Pacific Atmospheric Sulfur Experiment (PASE) is a comprehensive study of the chemistry of sulfur in the lower part of the remote marine troposphere. The experiment will be conducted east of the island of Kiritimati (Christmas Island), which past experiments have shown is an ideal location for such studies. State of the art instruments will be used to make accurate high speed airborne determinations sulfur dioxide, dimethyl sulfide, dimethyl sulfoxide, dimethyl sulfone, methane sulfonic acid, hydroxyl radical, ammonia, water vapor, ozone, hydrogen peroxide, methyl hydrogen peroxide, liquid water, temperature, pressure, wind velocity, cloud condensation nuclei, and size, composition and thermal properties of aerosols. Dimethyl sulfide, sulfur dioxide, water vapor and ozone will be determined at 25 samples per second allowing vertical fluxes of these species to be determined by eddy correlation. PASE will be performed using the NCAR C130 aircraft and will be conducted in a Lagrangian framework similar to that used in the Dynamics and Chemistry of Marine Stratocumulus Study (DYCOMS) I and II programs. The Lagrangian framework allows the budgets of dynamical properties, water vapor, ozone, dimethyl sulfide, and sulfur dioxide to be experimentally determined. Detailed modeling of the chemistry and dynamics of the marine trade wind regime is an integral part of PASE.

Highly relevant issues concerning how cloud condensation nuclei are produced in the marine atmosphere will be investigated. Related issues such as the photochemical formation of small particles of sulfuric acid in the outflow of cumulus cloud will be investigated and evaluated for their potential to grow to CCN by accreting gases such as water vapor, sulfur dioxide, sulfuric acid, and ammonia. The formation of nanometer size sea salt preCCN will be studied including their potential growth to CCN. Loss of sulfur dioxide and sulfuric acid to sea salt near the ocean surface will be intensively studied.

PASE will provide information on the Aerosol Indirect Effect (AIE) in the remote marine atmosphere and an evaluation of the CLAW hypothesis that describes how dimethyl sulfide oxidation can have important impacts on AIE. At the core of PASE is the chemistry of sulfur because much of the chemistry of AIE involves the products of dimethyl sulfide (DMS) oxidation and their interactions with sea salt aerosols.

Broader impacts: A concerted effort will be made on PASE to bring this type of research into the educational activities of participating universities. Each PI has been asked to include both undergraduate and graduate students in their budgets and to be involved in the research on Christmas Island. Financial support for three undergraduate students is requested in this proposal. A series of seminars by PI’s will be presented to students on Christmas Island and one of the data workshops. To further encourage student participation in the field phase one seat on each mission will be reserved for students who do not otherwise get to deploy on the C130. The undergraduate students deployed with the Bandy group will be enrolled in the undergraduate research courses at Drexel University, which are required of all Drexel Chemistry majors (Chemistry 493 and 497).

Finally, PASE is designed to bring a large number of highly capable investigators to focus on an important set of the scientific issues in global climate. PASE is an integrated study of the interactions between sulfur chemistry and aerosols which have long been postulated but not experimentally verified in a concerted program. PASE investigators are likely to make substantial contributions to resolving the issue of AIE and its relationship to sulfur chemistry. The results of this study have the potential to make substantial contributions to chemical and physical bases of global climate models.
Pacific Atmospheric Sulfur Experiment

Project Description

1 Introduction

The details of the marine sulfur cycle are major unresolved issues in atmospheric chemistry. In the marine boundary layer (MBL), the number of particles capable of nucleating cloud droplets is thought to be controlled or strongly influenced by biogenic dimethyl sulfide (DMS). The chemistry of DMS is extremely complex, with numerous unmeasured rate constants for reactions involving the intermediate species. A significant fraction of DMS forms sulfur dioxide (SO$_2$), which has at least four competing fates: dry deposition, oxidation in sea salt by ozone, oxidation in cloud water by H$_2$O$_2$, and homogeneous oxidation initiated by OH. Only the latter can produce gaseous sulfuric acid (H$_2$SO$_4$) that can potentially react with H$_2$O vapor and perhaps ammonia (NH$_3$) to create new particles that then accrete H$_2$SO$_4$, H$_2$O and NH$_3$ to produce much larger particles that are cloud condensation nuclei (CCN). Because of the impact of these CCN on cloud properties that in turn control their reflecting properties, sulfur chemistry can have an important influence on the earth’s radiation balance and climate.

Sulfur chemistry is an important part of the aerosol indirect effect (AIE), which includes all processes that affect cloud properties that in turn affect the radiation balance of the earth. The sulfur contribution to AIE is included (perhaps too simply) in the CLAW hypothesis named after the scientists that proposed it [Charlson et al., 1987]. The CLAW hypotheses states that DMS released from the ocean is largely converted to sulfuric acid (H$_2$SO$_4$), which combines with H$_2$O and possibly NH$_3$ to produce new particles as described above. These new particles can be the precursor particles of CCN required for the nucleation of cloud droplets. Larger numbers of CCN cause clouds to be whiter, reflecting more solar radiation back to space. This process in turn leads to less solar radiation striking the ocean, which decreases the number of phytoplankton producing the DMS. A reduction in DMS occurs, leading to less H$_2$SO$_4$, fewer CCN, and less reflecting cloud. More light reaches the surface producing more DMS, etc, and thus more CCN that lead to whiter clouds thus closing the cycle.

Significantly, it is the number of CCN rather than their mass, which is at issue, so the mechanism of sulfate formation makes a huge difference. For example, oxidation of SO$_2$ in cloud water is unlikely to increase particle number concentrations. Consequently a detailed understanding of the relationship between DMS emissions, oxidation mechanisms, and aerosol formation and growth processes is central to understanding the radiation balance in the remote marine boundary layer.

Formation of new particles by chemical reactions is not the only way new particles can be generated. Wave and bubble breaking also can produce small NaCl particles, which by accreting H$_2$SO$_4$, H$_2$O and NH$_3$ can grow to CCN.

CCN precursors also can be formed in cumulus cloud outflow mainly in the free troposphere (FT) and then transported by entrainment into the cloud formation region of the atmosphere. This process is known to occur but has not been studied to the degree necessary to evaluate fully its potential for producing CCN.

These three processes for producing CCN in the marine boundary layer have been modeled by several groups, of which Yoon and Brimblecombe [2002] is typical. Many parameters in these models had to be computed such as entrainment of preCCN from the troposphere, the formation rates of SO$_2$ and H$_2$SO$_4$ from DMS, the fluxes of SO$_2$ and DMS at the ocean surface, the top of the convective boundary layer (CBL), and the top of the buffer layer (BuL) [Russell et al., 1998], etc. In the proposed experiment these and other parameters will be measured thus dramatically reducing the number of adjustable parameters in these models and thereby constraining them to much tighter limits.

The time is right for such experiments. Newly developed instruments make possible the measurements of the concentrations and surface fluxes of DMS and SO$_2$. The concentrations of many of the relevant gaseous species such as OH, H$_2$SO$_4$ dimethyl sulfoxide (DMSO), dimethyl sulfone (DMSO$_2$) methane sulfonic acid (MSA), and aerosol products such as sulfate (SO$_4^{2-}$) and methane sulfonate (MS) with unprecedented speed, accuracy and lower limit of detection.

In this proposal a detailed study of sulfur in the remote marine boundary is described that was named the Pacific Atmospheric Sulfur Experiment (PASE) because much of the study is devoted to sulfur and will be conducted over the Central Pacific east of Christmas Island in August 2006. It would be flown on the NCAR C130 aircraft.

The proposed program is complementary to the RICO (Rain in Cumulus over the Ocean) program that studied the microphysics of rain formation in warm cumulus clouds. Both RICO and PASE type programs are needed to fully understand and quantify the effects of marine aerosols on clouds and on the radiation balance of the earth.

The work proposed will be performed in the marine trade wind regime. Labeling of the various regions follows the scheme suggested by Russell et al. [1998]. This is a three-layer system. The lowest layer is the convective
boundary layer (CBL), the intermediate layer is the buffer layer BuL and the upper layer is the free troposphere (FT).

PASE is a multidisciplinary program involving several principal investigators who are submitting their own proposals. The principal investigators, the focus of their proposals and the relationship to the work described in this proposal are discussed in a subsequent section. Letters of participations are included in supplementary materials. Also included in supplementary materials is a request to the government of Kiribati for permission to perform this experiment.

2 Sulfur Chemistry

Substantial progress has been made during the last 30 years in understanding the chemistry of atmospheric DMS. This progress was recently summarized by Davis et al. [1999] and extended by Chen et al. [2000]. That DMS was the major sulfur gas emitted to the atmosphere was shown through determinations of DMS in marine air by Lovelock [1972] and Maroulis and Bandy [1977] and in seawater by Andreae and Raemdonck [1983]. Given that source, it was not surprising that aerosols in pristine marine air contained substantial levels of non-sea salt sulfate and methane sulfonate (MS) [Savoie and Prospero, 1989] as products of DMS oxidation. Laboratory studies have shown that DMS oxidation can be initiated by OH, by halogen containing radicals, and by the NO3 radical [Davis et al., 1999]. In the clean atmosphere around Christmas Island, OH appeared to be the most important DMS oxidant starting reactions that lead to SO2, H2SO4, DMSO, DMSO2, MSA (gas phase methane sulfonic acid), MS (aerosol phase methane sulfonate) [Davis et al., 1999], and NSS (non-sea salt sulfate) aerosol. Although the basic chemical framework seems clear, many unknowns remain. In this section, we outline five specific questions we propose to address.

Instrumentation is now available for determining DMS and SO2 at 25 samples per second (sps) aboard ships and aircraft making possible the use of eddy correlation for determining surface and entrainment fluxes. Atmospheric sulfur chemistry has not been tested using direct measurements of DMS source- and SO2 loss-fluxes described in this proposal. Methods also are available for at least 1 sps determinations of DMSO and DMSO2 [Nowak et al., 2001; Xu, 1999], thus allowing these species to be profiled. It may even be possible to make 25 sps determinations of DMSO and DMSO2 so their fluxes could be computed by eddy correlation.

2.1 DMS and SO2 Chemistry

A major goal of the proposed research is to experimentally determine all the terms in the chemical budgets of DMS and SO2. The budgets of DMS and SO2 contain the surface fluxes of these species, the oxidative destruction of DMS and the gas phase formation and destruction rates of SO2; the quantities needed to test kinetic models of their chemistry.

Complete budgets for these species have not been obtained although some attempts have been made. Davis et al. [1999] and Chen et al. [2000] summarized these attempts. All reported budgets are incomplete because the necessary fluxes at the boundary layer top and bottom for DMS, SO2 and other species were not available. Consequently, fluxes were parameterized and thus contained adjustable variables that were selected by best fit to the available data. A major contribution of the proposed study is that DMS and SO2 budgets will be closed using directly determined eddy fluxes at the ocean surface and interfacial layers.

2.1.1 DMSO and DMSO2 Chemistry

Models of DMS oxidation chemistry include an OH-addition channel that produces MSA, DMSO and DMSO2 [Davis et al., 1998]. Since the efficiency of this channel apparently increases as temperature decreases, DMSO and DMSO2 concentrations should increase when the ambient temperature drops. The Christmas Island site has ocean temperatures on the high side near 26°C, which should make this channel relatively inefficient compared to ocean areas having lower temperatures. Photochemical production should cause MSA, DMSO and DMSO2 to increase during the daytime, while at night they should decrease due to uptake by aerosol surfaces and the ocean.

However, observations of DMSO and DMSO2 on Christmas Island in 1994 showed no diurnal variation [Bandy et al., 1996]. This is in contrast to the obvious anticorrelation of DMS and SO2 observed by Bandy et al. [1996]. More recently Nowak et al. [2001] found a similar lack of an identifiable diurnal variation for DMSO and DMSO2. Clearly, these data do not match model predictions, so something has been missed. As Nowak et al. [2001] point out, either the kinetic models are wrong or a non-photochemical source of DMSO has been missed. An objective of this program is to make more accurate measurements of DMSO, DMSO2, and related species over time and altitude, to resolve this issue.

2.1.2 BrO and DMS Chemistry

Because appropriate instrumentation is not available to study bromine chemistry in detail we must consider our efforts to be exploratory in nature. However, review of the literature suggests that the issue remains and must be considered.

The impact of gas and droplet halogen chemistry on photochemistry and in particular to DMS oxidation in...
clear and cloudy MBL’s, was examined numerically by von Glasow et al. [2002a, 2002b, 2004]. In these studies the inclusion of a BrO – DMS oxidation path contributed approximately 17% to 75% of the total DMS oxidation under equatorial Pacific (remote marine tropical) to “Cape Grim summer” conditions. This model predicts that the BrO-DMS path yields DMSO and has a significant impact on the DMSO to DMS ratio. Under the low nitrogen oxide conditions of the equatorial tropics, the other DMS oxidant is OH. Ozone is the key constituent regulating the relative importance of the BrO mechanism [von Glasow et al., 2004] as was also shown for ozone production [Chang et al., 2004]. Ozone chemistry effectively controls both the BrO source and the OH source. Further, the addition of BrO chemistry was shown to reduce the efficiency of DMS to SO2 conversion in the gas phase and the inclusion of heterogeneous halogen chemistry (HBrO) increased the production rate of MSA and non-sea salt sulfate. In clear air aerosol simulations, halogens contributed roughly 50% of the NSS production; in cloudy air simulations H2O2 accounted for more than 90% of NSS production. The reductions noted in SO2 also reduced gas phase H2SO4 production and reduced “nucleation” of new particles. BrO levels of consequence to DMS are estimated to be on the order 0.3-3 ppt.

The contribution of BrO and halogen chemistry to DMS oxidation in our study region is expected to be small. Direct measurements and diagnostic measures are available to assess this. BrO chemistry is associated with the loss of Br\(^{-}\) from sea salt aerosols. Evidence of Br\(^{-}\) loss, e.g. Br/Na ratios below that of seawater, and that of other halogens, e.g., F, would indicate the potential presence of halogen chemistry. Some PI’s will address this issue in more detail in their proposals.

2.2 Loss of SO2 to the sea salt aerosol layer

The absorption of SO2 and its oxidation to SO4\(^{2-}\) by O3 in water contained in sea salt particles is widely accepted as a major pathway for the removal of SO2 from the MBL. The newly formed sulfuric acid might then displace hydrochloric acid (HCl) and other chlorinated gases from these concentrated solutions. A paper by Martens et al. [1973] reported the depletion of chloride in Puerto Rican and San Francisco Bay marine aerosol, while Gravenhorst [1978] reported that SO2 was lost to marine aerosols of the North Atlantic. A transect from 30°N to 30°S in the Central Pacific also revealed that this loss was pronounced in the upwelling region of the equatorial Pacific near Christmas Island [Clarke et al., 1997].

Numerous reports of non-sea salt sulfate (NSS) enrichment and chloride depletion followed this initial work. The papers of Keene et al. [1990], Chameides and Stelson [1992], Suhre et al. [1995], Luria and Sievering [1991] are typical. These studies postulate the existence of suitable mechanisms for the oxidation of SO2 by O3 in marine aerosol, in agreement with field studies showing NSS enhancement and chloride (Cl) depletion. All predict that SO2 removal by marine sea salt aerosol is at least as efficient as removal at the sea surface. However, until now, removal of SO2 at the sea surface could not be directly observed. An important objective of this work is to determine the nighttime budgets of SO2 with high precision below 200m. In the cloud-free case the destruction term for SO2 above the ocean surface is only loss to aerosol because the photochemical loss is nil. The surface flux can be obtained by extrapolating the SO2 flux to the ocean.

2.3 Production of submicron NSS from DMS

What fraction of emitted DMS becomes submicron sulfate aerosol, which could affect CCN and thereby cloud radiative properties? In the absence of precipitation, aerosol concentrations will decrease only due to dry deposition and dilution by entrainment of FT air [Huebert et al., 1996]. MOUDI size distributions will be used to estimate the dry deposition loss, which is likely to be negligible for small sizes. Entrainment velocities at the top of the BuL and the CBL will be determined from fast H2O, SO2, DMS and O3 data. The daytime increase in NSS and MS concentrations can then be corrected for entrainment and converted to a production rate in both the CBL and BuL. Measurements of the physical size distributions in the FT and CBL then can be used to quantify the processes controlling both particle number and mass, for the AIE. Measurements using an early application of the aerosol volatility approach found virtually all of the accumulation mode aerosol mass and number were NSS in the productive equatorial Pacific. Repeated transects later demonstrated that both NSS concentrations and a surface ammonia flux were linked to gradients in surface water chlorophyll [Clarke et al., 1996]. We will also measure organic carbon (OC) aerosol, to tighten the agreement between physical and chemical size distributions.

2.4 Dependence of SO2 exchange velocities on wind speed

Surface fluxes of gases are thought to be the product of an interfacial concentration difference and an exchange velocity. This exchange velocity (which can be generalized to many gases) is thought to be a function of surface wind speed [Liss and Merlivat, 1986; Wanninkhof and McGillis, 1999], surface films, whitecaps, and other factors. Recent measurements of CO2 fluxes suggest that other water-side controlled gases like SO2 might show a
cubic dependence on wind speed [Wanninkhof and McGillis, 1999], although a quadratic has often been used [Wanninkhof, 1992]. We propose to examine these relationships using direct surface flux measurements of SO$_2$ obtained using eddy correlation. The negligible concentration of SO$_2$ in the surface ocean obviates the needs for seawater measurement.

3 Proposed Research

The important objective of this work is to uniquely obtain chemical budgets. The approach for doing this was developed by Bandy and Lenschow [Lenschow et al., 1988] for the Dynamics, and Chemistry of Marine Stratocumulus program (DYCOMS I) that was further refined in the DYCOMS II program [Faloona, et al., 2003; Stevens, 2003]. Fast determinations of DMS, SO$_2$, O$_3$ and H$_2$O make this kind of analysis possible at least for these species.

3.1.1 The study region

PASE will be conducted east of Christmas Island (Kiritimati, 2 N, 157 W). This region was chosen because its chemistry and meteorology are well characterized and it is an ideal outdoor laboratory to study the chemistry of DMS. The chemical and aerosol characteristics have been reported by Bandy et al. [1996], Huebert et al., [1996], Clarke et al. [1996], Davis et al. [1999], and Chen et al. [2000]. The meteorological characteristics were reported by [Lenschow et al., 1999]. These investigations contain considerable detail so only the most relevant characteristics will be discussed here.

Christmas Island is in the southeast trade wind regime, far from anthropogenic sources of sulfur. Soundings of the 25 Hz vertical velocity, water vapor mixing ratio, air temperature and ozone are shown in Figure 1. The CBL is characterized by a region of high and uniform fluctuations in vertical velocity that imply effective and rapid vertical mixing. Typical of turbulent layers, the sounding of water vapor is almost constant up to the CBL top where it rapidly decreases. The BuL is less well mixed because turbulence is weaker and intermittent. The top of the BuL is characterized by a further large drop in turbulence, water vapor, DMS, etc. at the trade wind inversion. Above the BuL is the free troposphere.

An important property of the Christmas Island trade wind regime in August and September is that there are long periods during which few clouds exist especially in the CBL [Bandy et al., 1996]. The budget studies of PASE will be carried in one of these common, very stable, nearly cloud-free periods in August. However, aging, growth, and uptake onto aerosol will be enhanced in the small non-precipitating clouds that are often present in the BuL [Bandy et al., 1996]. Studies of cloud processing is an important component of PASE. Focus will be on both the nonprecipitating clouds that are often present in the BuL layer during the stable periods and the outflow of convective cumulus clouds that penetrate the trade wind inversion that often appear at the end of stable periods. These cloud studies will be
discussed in greater detail in a subsequent section.

The characteristics of the CBL appear to be a general property of the marine trade wind regime. The soundings for DMS and vertical velocity in Figure 2 were obtained in the northeast trade wind regime in the Atlantic east of St. Croix, VI. Soundings for SO$_2$, vertical velocity and water vapor mixing ratio for Midway Island in the Pacific are shown in Figure 3. Each of these trade wind regimes has a turbulent, well mixed CBL and a less well mixed BuL.

Because fluxes and time derivatives of concentrations are the variables to be measured in this study, requirements of homogeneity are greatly reduced (Lenschow, private communication) compared to previous studies of the Christmas Island trade wind regime [Bandy et al., 1996; Chen et al., 2000; Davis et al., 1999]. However, homogeneity makes data analysis easier and to some extent more precise.

East of Christmas Island for a few hundred kilometers, the ocean appears to have a reasonably homogeneous flux of DMS. Evidence of this homogeneity was obtained in Mission 7 of PEM Tropics A that was flown over a track 100 km in length just east of Christmas Island. In this mission level legs were flown as circles 60 km in diameter (30 minutes in length) that were advected with the mean wind. The variability of the concentrations along the track was small and very repeatable [Lenschow et al., 1999] and fit on a smooth curve determined by the photochemistry of the system [Davis et al., 1999]. To draw this inference of homogeneity it is useful to recognize that the CBL mixes vertically within the CBL in less than 0.5 hours (I. Faloona, private communication). Horizontal mixing is slower, so any change in surface flux quickly appears as a change in DMS around the circle. Systematic changes of this type were not observed at Christmas Island [Lenschow et al., 1999]. Finally, Bandy et al. [1996] reported a repeatable diel variations of DMS and SO$_2$ over 4 days that could not have been achieved unless the upstream DMS flux was reasonably uniform and constant.

3.1.2 Flight Plans

CBL budgets for DMS, SO$_2$, O$_3$, H$_2$O and possibly DMSO and DMSO$_2$ will be determined using the flight plan shown in Figure 4. Each set of legs will begin and end with a sounding to identify the top (h) of the CBL by locating the large decrease in variance of vertical velocity at the top of the CBL. Thirty-minute circles will then be flown at 30 m, h/4, h/2 and 3/4h. This will be repeated 3 times. For nighttime missions the 30 m level can be flown only in daylight or twilight (for safety reasons). It is noteworthy that the soundings will be performed at 800 ft min$^{-1}$ so the total expected duration for the sounding is about 3 min. The column concentrations of DMS, SO$_2$, DMSO, DMSO$_2$, and any other species with fast measurement rates will be obtained from these soundings. Since there will be 4 soundings per flight there will be 4 determinations of the column concentrations of these species.
species, separated by about 2.5 hours. We will compute 3 time derivatives of the column concentrations of DMS, SO$_2$, DMSO, DMSO$_2$, and the other species with fast measurement rates.

Near-surface budgets of DMS and SO$_2$ and possibly DMSO and DMSO$_2$ will be determined using the flight profiles shown in Figure 5. To minimize the impact of any variation in surface flux these studies will be flown over the same circle geographically to the extent possible, without entering the aircraft plume. These profiles will be flown 5 times per mission. Most of this flight will be flown under low light conditions to minimize photochemistry.

3.1.3 Meteorological Framework

As described in 3.1.1 the experiment will be carried out in the well mixed CBL east of Christmas Island. For this CBL the following budget approach provides the basis for interpreting data to be obtained in this study.

The budget for scalar $s$ is given by the relationship

$$\frac{\partial \langle s \rangle}{\partial t} + \overline{u} \frac{\partial \langle s \rangle}{\partial x} + \frac{\partial}{\partial z} \left( \langle s \rangle \overline{w'} \right) = f(s) - d(s)$$

(3.1.1)

The rate of change of each species is controlled by horizontal advection, vertical fluxes, formation, and destruction. Here $s$ is the concentration of scalar $s$, $\overline{u}$ is the mean wind speed along the mean wind direction, $x$ is the direction of the mean wind, $w$ is the vertical velocity, $z$ is the altitude, and $\langle s \rangle \overline{w'}$ is the eddy flux at the altitude $z$. Also $f(s)$ is the chemical formation rate and $d(s)$ is the chemical destruction rate of $s$.

Integrating (3.1.1) from the surface through the top of the CBL yields

$$\frac{\partial \langle s \rangle}{\partial t} + \overline{u} \frac{\partial \langle s \rangle}{\partial x} - \langle s \rangle \frac{\partial \overline{h}}{\partial x} - \int_0^h \langle s \rangle \overline{w'} \, dz = f(s) - d(s)$$

(3.1.2)

where angle brackets denote a column concentration for the boundary layer defined by

$$\langle s \rangle = \frac{\int_0^h s \, dz}{h}$$

(3.1.3)

Here $h$ is the depth of the CBL, $J_0(s)$ is the flux at $z=0$, $J_h(s)$ is the flux at $z=h$, $F(s)$ is the column chemical formation rate of $s$, and $D(s)$ is the column chemical destruction rate of $s$. All missions will be flown in the Lagrangian framework (drifting patterns with the wind) so that $\overline{u}=0$. Equation (3.1.2) then simplifies to:

$$\frac{\partial \langle s \rangle}{\partial t} = f(s) - d(s)$$

(3.1.4)

All the terms on the left can be measured for DMS, H$_2$O, O$_3$ and SO$_2$. Budget analyses described below are based on (3.1.4).

3.1.4 How will (3.1.4) be used in this study?

The variable $s$ represents the concentrations of O$_3$, SO$_2$, DMS, H$_2$O, or any other scalar quantity. Each of the terms has the units of flux, e.g., pptv m$^{-1}$ s$^{-1}$ or molecules m$^{-2}$ s$^{-1}$. As illustrated in Figure 2, (3.1.4) represents the conservation of mass of $s$ in a cylinder that is moving at the mean wind speed along the direction of the mean wind. The chemical formation and destruction terms contain gas phase processes as well as gas-to-particle and particle-to-gas conversions. These issues are discussed in further detail in 3.5.

DMS data obtained during DYCOMS II illustrate the budget process. This program was a study of the dynamics of the stratocumulus regime west of San Diego that was

![Figure 6 Soundings for vertical velocity, liquid water, DMS and DMS vertical flux. The slope of the DMS vertical flux curve is the vertical flux divergence of DMS.](Figure 6 Soundings for vertical velocity, liquid water, DMS and DMS vertical flux. The slope of the DMS vertical flux curve is the vertical flux divergence of DMS.)
conducted in the summer of 2001. The legs in the CBL were flown as 30 min circles, just as planned in PASE. Soundings for vertical wind velocity, liquid water, DMS and DMS flux are shown in Figure 6. (The stratocumulus region near San Diego is a one-layer system, so there is no BuL.) The CBLs of the stratocumulus and trade wind regimes are dynamically similar. Note the high uniform turbulence in the CBL as illustrated by the fluctuations in vertical velocity in the CBL and the transition to very low fluctuations at the top of the CBL. The almost constant DMS levels in the CBL reflect good vertical mixing. The flux of DMS increases with altitude in this case because dry, DMS-free air is being entrained at the CBL top and the DMS must be brought from lower altitudes to keep the DMS concentration constant with altitude. Note that the slope of the DMS flux vertical profile is the flux divergence of DMS.

Extrapolation of the DMS flux profile to the surface yields 27.5 pptv cm s\(^{-1}\) for the surface flux of DMS, \(J_{o}(\text{DMS})\), and extrapolation to the CBL top yields 62 pptv cm s\(^{-1}\) for the flux for DMS at the CBL top, \(J_{h}(\text{DMS})\). This is a general strategy for obtaining these two important quantities in the chemical budgets of the CBL. Computation of the time derivative of the column concentration of a scalar is straightforward and is described in 3.2.1.

### 3.2 Strategy for computing real world chemical budgets

Because all terms on the left side of (3.1.4) will be experimentally determined, it is convenient to rewrite it in the form:

\[
C(s) = F(s) - D(s) \tag{3.1.5}
\]

where \(C(s)\) represents the difference between chemical formation and destruction, and can be experimentally determined:

\[
C(s) = \frac{\partial}{\partial t} <s> - J_o(s) + J_h(s) \tag{3.1.6}
\]

The program to determine complete CBL budgets will be designed so that one set of legs is flown at night. \(C(s)\) can be conveniently divided into nighttime processes that occur all the time and daytime processes that occur only during the daytime.

\[
C(s) = F_g(s) - D_g(s) + F_g(s) - D_g(s) \tag{3.1.7}
\]

\[
C^\prime(s) = F_g(s) - D_g(s) \tag{3.1.8}
\]

\[
C_n(s) = F_n(s) - D_n(s) \tag{3.1.9}
\]

\[
C^\prime_n(s) = C(s) - C_n(s) \tag{3.1.10}
\]

\(F_g(s)\) and \(D_g(s)\) are photochemical terms and are assumed to be gas phase processes as indicated by a \(g\) subscript. By flying one leg set at nighttime, \(C_n(s)\) is obtained. Using standard propagation of errors techniques, the error in \(C(s)\) is obtained from the equation:

\[
\delta C(s) = \sqrt{\sum_{i} \left( \frac{\partial C(s)}{\partial \delta} \right)^2 \left[ \delta F_i(s) \right]^2 + \left[ \delta D_i(s) \right]^2} \tag{3.1.11}
\]

\[
\delta C^\prime_n(s) = \sqrt{\left[ \delta C(s) \right]^2 + \left[ 0.1 \delta C(s) \right]^2} \tag{3.1.12}
\]

To estimate errors, \(C_n(s)\) is assumed to be 10% of \(C(s)\). Therefore

\[
\delta C^\prime_n(s) = \sqrt{\left[ \delta C(s) \right]^2 + \left[ 0.1 \delta C(s) \right]^2} \tag{3.1.13}
\]

Although not as precise or complete there is another approach that requires only vertical profile data and does not require flux measurements. The full budget equation can be rearranged to yield

\[
\frac{\partial}{\partial t} <s> = [J_o(s) - J_n(s)] + F_g(s) - D_g(s) \tag{3.1.14}
\]

\[
C(s) = \frac{\partial}{\partial t} <s> = \left[ \frac{\partial}{\partial t} <s> \right]_n = F_g(s) - D_g(s) \tag{3.1.15}
\]

This approach assumes that the terms in square brackets in (3.1.14) do not change rapidly with time and is the preferred approach for a species that cannot be determined at 25 sps but can be determined at 1 sps or faster.

### 3.2.1 Propagation of errors in \(C(\text{SO}_2)\)

In this section the propagated errors in \(C(s)\) are computed for \(\text{SO}_2\). The same strategy can be used to compute...
the propagated error in C(s) for DMS, DMSO and DMSO$_2$. Propagated errors for these species are summarized in Table 1.

From the soundings $<\text{SO}_2>$ can be computed at two different times, $t_1$ and $t_2$. From these data the time derivative of the SO$_2$ column concentration at each leg can be computed:

$$\frac{\delta <\text{SO}_2>}{\delta t} = \frac{<\text{SO}_2>_{2} - <\text{SO}_2>_{1}}{t_2 - t_1}$$  \hspace{1cm} (3.1.16)

The contribution of errors from instrumental noise is now computed for each sounding. At a data rate of 25 sps, 4500 measurements of SO$_2$ are obtained in each 180 s sounding. At a typical sensitivity of 60 counts per second per pptv and 60 pptv of ambient SO$_2$, a total of 648,000 counts are obtained in the 180 s interval. The standard deviation of this signal is the square root of the counts, which is 805. Here the error is estimated using the average of the SO$_2$ in the soundings. Note that this approximation is used only in making error estimates and not in the actual data processing.

The confidence interval for errors arising from detector noise is computed from the equation:

$$1.96 \frac{1 \sigma}{\sqrt{N}} \approx \text{counts}$$  \hspace{1cm} (3.1.17)

Here $t$ is the two tailed $t$ value (1.96), $\sigma$ is the standard deviation of the signal in counts (805 counts) and $N$ is the number of measurements (4500). In pptv the confidence interval is

$$\text{Confidence Interval in pptv} \approx \frac{1 \times 24 \times 60 \times 0.4}{60 \times 4500} = 0.04 \text{ pptv}$$  \hspace{1cm} (3.1.18)

Therefore

$$\delta \frac{\delta <\text{SO}_2>}{\delta t} = -1000 \left[ \delta \frac{d[\text{SO}_2]}{dt} \right] = -1000 \left( \frac{1000 \times \sqrt{(0.4^2 + 0.4^2)} \text{ pptv}}{7200 \text{ s}} \right) = 0.08 \text{ pptv ms}^{-1}$$  \hspace{1cm} (3.1.19)

Here the height of the boundary layer was assumed to be 1000 m and the error in the boundary layer height was negligible compared to other errors. Also the time between soundings is about 7200 s.

The error in the surface flux, $\delta J_0(\text{SO}_2)$, is computed using the fact that the eddy flux measurement technique can determine SO$_2$ fluxes to about 10% [Mitchell, 2001]. The surface flux of SO$_2$ on Christmas Island is estimated using the deposition velocity parameterization for $J_0$:

$$J_0(\text{SO}_2) = \nu_d[\text{SO}_2]_0 = 0.01 \text{ ms}^{-1} \times 60 \text{ pptv} = 0.6 \text{ pptv ms}^{-1}$$  \hspace{1cm} (3.1.20)

where $\nu_d$ is the deposition velocity and $[\text{SO}_2]_0$ is the SO$_2$ concentration just above the ocean surface. The estimated error in the deposition velocity is 10% so the absolute error in $J_0(\text{SO}_2)$ is 0.06 pptv ms$^{-1}$.

The error in the flux at the CBL top would also be about 10% [Mitchell, 2001]. The entrainment velocity at the CBL top is about -0.005 m s$^{-1}$. The jump in SO$_2$ is assumed to be 60 pptv. The estimated flux at the boundary top is

$$J_h(\text{SO}_2) = \omega_h [\text{SO}_2]_h = 0.005 \text{ ms}^{-1} \times 60 \text{ pptv} = 0.3 \text{ pptv ms}^{-1}$$  \hspace{1cm} (3.1.21)

Since this flux also can be determined to 10%, the error is $\delta J_h(\text{SO}_2) = 0.03 \text{ pptv m}^{-1}$. Assuming that $C_h(s)$ is $10\%$ of $C(s)$ the total error in $C'(s)$ is 0.1 pptv m s$^{-1}$.

To put these errors into perspective, the formation rate of SO$_2$ is about 2 pptv m s$^{-1}$ [Bandy et al. 1996; Mitchell 2001] so a 0.1 pptv m s$^{-1}$ error in $C'(\text{SO}_2)$ yields a relative propagated error of $\approx 5\%$.

Table 1. Estimates for uncertainty calculations

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$v^i$</th>
<th>$w^i$</th>
<th>$h^i$</th>
<th>$s^i$</th>
<th>$J^5$</th>
<th>$J^6$</th>
<th>$\delta J^7$</th>
<th>$\delta J^8$</th>
<th>$\delta C^9$</th>
<th>$\delta $&lt;s&gt;/dt$^{10}$</th>
<th>$\delta C'(s)^{11}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_2$</td>
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<td>0.01</td>
<td>1000.00</td>
<td>60.00</td>
<td>0.60</td>
<td>0.30</td>
<td>0.06</td>
<td>0.03</td>
<td>60000.00</td>
<td>0.08</td>
<td>0.10</td>
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<tr>
<td>DMS</td>
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<td>150.00</td>
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<td>0.75</td>
<td>0.20</td>
<td>0.08</td>
<td>150000.00</td>
<td>0.12</td>
<td>0.25</td>
</tr>
<tr>
<td>DMSO</td>
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<td>0.01</td>
<td>1000.00</td>
<td>20.00</td>
<td>0.20</td>
<td>0.10</td>
<td>0.02</td>
<td>0.01</td>
<td>200000.00</td>
<td>0.04</td>
<td>0.05</td>
</tr>
<tr>
<td>DMSO$_2$</td>
<td>0.01</td>
<td>0.01</td>
<td>1000.00</td>
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<td>0.01</td>
<td>200000.00</td>
<td>0.04</td>
<td>0.05</td>
</tr>
</tbody>
</table>

1Deposition velocity (ms$^{-1}$)  6 flux at CBL top (pptv m s$^{-1}$)
2 Entrainment velocity (ms$^{-1}$)  7 Error surface flux (pptv m s$^{-1}$)
3 CBL depth (m)  8 Error in flux at CBL top (pptv m s$^{-1}$)
4 Concentration (pptv)  9 Column concentration (pptv m$^{-2}$)
5 Surface flux (pptv m s$^{-1}$)  10 Error in time derivative of s (pptv m s$^{-1}$)
11 Error in C'(s) (pptv m s$^{-1}$)
3.2.2 Daytime Studies

The daytime studies must consider the fact that some species such as SO$_2$, DMSO and DMSO$_2$ can be destroyed by reaction with aerosol as well as photochemical processes. Loss to aerosol and photochemistry will be separately evaluated by flying a series of legs shown in Figure 4.

During daytime

\[ C'(SO_2) = F_g(SO_2) - D_g(SO_2) \]  
\[ C'(DMS) = -D_g(DMS) \]  
\[ C'(DMSO) = F_g(DMSO) - D_g(DMSO) \]  
\[ C'(DMSO_2) = F_g(DMSO_2) - D_g(DMSO_2) \]

The gas phase formation rate of DMS is assumed to be negligible. The photochemical loss rate of SO$_2$ due to reaction with OH is slow and can be computed with small relative error. For example the reaction of OH and SO$_2$ has a rate constant of $3.88 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The concentration of SO$_2$ is about 60 pptv or $1.47 \times 10^9$ molecules cm$^{-3}$, the daytime averaged OH is about $10^6$ molecules cm$^{-3}$ and the depth of the CBL is about 1000 m. Using these estimates $D(SO_2)$ from photochemistry is estimated to be 0.023 pptv m s$^{-1}$. Taking a conservative estimate of error of 30%, the contribution of this term to the overall error is 0.015 pptv m s$^{-1}$ which is acceptable. For convenience this correction is included in $C'(SO_2)$. Therefore,

\[ C'(SO_2) = F_g(SO_2) \]

The efficiency of conversion of DMS to SO$_2$ can be computed:

\[ %Eff = 100 \left[ \frac{F_g(SO_2)}{D_g(DMS)} \right] \]

Here %Eff is the efficiency of conversion of DMS to SO$_2$ and ranges from 0 to 100%. To estimate an error in %Eff, the formation rate of SO$_2$ is assumed to be 1 pptv m s$^{-1}$ and the destruction rate of DMS is assumed to be -2 pptv m s$^{-1}$. Using the data in Table 1 leads to a propagated error in %Eff of 15%. If the experiment is repeated 5 times the propagated error would be reduced to 7%.

The reaction of OH and DMSO$_2$ is probably negligible compared to other processes such as the loss to aerosol [Davis et al., 1998], so the gas phase chemical column destruction rate of DMSO$_2$, $D_g(DMSO_2)$, is negligible. Consequently, $F_g(DMSO_2)$ is uniquely determined:

\[ C'(DMSO_2) = F_g(DMSO_2) \]

The fraction of DMS leading to DMSO can be approximated by that which is not converted to SO$_2$:

\[ F_g(DMSO) = \left[ D_g(DMS) \right] \left[ 1 - \left( \frac{%Eff(SO_2)}{100} \right) \right] \]

In this way the destruction rate of DMSO can be determined as a function of time. Also the efficiency of the formation of DMSO$_2$ from DMSO can be estimated

\[ %Eff = 100 \left[ \frac{F_g(DMSO_2)}{D_g(DMSO)} \right] \]

Nighttime circles are flown in the same way as the daytime circles except that the 30 m leg must be flown in twilight for safety reasons.

3.2.3 Full Nighttime Budgets.

At night we assume (for now) that the chemical formation rates of most s are negligible. Hence

\[ C(s) = -D(s) \]

D(s) is probably negligible for DMS but not necessarily for the other species where it contains a contribution from loss to aerosol. However, in this case D(s) will be small because most of the sea salt aerosol removing s is located below the lowest leg flown. In this case most of the loss of s to aerosol is included in $J_0(s)$. A separate experiment to study this issue is described in 3.2.4.

3.2.4 Studies of s just above the ocean surface
Just above the ocean surface a layer of basic sea salt particles having large surface area is thought to remove $s$. Several missions will be flown to provide quantitative determination of the removal of $s$ by aerosol. This study will be focused on the region below 200 m where a large fraction of the loss of $s$ to aerosol is expected [Suhre et al., 1995]. In this study 3 circles will be flown at 30, 100, and 200 m. Three flight levels were chosen because the reactivity of $s$ in this region may change with height producing nonlinear changes in $J_{ds}(s)$ with height within this layer. The choice of three levels was a compromise between available time on station and the need to account for this nonlinear behavior. The 30 and 100 m circles will be flown during twilight for safety reasons.

The relative contribution of loss of $s$ to the sea surface and loss of $s$ to aerosol can be estimated. The budget equation for $s$ in integral form for this region from the surface to 200 m is

$$C(s) = -D(s)$$

(3.1.32)

$J_{ds}(s)$ is the true surface flux that will be obtained by fitting the fluxes at 30, 100 and 200 m to a quadratic and then extrapolating $J(s)$ to the surface to obtain $J_{ds}(s)$. The percentage loss of $s$ to aerosol below 200 m compared to the total loss in the region being studied including that lost at the ocean surface is given by the expression:

$$% \text{Lost Aerosol} < 200m = \frac{\left| J_{ds}(s) \right|}{\left| J(s) \right|} \times 100$$

(3.1.33)

This can be done only for any species that can be determined at 25 sps and will include both DMS and SO$_2$.

To compute an estimated error in the loss of $s$ to aerosol we assume that the rate of loss of $s$ to aerosol is equal to the rate of loss of $s$ to ocean surface. For SO$_2$ the propagated error in the % lost to aerosol is 16%. This error can be decreased by repeating this experiment 5 times under conditions of similar wind speeds in which case the error would be reduced to 7%.

The many additional measurements in PASE allow a more detailed study of the boundary layer budget of sulfur to be performed near the ocean surface. For instance, the aerosol surface area will be measured, allowing an estimate of the loss rate of SO$_2$ to aerosol to be compared with the result from the gas phase analysis described in this section. The observed deficit of Cl and Br in various sizes of aerosol can be combined with an estimate of the flux of sea salt aerosol to estimate the source of gas phase halogens from the sea salt aerosol. This will be compared to the rate at which SO$_2$ is lost to aerosol.

### 3.2.5 Dependence of $J_{ds}(s)$ on wind speed

In the summer of 1994 the Christmas Island meteorology occurred in regimes in which the atmosphere was near steady state for 3-4 days in which the wind speed gradually increased from 5 to 10 m s$^{-1}$. During days 6 and 7 the wind speed increased gradually to about 12 m s$^{-1}$. This kind of variability provides an opportunity to investigate the surface fluxes of $s$ and the losses of $s$ to aerosol during a more than doubling of the wind speed. Models indicate a significant change in SO$_2$ surface flux and loss to aerosol as the wind speed increases. Some models suggest the magnitude of exchange velocities for gas emission increase with the cube of the wind speed [Wanninkhof and McGillis, 1999]. Computation of exchange velocities requires the surface ocean concentration measurements. However, the concentration of SO$_2$ in the surface ocean is negligible, thus the exchange velocity of SO$_2$ can be determined by extrapolating vertical fluxes made at higher altitudes to the ocean surface. The wind speed dependencies of the DMS, SO$_2$, H$_2$O and O$_3$ surface fluxes will be compared. If there is good agreement in the wind speed dependencies, an estimate of the DMS ocean concentration could be made using the exchange velocity determined from the SO$_2$ data.

### 3.2.6 Nighttime budget of DMS

At nighttime both the chemical formation and destruction rates of DMS should be negligible. Therefore

$$F(DMS) = D(DMS) = 0$$

(3.1.34)

As described above $C(DMS)$ can be determined to about 0.25 pptv m s$^{-1}$. Since the chemical formation of DMS in the atmosphere is assumed to be negligible the magnitude of the chemical destruction rate of DMS and the formation rate of SO$_2$ during nighttime can be shown to be $\leq 0.25$ pptv m s$^{-1}$. Although the destruction rate of DMS and the formation rate of SO$_2$ should be zero at night, this experiment allows us to test the assumption that halogen and nitrate radical reactions are unimportant at night in this region.

### 3.3 Determination of entrainment velocities

Although not used in the budget calculations, several determinations of the entrainment velocity will be obtained in this study. This parameter is very important in developing dynamical models of the CBL that is of interest to meteorologists and modelers. The entrainment velocity is defined by the relationship
Here \( \overline{S'w'} \) is the eddy flux at the CBL top obtained by extrapolating eddy fluxes obtained at various altitudes in the CBL to the CBL top. Also \( w_c \) is the entrainment velocity and \( \Delta s \) is the jump in \( s \) at the CBL top. In the DYCOMS II program DMS flux data were used to obtain good estimates of the entrainment velocity [Faloona et al., 2003; Stevens, 2003]. Estimates of the entrainment velocities will be obtained from DMS, \( \text{H}_2\text{O} \), \( \text{SO}_2 \), \( \text{O}_3 \), momentum and heat during PASE.

3.4 Measurements

During PASE we will determine most of the chemical species required to characterize the photochemical environment of the study region. On the aircraft, these measurements include \( \text{OH} \) (Mauldin), \( \text{H}_2\text{O}_2 \), \( \text{CH}_3\text{OOH} \) (Heikes), \( \text{O}_3 \) and \( \text{CO} \). NO will not be determined because its concentration is known to be <5 pptv in the study area [Davis et al., 1999] and thus will play a secondary role in the photochemistry of this regime. Because sulfur plays a huge role in the chemistry of AIE a large suite of gas phase species will be determined. These include DMS, \( \text{DMSO}_2 \), \( \text{TU} \), \( \text{SO}_2 \) (Thornton) and \( \text{H}_2\text{SO}_4 \), \( \text{NH}_3 \) and \( \text{MSA} \) (Mauldin).

Because the products of those gas-phase reactions are often aerosols, a large suite of aerosol physical and chemical measurements also will be made. Continuous fast size-resolved measurements of ambient aerosol surface area will be determined to estimate rates of loss of gaseous sulfur species to aerosol (Clarke). These measurements will include ambient size-distributions, dry size distributions and both wet and dry scattering coefficients that can be used to confirm both size distribution measurements. Continuous measurements of thermally resolved dry aerosol size distributions will be used to estimate the 3-D changes in aerosol size due to both nucleation and uptake of volatile components (Clarke). These size-resolved measurements will address issues related to the contributions of entrainment and DMS derived sulfates to aerosol variability. It will also provide evaluation of the role of refractory sea-salt aerosol, its flux, and its contributions to aerosol volume, surface area and number.

The aerosol chemical measurements include a Particle-Into-Liquid Sampler (PILS) coupled to a dual channel ion chromatograph (IC) that will be used to measure the bulk chemical composition of ionic constituents (Webber). This will include cations sodium, ammonia, potassium, magnesium, calcium, and anions chloride, nitrate, sulfate, and methane sulfonate (MS) in small particles [up to 1 micro meter]. The PILS measurements will complement a recently developed Aerosol-Chemical Ionization Mass Spectrometer (Aerosol-CIMS) (Webber). This instrument will provide 1 Hz (or possibly even faster) measurements of bulk sulfate and methane sulfonate with high sensitivity (LOD ng m\(^{-3}\)). Aerosol chemistry will also be collected using the Total Aerosol Sampler, TAS, which collects even the largest sea salt particles without inlet bias (Huebert) and analyzed for cations and anions (Howell). The other methods may miss the coarse fraction of NSS, which results from the ozone oxidation of \( \text{SO}_2 \) in sea salt. A MSP Flying MOUDI (MOI) with a low-turbulence inlet (LTI) on the aircraft will be used to get size-resolved chemistry from the aircraft (Howell). Because many of the mission legs will be flown as 30 minute level legs, integrated samples taken over a complete leg will provide high precision concentration data for these aerosol substances.

3.5 Cloud Processes and New Particle Production

Clouds form upon cloud condensation nuclei (CCN) that have the size and chemical properties allowing them to activate at prevailing cloud supersaturations. The increased surface area of the activated droplets can enhance the rate of gas to particle conversion and promote aqueous phase reactions that can increase net solute mass as a result of non-precipitating cloud cycles. This growth process can provide a sink for gas phase \( \text{SO}_2 \) and also result in a so-called Hoppel minimum in the size distribution between unactivated and activated sizes [Hoppel and Frick, 1994]. The diameter of this minimum provides an indication of representative cloud supersaturations for the region [Cantrell et al., 1999]. Ground based measurements of diurnal variations in this minimum at Christmas Island were interpreted to reflect photochemical production and cloud processing [Clarke et al., 1996]. Recently, airborne studies near tropical clouds have been argued to demonstrate the effectiveness of this process [Jimenez et al., 2004] although the instruments were not ideal for this purpose and uncertainties were large. We will explore this process in greater detail with the far more complete and faster measurements available during PASE. These flights will require measurements below, in, above and around non-precipitating clouds to examine changes in the size distributions and chemistry. Stratification of observed changes in terms of cloud air sources identified by conservative variables (e.g. DMS and equivalent potential temperature) will be employed [Paluch, 1979].

Cloud outflow regions have also been shown to be a source region for new aerosol particles [Clarke et al., 1998] and often consistent with binary nucleation of sulfuric acid [Clarke et al., 1999]. These near cloud environments were found generally well above 2 km in the tropics although in highly productive regions after heavy rain we found evidence of boundary layer nucleation [Clarke et al., 1998] linked directly to the sulfur cycle. We will revisit the formation of new particles in the outflow region of marine cumulus clouds. Our fast OH, DMS, \( \text{SO}_2 \), \( \text{DMSO}_2 \), \( \text{H}_2\text{SO}_4 \),
H$_2$O, NH$_3$, aerosol composition and liquid water instruments replace very slow instruments which could not resolve the outflow regions observed in earlier experiments. PASE will have a greatly improved capability to make progress on this problem. The studies will be carried out as they were in ACE-1 where the favorable clouds were first detected by satellite observations but the study clouds were located after the experiment was airborne. Flights will be made toward the Equator (ITCZ) to encounter suitable cloud formations.

The large number of hours flown in the marine boundary layer in the Sulfur Chemistry investigation will provide ample opportunity for the observation and characterization of new particles including their entrainment from the FT and their conversion to CCN. Of particular importance is a continued investigation of the possibility that primary emissions of small refractory particles occur in the wave-breaking processes [Clarke et al., 2003; Martensson et al., 2003] and grow to CCN by accreting H$_2$SO$_4$ onto nm size salt particles (O’Dowd et al., 1999 and references therein). Models based on the chemistry proposed by Bandy and coworkers will also be tested (Bandy and Ianni, 1998; Ianni and Bandy, 1999, 2000).

### 3.6 Peroxides

Hydrogen peroxide concentrations, and to a lesser extent methyl hydroperoxide concentrations, in the marine boundary layer are impacted by physical processes as well as photochemical production and loss [Thompson and Cicerone, 1982; Thompson et al., 1993; Heikes et al., 1996; Chen et al., 2001; Chang et al., 2004]. Surface deposition and entrainment fluxes of several chemical constituents (DMS, SO$_2$, H$_2$O and O$_3$) will be determined in PASE using 10 Hz or faster instrumentation and correlative Reynolds flux methods. The entrainment velocities developed from the correlative methods will be combined with slower measurement gradient flux methods to evaluate entrainment fluxes for H$_2$O$_2$ and CH$_3$OOH between the free-troposphere buffer layer and marine boundary layer as described in Lenschow et al (1999). Chang (2002) and Chang et al. (2004) theoretically showed that the entrainment of H$_2$O$_2$, CH$_3$OOH, and CH$_3$O played a minor role compared to photochemistry in setting the mixing ratio of these species in the MBL. However, the entrainment of O$_3$, nitrogen oxides, or hydrocarbons was shown to impact their own mixing ratio, as well as, those for H$_2$O$_2$, CH$_3$OOH, and CH$_3$O via photochemistry. PASE permits a venue to evaluate their theoretical results.

### 3.7 Photochemical Models

A photochemical model will be developed based on that of Davis et al. [1999] that was used to study the chemistry of sulfur in the tropical marine atmosphere including the Christmas Island trade wind regime. These studies will be performed by Dr. Yuhang Wang as the principal investigator and Dr. Doug Davis as a co-investigator. It will be modified to reflect knowledge gained about the chemistry, sources and sinks of species such as DMSO and DMSO$_2$.

### 3.8 Flight Plans

In July or August 2005 the C130 will be ferried from RAF to Christmas Island. Some portions of this ferry can be used for research. However, this is not the primary goal of the mission.

The field phase of the program will be conducted about 250 km east of Christmas Island (Kiritimati). Approximately 5 weeks onsite will be devoted to this study so that the best available meteorological conditions can be chosen for study. As mentioned above the stable meteorological phases tend to be 3-4 days in length with the overall length of a stable-unstable period being approximately 7 days. In 5 weeks approximately 4 stable periods are expected which provides ample opportunities to complete this research. The plan presented below assumes that the flights will be flown on every opportunity that does not exceed crew rest requirements. There also may be some adjustments if critical measurement systems are not operational.

Stable meteorological phases are easily recognized. The beginning of such a phase is characterized by very steady winds at speeds of 4-6 m s$^{-1}$ and a direction of almost 100°. Also the skies are almost cloud free (cloud free in CBL) with very bright sunshine. Decision to fly can be made the previous evening with good prospects for the flight program the next day.

A detailed discussion of using satellite and other meteorological information to guide aircraft deployment is included in the Heikes and Merrill proposal (University of Rhode Island). Relevant portions are included in this proposal.

**Table 2 Flights for Budget Studies**

<table>
<thead>
<tr>
<th>Flight</th>
<th>Time</th>
<th>Duration</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Night</td>
<td>9</td>
<td>Nighttime budgets</td>
</tr>
<tr>
<td>2</td>
<td>Night</td>
<td>9</td>
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<td>Night</td>
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<td>Nighttime budgets</td>
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<tr>
<td>10</td>
<td>Night</td>
<td>9</td>
<td>Surface Fluxes</td>
</tr>
</tbody>
</table>

*Nighttime flights will conform to NCAR RAF safety requirements.*
Precipitation in the vicinity of Christmas Island and the central and eastern equatorial Pacific in general is a product of cumulus clouds associated with easterly waves propagating through the region. The classical description of these waves gives a length of 3000-4000 km, phase speed of 8-10 m/s and period of 4-5 days (Holton, An Introduction to Dynamic Meteorology, 4th Ed., Elsevier Academic Press, 2004). Mean surface winds in this region for July and August are on the order of 4-5 m/s (8-10 knots; US Navy Climatic Atlas for the South Pacific, 1979). Hence, the waves may be thought to move through an air mass. These characteristics correspond to the phenomenological observations of cloud, rain and fair-weather conditions noted by Bandy during the 1994 experiment at Christmas Island. The 2001-2004 TOGA-COARE TAO daily data (viewable at www.pmel.noaa.gov/tao/data_delivery) suggest clouds (diagnosed from shortwave radiation) and precipitation are more episodic than cyclic in July and August, with on-order of 10 events within a July-August interval.

The easterly waves tend to be asymmetrical. The smaller trough portion is associated with cloud and precipitation processes resulting in scavenging of soluble gases and aerosols. Petersen et al., [2004] describe convection and precipitation structure associated with 3 easterly waves in the eastern Pacific during September 2001. Briefly, three of their findings are relevant: rain is predominantly ahead of or west of the surface trough, approximately 85% of the precipitation was contributed by "convection" and 15 % by "stratiform", and "heavy convection" precedes the trough by 0-2 days and "light convection" and "stratiform" comes 1-3 days after the trough passage. Daily average and 10 minute average data from TAO buoys bracketing Christmas Island indicate precipitation periods are typically a few 10’s of minutes in duration with isolated occurrences of rain episodes on 2 or more consecutive days. Cloudy periods, significant enough to affect short-wave radiation and MBL chemistry, exhibit similar time intervals. The broader ridge portion of the easterly waves corresponds with suppressed convection and relatively cloud-free conditions. The buoy data show these periods to persist for 4-6 days. The ridge is identified as the best meteorology for studying marine sulfur fluxes and photochemistry. The trough portion would be best for examining cloud outflow of cloud and BuL processes described in previous sections. These flights will be flown when conditions are favorable. Satellite and meteorological support is described briefly in a previous section and in detail in the Heikes and Merrill proposal.

In addition to these flights, three 9 hours missions will be flown to investigate the formation of nuclei in the outflow of cloud and BuL processes described in previous sections. These flights will be flown when conditions are favorable. Satellite and meteorological support is described briefly in a previous section and in detail in the Heikes and Merrill proposal.

3.9 Data Processing and Dissemination

It is the responsibility of the mission scientist to archive all the data produced by this experiment. Workshops to discuss the data and plan publications will be held 6 and 12 months after the completion of the experiment. The data archive will enter the public domain through a web site at NCAR 1.5 years after completion of the experiment. It is the intent to publish a special volume in an appropriate journal.

3.10 Other Activities

PASE will have a substantial instructional component both at the undergraduate and graduate level. Several undergraduate and graduate students will be involved in both the field and interpretation phase of the program. Each PI has agreed to present a seminar to students during the field campaign at Christmas Island. PI’s will also be encouraged to request that students attend workshops and make presentations when appropriate. Finally one seat per flight will be reserved on the C130 for an undergraduate or graduate student who does not ordinarily get to fly because of assignment issues. Finally the mission scientist will offer Drexel students the opportunity to participate in PASE data interpretation through our Chemistry research courses Chemistry 493 and 497, which are required of all chemistry majors.

Finally PASE is designed to bring a large number of highly capable investigators to focus on the important scientific issues. Without programs of this type the investigations of each investigator tends to study such problems in an unconnected and fragmented way. In PASE the important issues were identified which the integrated efforts of the PASE investigators are likely to make substantial contributions to resolving.
Dr. Alan Bandy is the mission scientist and is responsible for the execution of the mission and organizing the interpretation and publication of the data. Dr. Donald Thornton (Drexel) will make the fast SO$_2$ measurements, Dr. Fang Huang Tu (Drexel) will perform the DMS, DMSO and DMSO$_2$ measurements. OH, H$_2$SO$_4$, MSA and NH$_3$ will be determined by Dr. Lee Mauldin (NCAR). Dr. Anthony Clarke will perform aerosol size, thermal properties and composition measurements. Dr. Rodney Weber (Georgia Tech) and Dr. Steve Howell (Hawaii) will make aerosol composition measurements. Drs. Brian Heikes, John Merrill (Rhode Island) and Daniel O'Sullivan (Naval Academy) will provide H$_2$O$_2$ and CH$_3$OOH data and meteorological support. Drs. Ian Faloona (UC-Davis) and Donald Lenschow (NCAR) will direct mission planning and the aircraft mission. Drs. Yuhang Wang and Douglas Davis (Georgia Tech) will provide photochemical modeling. Dr. Jim Hudson (Desert Research Institute) will make CCN measurements.

Measurements of OH, HO$_2$, H$_2$SO$_4$, MSA and NH$_3$ will be determined by Dr. Lee Mauldin (NCAR) (Davis et al., 1999; Nowak et al., 2002; Cantrel et al., 2003). Support of the determinations of OH, H$_2$SO$_4$, MSA and NH$_3$ and other selected radicals by Dr. Lee Mauldin (NCAR) is included here as a subcontract. The above compounds will be measured using a multi-channel selected ion chemical ionization mass spectrometer (SICIMS) which is an improved version of the instrument used previously aboard the NCAR C-130 for the NSF-sponsored TOPSE study. With the exception of ammonia, these compounds have all been successfully measured on a near simultaneous basis in several previous airborne studies. Measurements of OH, H$_2$SO$_4$, and MSA will be on a time shared basis for 15 sec each once every 30 sec, resulting in a detection limit of 0.1 pptv (parts per trillion by volume) in 1 minute and 0.02 pptv in 5 minutes respectively for each species. Peroxy-radicals will be measured on an exploratory basis using a second separate mass spectrometer channel. Either HO$_2$ or HO$_2$+RO$_2$ will be measured once every 30 sec, with a 0.1 pptv detection limit for a 1 min. integration. NH$_3$ will be measured using a third mass-spectrometer channel once every 15 sec with a detection limit of ~30 pptv for a 2 minute integration.

5 ATD/RAF Airborne Scientific Instrumentation requested

The following RAF instruments will be requested in addition to the standard airborne scientific measurements supplied by RAF: Lyman-alpha hygrometer, Gerber probe (liquid water content), cloud particle size distribution (0.5 - 47 μm), cloud particle size distribution (40 - 640 μm), aerosol particle size distribution (0.1 - 3.0 μm), aerosol particle size distribution (0.3 - 20 μm), fast-response chemiluminescence ozone concentration, video recording (fwd) with optional date/time stamp, video recording (side) with optional date/time stamp, video recording (down) with optional date/time, audio recording (on video tape) stamp. [1 sec digital photos should be available in at least the forward direction]

6 Results from Prior NSF Support

OPP-9809162, Investigation of the sulfur chemistry of the Antarctic troposphere (ISCAT), $391,813, 5/14/98 - 12/31/02

SO$_2$, DMS, DMSO, DMSO$_2$ and MSIA (methane sulfonic acid) were determined at the South Pole during November and December of 1999 using Atmospheric Pressure Ionization Mass Spectrometry. These data and those of participating principal investigators were processed and archived. SO$_2$ was the predominant sulfur gas other than carbonyl sulfide. After 18 Dec 2000 the meteorological conditions changed, and the concentration of the sulfur gases (other than carbonyl sulfide) were less than 5 parts per trillion by volume. Sulfur dioxide was frequently observed at the clean air station from aircraft and local sources (primarily vehicles).


Sulfur dioxide was determined on ACE-ASIA with a frequency of 2 Hz and a lower limit of detection of 3 pptv. The data were processed and submitted in the ACE Asia archive (CODIAC, JOSS, UCAR). The SO$_2$ data clearly showed transport was predominantly at altitudes below 2000 m above sea level.

Mian Chin, Paul Ginoux, Robert Lucchesi, Barry Huebert, Rodney Weber, Tad Anderson, Sarah J. Masonis, Byron


ATM-0004444, A Study of the Dynamics of the Marine Stratocumulus, 2/1/2001-1/31/2003, $190,396

Dimethyl sulfide was determined with a frequency of 25 Hz. The data were processed and archived with the DYCOMS II data in CODIAC (JOSS, UCAR). DMS was used to determine the entrainment velocity at the stratocumulus cloud top. The entrainment velocity determinations from DMS, ozone, and thermodynamic properties agreed within experimental limits. DMS surface fluxes were also obtained.


ATM-342672, Chemistry of Sulfur Dioxide and Dimethyl Sulfide in the Tropical Marine Boundary Layer, 2/1/2004-7/31/2005, $248594

Work is in progress testing atmospheric pressure ionization mass spectrometry techniques for dimethyl sulfoxide and dimethyl sulfone. Field tests for DMSO indicated possibility to obtain <1 Hz time resolution for DMSO and DMSO2.


Field phase of RICO was conducted in December 2004 and January 2005. Data reduction and analyses are in progress. An undergraduate student will be involved in the data analyses for the summer of 2005.


Work is in progress testing atmospheric pressure ionization mass spectrometry techniques for hydrogen peroxide. An undergraduate student will be involved in the research for the summer of 2005.


