MARINE AEROSOL AND GAS EXCHANGE AND GLOBAL ATMOSPHERIC EFFECTS

Barry J. Huebert[1], Timothy S. Bates[2] and Neil W. Tindale[3]

[1]Department of Oceanography
University of Hawaii
Honolulu, HI 96822 USA
[2]NOAA/PMEL
7600 Sand Point Way
Seattle, WA 98115 USA
[3]Departments of Meteorology and Oceanography
Texas A&M University
College Station, TX 77843 USA

ABSTRACT

It is becoming clear that the global climate system is controlled by numerous links between the biosphere and the atmosphere. The objective of IGAC's Marine Aerosol and Gas Exchange: Atmospheric Chemistry and Climate (MAGE) Activity is to quantify those links through interdisciplinary multinational research on air/sea exchange and its biological controls and impacts. We seek to bring together scientists from a variety of disciplines to study the interfaces between them. Wherever possible, we encourage collaborative work between marine scientists who look up at the interface from the water column and atmospheric chemists, whose work in the atmosphere has frequently treated the ocean's surface as a featureless source or sink.

Several problems require this interdisciplinary approach. Marine biological productivity in some areas is controlled by the supply of nutrients from the atmosphere. In certain nitrogen-rich regions, for instance, the supply of iron from atmospheric aerosols may limit productivity. In other areas, the wet and dry deposition of atmospheric nitrate and ammonium may be a significant source of fixed nitrogen to biological communities. MAGE helped to organize an international group of scientists who studied the effect of atmospheric iron on biological productivity, phytoplankton speciation, and DMS production as a part of the Equatorial Pacific JGOFS (Joint Global Ocean Flux Study) experiment in the spring of 1992. A second MAGE/JGOFS cruise studied the fluxes of biogenic gases through the air/sea interface in the same region.

Global Atmospheric-Biospheric Chemistry
Edited by R.G. Prinn, Plenum Press, New York, 1994

To quantitate the impact of marine biota on atmospheric aerosols, cloud properties, and climate, one must precisely measure (and then parameterize for use in models) the emission of trace gases from the ocean's surface. MAGE is seeking to develop new strategies for measuring some of these elusive fluxes. During the Atlantic Stratocumulus Transition Experiment (ASTEX) in June of 1992, MAGE organized scientists from five countries to study air/sea fluxes, their biological forcing, and their atmospheric effects. Three aircraft, two ships, two islands, and a dozen constant-density balloons were used to test a Lagrangian strategy for studying two airmasses. By repeatedly sampling the same air, we hoped to reduce the perennial problem of deconvoluting transport and chemistry so that we can clearly understand processes and fluxes. In this way we will improve our understanding of the marine nitrogen budget (including both ammonia emissions and nitrate deposition), as well as the climatically-important sulfur cycle and DMS emissions.

INTRODUCTION

The composition of the marine atmosphere is strongly influenced by sources and sinks at the ocean's surface. At present, these sources and sinks are poorly characterized relative to the needs of climate modelers. MAGE seeks to understand these interactions more fully, so that useful predictive descriptions of air/sea exchange can be included in climate and marine biological models.

There are numerous ways in which the air/sea exchange of gases and aerosols affects the earth's climate. MAGE is studying several:

1. Since atmospheric input of iron and fixed nitrogen may control primary productivity in certain marine ecosystems, the ocean's ability to produce biomass and bury atmospheric CO_2 is in part limited by the quantity of nutrients the atmosphere delivers to remote marine regions (Duce, 1986). Thus we have to understand atmospheric processes such as transport and surface deposition of non-carbon substances to model the CO_2 cycle and the greenhouse effect.
2. Numerous biogeochemical cycles are affected by surface fluxes: ammonia may be redistributed between regions by emission to the atmosphere and conversion to aerosol, followed by deposition to other locations (Liss and Galloway, 1993). Air/sea exchange is a critical part of balancing the budget of reduced nitrogen in surface water and using the Redfield ratio to predict the potential burial of atmospheric carbon (Duce, 1986).
3. The production of cloud condensation nuclei (CCN), which control cloud radiative properties (Albrecht, 1989), is thought to be the result of marine dimethyl sulfide (DMS) emissions (Andreae, 1986; Charlson *et al.*, 1987). Both this indirect impact of aerosols on the earth's radiation budget and the direct scattering of sunlight by particles (Charlson *et al.*, 1992) are thus strongly influenced by air/sea exchange.
4. The mechanisms that form and remove marine aerosols cannot be studied without knowing the rates of supply and removal of reactants and products (Langner *et al.*, 1993). The importance of SO_2, for instance, as a precursor to sulfate aerosol, depends heavily on knowing how much SO_2 is dry-deposited to the ocean's surface before it can be oxidized (Huebert *et al.*, 1993).

Existing methods for estimating surface fluxes are inadequate for many of the intended uses. In the case of DMS, for instance, some authors consider the uncertainties from thin-film flux estimates to be a factor of two or three (Andreae, 1986). But in view of the importance of marine aerosols to the earth's radiation budget, we need to know their source strength to at most tens of percent, not factors of several (Penner *et al.*, this volume).

MAGE has sponsored two field programs and is planning another. In the Equatorial Pacific Ocean in early 1992, MAGE conducted two shipboard studies alongside the U.S. JGOFS program. One group focused on gas emissions from the ocean and their effect on atmospheric chemistry, the other group focused on the deposition of aerosol particles to the ocean and their affect on ocean biological productivity. In June of the same year, MAGE used two ships and three aircraft to develop a Lagrangian observing strategy during the ASTEX/MAGE program near the Azores. Although it is still too early to report significant scientific results from those programs, some early insights are discussed below. MAGE has paid particular attention to the potential for doing Lagrangian experiments in the atmosphere, to isolate surface exchange processes from the confounding effects of horizontal advection. To further this goal MAGE is cosponsoring an Aerosol Characterization Experiment (ACE-1) in the vicinity of Cape Grim, Tasmania, in January and February of 1995.

JGOFS/MAGE

Many of today's most pressing problems cannot be understood without truly interdisciplinary research. MAGE helped organize two teams of atmospheric chemists and biologists, who took advantage of the U.S. Equatorial Pacific (EQPAC) JGOFS cruises in the spring of 1992 to work alongside the oceanographic community's best carbon-cycle researchers. The JGOFS and MAGE programs are quite complementary in that they share a common reservoir, the surface ocean. Whereas JGOFS focuses on the exchange of biogenic elements between the surface ocean and deep ocean, MAGE focuses on the exchange between the surface ocean and atmosphere. Both processes depend on the biology, chemistry and physics in the surface ocean. The biology and chemistry of the surface ocean in turn, depend on inputs of nutrients from the atmosphere and deep ocean. Together the two programs are beginning to quantify the important biogeochemical processes in the surface ocean that influence the earth's climate.

R/V Vickers Cruise

The first MAGE/JGOFS cruise took place during February and March of 1992 aboard the R/V Vickers. The main focus of this cruise was to:

1. Study the cycling of trace gases in the upper water column using measurements of key species as a function of depth and microbiological/photochemical rate studies.
2. Calculate the air-sea exchange of these trace gases using shipboard measurements of the important seawater and atmospheric species, air sea exchange models and micro-budget flux estimates.
3. Compare the atmospheric gas phase and aerosol phase chemistry over a wide variety of oceanic regimes.

The measurements included sulfur, halogen, nitrogen and carbon compounds in both biologically productive and oligotrophic waters along 140°W in the equatorial Pacific (Figure 1). Although the data from the cruise are still being analyzed there are already several interesting results.

Seawater dimethylsulfide (DMS) concentrations, and hence the flux of DMS to the atmosphere was much higher in the southern hemisphere than the northern hemisphere (Figure 2). The high concentrations of DMS were likely a result of lower microbial consumption rates. The entire seawater sulfur cycle in the equatorial pacific near 12°S was quite different from expected, based on previous measurements (Bates *et al.*, 1993) in temperate latitudes (48°N). At 12°S dimethyl-sulfoxide (DMSO), a photochemical

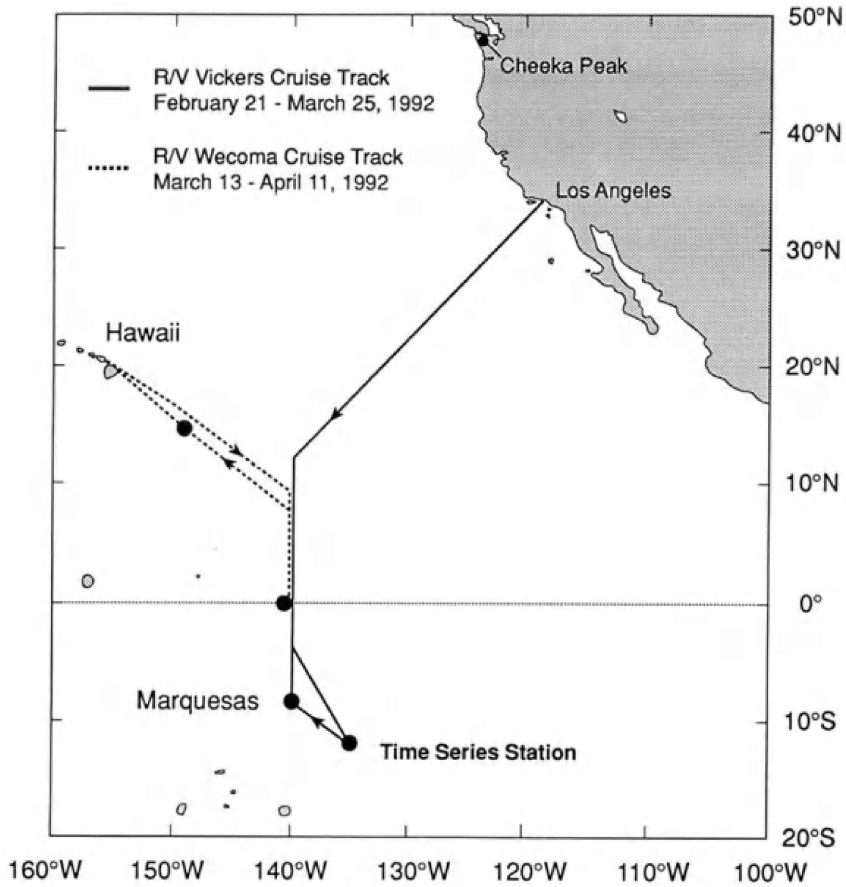

Figure 1. IGAC-MAGE Equatorial Pacific Field Study: Cruise tracks for the R/V Vickers and R/V Wecoma.

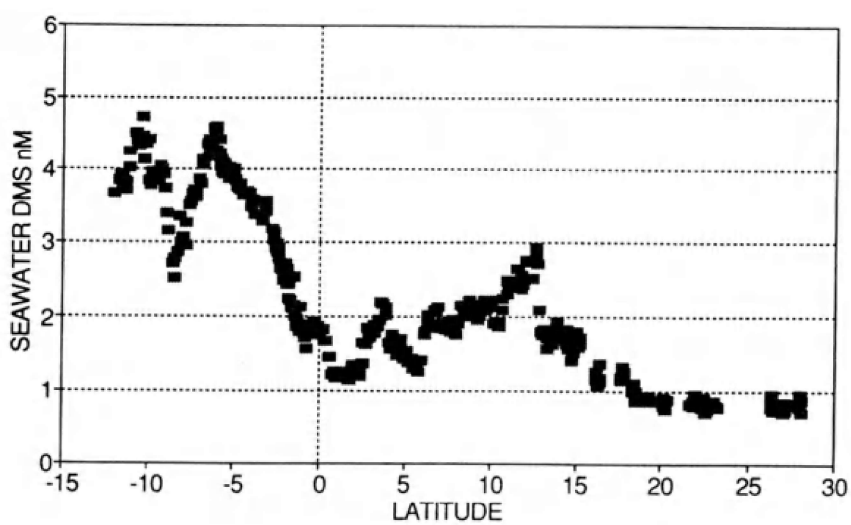

Figure 2. Seawater DMS concentrations along the Vickers cruise track. These data from the southbound leg were essentially identical to the values obtained during the return northbound leg. This implies that the features observed here were stable on the time-scale of one to two weeks.

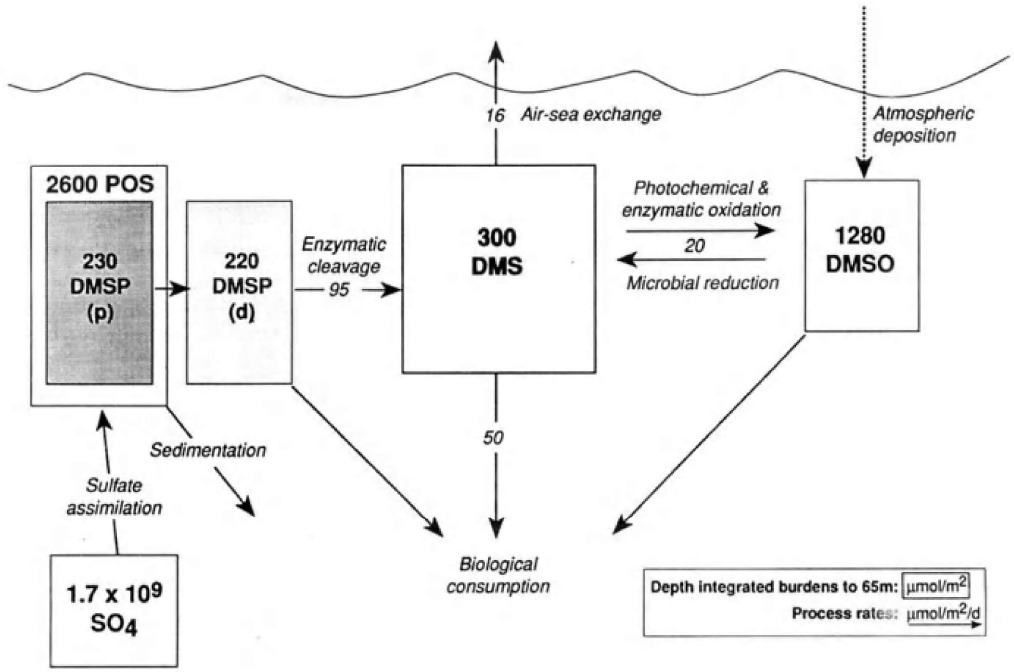

Figure 3. Seawater sulfur cycle at 12°S, 135°W. Note that the particulate DMSP burden was only about 10% of the total particulate organic sulfur burden and was approximately equal to the DMS burden. In this region the major sinks for DMS (air-sea exchange, biological consumption, and photochemical oxidation) are all of the same order of magnitude. (Data from R. Kiene, D. Kieber and P. Matrai, private communication.)

oxidation product of DMS, was the dominant sulfur species (Figure 3) and dimethylsulfoniopropionate (DMSP), the precursor of DMS, was present at concentrations similar to DMS. In contrast, DMSP concentrations were 25 times higher than DMS concentrations at the temperate latitude site. At 12°S air-sea exchange, photo-oxidation and biological consumption were all important sinks for DMS. Some of the extensive biological and chemical measurements from the JGOFS work may help explain why the biological consumption of DMS is so low in this region. These data will be described in more detail in a manuscript by R. Kiene and coworkers.

A time-series station at 12°S provided an opportunity to obtain a detailed picture of the atmospheric diurnal cycle of several trace gases. DMS concentrations, for example, markedly decreased during the day as a result of photochemical oxidation (Figure 4). This diurnal cycle can be coupled to an atmospheric photochemical model to estimate the DMS air-sea exchange rate needed to maintain the atmospheric DMS concentrations. This calculation, based on atmospheric DMS concentrations and an atmospheric photochemical model, is totally independent from the more traditional air-sea exchange calculations based on seawater DMS concentrations and a wind speed/transfer velocity relationship. At this 12°S station both methods produced nearly identical results with DMS fluxes in the range of 10 to 20 µmole/m^2/day. The details of this study will be described in a manuscript by S. Yvon and coworkers.

The gases that are emitted from the ocean affect the chemical composition of the atmosphere, the oxidative capacity of the atmosphere and the production of aerosol particles. DMS, for example, is the major natural source of sulfur to the atmosphere and is the primary precursor to aerosol particles in the remote marine atmosphere. The number and size distributions of aerosol particles are a functions of precursor source strength (DMS emissions), the existing aerosol size distribution, relative humidity, temperature and

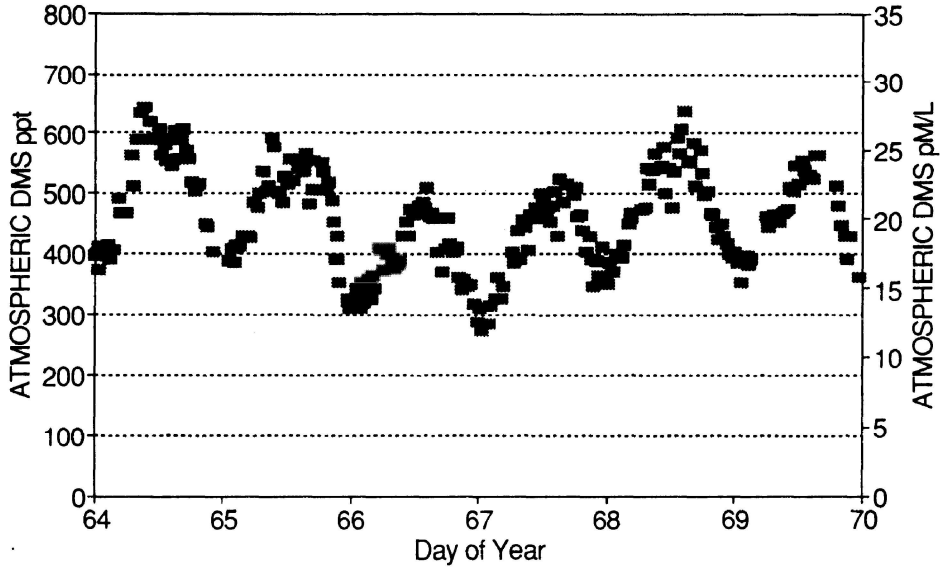

Figure 4. Atmospheric DMS concentrations at 12°S, 135°W. Time is shown in GMT. DMS concentrations decrease during the day as a result of photochemical oxidation. There were no significant changes in the marine boundary layer height during this time period.

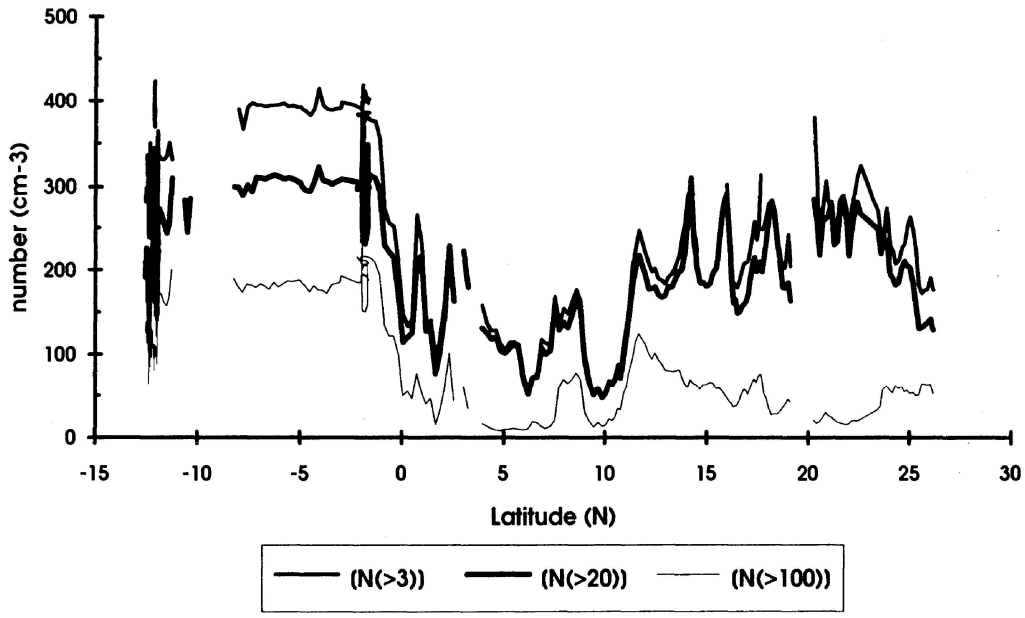

Figure 5. Aerosol concentrations on the northbound leg of the Vickers cruise track. The concentrations are given as number of particles per cm^3 with diameters greater than 3, 20 and 100 nm. Note that in the northern hemisphere there were few particles with diameters <20 or >100 nm. This single mode particle distribution implies that the particles were a few days old but yet had not had sufficient time to grow large enough to serve as cloud condensation nuclei (CCN). In the southern hemisphere the particle number size distribution was trimodal, suggesting that in addition to the nuclei mode there were also newly formed particles (an ultra-fine mode) and an aged accumulation mode. In this region most of the particles had diameters > 40nm diameter and were active CCN at 0.65% supersaturation. (Data from D. Covert and V. Kapustin, private communication.)

atmospheric circulation. The detailed aerosol chemical, physical and optical measurements collected aboard Vickers will provide a valuable data set for modeling aerosol formation and growth. Many of the processes important to aerosol formation and growth were evident along the Vicker's cruise track. For example, at the northern end of the cruise track along 140°W the aerosol particles were present in primarily a single mode with diameters around 20 to 30 nm (Figure 5). This size distribution is likely a result of subsidence from the free troposphere. Further south the aerosol size distribution was tri-modal suggesting a mixture of freshly formed aerosol and more aged boundary layer aerosol. The details of the aerosol physical measurements will be a manuscript by D. Covert and coworkers.

For up-to-date information on the above R/V Vickers manuscripts and others, contact Dr. Tim Bates, NOAA/PMEL, 7600 Sand Point Way, Seattle, WA 98115. (Phone: 206-526-6248, Internet: bates@pmel.noaa.gov.)

Wecoma Cruise: FeLINE II

The input of atmospheric material to the ocean has been suggested as a mechanism for limiting primary production in nutrient rich open ocean surface waters (Duce, 1986; Martin *et al.*, 1991). There is growing evidence, for instance, that eolian iron is particularly important as a limiting micronutrient (Young *et al.*, 1991). In three regions of the Pacific Ocean the input of eolian iron may regulate production in surface waters. These are the high latitude open ocean in the Gulf of Alaska and the Southern Ocean, and the band of nutrient rich surface water that exists in the central and eastern equatorial Pacific.

The equatorial Pacific (0, 140°W) was chosen as the study site for the 1992 MAGE FeLINE-II cruise (Figure 1). The main objectives of FeLINE-II included the study of: aerosol iron input, phytoplankton productivity and photosynthesis, dimethyl sulfide (DMS) production, dissolved organic carbon (DOC) production and consumption, photochemical cycling of iron and hydrogen peroxide in surface waters, and the oceanic vertical distribution of trace metals (primarily Fe and Zn).

Over a dozen shipboard incubation experiments (enrichment experiments) were completed during the cruise, evaluating the roles of iron (in several chemical forms), aerosol particles and leachate, nitrate, photosynthetically active radiation (PAR) and UV light, cobalt and vitamin B12 on phytoplankton productivity. Most of these factors were also measured in samples collected during conductivity-temperature-depth (CTD) casts and in trace metal clean samples collected using 30-liter GoFlo bottles deployed on Kevlar line.

Most of the experiments conducted during this cruise were collaborations between groups, which resulted in a much stronger and more flexible research program than would have resulted if the groups had worked independently. Highlights of the individual groups' efforts are summarized below.

The Moss Landing Marine Laboratories group examined the photochemistry of iron in surface waters and its implications to iron bioavailability. Their decktop incubation experiments showed enhanced growth from all of the iron additions, with the most dramatic enhancement in carboys enriched with atmospheric aerosol particles (Figure 6). They also observed clear diurnal patterns in iron levels, with a maximum at midday. This is consistent with a model involving the reductive dissolution of colloidal iron, its subsequent oxidation, and the uptake of dissolved iron (III). These results indicate that photochemical reactions can produce sufficient bioavailable iron (from what was previously unavailable colloidal iron) to support primary production in the euphotic zone in this area (Johnson *et al.*, 1993).

A University of Rhode Island (URI) team studied the influence of ultraviolet radiation, photo-chemical cycling, and rain events on the distribution of iron and hydrogen peroxide, and the speciation and bioavailability of iron. They:

1. quantified the air-sea fluxes of peroxides and cathodic-stripping voltammetric (CSV) labile iron during a rain squall (Figure 7), and documented the influence of such a rain event on the horizontal and vertical distribution of labile iron and peroxides in the surface waters of the region (Figure 8),
2. compared the effects of iron-containing rainwater additions on phytoplankton growth in nutrient-rich and nutrient-depleted surface waters,
3. determined CSV labile iron vertical distributions in euphotic and deeper waters,
4. characterized the temporal and latitudinal variability in the spectral distribution of downwelling ultraviolet and photosynthetically active radiation in euphotic waters,
5. examined the importance of natural UV levels to iron availability, phytoplankton growth and the photo-redox cycling of iron and peroxides (Hanson *et al.*, 1993).

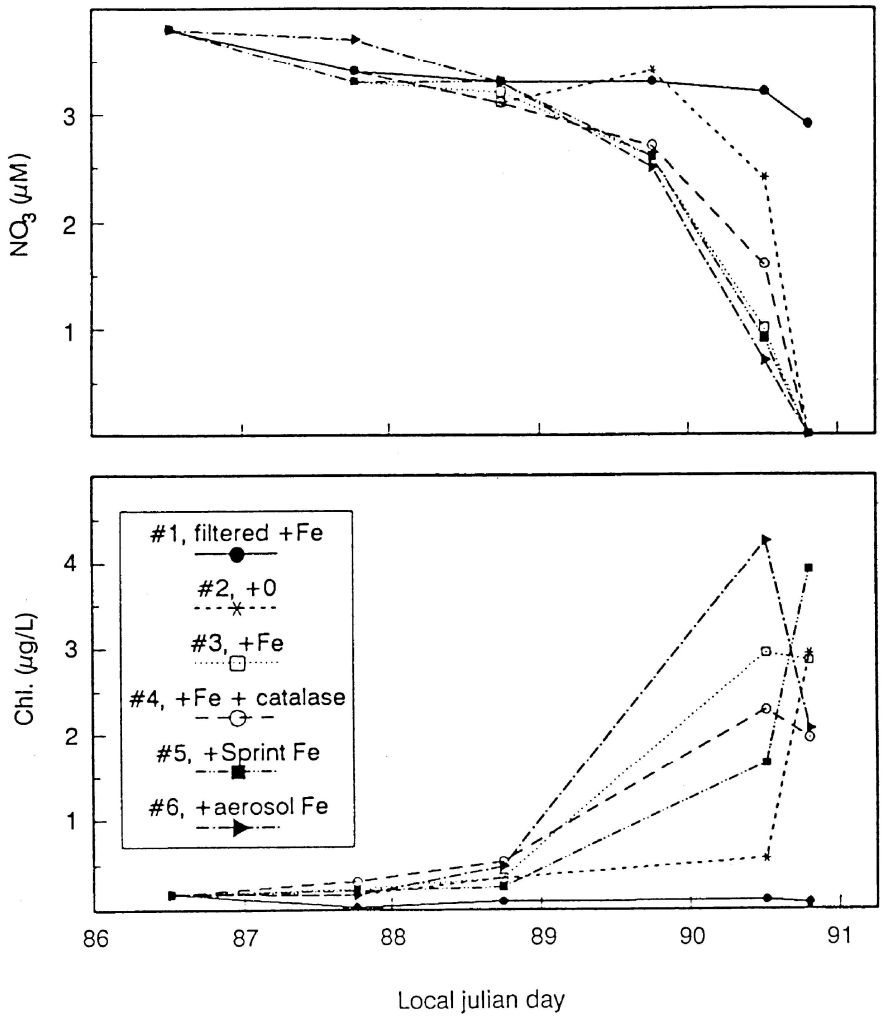

Figure 6. Nitrate **(top panel)** and chlorophyll **(bottom panel)** concentrations measured over time in carboys containing seawater collected at 0°N, 140°W. Seawater in Carboy #1 was filtered and 0.22 μm $FeNH_4(SO_4)_2$ was added to a final concentration of 10 nM. Carboy #3 contained unfiltered seawater with 10 nM $FeNH_4(SO_4)_2$. Carboy #4 was similar to #3, except that the enzyme catalase was added every day to keep H_2O_2 concentrations less than 5 nM as compared to ambient concentrations near 25 to 30 nM. Seawater in Carboy #5 was unfiltered and contained 10 nM Fe added as sodium ferric ethylenediamine di-(o-hydroxyphenyl) acetate. Seawater in Carboy #6 was unfiltered and approximately 10 nM iron was added in the form of aerosol particles collected on Oahu, Hawaii. (Data from Johnson *et al.*, 1993.)

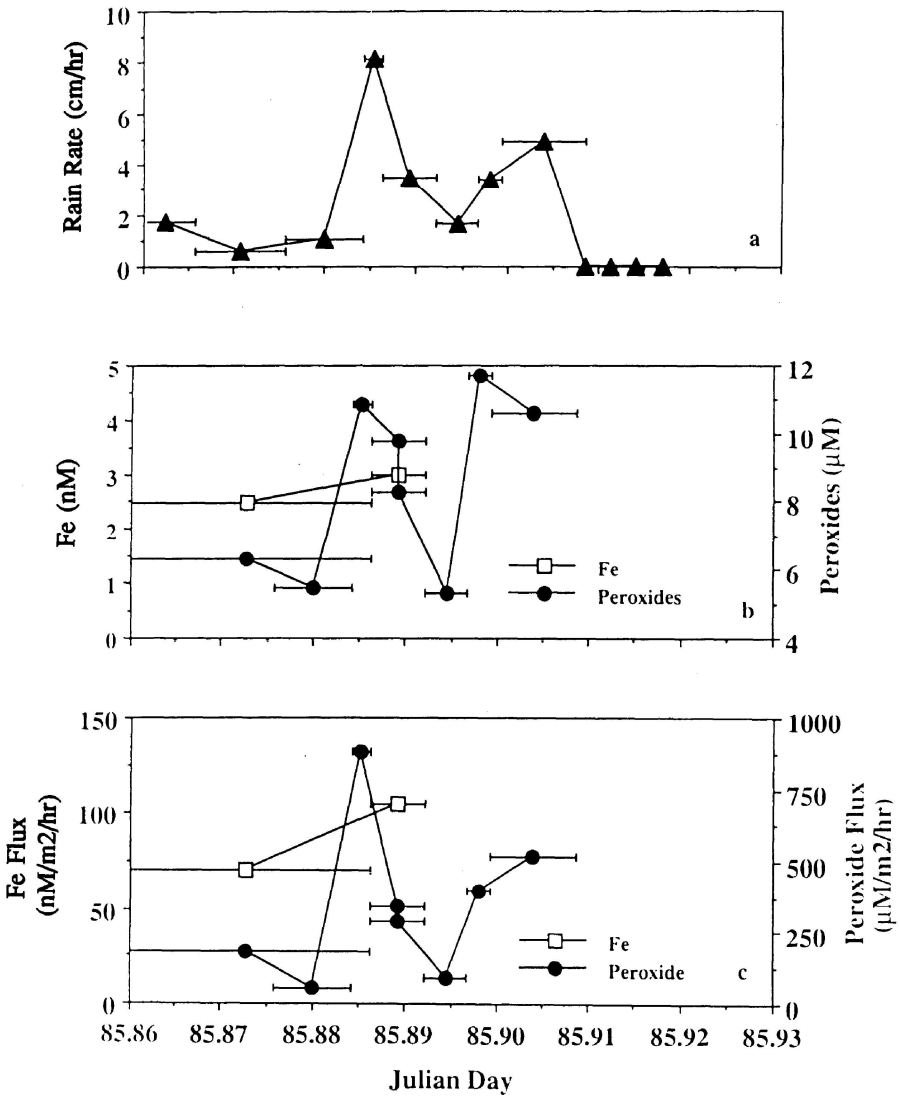

Figure 7. Time course of precipitation observations during the squall. **(top panel)** Average rain rate in cm per hour for the time period of collection (horizontal bars); **(middle panel)** concentrations of dissolved iron (open squares) and peroxides (open circles) in the precipitation; and **(bottom panel)** calculated wet depositional fluxes of dissolved iron (open squares) and peroxides (closed circles). (Data from Hanson *et al.*, 1993.)

The University of East Anglia group (G. Malin, S. Turner and P. Liss) studied the transfer of volatile DMS from the surface waters to the atmosphere. This link between the atmosphere and ocean is made through the action of phytoplankton which synthesize DMSP (the dissolved, non-volatile precursor to DMS) as an osmolyte and cryoprotectant.

Another URI effort involved deckboard incubation experiments in which surface waters were enriched with aerosol leachate, inorganic iron, cobalt, nitrate and vitamin B12. The results indicated that the addition of cobalt alone does not influence phytoplankton growth. However, the addition of cobalt and iron together may have allowed more rapid growth (as indicated by the increase in chlorophyll) than was observed in a solely iron stimulated population. For iron stimulation to be observed, nitrate had to be present (in situ, or added). Again, enhanced growth was seen in deckboard enrichment experiments with the addition of natural aerosol material (D. Swift, private communication).

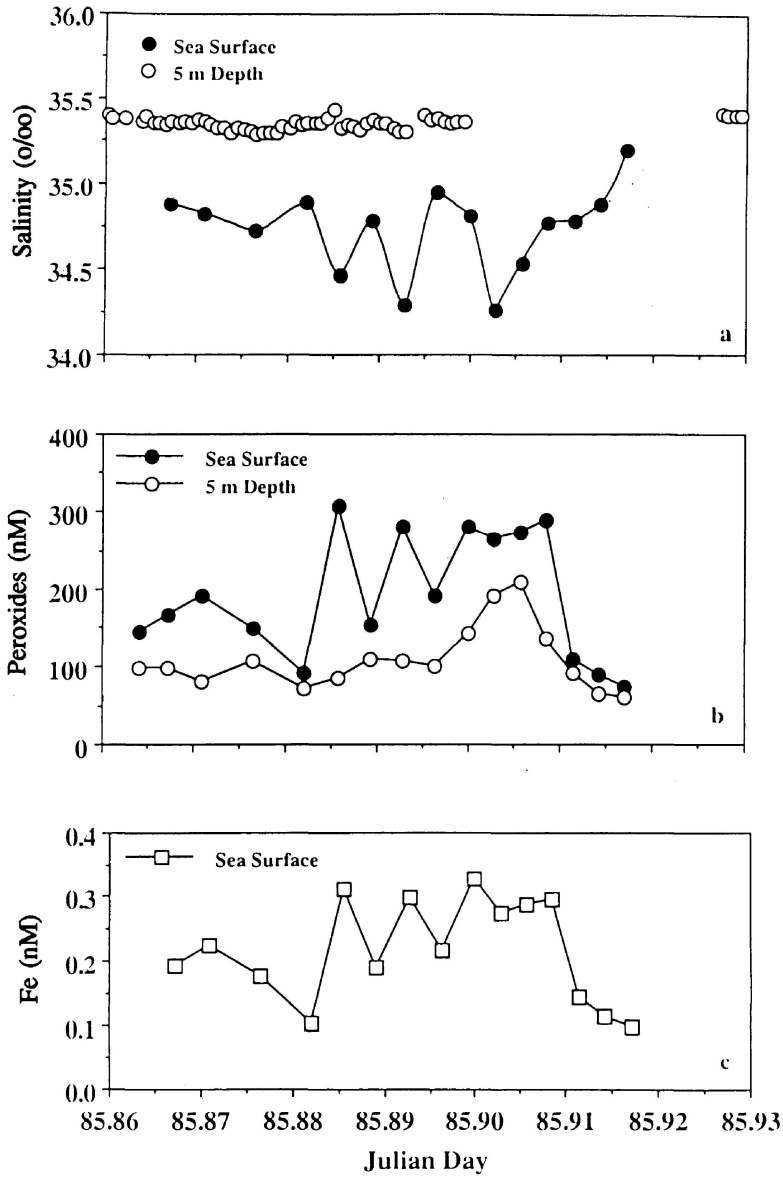

Figure 8. Time course observations of seawater during the squall. **(top panel)** Salinity of surface (closed circles) and water at 5 m depth (open circles); **(middle panel)** concentration of total peroxides in seawater samples collected from the surface (closed circles) and 5 m depth (open circles); and **(bottom panel)** the concentration of dissolved iron as determined by ACSV in sea surface samples. (Data from Hanson *et al.*, 1993.)

The persistence of high nutrient, low biomass waters along the equatorial Pacific at 140°W is thought to result from some form of resource sub-utilization. The two hypotheses put forth to explain this phenomenon involve either resource limitation or grazing pressure. R. Greene, Z. Kolber, and P. Falkowski (Brookhaven National Laboratory) examined the variability in the quantum yield of chlorophyll fluorescence using a fast repetition rate fluorometer. The parameter derived (denoted ~hm) is a quantitative measure of photochemical energy conversion efficiency in photosystem II. They found that ~hm was relatively low throughout the nutrient-rich equatorial waters (and higher in more oligotrophic waters) indicating greater physiological limitation of the photochemical energy conversion efficiency in the natural phytoplankton populations at the equator. Shipboard enrichment studies (Figure 9) showed that ~hm increased following addition of

nanomolar concentrations of inorganic iron and aerosol dust leachate. This response suggests that iron (rather than relaxed grazing pressure) increased the photosynthetic efficiency of the phytoplankton, resulting in increased productivity in the shipboard enrichments. The Brookhaven results indicate that low iron availability limits photochemical energy conversion efficiency and is the principle mechanism controlling rates of photosynthesis in these nutrient-rich equatorial Pacific waters.

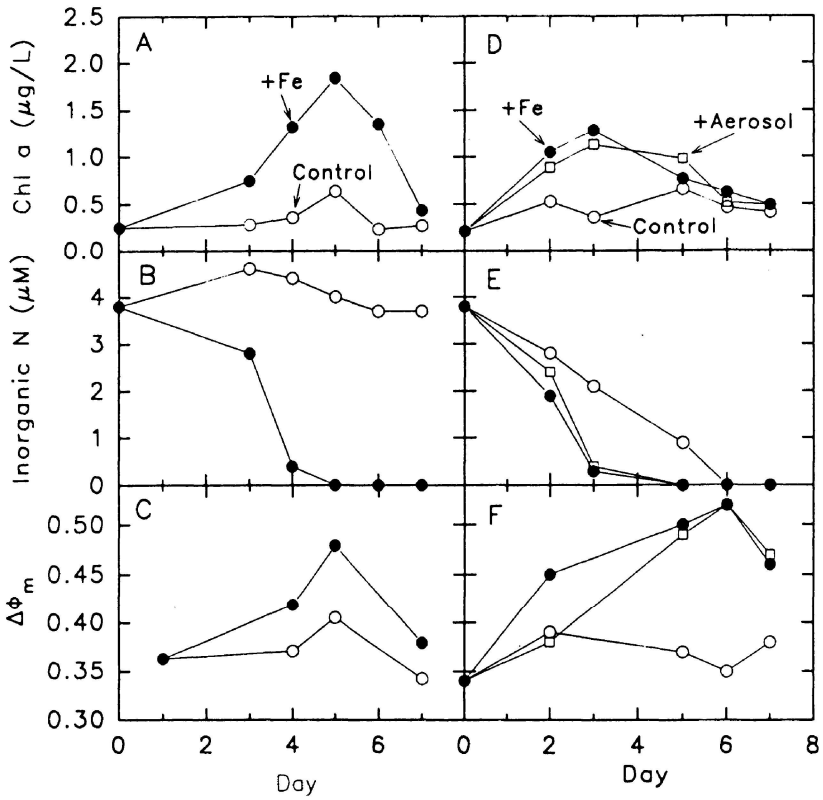

Figure 9. Changes in Chl a (μg L^{-1}, panels A and D), inorganic nitrogen (μM, panels B and E), and the quantum yield of fluorescence ($\Delta\phi_m$, panels C and F) in shipboard incubations. The panels on the left show results from experiments initiated on March 23, 1992 with addition of inorganic Fe to a final concentration of 4.5 nM Fe (depicted as +Fe). The panels on the right show results from experiments initiated on March 28, 1992 with addition of inorganic $FeSO_4$ (4.5 nM Fe final concentration) and Fe as aerosol dust leachate (2 nM Fe final concentration, depicted as +aerosol). Control bottles were natural samples without enrichment. (Data from Greene *et al.*, 1993.)

Several links between the marine sulfur cycle, atmospheric iron availability and non-seasalt sulfur in ice cores emphasize the climatic significance of DMS. Preliminary results indicate that the production of both DMS and DMSP, in the dissolved and particulate phase, is enhanced in the presence of added iron. Although preliminary in nature, there is also strong evidence that the production of chloroiodomethane is also dramatically increased in the presence of iron.

J. Martin's group (Moss Landing Marine Laboratory) conducted iron enrichment experiments on both the FeLINE-II and JGOFS-EQPAC cruises. Dissolved iron concentrations in the equatorial Pacific were extremely low (less that 0.03 nM) in the surface waters, in contrast to the 10 nM concentrations found in coastal waters. Results from their enrichment experiments indicated enhanced growth in both addition treatments and controls although the treatments usually showed greater growth more quickly. The

subsequent growth in the controls remains a mystery. Several explanations may account for this observation: (1) an increased Fe source, (2) contamination of the controls, or (3) reduced grazing pressure as a result of enclosure. Although the evidence for increased Fe deposition during this time is positive, it is highly tentative and requires further examination (see below). Recently several investigators have suggested that phytoplankton growth may be controlled by a balance of factors including nutrients, Fe limitation, and grazing. It is possible that containment alone was responsible for some of the observed effects under the conditions of this oceanographic regime. This points to the need for an uncontained iron enrichment experiment.

The atmospheric group of N. Tindale and B. Duce from Texas A&M University collected both air and rain samples on station and underway, in order to measure the concentration and flux of aerosol particles during a transect through the Intertropical Convergence Zone (ITCZ). Portions of aerosol and rain water samples were provided to the other groups for use in their enrichment experiments on both the FeLINE and JGOFS cruises. Aerosol concentrations in this region were extremely low, especially south of the ITCZ in southern hemisphere air. Preliminary results indicate there was a higher atmospheric concentration of aerosol iron in the EQPAC region in 1992 than in an earlier cruise in 1990, yet these differences are small and are not yet completely resolved. It is unclear whether the difference in atmospheric concentrations would lead to a significant difference in the flux of iron from the atmosphere to the ocean surface.

For up-to-date information on the R/V Wecoma cruise results, contact Dr. Neil Tindale at the Department of Meteorology, Texas A&M University, College Station, TX 77843 USA. (Phone: 1-409-862-4401, Internet: tindale@ariel.tamu.edu.)

ASTEX/MAGE: Lagrangian Measurements

To quantitate the impact of marine biota on atmospheric aerosols, cloud properties, and climate, one must precisely measure (and then parameterize for use in models) the emission of trace gases from the ocean's surface (Bates and Cline, 1985; Langner *et al.*, 1993). MAGE is trying to develop new strategies for measuring these fluxes. During the Atlantic Stratocumulus Transition Experiment (ASTEX) in June of 1992, MAGE organized scientists from five countries to study air/sea fluxes and their atmospheric effects. ASTEX/MAGE was a large boundary-layer, cloud, and radiation experiment conducted in the region of the Azores.

Surface fluxes and atmospheric reaction rates are often very difficult to derive from Eulerian observations (at a fixed point). Following one parcel of air and observing its changes over time (the Lagrangian reference frame) would make the rates much easier to deduce. The difficulty is that one must first know where an air parcel is moving and then follow it with a large suite of analytical instruments. It took the combined efforts of two research ships (the Woods Hole R/V Oceanus and NOAA's R/V Malcolm Baldrige), three aircraft (NCAR's Electra, the UK C-130, and the Univ. of Washington's C-131), 12 GPS-tracked balloons, real-time trajectory predictions, and the cooperation of literally hundreds of scientists from several countries to test a Lagrangian strategy during ASTEX/MAGE.

The analysis of Lagrangian data is based on a continuity equation, which has previously been used in various forms for evaluating fluxes of heat, momentum, and ozone in the marine boundary layer (Lenschow *et al.*, 1981; Kawa and Pearson, 1989). For a substance S in a Lagrangian parcel,

$$\frac{d}{dt}\langle S\rangle = J_o(S) - J_h(S) + F(S) - D(S) \tag{1}$$

Here, J_o is its surface flux, J_h is the flux at top of the mixed layer (i.e. entrainment of free tropospheric air), F is the column formation rate (from chemical reactions), D is the column destruction rate, and <S> is the column concentration of S. Implicit in this equation is the Lagrangian assumption that transfer through the sides of the parcel is not causing significant concentration change. Although neither advection nor dispersion appears in the budget equation above, they will contribute to the uncertainty in quantities derived from Equation 1, and must be explicitly included in a propagation of errors analysis.

To track the air's movements, we tagged our airmasses with constant-density balloons and inert perflourocarbon tracers. After being launched from the Oceanus (upwind of Santa Maria Island) the balloons floated with the air and radioed their GPS-derived positions to the aircraft, which were flying nearby. By using a continuous relay of the three aircraft, the airmass was under continual observation for about 42 hours. The Malcolm Baldrige, positioned to intercept the air as the balloons floated out of aircraft range downstream, did a detailed characterization of its gases and aerosols for comparison with the upstream values.

Two Lagrangian experiments were attempted during ASTEX/MAGE, with varying degrees of success. The first took place in extremely clean marine air. Cloud condensation nuclei (CCN) counts of less than 50 cm^{-1} ensured that cloud formation would generate a small number of large droplets, with the result that drizzle was frequently observed. While air which maintains its low aerosol concentrations by drizzling is an interesting case, the addition of just 0.1 mm of water on each balloon's top was enough to drop it to the surface, drowning the transmitter.

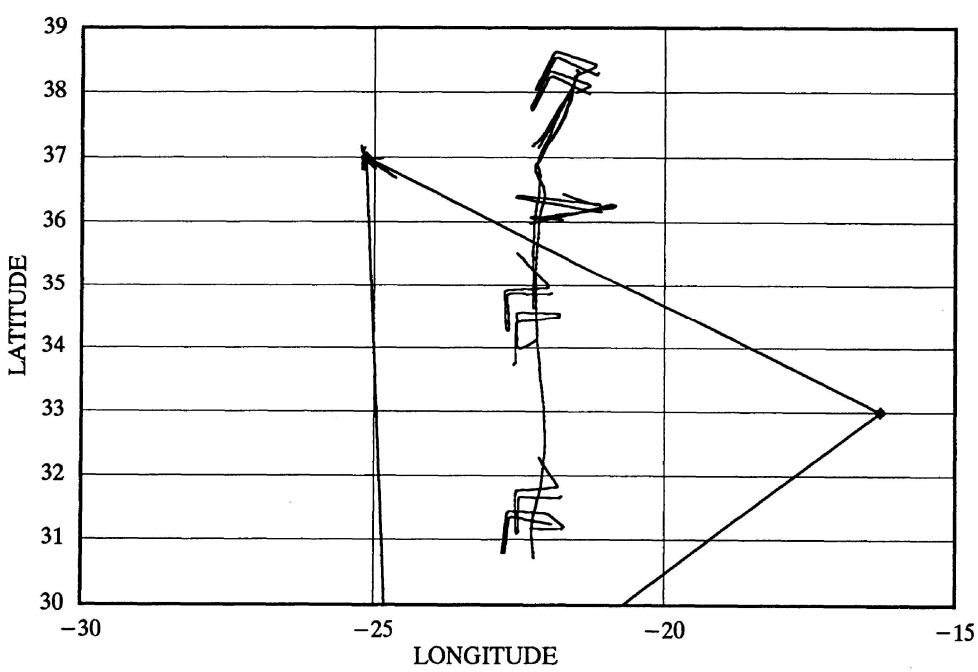

Figure 10. ASTEX/MAGE Lagrangian #2. The upper left corner of the triangle is Santa Maria, Azores; the right apex is Porto Santo, Madeira; and a ship occupied the lower apex. The wavy vertical lines are the tracks of five balloons, starting from the top of the figure where they were launched by the R/V Oceanus and ending by passing over the R/V Malcolm Baldrige at the bottom (ships not shown). Only one balloon survived to the end of the experiment. The back-and-forth patterns are Electra boundary layer sampling legs from flights 11–14 (one every 12 hours).

The second Lagrangian was a perfect contrast to the first: the air was heavily polluted by European aerosols, which suppressed precipitation and maintained high particle concentrations. We followed one balloon for the entire 42 hour observational period. Seven coordinated aircraft flights (four of which are diagrammed in Figure 10) generated an unmatched set of observations on how boundary layers decouple and develop over time.

We learned important lessons about how to conduct a Lagrangian experiment:

1. High-quality long range communications between all platforms is essential.
2. The balloons must be robust, so that they can withstand drizzle and modest downdrafts without loss. Protocols need to be established for how each platform would respond to the loss of one or more balloons.
3. The launch point of the balloons needs to be selected with some knowledge of the homogeneity of the airmass. Working on a boundary between airmasses (Figure 11) makes it harder to isolate the chemistry in either airmass from the effect of dynamics.
4. The best possible meteorological data and predicted trajectories need to be used to position ships and aircraft, to ensure that the aircraft can reach the starting and ending points of the tagged trajectory.
5. Even though advective effects are minimized, several techniques should be used to characterize the remaining atmospheric transport processes (entrainment, surface fluxes, and dispersion), so that chemical conversions can be isolated from these (inescapable) dynamic effects.
6. Natural and manufactured tracers should be used to confirm the extent to which the original airmass is still intact at the end of the experiment. The ability to analyze tracer samples in real-time (preferably on the aircraft) is essential for optimizing experimental strategies.
7. Extreme care must be used to avoid sampling contaminants from the ships and aircraft used in the study. The experimental plan should include measurements of the exhaust impact.
8. It is essential that 10 to 20% of the flight hours and ship days be devoted to instrument intercomparisons between platforms, to ensure that observed differences can be interpreted.

During most of the ASTEX/MAGE experiment, the deep marine boundary-layer was decoupled, meaning that a secondary inversion divided the moist air into a surface layer and one largely isolated from the ocean. Significant differences in chemistry between the layers created concentration gradients within the boundary layer (Figure 12). Some of the variability in the measurements of NSS vs. time (Figure 13) was due to the fact that the filter samplers collected material from altitudes where the concentrations differed.

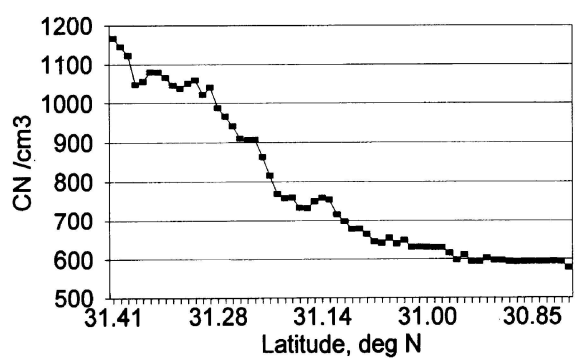

Figure 11. Condensation nuclei data along one boundary layer sampling leg. The CN gradient results from our sampling on the boundary between clean marine and polluted continental air. (Data from T. Clarke, private communication.)

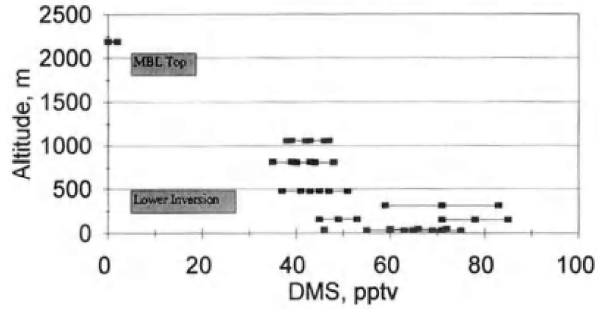

Figure 12. DMS concentrations versus altitude for Electra flight 7. A secondary inversion between 400 and 800 m decoupled the surface mixed layer from the upper boundary layer. This stratification produced vertical gradients of many chemical species. (Data from B. Blomquist, A. Bandy and D. Thornton, Drexel University, private communication.)

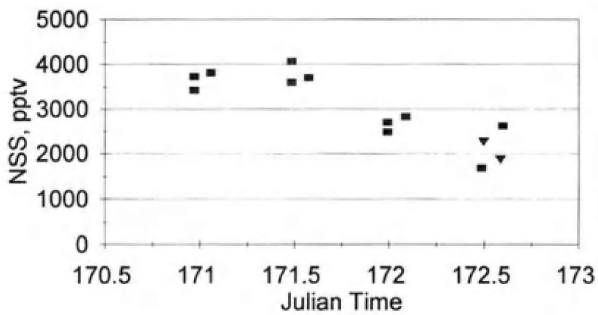

Figure 13. Evolution of non-seasalt sulfate concentrations during Lagrangian #2. The squares represent Electra samples. On each of the first three flights, one pair of samples was collected simultaneously with parallel samplers. The triangles indicate measurements from the R/V Malcolm Baldrige as the Lagrangian parcel passed over. (Malcolm Baldridge data from A. Pszenny, private communication.)

We could have modified our sampling strategies to account for the vertical gradients, had we been sufficiently aware of their impact. This is one of many lessons learned during ASTEX/MAGE that will improve our ability to separate dynamics and chemistry on subsequent Lagrangian experiments. We learned that the balloons can be ballasted differently to reduce their chances of being dunked, and that we should use a few "smart" balloons (which can adjust their buoyancy in flight) to ensure balloon survival. We also learned that satellite data and a pre-Lagrangian survey flight should be used to avoid starting the experiment in a region of sharp horizontal concentration gradients. ASTEX/MAGE brought us much closer to implementing a practical Lagrangian strategy.

Although the data from ASTEX/MAGE are still being analyzed, preliminary results suggest that the Atlantic Ocean near the Azores was a net source of ammonia vapor during the second Lagrangian experiment. To maintain the (relatively constant) ammonium aerosol concentrations in the presence of rapid dilution by clean free-tropospheric air, the ocean's surface had to be emitting tens of micrograms of ammonia nitrogen per square meter per day. This calls into question the idea that precipitation ammonium is a new (as opposed to recycled) fixed-nitrogen source to the oceans (Duce, 1986). Similar analyses of other species budgets are now underway.

Lagrangian observations can play an important role in the study of atmospheric chemistry, marine aerosol dynamics, boundary layer dynamics, and cloud/climate interactions. They offer a unique way of constraining fluxes and reaction rates by observing the effect of those processes on a parcel of air. Their implementation, however,

requires cooperation on an international scale: MAGE is involved because such experiments are beyond the capabilities of any one group, discipline, or nation working alone.

For further information about ASTEX/MAGE, contact Barry Huebert, Department of Oceanography, University of Hawaii, Honolulu, HI 96822 USA (Phone: 1-808-956-6896, Internet: huebert@okika.soest.hawaii.edu).

Future MAGE Experiments: ACE-1

Under the umbrella of the International Global Atmospheric Chemistry Program (IGAC), MAGE and a sister project Multiphase Atmospheric Chemistry (MAC) are planning to employ a Lagrangian experiment to study DMS, aerosols, clouds, and climate during the Aerosol Characterization Experiment (ACE-1) in the vicinity of Cape Grim, Tasmania in early 1995. The new NCAR C-130 will support an even comprehensive chemical experiment, and one or two ships will be used to study the surface water forcing of air/sea exchange.

Anyone interested in learning more about ACE-1 should contact either Barry Huebert (the MAGE Convenor), or the MAC Co-convenors, Tim Bates or John Gras (Division of Atmospheric Research, CSIRO, Private Bag 1, Mordialloc, Vic. 3195, Australia. Phone: 61-3-586-7666, Internet: jlg@dar.csiro.au).

REFERENCES

Albrecht, B.A., 1989, Aerosols, cloud microphysics, and fractional cloudiness, *Science*, 245:1227-1230.

Andreae, M.O., 1986, The ocean as a source of atmospheric sulfur compounds, *in:* "The Role of Air-Sea Exchange in Geochemical Cycling," P. Buat-Menard (ed.), D. Reidel, Hingham, MA, U.S., pgs. 331-362.

Bates, T.S. and J.D. Cline, 1985, The role of the ocean in a regional sulfur cycle, *J. Geophys. Res.*, 90:9168-9172.

Bates, T.S., R.P. Kiene, G.V. Wolfe, P.A. Matrai, F.P. Chavez, K.R. Buck, B.W. Blomquist and R.L. Cuhel, 1993, The cycling of sulfur in surface seawater of the northeast Pacific, *J. Geophys. Res.*, in press.

Charlson, R.J., J.E. Lovelock, M.O. Andreae and S.G. Warren, 1987, Oceanic phytoplankton, atmospheric sulfur, cloud albedo, and climate, *Nature*, 326:655-661.

Duce, R.A., 1986, The impact of atmospheric nitrogen, phosphorus, and iron species on marine biological productivity, *in:* "The Role of Air-Sea Exchange in Geochemical Cycling," P. Buat-Menard (ed.), pgs. 497-529, D. Reidel, Hingham, MA, U.S.

Greene, R.M., Z.S. Kolber, D.S. Swift, N.W. Tindale and P.G. Falkowski, 1993, Physiological limitation of phytoplankton photosynthesis in the eastern equatorial Pacific determined from natural variability in the quantum yield of fluorescence, *Limnol. Oceanogr.*, in press.

Hanson, A.K., N.W. Tindale, M.A.R. Abdel-Moati, J.E. Prentice, D.W. O'Sullivan, 1993, Influence of a rain event on iron, peroxide, and phytoplankton in the surface waters of the equatorial Pacific ocean, in preparation.

Huebert, B.J., T.S. Bates, A. Bandy, S. Larsen and R.A. Duce, 1990, IGAC/MAGE: International Planning for Air/Sea Exchange Research, *EOS*, 71(35).

Huebert, B.J., S.G. Howell, P. Laj, J.E. Johnson, T.S. Bates, P.K. Quinn, S.A. Yvon, E.S. Saltzman, V. Yegorov, A.D. Clarke and J.N. Porter, 1993, Observations of the atmospheric sulfur cycle on SAGA-3, *J. Geophys. Res.*, 98:16,985-16,996.

Johnson, K.S., K.H. Coale, V.A. Elrod and N.W. Tindale, 1993, Iron photochemistry and bioavailability in equatorial Pacific waters, *Marine Chem.*, in press.

Kawa, S.R. and R. Pearson, Jr., 1989, Ozone budgets from the dynamics and chemistry of marine stratocumulus experiment, *J. Geophys. Res.*, 94:9809-9817.

Langner, J., T.S. Bates, R.J. Charlson, A.D. Clarke, P.A. Durkee, J. Gras, J. Heintzenberg, D.J. Hoffman, B. Huebert, C. Leck, J. Lelieveld, J.A. Ogren, J. Prospero, P.K. Quinn, H. Rodhe and A.G. Ryaboshapko, 1993, "The global atmospheric sulfur cycle: An evaluation of model predictions and observations," Report No. CM-81, ISSN 0280-445X, Dept. of Meteorology, Stockholm Univ.

Liss, P.S., J.N. Galloway, 1993, Air-Sea exchange of sulphur and nitrogen and their interaction in the marine atmosphere, *in:* "Interactions of C, N, P and S Biogeochemical Cycles and Global Change," R. Wollast, F. T. Mackenzie and L. Chou (eds.), Springer-Verlag, pgs. 259-281.

Lenschow, D.H., R.J. Pearson and B.B. Stankov, 1981, Estimating the ozone budget in the boundary layer by use of aircraft measurements of ozone eddy flux and mean concentration, *J. Geophys. Res.*, 86:7291-7297.

Martin, J.H., R.M. Gordon, and S.E. Fitzwater, 1991, The case for iron, *Limnol. Oceanogr.*, 36:1793-1802.

Yin, F., D. Grosjean and J.H. Seinfeld, 1990, Photooxidation of DMS and DMDS. I: Mechanism development, *J. Atmos. Chem.*, 11:309-364.

Young, R.W., K.L. Carder, P.R. Betzer, D.K. Costello, R.A. Duce, G.R. Ditullio, N.W. Tindale, E.A. Laws, M. Uematsu, J.T. Merrill and R.A. Feely, 1991, Atmospheric iron inputs, primary productivity, and phytoplankton responses in the north Pacific, *Global Biogeochem. Cycles*, 5:119-134.