.0	.38	.30	.29	.23

$\underbrace{7.0 \quad 9.7 \quad 5.9 \quad 2.2 \quad 1.9}_{\text{MARINE > CONTINENTAL}}$ 1.2 1.0 $\underbrace{.38 \quad .30 \quad .29 \quad .23}_{\text{CONTINENTAL > MARINE}}$

FIGURE 3 PERCENTAGE OF PARTICLES BETWEEN 0.5 AND 5 MICRON ACCORDING TO COMPOSITION

	LESS THAN ATOMIC NUMBER 11 (∠ Na)	Na Cl ONLY	SALTS OTHER THAN NaCl	Si CONTAINING COMPOUNDS
CONTINENTAL				
16M LEVEL	39	15	35	11
4M LEVEL	33	27	31	10
MARINE				
16M LEVEL	8	90	2	0
4M LEVEL	6	91	3	1

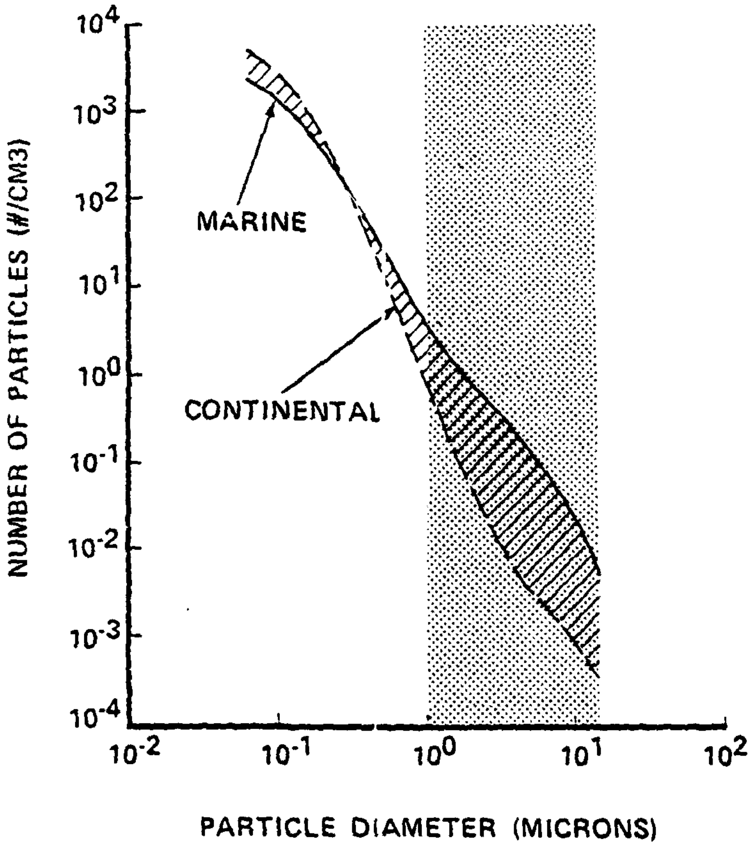

FIGURE 4: PARTICLE SIZE DISTRIBUTION

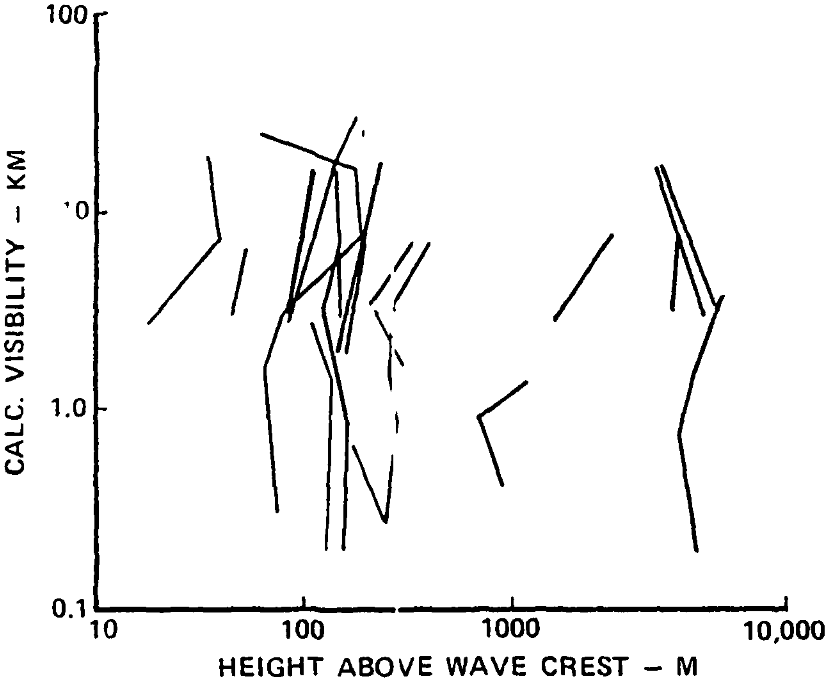

FIGURE 5: CALCULATED VISIBILITY AS A FUNCTION OF SAMPLING HEIGHT ABOVE WAVE CREST

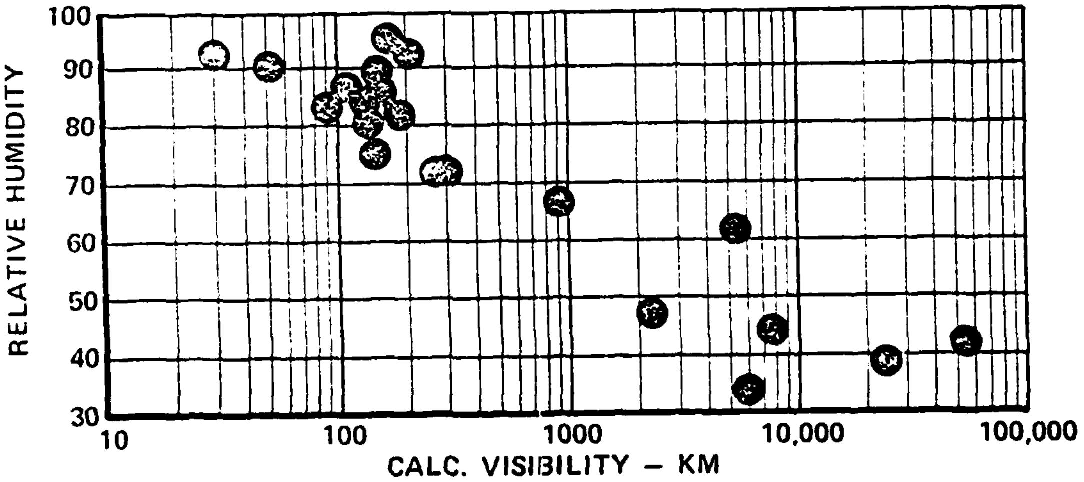

FIGURE 6: CALCULATED VISIBILITY AS A FUNCTION OF RELATIVE HUMIDITY

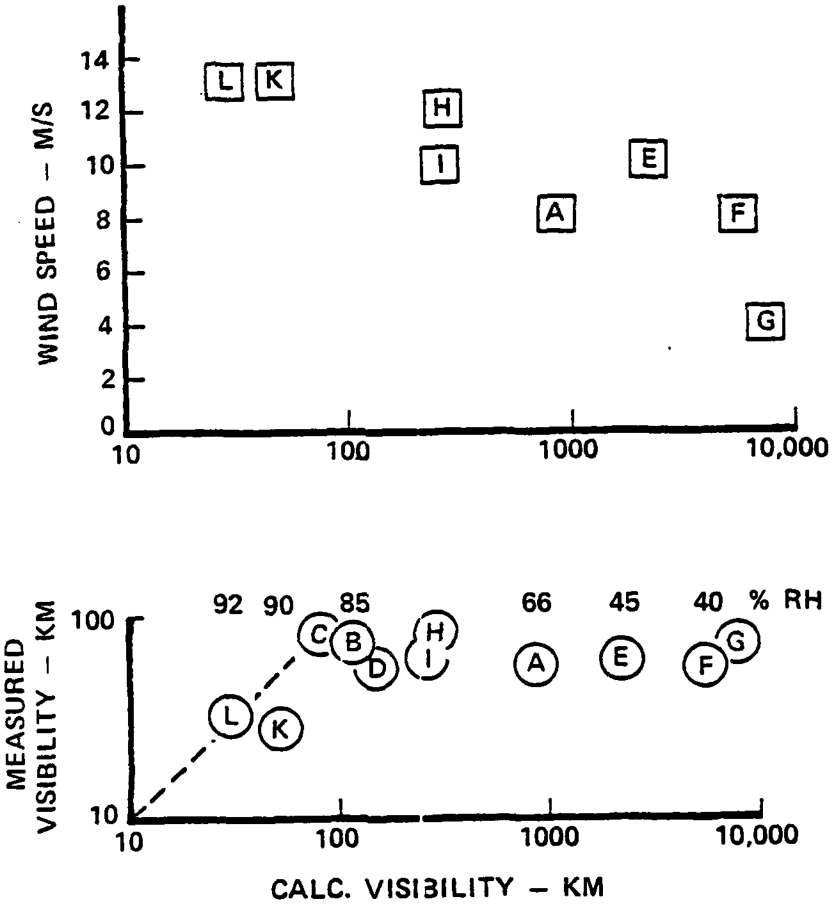

FIGURE 7: CALCULATED VISIBILITY AS A FUNCTION OF WIND SPEED AND MEASURED VISIBILITY

2.3 Technical paper presented at the Second Conference on Coastal Meteorology, January 1980, Los Angeles, California.

AEROSOL IN THE MARINE BOUNDARY LAYER

BY

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AEROSOLS IN THE MARINE BOUNDARY LAYER*

BY

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1. INTRODUCTION AND SUMMARY

During seven at-sea field studies conducted since 1974, a considerable quantity of data was acquired describing the aerosol characteristics of the marine boundary layer in coastal areas off the west coasts of the United States and Europe, off the coasts of New England and Nova Scotia, in the northern Gulf of Mexico, in the Mediterranean and in the mid-Atlantic. These field studies included participation in Panama City I and II, CEWCOM-76 and CEWCOM-78. Observations of aerosol size spectra (0.01 - 30.0 μm diameter), cloud condensation nuclei, bulk aerosol composition, individual particle (>0.2 μm diameter) composition, visibility and relative humidity and other meteorological parameters were acquired in the lowest 20 m of the marine atmosphere. These data show that the marine aerosol population varies considerably in both size spectra and composition, particularly in coastal areas, and does not necessarily comprise primarily sea salt aerosols. The data further demonstrate that what is thought to be "clean" (natural) marine aerosol at one location should not be extrapolated to describe other "clean" marine situations elsewhere nor necessarily be termed "natural". The purpose of this paper is to provide a summary of these data.

The data presented here were obtained as part of Calspan's participation in a broader Navy-sponsored study of marine fog and marine boundary layer characteristics. Specific at-sea studies from which data are provided in this paper are as follows:

1. August 1974, offshore area of northern California (to 140 km offshore) aboard the Naval Postgraduate School's R/V ACANIA (Ref. 1).
2. August 1975, offshore along the New England coast (200-400 km offshore) and off the southern coasts of Nova Scotia and Newfoundland (to 200 km) aboard the Naval Research Laboratory's USNS HAYES (Ref. 2 and 3).
3. September-October 1976 (CEWCOM-76), offshore area of southern California between San Diego and Point Conception to 500 km offshore aboard ACANIA (Ref. 4).

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4. February 1977 and November-December 1978 (Panama City I and II), 20 km offshore of Panama City, Florida, in the Gulf of Mexico aboard the Naval Coastal Systems Center's offshore platform, STAGE I (Ref. 5, 6 & 7).

5. May-June 1977, a Transatlantic-Mediterranean cruise, via Nova Scotia to Athens, Greece, aboard the HAYES (Ref. 8).

6. May 1978 (CEWCOM-78), offshore between San Diego and Point Conception to ∿150 km offshore aboard ACANIA (Ref. 9, 10 & 11).

The instrumentation utilized in these studies included: a TSI Electrical Aerosol Analyzer and Calspan impactors for aerosol and sea spray size spectra (0.01 - 30 μm diameter), a Gardner Small Particle Detector for total aerosol concentration, a Calspan thermal diffusion chamber (static) for cloud condensation nucleus (CCN) activity spectra, an MRI Integrating Nephelometer for visibility and scattering coefficient, Battelle-type and Casella cascade impactors to collect samples of aerosols for individual particle analysis via scanning electron microscopy (SEM) and elemental energy dispersive x-ray analysis (EDXA), lo-vol filter samples (Fluoropore teflon-membrane, 0.5 μm pore size) for bulk aerosol chemistry via wet-chemical and wave dispersive x-ray fluorescence (XRF) analysis, and standard meteorological instrumentation for winds, temperature, dewpoint, etc. Detailed descriptions of specific cruise objectives, cruise scenarios, instrumentation set-up, and data sets may be found in the indicated references.

2. AEROSOL CONCENTRATIONS AND SIZE SPECTRA

Typical and average values for aerosol and CCN observed during respective portions of the aforementioned studies (in the absence of fog and storm conditions) are summarized in Table 1. (The Gulf of Mexico data are averaged for on-shore (marine) and off-shore (continental) wind conditions, while other data show the general range of temporal variations in aerosol concentrations.) Shown in Table 1 are concentration (per cm^3) values for Aitken (total) particulates, those greater than 0.1 and 1.0 μm diameter, and those active as CCN at 0.2% and 1.0% supersaturation. These data show that, in the coastal areas (within 300 km off shore but away from the immediate coastline), total particle concentration is typically $< 6000\ cm^{-3}$, that ∿25-50% of the particles are in the size range 0.1 to 1.0 μm diameter, with the remainder being < 0.1 μm in diameter, and that ∿50% of the particles are active at 1.0% supersaturation. Total-particle and CCN concentrations generally decrease with distance offshore, although high concentrations are often observed well at sea as was the case off the coast of Portugal. Concentrations of large-particles

(< 1.0 μm diameter) exhibit a relatively constant range of ∿0.5 to 5.0 cm^{-3} in the marine atmosphere. Minimum particle concentrations were observed in the mid-atlantic and far-offshore West Coast and may be representative of "clean" marine conditions. At any particular location, however, observed aerosol concentrations exhibit temporal variations of nearly an order of magnitude.

Measured aerosol size spectra were fitted with Junge distributions of the form

$$dN/d\log r = C\, r^{-\beta}$$

where dN is the number of particles per cm^3 in the size range dlog r, and β and C are constants for a given distribution. The Junge distribution applies to the approximate aerosol size range 0.1 to 10.0 μm diameter and provides a mathematical description of the aerosol spectrum. Junge distributions are shown for the northern Gulf of Mexico (for both onshore and offshore winds), along the coast of Portugal (200-1200 km offshore), in the Mediterranean (150-250 km offshore), and for CEWCOM-78 (for data obtained at San Nicolas Island and for data obtained elsewhere within the Channel Islands area to ∿150 km offshore of southern California) and compared with Junge's data (Ref. 12) for polluted continental aerosol. It is seen that the coastal aerosol population differs from continental aerosols spectra in that it comprises higher concentrations of larger aerosols (i.e., >∿5 μm diameter) and lower concentrations of smaller particles (i.e., < 1.0 μ diameter). (The Panama City continental data are weighted to clean airmass characteristics because we experienced a number of early-Winter frontal passages; hence aerosol concentrations were low in the observed fresh airmasses.)

Average CCN activity spectra for a number of at-sea coastal locations are presented in Figure 2. These spectra represent the aerosols which would be expected to change size as a function of relative humidity and hence be responsible for fluctuations of visibility in the marine atmosphere. Minimum values observed in the mid-Atlantic and far offshore of California may be representative of "clean" marine CCN activity spectra. As with the general aerosol population, the highest concentrations of CCN are found on the average closest to the coast, suggesting that continental sources are responsible for the greater fraction of the CCN population. The data in Figure 2 show that average CCN concentrations exhibit spatial variability of an order of magnitude, comparable to temporal variations (see Table 1).

3. THE CHEMISTRY OF AEROSOLS IN THE MARINE ATMOSPHERE

In the marine atmosphere, particularly in coastal areas, the composition (as well as the size spectra) of ambient aerosols is dependent on airmass history and wind trajectories. The influence of winds on the composition of aerosols observed in coastal areas is illustrated by the data presented in Figure 3. In the figure, the airborne concentrations of selected constituents of aerosols sampled during a 4-week period (November-December 1978) from an offshore platform located 20 km southwest of Panama City, Florida, in the Gulf of Mexico are plotted as functions of wind direction. The samples were collected on 47 mm Teflon membrane filters (0.5 μm pore size) with flow rates of ∿30 ℓ/min over sampling periods of from 3 to 20 hours. The results of XRF analyses of the filter samples were averaged for 45° increments in wind direction. (At the platform, winds from the southerly hemisphere between 150°T and 260°T have substantial marine fetch, while northerly winds from 315°T to 090°T have a maximum of 40 km fetch over water after leaving the continent.) The data show that with increasingly maritime air (i.e., with more southerly winds) airborne concentrations of Cl, Na, and Mg (the major constituents of seawater) increased by about an order of magnitude, while concentrations of Si and Al (both originating in soils) decreased; S concentrations remained relatively constant. (Sulfur is the fourth most abundant constituent of seawater, but it is also a major component of continental aerosols.)

Mass loading (airborne concentration) data for these and other observed constituents of marine aerosols are summarized for different marine locations in Table 2. It is readily seen that average concentrations of all constituents of the observed aerosols differed by approximately a factor of 10 between locations. Note that measurable concentrations of such continental materials as Al, Si (and even Mn and Fe) are found far at sea while concentrations of Cl can be quite small in the marine environment. Note that, comparing even the previously defined "clean" marine locations (mid-atlantic and far offshore California), mass loading of the various constituents varies considerably.

The ratio of the concentration of elemental constituents to that of sodium in ambient aerosols in the marine boundary layer, when compared to that of sea water, provides a useful indicator of the continental or maritime characteristics of the aerosol. For example, the sodium ratios for Al and Si in bulk sea water are extremely small (i.e., $\sim 10^{-4}$), and any detectable airborne quantities in the marine atmosphere must be attributed to continental sources. Further, the sodium ratios for Cl and Mg in sea water are relatively constant, and aerosol values which approach those of sea water are indicative of sea salt aerosols. Sodium ratios for the data presented in Table 2 are tabulated in Table 3 and compared against those of sea water to produce enrichment ratios (factors) which are tabulated in Table 4. The enrichment ratio (E) is simply the sodium ratio of an element (X) in a sample divided by the sodium ratio for that species in

$$E(x) = \frac{(x/_{Na})\ \text{sample}}{(x/_{Na})\ \text{sea water}}$$

sea water. If the sample is pure marine (sea salt) aerosol, the enrichment ratio is 1. (Due to limitations and inaccuracies imposed by sampling conditions, sample handling, trace ambient concentrations, filter background and analysis procedures, we consider values ranging from ∿0.7 to ∿1.5 as indicative of pure marine.) Enrichment ratios >1.5 indicate an excess of specific species (relative to sodium) from either fractionation processes at the sea surface or, more likely, continental sources.

All elements considered, the analysis presented in Table 4 suggests that, averaged over the sampling times and respective cruise areas, pure marine aerosols (sea salt) were not observed at any time during the at-sea studies. The closest approach to pure marine aerosol was observed off the coast of southern California (beyond 100 km) in September 1976; but even there a substantial excess of sulfate aerosol matter was observed. The data show that, in addition to elements expected from sea water, there are always at least background levels of materials of continental origin (e.g., S, Al, Si, etc.) in the bulk aerosol observed in the marine atmosphere and that the relative concentrations can vary over a considerable rang

During recent field studies, Calspan has collected aerosol samples with 6-stage Battelle and 4-stage Casella cascade impactors for analysis via SEM and EDXA. The combination of these two techniques allows (1) visualization of the impacted particle where size measurements can be obtained and (2) determination of elemental composition of individual particles with specific identification of elements from sodium (atomic number 11) and greater in atomic number. (Data can be obtained only for particles >0.2 μm diameter; maximum particle sizes are generally < 15.0 μm.) The samples are collected on cellulose acetate proprionate substrates with flow rates of ~12 ℓ/min and sampling times of 1-2 minutes. (The substrate is a smooth, carbonaceous material devoid of interfering elemental composition. A phosphorus peak from a plasticizer in the material is occasionally seen in the x-ray energy spectrum when long count times are used.) A typical example of the particle collections is shown by the SEM photograph (Figure 4) of one stage of a sample obtained in the mid-Atlantic during May 1977. (Note the 10 μm marker at the bottom of the picture.) As shown by the sample, particles in general, are usually rectangular, irregular, or globular in shape; very few readily identifiable cubic NaCl crystals are seen.

After length and width dimensions are measured, the elemental composition of individual particles is determined using energy-dispersive x-ray analysis (EDXA). Examples of the x-ray energy spectrum for each of four different individual particles are presented in Figure 5. 'A' shows the spectrum for a frequently observed group of particles which contained no elements of atomic number equal to or >Na. (The phosphorus peak, P, came from a plasticizer in the cellulose acetate substrate when long count-times were required.) 'B' shows an example of a 'pure' NaCl particle, thought to be sea salt. 'C' shows the spectrum of an aerosol particle of mixed inorganic salts, heavy metal and silicate composition. 'D' shows the spectrum of a particle of mixed composition containing only inorganic salts. From this kind of analysis, it was found that individual particles could be grouped into five categories according to total elemental composition:

(1) those with atomic numbers lower than Na;
(2) NaCl only--sea salt;
(3) other inorganic salts without NaCl;
(4) NaCl with minor amounts of other inorganic salts;
(5) and Si containing compounds.

The percentages of particles found in each of these five composition groups at different locales are shown in Table 5. Inspection of the data reveals that the aerosol populations differ dramatically in composition, comparing one location to another. At times in the marine atmosphere, "pure" NaCl aerosols account for 80% of the aerosol population (>0.2 μm diameter); at other times only 15-20% of the particles are NaCl. In the absence of high proportions of NaCl particles, aerosols composed of elements with atomic numbers lower than Na (probably organics, as will be discussed later) can comprise 15-35% of the observed aerosols, depending on location. Likewise, other inorganic salts (without admixtures of NaCl) can account for 15-45% of the aerosol population in coastal areas. A background level of silicate-containing aerosols, accounting for 2-20% of the aerosols >0.2 μm, is always found. These observed differences in the chemical species comprising the aerosol populations, respectively, of the Atlantic, Coastal Europe, Coastal California, the Mediterranean, and the Gulf of Mexico suggest significant implications in terms of the response of the aerosol to changes in relative humidity and hence, to effects on visibility, depending on the compositional combination of the observed elements within individual particles.

3.1 Chemical Species Composed of Elements of Atomic Number Less Than Na

There are ten elements of atomic number less than sodium which could make-up the particulates containing only those elements. However, only four of those have a high probability of being found in the atmosphere: H, N, C, O. If the particles are inorganic, then a cation and an anion combination must be formed from those four elements. The only logical cation formed from H, N, C and O in the atmosphere as particulate is the ammonium ion (NH_4^+). There are several combinations of C, N, O and H which may form inorganic anions, the most likely of which are NO_3^- and CO_3^{--}. It is unlikely, however, that ammonium nitrate was the primary aerosol, since it sublimes under the evacuated conditions of the SEM and would not have been detected as a particle. Ammonium carbonate is not commonly found in the atmosphere. The lack of available inorganic ions, therefore, leaves the strong probability that these aerosols were organic material, their sources being combustion products, photochemical processes or natural continental organics.

3.2 Particles Composed Solely of NaCl

A second categorization of the aerosols observed during the cruise were those composed solely of NaCl. Some of these particles were cubic in shape, but most were rounded, globular and irregular. These particles are thought to be sea salt aerosols whose other major constituents are at least an order of magnitude lower in concentration and hence did not show up in the x-ray analyses (e.g., Figure 5b).

3.3 Aerosols Comprised of Inorganic Salts Other Than NaCl

The third chemical classification of aerosols observed during these studies was that of inorganic salts which did not contain NaCl. These particles were found to comprise substantial portions of the aerosol population, particularly for Coastal Europe and California and in the Mediterranean. While more than 20 different element-combinations were observed, this group consists primarily of particles containing S, Ca or Cl alone or combinations of these elements. The most frequently observed other elements in combination with these three were K and Fe. The highest portions of S-only particles were found along the European Coast, in the Mediterranean, and in the Gulf of Mexico. Cl-only particles were found chiefly in the Mediterranean and in the Gulf of Mexico. Ca-only aerosols were found in all coastal areas, while combinations Ca-S aerosols were found primarily in the Mediterranean and off the coast of southern California. The candidate chemical species containing only Ca and elements of $<$ Na in atomic number are probably limited to CaO, $CaCO_3$ (calcite) or $Ca(NO_3)_2$. Particles which contained only elemental S or Cl were very likely ammonium sulfate $(NH_4)_2SO_4$ and ammonium chloride NH_4Cl, respectively, since the NH_4^+ ion is the only available cation from the group of elements of $<$ Na in atomic number. The aerosols which contained only Ca and S were probably $CaSO_4$, the common sedimentary mineral, gypsum.

3.4 Mixed Aerosols Composed of NaCl and other Inorganic Salts

The fourth chemical classification contained particles that were primarily NaCl with a small amount of co-precipitated inorganic salts such as those described above. The relative amount of inorganic salt that was observed co-precipitated with NaCl was always less than 10 percent of the amount of NaCl present, based on the Cl x-ray peak. S was the most common co-precipitate, and a combination of S and Ca was the most common mixture associated with NaCl. The data show that these common elemental admixtures to NaCl were uniformly distributed over the Atlantic and in all coastal areas, including the Mediterranean and Gulf of Mexico. These particles probably result from coagulation processes involving marine and continental aerosols.

3.5 Silicate-Containing Aerosols

The final chemical composition group consisted of particles which contained the common soils element Si. More than 40 different elemental combinations were observed containing Si. The most frequently observed Si-containing compound was pure Si and is presumed to have been SiO_2. The remainder of the Si-containing compounds generally were different in chemical composition at different sampling sites, containing various combinations of the common co-precipitates discussed earlier. The most complex of these apparently mixed aerosols were observed in the central Mediterranean.

4. CONCLUSIONS

It must be recognized that the aerosol data presented here were acquired under specific meteorological circumstances(in the absence of fog and storm conditions) and what was observed is not necessarily typical in an absolute sense. However, the data demonstrate that the marine aerosol population does vary considerably in both size spectra and chemical composition, particularly in coastal areas and does not necessarily comprise primarily sea salt aerosols.

1. In the marine atmosphere, total particle concentrations are typically average < 6000 cm^{-3}, and average concentrations of aerosols of >1.0 μm diameter are usually 1-10 cm^{-3}.

2. Concentrations of both aerosols and CCN exhibit temporal and spatial fluctuations of an order of magnitude, but, in general as expected, decrease with distance from shore.

3. Similarly, the airborne concentrations (mass loading) of various chemical components of the marine aerosol also varies temporally and spatially by about an order of magnitude.

4. The marine aerosol, on the average, is not solely composed of sea salt. At times sea salt aerosols can comprise 80% of the marine aerosol burden; at other times as little as 15%. There appears to always be a continental-source component to the marine aerosol burden. The continentally-derived materials most frequently observed in the marine atmosphere are of organic, sulfate, and common mineral origin.

5. Because marine aerosol composition, particularly of the larger more optically effective particles, varies considerably and is not necessarily sodium chloride, aerosol response to changes in relative humidity will vary from one locale to another and will be other than that predicted from assumptions of sodium chloride composition.

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Table 1

Observed Aerosol Concentrations in the Marine Boundary Layer *

		Visibility (km)	RH (%)	Total Part. Conc. (cm^{-3})	Particle Concentration at Diameters >0.1μm (cm^{-3})	>1.0μm (cm^{-3})	-----CCN @----- 0.2% SS (cm^{-3})	1.0% SS (cm^{-3})
Coast of Portugal (within 1200 km)	May 77	20-50	75-90	900-5000	400-2000	0.9-3.0	300-500	600-1000
Mediterranean (150-250 km offshore)	Jun 77	25-60	65-80	800-3500	250-1500	0.7-3.0	150-900	400-2000
Coast of Nova Scotia (within 150 km)	Aug 75	-	-	400-2000	-	-	130	450
New England Coast (200-400 km offshore)	Aug 75	-	-	2000-6000	-	-	580	1350
New England Coast (within 300 km)	May 77	20-80	65-75	4000-15000	1000-5000	0.3-6.0	350	990
Gulf of Mexico (20 km offshore)								
Marine (Panama City, FL)	Feb 77	43	65-95	3400	-	0.1-1.3	-	-
Marine	Nov 78	23	75-95	1700	300-1200	1.0-10.0	730	1450
Continental	Feb 77	32	40-75	5500	-	0.1-1.2	-	-
Continental	Nov 78	20	35-85	3800	1500-3500	0.1-1.0	1010	2130
Offshore Coast of S. California								
(within 150 km)	Oct 76	10-40	70-95	400-4000	-	-	50-1000	400-2200
(within 150 km)	May 78	10-30	75-95	300-10000	100-2000	6.0	100-700	300-3500
(beyond 150 km)	Sep 76	30-80	70-95	< 200-600	-	-	20-200	100-400
Off N. California (100-150 km)	Aug 74	-	-	-	-	-	60	200
Mid-Atlantic	May 77	80	50-75	< 200-500	30-150	0.8-4.0	60-140	90-200

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*Single numbers represent averages; multiple figures are typical range values and do not include extremes.

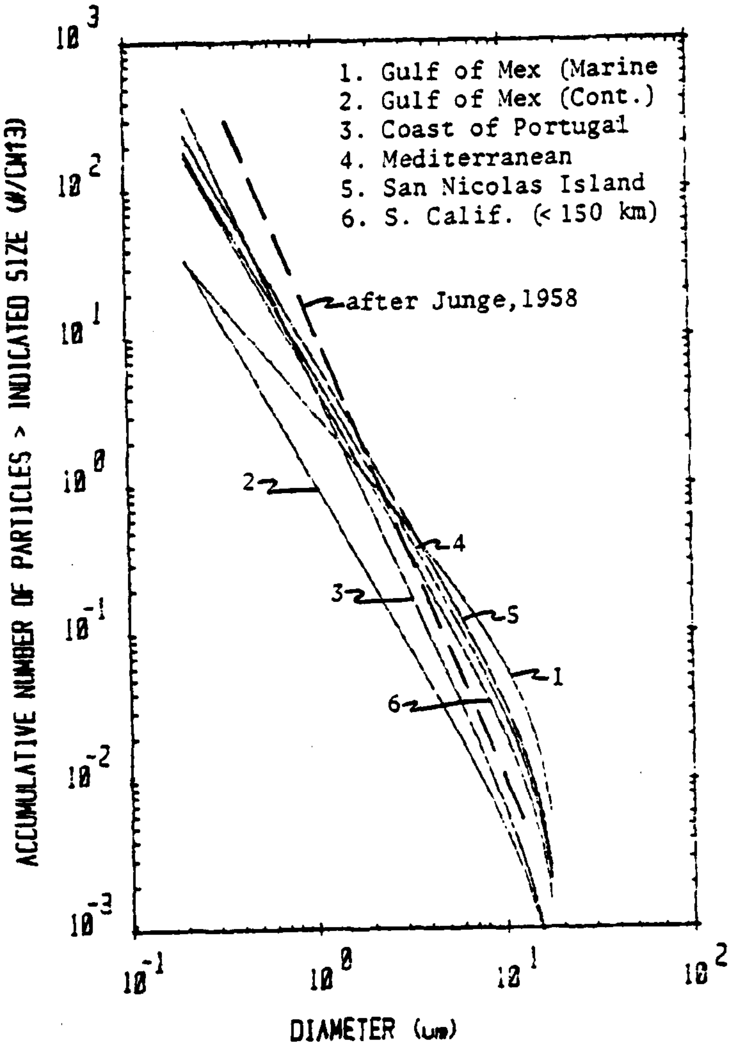

Figure 1. Average Junge Distributions for the Indicated Cruise Areas

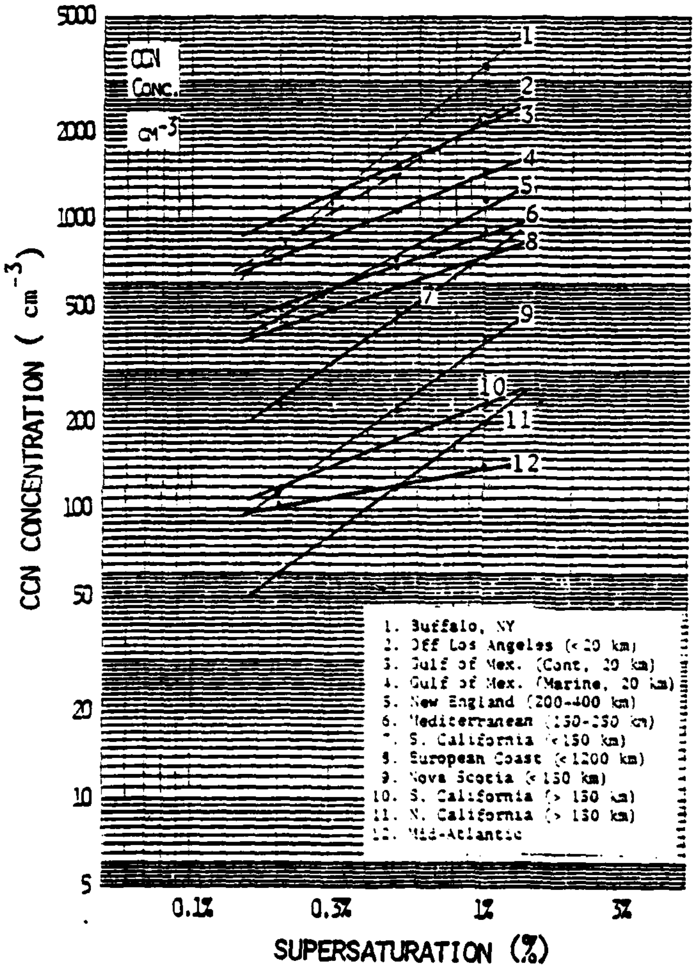

Figure 2. Average CCN Activity Spectra Observed in the Marine Atmosphere (except for Buffalo, NY data)

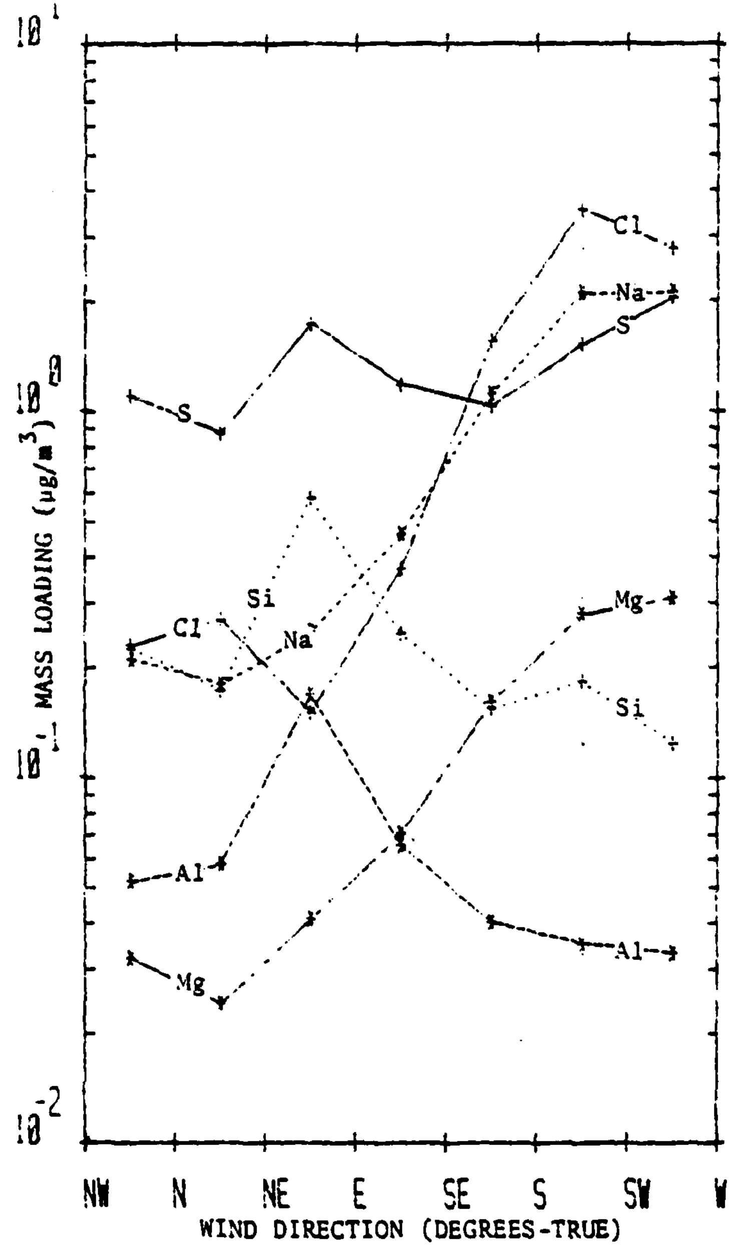

Figure 3. Average Airborne Concentration of the Elemental Constituents of Aerosols Observed 20 km Offshore in the Northern Gulf of Mexico, November-December 1978

Table 2
Average Airborne Concentrations of Selected Constituents of Marine Boundary Layer Aerosols

Absolute Concentrations ($\mu g/m^3$)

		Na	Cl	S	SO_4^{--}	Mg	K	Ca	Al	Si	Mn	Fe
Off N. American Coast(Atlantic) (within 300 km)	May 77	1.0	2.81	1.4	1.4	.38	.08	.44	.22	.44	.01	.50
New England Coast (200-400 km offshore)	Aug 75	1.3	< .02	-	14.0	.12	.22	.13	.26	-	-	-
Off Portuguese Coast (within 1200 km)	May 77	0.2	0.17	1.5	2.1	.08	.03	.09	.05	.11	.02	.06
Mediterranean	Jun 77	0.2	0.17	1.7	3.9	.09	.04	.14	.07	.15	.02	.10
Off Nova Scotia (within 150 km)	Aug 75	0.9	< .02	-	4.0	.05	.19	.09	.22	-	-	-
N. Gulf of Mexico (20 km offshore)												
on-shore wind	Nov 78	1.8	3.01	1.4	-	.25	.12	.17	.03	.16	-	0
off-shore wind	Nov 78	0.2	0.27	1.1	-	.04	.06	.07	.09	.29	-	.06
Coast of South California												
within 100 km	Oct 76	2.1	1.20	-	8.4	.31	.20	.19	.013	-	-	-
within 150 km	May 78	2.1	4.35	0.4	-	.35	.36	.62	.10	.54	0	0
beyond 100 km	Sep 76	2.4	3.10	-	2.5	.30	.14	.08	.004	-	-	-
Mid-Atlantic	May 77	0.4	1.38	0.3	0.3	.10	.02	.06	.02	.03	0	.02

Table 3
Sodium Ratios of Selected Constituents of Marine Boundary Layer Aerosols

Sodium Ratios (X/Na)

		Cl	S	SO_4^{--}	Mg	K	Ca	Al	Si	Mn	Fe
Off N. American Coast (Atlantic) (within 300 km)	May 77	2.81	1.4	1.4	.38	.08	.44	.22	.44	.01	.50
New England Coast (200-400 km offshore)	Aug 75	< .02	-	10.8	.09	.17	.10	.20	-	-	-
Off Portuguese Coast (within 1200 km)	May 77	0.85	7.5	10.5	.40	.15	.45	.25	.55	.05	2.5
Mediterranean	Jun 77	0.85	8.5	19.5	.45	.20	.70	.35	.75	.05	2.5
Off Nova Scotia (within 150 km)	Aug 75	< .02	-	4.4	.06	.21	.10	.24	-	-	-
N. Gulf of Mexico (20 km offshore)											
on-shore wind	Nov 78	1.64	0.8	-	.14	.07	.09	.02	.09	0	0
off-shore wind	Nov 78	1.13	4.7	-	.16	.25	.31	.36	1.22	0	.30
Coast of South California											
within 100 km	Oct 76	0.57	-	4.0	.15	.10	.09	.006	-	-	-
within 150 km	May 78	2.09	.19	-	.17	.17	.30	.05	.26	0	0
beyond 100 km	Sep 76	1.29	-	1.0	.13	.06	.03	.002	-	-	-
Mid-Atlantic	May 77	3.45	0.8	0.8	.25	.05	.15	.05	.08	.03	1.25
Textbook Seawater		1.8	.084	.25	.12	.04	.04	10^{-6}	$3x10^{-4}$	$2x10^{-7}$	10^{-4}

Table 4
Enrichment Ratios (Relative to Sodium Ratios of Sea Water) for Selected Constituents of Marine Boundary Layer Aerosols

Enrichment Ratios $\frac{X/Na\ (Sample)}{X/Na\ (Sea\ Water)}$

		Cl	S	SO_4^{--}	Mg	K	Ca	Al ($x10^5$)	Si ($x10^3$)	Mn ($x10^5$)	Fe ($x10^4$)
Off N. American Coast (Atl) (within 300 km)	May 77	1.6	17.0	5.6	3.2	2.0	11.0	2.2	1.5	0.5	0.5
New England Coast (200-400 km offshore)	Aug 75	< .01	-	43.0	0.8	4.3	2.5	2.0	-	-	-
Off Portuguese Coast (within 1200 km)	May 77	0.5	89.0	42.0	3.3	3.8	11.0	2.5	1.8	2.5	2.5
Mediterranean	Jun 77	0.5	101.0	78.0	3.8	5.0	18.0	3.5	2.5	2.5	2.5
Off Nova Scotia (within 150 km)	Aug 75	< .01		18.0	.5	5.3	2.5	2.4	-	-	-
N. Gulf of Mexico (20 km offshore)											
on-shore wind	Nov 78	0.9	9.5	-	1.2	1.8	2.3	0.2	0.3	0	0
off-shore wind	Nov 78	0.6	55.0	-	1.3	6.3	7.8	3.6	4.1	0	0.3
Coast of South California											
within 100 km	Oct 76	0.3	-	16.0	1.3	2.6	2.4	.06	-	-	-
within 150 km	May 78	1.2	2.2	-	1.4	4.7	7.9	0.5	0.9	0	0
beyond 100 km	Sep 76	0.7	-	4.2	1.1	1.6	0.8	.02	-	-	-
Mid-Atlantic	May 77	1.9	9.5	3.2	2.1	1.3	3.8	0.5	0.3	1.5	1.3

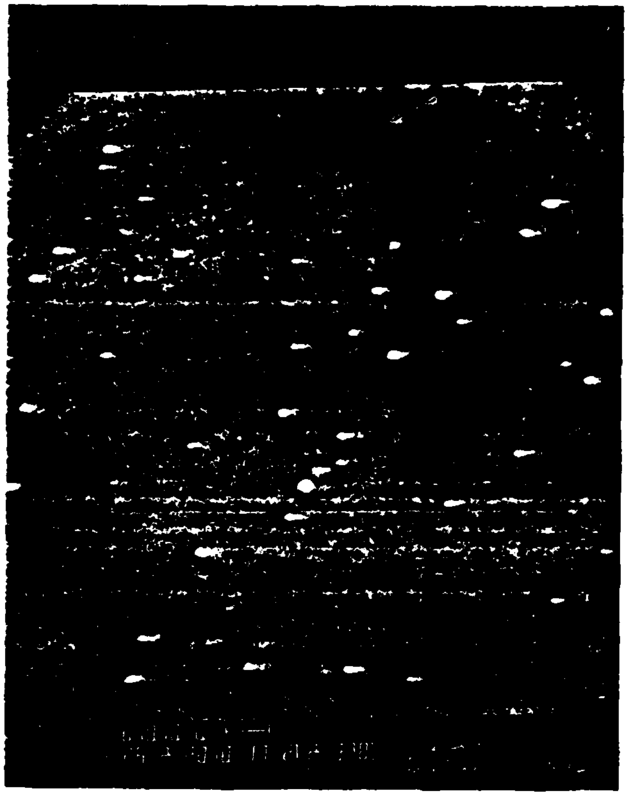

Figure 4. A Scanning Electron Microscope Microphotograph of a Cascade Impactor Sample of Marine Aerosols Obtained in the Mid-Atlantic on 23 May 1977

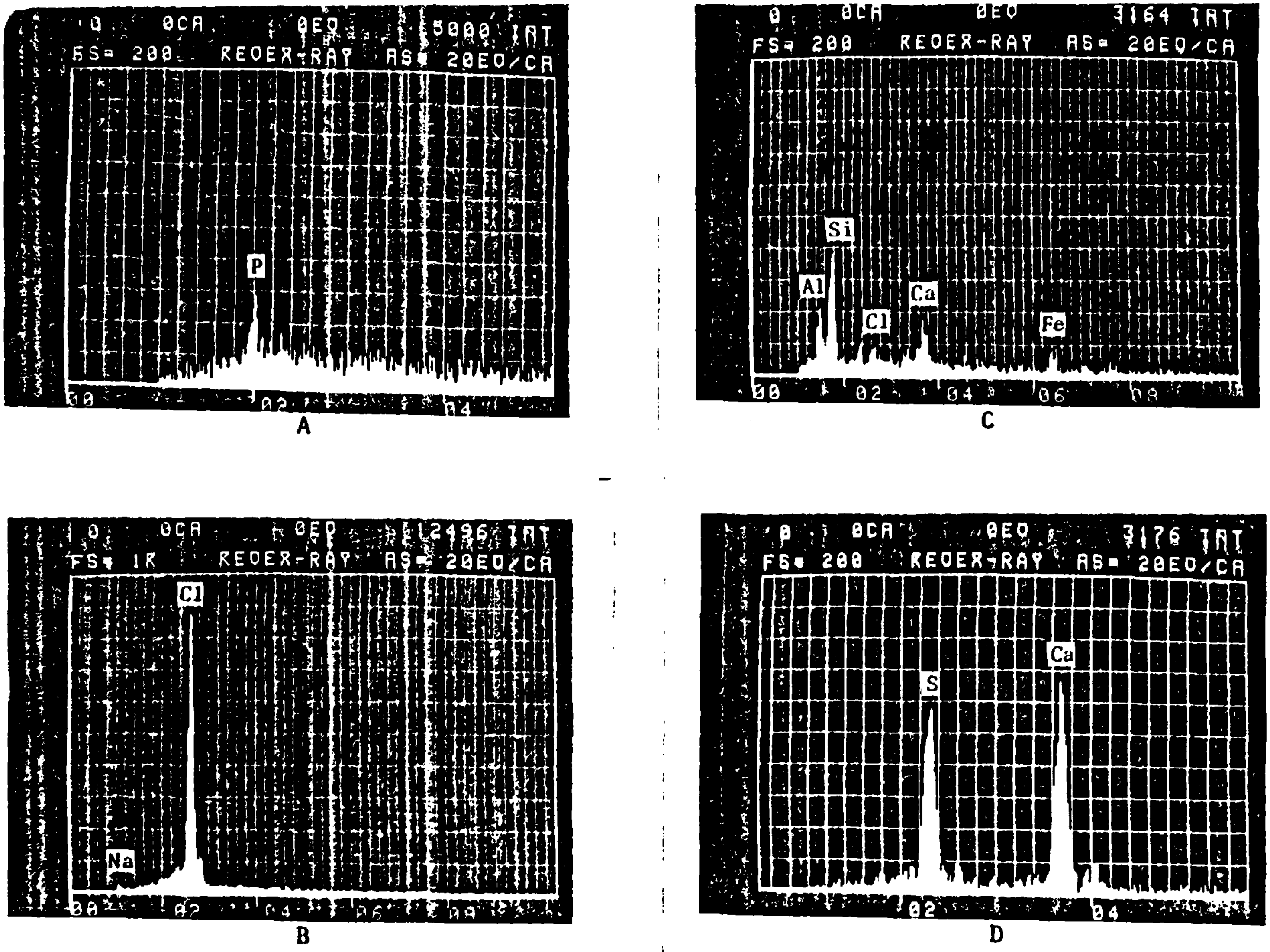

Figure 5. Examples of Individual Elemental X-Ray Energy Spectra of Four Different Marine Aerosol Particles Collected with a Cascade Impactor

Table 5
The Percentage of Particles in the Size Range 0.2-10 μm Diameter As Functions of Composition and Sampling Location

		< Na* (%)	NaCl (%)	Mixed: NaCl and Other Salts (%)	Other Salts Without NaCl (%)	Si (%)	Total Particulates Counted
Coast of Portugal (within 1200 km)	May 77	33	25	17	13	12	200
Mediterranean	Jun 77	17	22	8	44	9	400
New England Coast (within 300 km)	May 77	2	81	11	3	2	150
Gulf of Mexico (20 km offshore)							
Marine	Nov 78	14	80	1	2	3	239
Continental	Nov 78	27	25	3	34	11	280
Coast of South California (within 150 km)	May 78	39	15	1	24	21	1350
Mid-Atlantic	May 77	12	68	10	8	2	300

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*Particles composed exclusively of elements with atomic numbers lower than Na