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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 3/19/97	3. REPORT TYPE AND DATES COVERED Final (see report)		
4. TITLE AND SUBTITLE Oxidation-reduction Photochemistry in Marine Systems		5. FUNDING NUMBERS ONR Grant No0014-89-J-1258		
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9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Dr. Ron Ferek, Code 322 Office of Naval Research, Room 804 800 North Quincy Street Arlington, VA 22217-5660		10. SPONSORING/MONITORING AGENCY REPORT NUMBER		
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION / AVAILABILITY STATEMENT <b>DISTRIBUTION STATEMENT A</b> Approved for public release; Distribution Unlimited		12b. DISTRIBUTION CODE		
13. ABSTRACT (Maximum 200 words) The principal net process in natural water photochemistry is light-catalyzed oxidation of a various organic compounds ("Dissolved Organic Carbon", DOC), with concurrent reduction of dissolved oxygen: $DOC + O_2 + hv \rightarrow \text{Oxidized DOC (e.g. CO, CO}_2, \text{carbonyl compounds)} + HOOH$ . We explored the hypothesis that HOOH forms by one-electron reduction of oxygen to superoxide ( $O_2^-$ ), which then "dismutates" to HOOH. We also quantified $O_2^-$ fluxes and defined some HOOH reaction paths. 1. $O_2^-$ fluxes were quantified in two seasons in the eastern Caribbean; they correlated with total free radical fluxes and with runoff of the Orinoco and Amazon Rivers. 2. Isotopic methods were applied to characterize the slower chemical and biological decay of HOOH. 3. Pulse radiolysis fast-kinetics studies in seawater medium elucidated in detail the kinetics and nature of the dismutation (proton and Cu catalysis) that forms HOOH. 4. A method for directly measuring the steady-state <i>in situ</i> concentration (not flux) of $O_2^-$ in sunlit surface waters was developed and deployed at sea on the R/V <i>Columbus Iselin</i> , which went hard aground on day 3; ONR declined to continue support. 5. A quantitative timeseries model of CO photochemistry was developed.				
14. SUBJECT TERMS photochemistry, upperocean, free radicals, superoxide, hydrogen peroxide		15. NUMBER OF PAGES		
		16. PRICE CODE		
17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT	

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)  
Prescribed by ANSI Std. Z39-18  
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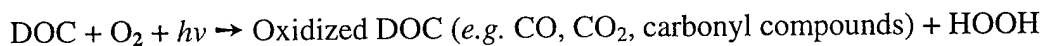
## FINAL REPORT

### Oxidation-reduction Photochemistry in Marine Systems ONR Grant N00014-89-J-1258 Grant Period 10/1/88-12/31/95

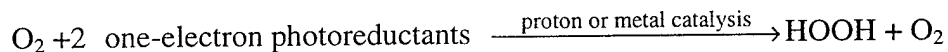
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#### ABSTRACT

While natural water photochemistry comprises a complex array of paths; the principal net process is light-catalyzed oxidation of a various organic compounds ("Dissolved Organic Carbon," DOC), with concurrent reduction of dissolved oxygen:



We explored the "reduction side" by verifying the hypothesis that HOOH forms by one-electron reduction of oxygen to superoxide ( $\text{O}_2^-$ ), which "dismutates" to HOOH, and by quantifying the associated  $\text{O}_2^-$  fluxes and defining some of the reaction paths of HOOH:

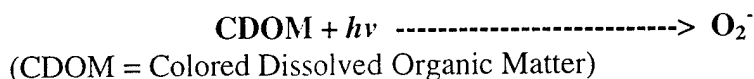


1. Superoxide fluxes were quantified in two seasons throughout the eastern Caribbean. They correlated with total free radical fluxes and with the terrestrial runoff of the Orinoco and Amazon Rivers.
2. Isotopic methods related to those developed for measuring superoxide formation fluxes were also applied to characterize the slower chemical and biological decay of HOOH.
3. Pulse radiolysis/fast kinetics studies in seawater medium elucidated in detail the kinetics and nature of the dismutation (proton and Cu catalysis) that forms HOOH.
4. A method for directly measuring the steady-state *in situ* concentration (not flux) of  $\text{O}_2^-$  in sunlit surface waters was developed and deployed at sea on the R/V *Columbus Iselin*. The ship went hard aground three days on day 3; ONR declined to continue support.
5. A quantitative time-series model of CO mixed-layer photochemistry was developed.

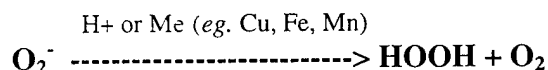
## REPORT

The underlying hypothesis of this work was that important sunlight-driven photochemical reactions in the upper ocean are generally coupled oxidation-reduction reactions (1, 2). These little-known processes oxidize an array of (unknown) organic carbon compounds, concurrently reducing oxygen in a series of processes that, we hypothesize, are (relative to carbon's complexity) straightforward and characterizeable: Key steps are:

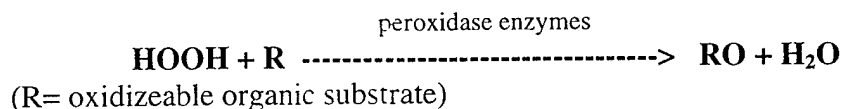
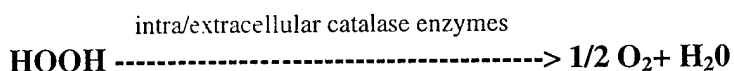
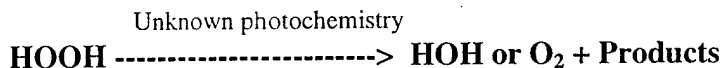
1. Superoxide ( $O_2^-$ ) radical formation:



2. Superoxide loss by catalyzed dismutation, forming hydrogen peroxide:



3. HOOH loss processes:



The thrust of this project has been to explore this hypothesis by characterizing these processes, especially the "chemical" ones 1 and 2, both in quantitative (flux) terms, and mechanistically in terms of basic chemical kinetics and mechanisms and their interactions with the upper ocean's chemical environment (*e.g.* pH variability).

First, a number of novel new methods were developed for this work (3-5).

Second, these were applied in the first major fieldwork phase of this project, which consisted of intensive investigations (jointly with other ONR PI's and in our lab with related NSF-funded projects) exploring the effect of the Orinoco River's photochemically reactive freshwater outflow on the basin-scale photochemistry of the eastern Caribbean by means of cruises in spring and fall, 1988; (*eg* refs 6-11). The major results were published as a Special Section of JGR in 1993 (12). Copies were forwarded to ONR, and three additional copies are submitted with this report).

Third the kinetics of superoxide dismutation were studied pulse radiolysis methods (13); this initial study characterized the proton-catalyzed reaction, indicated that a metal-

catalyzed, chelator-resistant activity existed in river waters, and showed that a number of common trace constituents in seawater had no catalytic activity (eg nitrite, manganese (II), iodate). Subsequent work with Drs. James Moffett and Bettina Voelker is underway, (initial ONR funding, then funded by NSF), to study in more detail the Cu-catalyzed dismutation. When this work is published, it will acknowledge (in part) this grant. Basically, we have now (A) fully characterized the (efficient) SOD-like activity of inorganic Cu species in seawater and explained them in terms of elementary rate constants for Cu(I) oxidation and Cu (II) reduction by superoxide, (B) found that "weak ligand" organic-Cu complexes in seawater (eg humic acid complexes) are also catalytically active with only slightly lower rates than inorganic Cu, (C) found that a "strong" Cu complex involving a chelator excreted by phytoplankton cultures is, surprisingly, also catalytically active, though at only about one-tenth the rate of the other Cu species examined, and (D) shown that there is an ubiquitous "chelation-resistant" (eg metal-independent or complex with extremely strongly bound metal process that contributes enough activity to make the proton catalyzed dismutation irrelevantly slow in all waters examined to date.

Using newly developed  $^{18}\text{O}$  labeling methods, we also investigated the peroxidase vs catalase pathways of dark HOOH decomposition (14), and whether there were light-dependent reactions of HOOH in the eastern Caribbean (10). The latter study revealed low rates of light reactions, validating the use of "dark" HOOH decay rates in quantitative models of HOOH cycling, such as those of Sikorski and Zika (Special Section, (12).

Finally, based on initial expectations (12) that the sea-surface superoxide concentrations near noon might approach 10 nM - a truly astonishing concentration for a reactive free radical, far exceeding that of many important free metal ion concentrations, we designed apparatus and procedures for directly detecting  $\text{O}_2^-$  steady-state concentrations *in situ*- (A) in real time but tentatively by detecting NO loss (3,9), and (B) confirmed later by  $^{15}\text{N}$ -NO methods) to determine whether these expectations of high  $[\text{O}_2^-]$  were correct and hence whether our understanding of superoxide chemistry was sound. The method was based on the same labeled NO trapping technique used previously.

The concept is shown in Figure 1. Figure 2A, B depicts the device as developed in the lab, where it successfully detected (artificially generated) superoxide at low levels (Figure 3). On the fateful 1994 fieldwork cruise of *R/V Iselin*, we learned how to tow the *in situ* probe stably alongside and carried out initial optimizations during the first two days. Retiring early, we expected to do the first true experiment the next day: a pre-dawn to midday *in situ* run. At ca 2200 in perfect weather, the ship ran hard aground. The next morning we found ourselves being evacuated rather than measuring superoxide levels (Fig.4).

As a "postlude" to this frustrating ending, if the considerable progress we have made in the lab holds in the field for freshly collected "blue water," then we would not have been able to detect any  $\text{O}_2^-$ . The presence of a number of SOD activities not previously known

would reduce its lifetime from the presumed ~1000 seconds to order 5-50 seconds reducing steady-state concentrations to near or below the limit of detection.

Under ONR funding, we also published two other studies related to free-radical and photochemistry in natural waters in collaboration with other groups (15,16).

Last, but far from least, this project also funded in part the M.S. thesis of A.J. Kettle (17), (advisors: Bill Martin, Jim Price, and O. C. Zafiriou;) (other support was from NASA and NSF). In this major study, a 9-day time-series of the short-lived photoproduct CO in the upper ocean was modeled successfully (Figure 5) taking into account vertical mixing, gas exchange, microbiological consumption, and photoproduction. A paper based and significantly extending his thesis is in preparation and will also acknowledge ONR funding. This quantitative approach has, we feel, great future promise.

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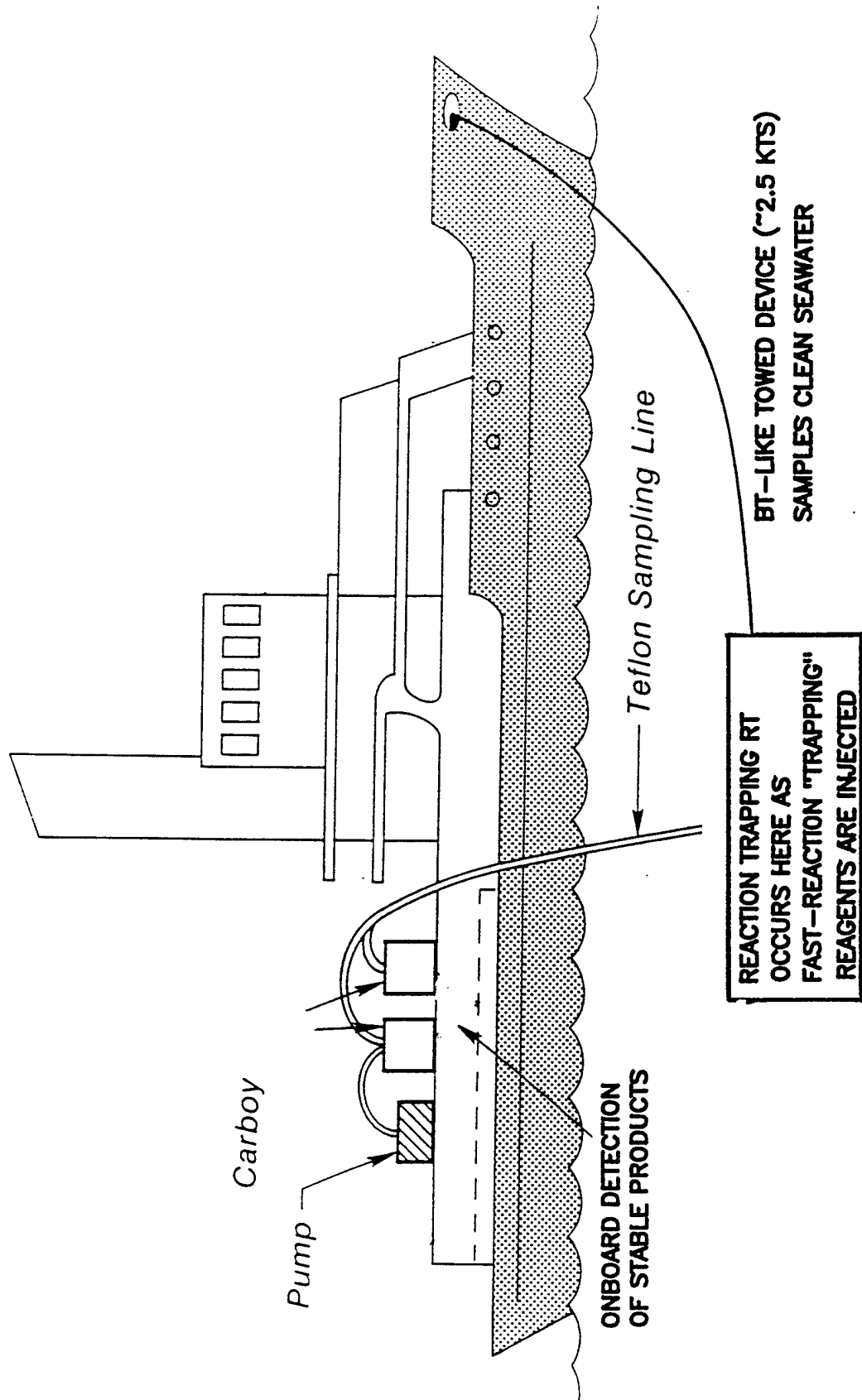


Figure 1.

Notes on Optimizing the In Situ  $O_2^-$  Trapping Apparatus  
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Plumbing Diagram

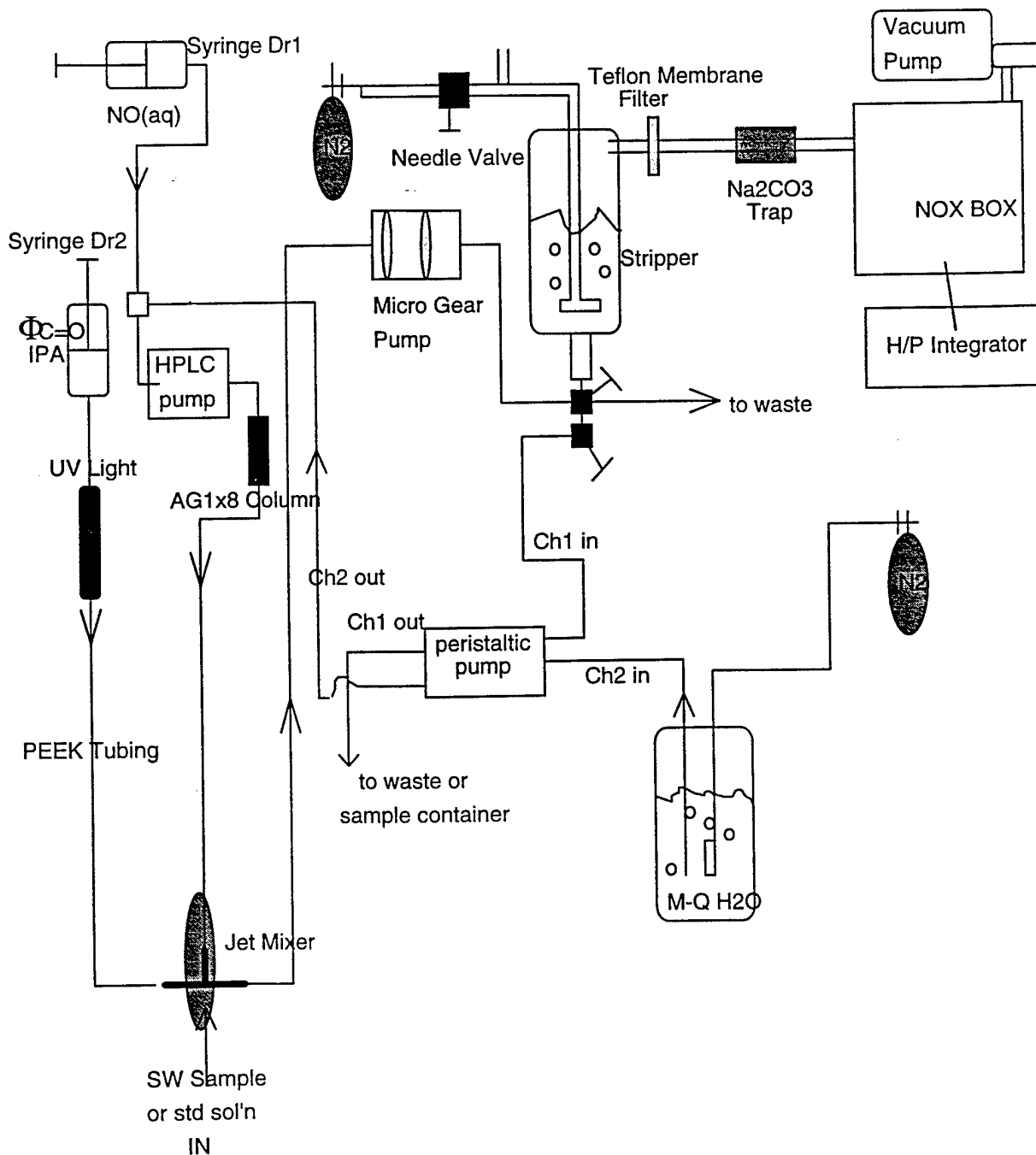


Figure 2A.

# IN SITU CHEMICAL TRAPPING OF SUPEROXIDE

MIXING "T"  
AUG 1994

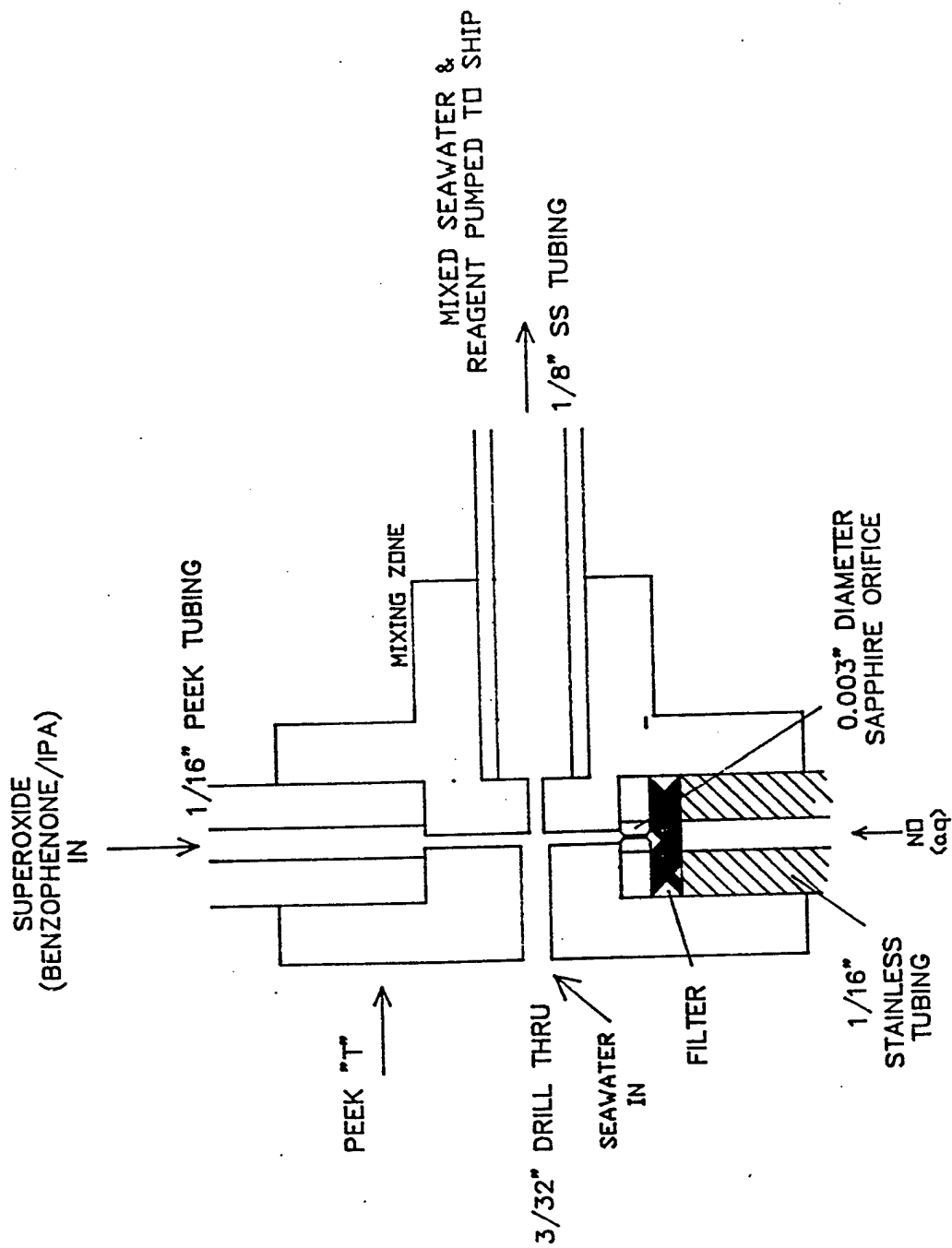


Figure 2B.

TITRATION OF NITRIC OXIDE IN SEAWATER BY UV GENERATED O<sub>2</sub>-  
USING IN SITU O<sub>2</sub> - SAMPLING PROBE

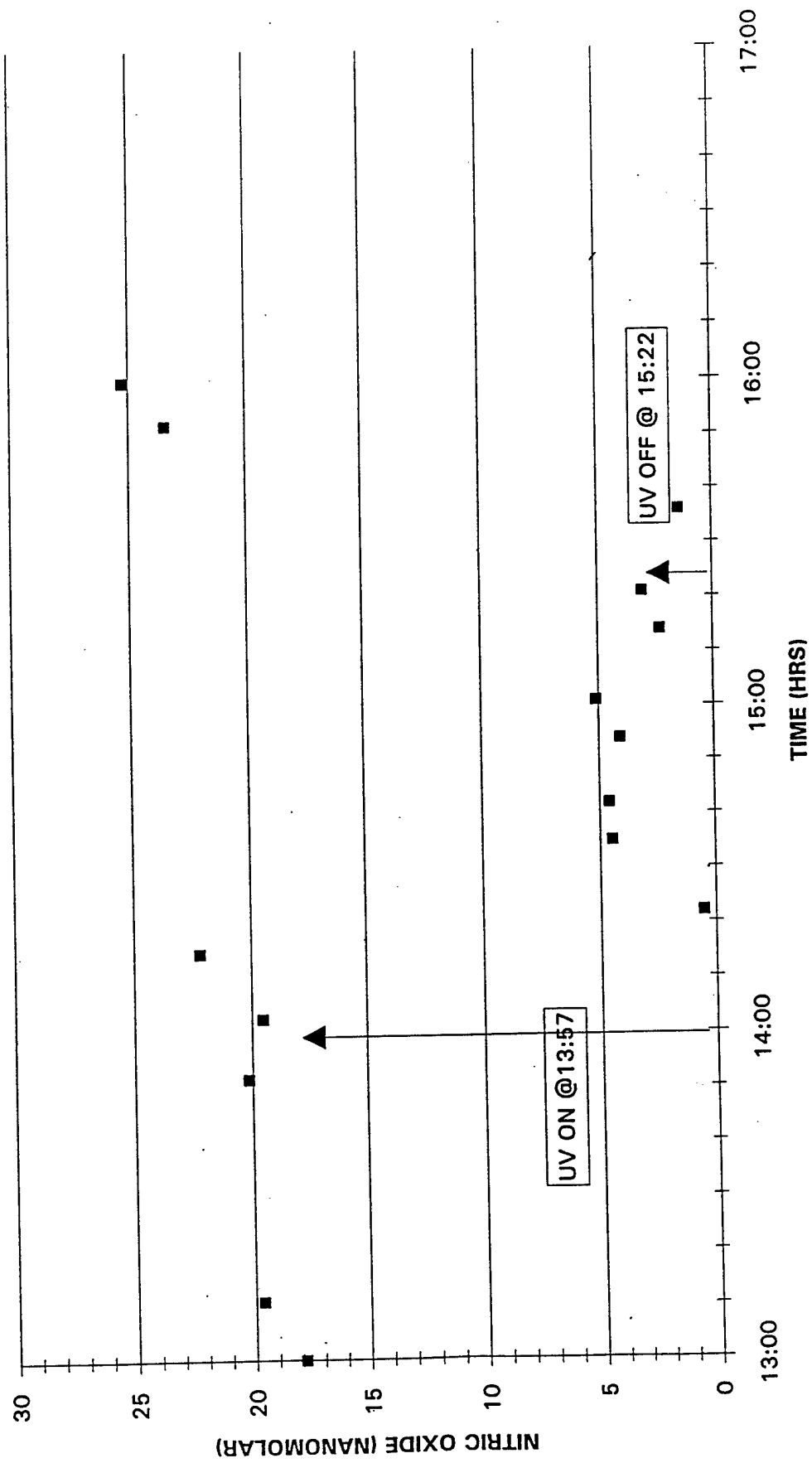
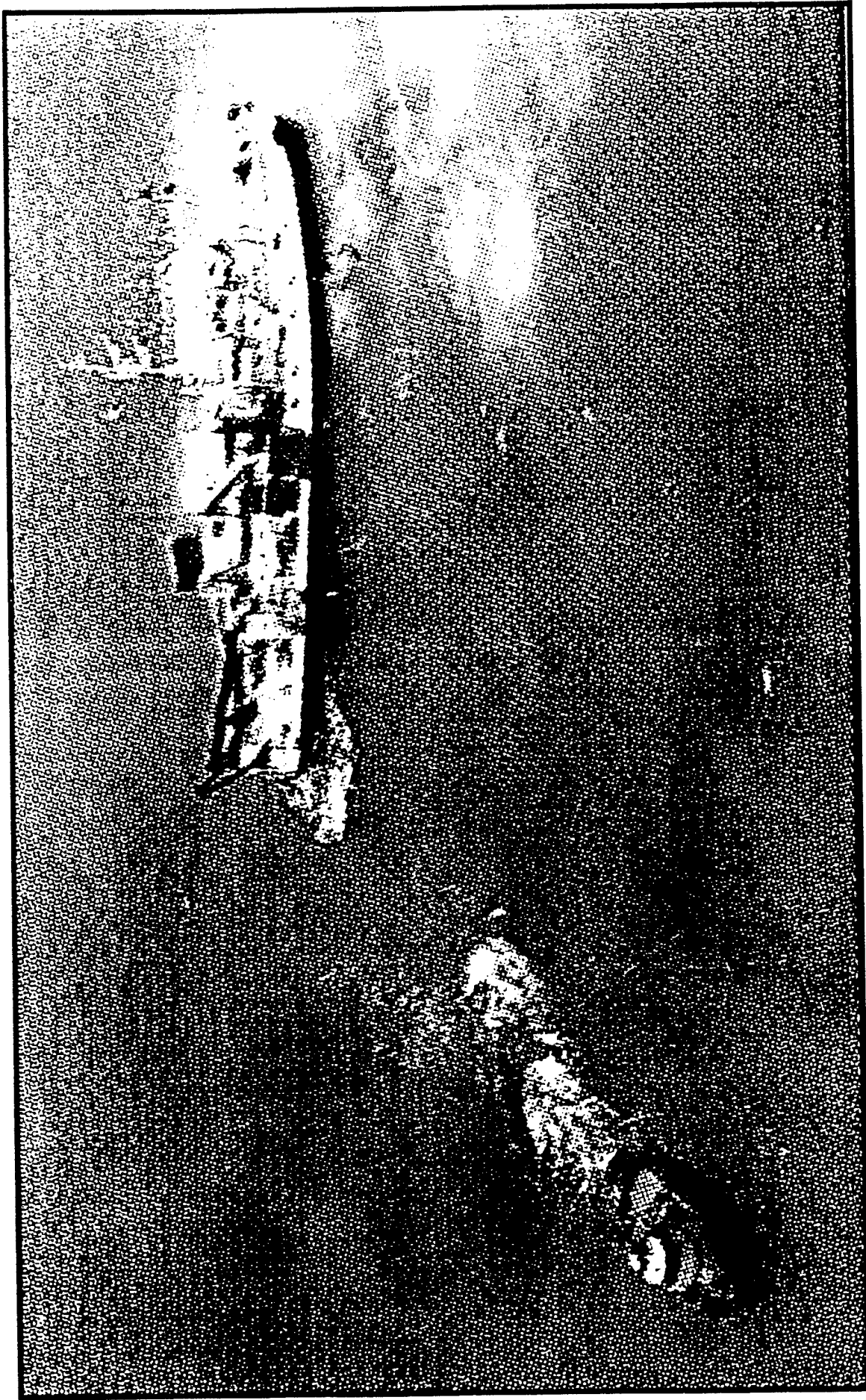


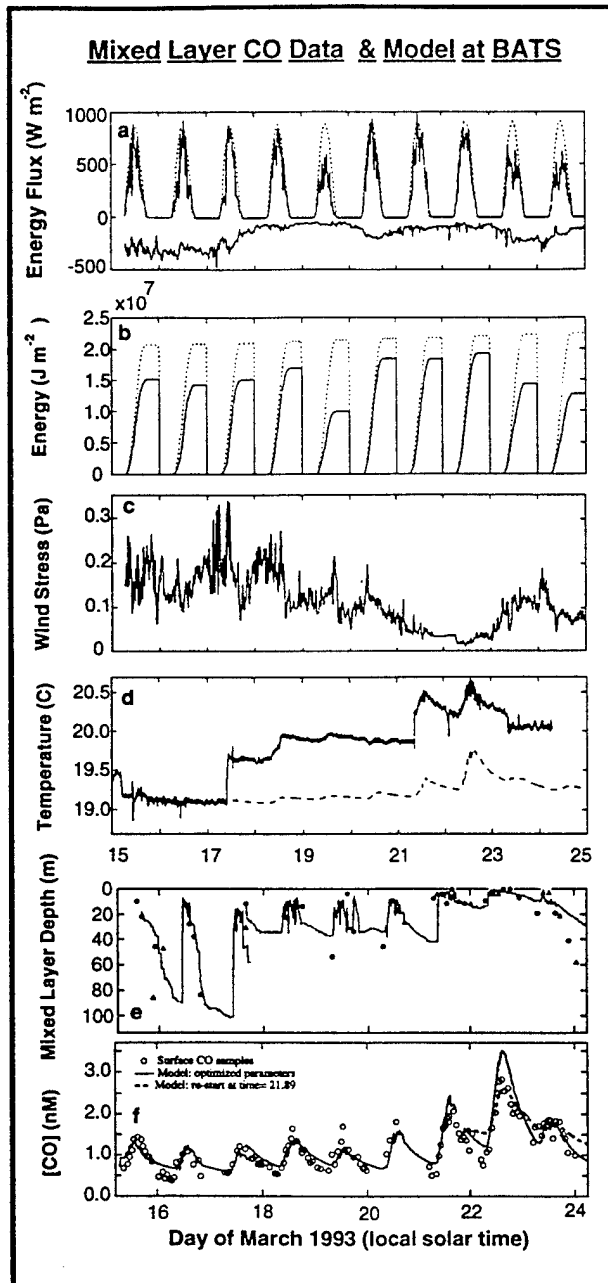
Figure 3.

# Miami Herald



PAUL DEMORANVILLE/ for the Herald

Figure 4.



The physical model is Price-Weller-Pinkel (PWP, 1-D) upper ocean physics; the biogeochemical model uses PWP physics with spectrally resolved insolation and underwater light fields, a first-order biological CO loss term, and CO production terms, one light-dependent (large) and one constant (small) (Kettle, 1994). (a) insolation (positive values, measured- solid line; cloudless sky value- dotted line), and heat losses (negative values, solid line). (b) Daily integrated measurements (solid) and estimated clear sky values (dotted). (c) wind stress magnitude (d) SST-measured (solid) and modeled (dotted). **Note sharp jumps due to advected thermal fronts.** (e) Mixed layer depth estimates from XBTs (triangles), CTDs (circles), and model (solid line). (f) measured sea surface [CO] (circles) and model, optimized with respect to [CO] from both profiles (not shown) and sea surface [CO] (circles).

Figure 5.