# MECHANISMS OF SULFATE PRODUCTION IN THE REMOTE

### EQUATORIAL PACIFIC MARINE BOUNDARY LAYER

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#### DEDICATION

I dedicate this work to my family, who provide me with all the tangibles and intangibles that I could ever need.

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#### ABSTRACT

The importance of the mechanisms of sulfate production in the remote marine atmosphere is an unresolved issue that hinders our ability to properly model aerosolclimate feedbacks in this region. The Pacific Atmospheric Sulfur Experiment (PASE) was designed to address this question by characterizing tropical sulfur chemistry in the vicinity of Christmas Island. We collected size-segregated aerosol samples on daytime and early morning flights from the NCAR C-130 aircraft in August and September of 2007. Using sulfur gas fluxes also measured in PASE, we constructed a non-sea-saltsulfate (NSS) budget to investigate the fate of DMS-derived sulfate.

Average NSS concentrations during PASE (145 ppt) were ~30% lower than those during a 1994 tower-based experiment in the same location. A mean of 11% of NSS occurred on the coarse mode. Over the course of a day, a portion of this supermicron NSS is subject to dry deposition to the ocean, leaving dilution by entrainment as the primary mechanism for reducing the fine NSS. In addition to the predominantly submicron mass size fraction of NSS, depletion of SO<sub>2</sub> in the BuL during cloud encounters supports the significance of cloud processing in this region. In the absence of sulfur input from the free troposphere (FT), conversion of SO<sub>2</sub> on sea-salt particles represents a DMS sink comparable in size to in-cloud oxidation of SO<sub>2</sub> and dry deposition of SO<sub>2</sub>.

Elevated CO observed throughout the second half of the project suggested that continental sources were contributing S, Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup>, which probably reduced coarse aerosol pH. Back trajectories and satellite images show that long-range transport brought

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South America biomass burning aerosol to the equatorial Pacific. Despite its remoteness, we found evidence of continental air on  $40 \pm 10\%$  of the research flights. SO<sub>2</sub> profiles that penetrated the FT revealed large pollution layers aloft, demonstrating the need to account for continental sulfur sources when budgeting remote MBL sulfur chemistry. Entrainment of FT NSS and SO<sub>2</sub> (and its subsequent conversion to NSS in cloud) may be required to account for the observed fine-mode NSS mass in the MBL. During periods of long-range transport, extensive entrainment of continental sulfur competes with and may even overshadow local sulfate production from DMS oxidation.

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## CHAPTER 1 INTRODUCTION

Aerosol in the remote marine boundary layer (MBL) primarily consists of two species: supermicron sea-salt aerosol (SSA) and submicron sulfate aerosol. SSA particles are the predominant aerosol (by mass) in the remote marine boundary layer and are mechanically generated from the breaking of waves. Sulfate aerosol, formed as an oxidation product of dimethyl sulfide (DMS) emitted by phytoplankton, also represents a significant fraction of the aerosol burden in the remote MBL. Because sulfate dominates aerosol number (Figure 1) in the remote marine atmosphere, its formation mechanisms have been widely studied and modeled (e.g., Chameides and Stelson, 1992; Sievering et al., 1992; Hegg et al., 1992; Huebert et al., 1996; O'Dowd et al., 1997; Clegg and Toumi, 1998; Gurciullo et al., 1999; Davis et al., 1999). However, researchers have yet to fully expound the details of remote MBL sulfur's production and fate due to a shortage of process studies. This deficiency of concern because of atmospheric sulfur chemistry's link to climate.

Well-recognized as the largest uncertainty in global climate forcing, aerosols directly impact climate by scattering light and participating in chemical reactions and geochemical cycles. They can also indirectly impact climate by acting as cloud condensation nuclei (CCN), thereby influencing the formation and properties of clouds. This effect is particularly important over the ocean, where an increase in cloud cover has the potential to alter the albedo from that of water, 0.06 at the lowest, to that of stratocumulus clouds, 0.6 (von Glasow and Crutzen, 2004). Hence, understanding the

chemical processes that dictate the size, number, and composition of particulate matter leads to better predictions about short term climate forcings.

Aerosol properties such as concentration, size, and water solubility directly influence the ability of aerosol particles to serve as CCN. However, CCN denotes only the particles that can activate to form cloud droplets at relevant ambient supersaturations. In remote marine cumulus, typical supersaturations range from 0.3% to 0.8% (Pruppacher and Klett, 1997). Accumulation-mode sulfate particles can act as CCN in the MBL, so increases in NSS number concentration probably lead to increases in the CCN number. The resulting influence on cloud properties such as coverage, albedo, and lifetime has motivated many studies on the link between sulfate and CCN on regional and global scales.

The CLAW hypothesis (Charlson et al., 1987) spawned interest in the notion that oceanic biota can affect Earth's radiation balance via the release of gaseous sulfur compounds into the troposphere. Because DMS is the largest marine source of natural sulfur (Bates et al., 1992), its atmospheric cycling plays a significant role in the generation of sulfate aerosol. Once it is released, DMS undergoes gas-phase oxidation that can take two main pathways, both resulting in a variety of products that can condense onto pre-existing particles or participate in multiphase chemistry with particles or cloud drops (Figure 1). These two reaction pathways involve either the addition of an OH or the abstraction of an H atom, with OH acting as the main oxidizing agent. The most important gas-phase products are sulfur dioxide (SO<sub>2</sub>), dimethylsulfoxide (DMSO), dimethylsulfone (DMSO<sub>2</sub>), methanesulfonic acid (MSA), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), and methanesulfinic acid (MSIA). Considerable effort has been made to clarify the

atmospheric processing of these trace species in hopes of elucidating the generation, transformation, and removal of sulfurous gases in the MBL. The oxidation of SO<sub>2</sub> to sulfate has been the focus of many studies (e.g. Penkett et al., 1978; Schwartz, 1987; Chameides and Stelson, 1992; Sievering et al., 1990; Sievering et al., 1992; Huebert et al., 1996; Davis et al., 1999; Gurciullo et al., 1999; von Glasow et al., 2002; Alexander et al., 2005; Zhu et al., 2006) exploring the link between the sulfur cycle and cloud nucleation over the ocean (Figure 3).

 $SO_2$ 's relative yield from DMS has been difficult to quantify.  $SO_2$  can follow a variety of pathways in the marine troposphere, including gas phase and aqueous phase chemistry (Figures 2 and 3). The principal sinks of  $SO_2$  are wet and dry deposition and chemical destruction.  $SO_2$  is effectively removed by dry deposition and its lifetime against dry deposition is thought to be 1-2 days (Seinfeld and Pandis, 2006). Transformation of SO<sub>2</sub> to other sulfur species is accomplished by oxidation in the gas phase and aqueous phase, which includes reaction with H<sub>2</sub>O<sub>2</sub> in cloud and reaction with O<sub>3</sub> in the liquid water associated with SSA (or mineral dust) particles. Other important aqueous-phase oxidants include CH<sub>3</sub>OOH, OH, O<sub>2</sub>, and NO<sub>2</sub>. Uptake of SO<sub>2</sub> by cloud droplets and SSA prior to reaction in the aqueous phase depends on these physical mechanisms: diffusion in the gas phase, mass transfer at the interface, collision success rate of SO<sub>2</sub> at the interface, and diffusion within the cloud or particle liquid water. Chemical parameters such as supply of oxidant, pH of the solution, acid-base dissociation, and solubility affect the transformation of SO<sub>2</sub> to secondary sulfate. The solubility of SO<sub>2</sub> (as well as the associated S(IV) species) is strongly pH dependent, rendering it more soluble at pH > 6. [HCO<sub>3</sub><sup>-</sup>], which dictates the buffering capacity of

SSA, governs the amount of  $SO_2$  that the particle can accommodate. Once  $SO_2$  is dissolved in water, it dissociates as follows:

$$SO_2 \cdot H_2 0 \leftrightarrow HSO_3^- + H^+$$
(1)  
$$HSO_3^- \leftrightarrow SO_3^{2-} + H^+$$
(2)

with Equation 1 having a  $pK_{a1}$  of 1.9 and Equation 2 having a  $pK_{a2}$  of 7.2. Referred to as S(IV) because sulfur is in the oxidation state 4, these compounds can then react with dissolved  $H_2O_2$  and  $O_3$ , which are regarded as the most important aqueous-phase oxidants. The aqueous phase reactions are:

$$S(IV) + H_2O_2 \rightarrow S(VI) + H_2O$$
(3)  
$$S(IV) + O_3 \rightarrow S(VI) + O_2$$
(4)

In cloudwater typical of marine conditions with a pH  $\leq$  5 (Chameides, 1984), H<sub>2</sub>O<sub>2</sub> is the dominant oxidant (Equation 3) since its reaction with S(IV) is pH-independent (Penkett et al., 1978). Oxidation of S(IV) by O<sub>3</sub> (Equation 4) is only important at pH > 6, making alkaline SSA particles an ideal reaction medium. Although alkalinity is supplied by seawater (pH  $\approx$  8), production of sulfate (S(VI)) and condensation of acidic vapors (H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>) consumes the alkalinity, terminating the oxidation of S(IV) by O<sub>3</sub> (Equation 4).

Clouds are important in the atmosphere for chemical and dynamical reasons. They provide a great deal of surface area and liquid water volume for reactions to take place. They also take part in the transport of air between the boundary layer and buffer layer. It is well-established that cloud processing is a major global source of sulfate aerosol (Seinfeld and Pandis, 2006). Aqueous-phase oxidation of SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup> by H<sub>2</sub>O<sub>2</sub> in cloud droplets has been postulated to be the most important pathway for conversion of  $SO_2$  to NSS (Hegg, 1985), though this is debated by some who argue that SSA dominates the production and removal of NSS (Sievering et al., 1991; Chameides and Stelson, 1992; Suhre et al., 1995; O'Dowd et al., 1997; Mari et al., 1999; Faloona et al., 2010). These authors thought that cloud processing is not as important as the SSA mechanism for supermicron NSS production in remote MBL studies; Gurciullo et al., (1999) calculated that as much as 50-75% of the coarse fraction of NSS mass originated from oxidation in SSA water, with the rest being attributed to cloud processing. However, Gurciullo et al., (1999) contended that a significant fraction (45-65%) of the total NSS (0.4-16  $\mu$ m) can be attributed to cloud processing, which primarily affects the submicron aerosol mass. Peter et al. (2006) suggested that new particle formation can occur in cloud, further demonstrating the strong effect that cloud can have on the fine aerosol population. MBLbuffer layer interactions have not been well characterized, leaving open to question the reservoir in which SO<sub>2</sub> is primarily oxidized.

Though it is generally assumed that formation of NSS on coarse SSA particles occurs by uptake of SO<sub>2</sub> gas to these hydrated particles, there are other mechanisms that could explain some of the NSS mass associated with SSA. Cloud drops with an SSA core could accumulate submicron NSS through collision/coalescence. Additionally, drizzle with SSA and acquired NSS mass could move these species, which became associated in cloud, into the MBL upon evaporation. This is a viable mechanism for cloud-induced coarse-mode NSS formation. Condensation of homogeneously-produced  $H_2SO_4$  vapor onto supermicron particles is another mechanism that places NSS mass on coarse SSA. Further study is needed to understand how the NSS-SSA association occurs.

Through the homogeneous oxidation to  $H_2SO_{4(g)}$  by OH, new aerosol particles can form, thus translating to an increase in cloud albedo. The gas-phase reactions are:

$$SO_2 + OH \cdot + M \to HOSO_2 \cdot + M$$
 (5)

$$HOSO_2 \cdot +O_2 \to HO_2 \cdot +SO_3 \tag{6}$$

$$SO_3 + H_2O + M \to H_2SO_4 + M \tag{7}$$

where the "•" denotes a radical species and *M* represents air molecules. The gaseous sulfuric acid formed can nucleate new particles in certain conditions and increase aerosol number concentration (Clarke et al., 1998; Weber et al., 1999). Aqueous-phase pathways reduce the gas-phase concentration and therefore the potential for new particle formation; however, once formed, new particles must undergo growth process via aqueous pathways to become large enough to influence clouds. The uptake of SO<sub>2</sub> onto SSA is an example in which these particles act as a sink for sulfate mass that could otherwise have contributed to nucleation and/or growth of small aerosol. Either could potentially lead to a forcing of the climate either directly (scattering of solar radiation) or indirectly (increasing CCN) as predicted by the CLAW hypothesis.

In particles, sulfur is found in both the S(IV)  $(SO_2 \cdot H_2O + HSO_3^- + SO_3^{2-})$  and  $S(VI) (H_2SO_4 + HSO_4^- + SO_4^{2-})$  oxidation states. Secondary S(VI) formed from the oxidation of S(IV) is referred to as non-sea-salt-sulfate (NSS). NSS refers to the sulfate produced from the homogeneous and heterogeneous reactions described above as opposed to the primary sea-salt sulfate that originates from the preexisting concentration of sulfate in seawater. We measure this NSS by subtracting the sea-salt sulfate component from total sulfate based on the constant ratio of sulfate to sodium in seawater.

The portion of NSS production occurring in SSA particles is a contentious issue. Some authors restrict aqueous-phase sulfate formation to cloud chemistry (e.g. Easter and Hobbs, 1974; Hegg and Hobbs, 1981; Hegg and Hobbs 1982; Seigneur and Saxena, 1987), though successive studies proposed that NSS production could proceed in the alkaline liquid water content of SSA based on the rapid rate of Equation 4 at a pH close to that of seawater (Chameides and Stelson, 1992; Sievering et al.,1991; Faloona et al., 2010). Hence, there are many implications of the alkalinity budget in MBL particles. Titration of the SSA alkalinity by acidic S(VI) compounds terminates sulfate formation by O<sub>3</sub> as the pH drops. The acidification of these particles (as sulfuric and nitric acids deposit onto or are formed on SSA) causes the displacement of Cl<sup>-</sup> through the release of HCl vapor (Keene et al., 1990; McInnes et al., 1994; Vogt et al., 1996). HCl volatilization occurs via these heterogeneous reactions:

$$HNO_{3(g)} + NaCl_{(p)} \rightarrow HCl_{(g)} + NaNO_{3(p)}$$
(8)

$$H_2SO_{4(p)} + 2 NaCl_{(p)} \rightarrow 2 HCl_{(g)} + Na_2SO_{4(p)}$$
 (9)

Because HBr is more soluble and a stronger acid than HCl, the analogous depletion of Br<sup>-</sup> from SSA had been thought to be negligible (Chameides and Stelson, 1992). However, recent model studies suggest that oxidation reactions enhanced by acidification of deliquesced SSA particles release bromine and chlorine, which can influence gas phase chemistry in the MBL (Hermann et al, 2003; von Glasow et al., 2004; Newberg et al., 2005). The influence that SSA-generated reactive halogen species have on DMS oxidation can be seen in Figures 2 and 3.

#### **Christmas Island (Kiritimati)**

During a ground-based experiment (hereafter referred to as the 1994 experiment) conducted on Christmas Island (2°N, 157°W) from 21 July to 13 August, 1994, Huebert et al. (1996) measured NSS and MS<sup>-</sup> concentrations from a 30 m tower, Clarke et al. (1996) measured aerosol physicochemical properties, and Bandy et al. (1996) measured DMS and SO<sub>2</sub>. Located in the remote equatorial Pacific, Christmas Island (Kiritimati) belongs to the Republic of Kiribati and is situated south of the Intertropical Convergence Zone (ITCZ) downwind of the biologically-productive equatorial upwelling regime at that time of year. Studying particulate sulfur chemistry in relatively uniform meteorological conditions far from major anthropogenic influences simplified the chemical budgeting of in-situ production and destruction rates. Measurements of particulate sulfur (NSS and MS<sup>-</sup>) and gaseous sulfur (DMS and SO<sub>2</sub>) revealed diurnal patterns linking  $SO_2$  and NSS. Huebert et al. (1996) used a simple box model to constrain the amount of NSS and MS<sup>-</sup> production resulting from the oxidation of SO<sub>2</sub>. The diurnal variations in DMS and SO<sub>2</sub> were reconstructed using pseudo-first-order coefficients to constrain processes such as photochemistry, dry deposition, and dilution by entrainment. Clarke et al. (1996) inferred that cloud processing and photochemical mechanisms controlled growth of submicron aerosol in the MBL while replenishment of aged nuclei from the free troposphere contributed aerosol number. Nucleation of new particles was not observed in the Christmas Island MBL. Bandy et al. (1996) reported a high conversion efficiency of DMS to SO<sub>2</sub> based on linear regressions of their time series data and posited dry deposition to be the most effective  $SO_2$  removal mechanism with the possibility for the secondary importance of loss of SO<sub>2</sub> to aerosol.

Though Christmas Island is an ideal setting for the study of DMS oxidation chemistry, this ground-based experiment lacked highly time-resolved DMS and SO<sub>2</sub> measurements, measurements of important (non-sulfur) atmospheric species, and dynamical properties. In addition, the 1994 experiment suffered from its confinement to a stationary location in the MBL where variations with altitude could not be characterized nor could fluxes be measured. We returned to this environment with an aircraft equipped with state-of-the-art instrumentation to intensively study the interactions between sulfur chemistry, aerosols, and the aerosol indirect effect.

The PASE (Pacific Atmospheric Sulfur Experiment) airborne field campaign sampled the remote equatorial Pacific troposphere near Christmas Island during August and September of 2007. In this region, the marine troposphere was typically divided into three distinct layers (Conley et al., 2009): the marine boundary layer (MBL, also referred to as the BL), a buffer layer (BuL), and the free troposphere (FT), though the BuL was sometimes absent or ambiguous. Figure 4 shows midflight vertical profiles of potential temperature ( $\theta$ ), vertical wind velocity, and H<sub>2</sub>O mixing ratio for a typical flight with the tropospheric layers labeled. The turbulent MBL is in contact with the surface of the ocean and remained shallower than 700 m in PASE (Conley et al., 2009). This layer is in a state of free convection (vigorous updrafts and downdrafts). Scattered and patchy trade cumulus clouds evolve throughout the day to cap the MBL. Shallow convective pumping can carry MBL air aloft into the buffer layer, while entrainment brings BuL air back down to the MBL. The more stable BuL, found between the MBL and the FT, can be thought of as a reaction chamber where air parcels from the MBL and FT have time to

mix and react in the presence of clouds and the absence of surface sources or sinks. The BuL is capped by the trade wind inversion at roughly 1500 meters.

Above the BuL is the FT, which extends to the tropopause. Particles and gases in the FT experience increased lifetimes against deposition because of their isolation from the ocean surface. This layer also usually has lower concentrations of trace species as a consequence of its vertical distance from the Earth's surface and separation from the mixed boundary layer; however, deep convection (and volcanic eruptions) can loft gaseous and particulate species into the FT until they are removed by chemical reaction, wet and dry deposition, and subsidence to the lower troposphere. The FT is optimal for long-range transport of pollutants (Andreae et al., 1983). In regions of subsidence, air originating in the free troposphere can entrain into the buffer layer and deepen the BuL unless divergence occurs. These processes affect the (vertical) spatial distribution of chemical species and so have the potential to influence their lifetimes and extent of oxidation in the atmosphere.

The National Center for Atmospheric Research (NCAR) C-130 flew sustained (30-min or more) legs at varying altitudes beginning at ~40 m throughout the MBL and BuL with periodic profiles into the FT. Rapid measurements of DMS and SO<sub>2</sub> fluxes by eddy covariance allowed for constraint of the sulfur budget, including the SO<sub>2</sub> depositional flux to the ocean surface and fluxes at the top of the MBL. Concomitant measurements of essential atmospheric constituents such as OH, H<sub>2</sub>SO<sub>4</sub>, MSA, H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, H<sub>2</sub>O vapor, and CO as well as measurements of dynamic and thermodynamic parameters reduce uncertainty in modeling sulfur chemistry. Measurements of aerosol chemical, physical, and optical properties in addition to measurements of CCN concentrations

complete the suite of direct observations needed to elucidate the connection between DMS oxidation, marine aerosols, and their effects on clouds.

Some results from the PASE DMS and  $SO_2$  measurements have already been published. Conley et al. (2009) presented a closure of the DMS flux budget. Faloona et al. (2010) proposed an  $SO_2$  flux budget for the MBL as shown in the blue text of Figure 5. However, their conclusions concerning the removal of  $SO_2$  to coarse SSA are not consistent with observed NSS size distributions (discussed below) or those from the 1994 experiment (Huebert et al., 1996). We will address this matter in our treatment of the NSS budget since the fate of  $SO_2$  and its effect on NSS production is a central unresolved issue of the marine sulfur cycle.

#### **PASE Aerosol Objectives**

Our aim is to quantify the properties of MBL particles such as size, chemical composition, concentration, residence time, and spatial distribution to better understand the multiphase interactions of  $SO_2$  with aerosols and clouds. We use size-segregated chemical composition and detailed size distributions to constrain the chemical mechanisms responsible for oxidizing S(IV). This knowledge can be used to inform climate models and develop more accurate predictions for the aerosol-cloud-climate feedback system.

Though our focus is on particulate species, the gas-phase data generated on this field program provide constraints for the sulfur aerosol formation rates as do comparisons to the 1994 experiment. Viewed in the context of the structure of the remote marine troposphere, the atmospheric sulfur chemistry is clearly subject to influences from other

parameters, including microphysical and dynamical phenomena. Even though we set out to sample isolated Southern Hemispheric air, we witnessed long-range pollution transport, which will be discussed later.

#### **Coarse aerosol**

In a chapter addressing the influence of aerosols on the Earth's climate, IPCC-AR4 report stated that, "Sea salt is [...] responsible for a large fraction of the non-sea salt sulphate formation" (IPCC 2007). The validity of this statement is one of the focal points of this study. The formation of NSS on coarse SSA begs examination because a) it prevents generation of fine sulfate aerosol that might evolve to have CCN potential and b) there are large uncertainties in the SSA size distribution and deposition flux, exposing the difficulties in modeling open-ocean aerosol. Various pathways, mechanisms, and precursors for NSS formation will be explored to gain insight into the importance of coarse marine aerosol.

SSA is a source for the reactive inorganic halogens bromine and chlorine in the MBL (Keene et al., 1990; Vogt et al., 1996; Sander et al., 2003). Recently, increased interest in the role of halogen chemistry in DMS oxidation (von Glasow and Crutzen, 2004) has led to model predictions that the SO<sub>2</sub> yield from DMS is depressed when inorganic halogen chemistry is included. Additionally, particulate sulfur production is enhanced when halogens are taken into account. From their model, von Glasow and Crutzen report that halogen chemistry (Equation 10) increases DMS oxidation rates, but it mainly forms DMSO, leading to smaller DMS to SO<sub>2</sub> conversion efficiency (Figure 2).

$$CH_3SCH_{3(g)} + BrO_{(g)} \to CH_3S(O)CH_{3(g)} + Br_{(g)}$$
 (10)

In another model study, Zhu et al. (2006) also calculated that increasing BrO reduces the yield of SO<sub>2</sub> from DMS and increases MS<sup>-</sup>/NSS ratio. Tracking Br<sup>-</sup> and Cl<sup>-</sup> deficits (or enrichments) is a way to constrain the possible influence of halogens on sulfur species in the remote MBL.

To infer atmospheric processing of supermicron aerosols, we utilize calculations of elemental enrichments/deficits. Using published ratios of chemical species to Na<sup>+</sup> in bulk seawater, we can quantify whether there is an excess or deficit of a given element on the coarse mode (Keene et al., 1986). The surface area-to-volume ratio is another valuable indicator of MBL processes that can be calculated for cascade impactor size distributions. The relative rates of condensation, evaporation, diffusion, and heterogeneous oxidation control these ratios. Molar or mass ratios of different species from the same sample can be measured more accurately than the concentrations themselves. In order to properly identify the chemical processes affecting marine aerosols, quantification of such ratios and non-sea-salt components is essential.

Deviations from the expected seawater ratios indicate the type and magnitude of interactions between coarse aerosol and the remote MBL environment; an excess infers greater uptake of an element's gaseous precursor onto a particular size range or in-cloud coagulation while a deficit suggests volatilization of an element. It is important to determine how the uptake of nitric acid depends on particle surface area because acidification of SSA impacts particulate sulfur formation. Nitric acid (HNO<sub>3</sub>) sticks to wetted supermicron particles, virtually irreversibly (if the particle remains hydrated) due to its very high solubility. Small SSA particles with greater surface area to volume ratios are more effective at nitric acid uptake (there is no aqueous-phase reaction involved),

thus acidifying these particles. Possible limitations to the reaction of HNO<sub>3</sub> (or any gas) with SSA may include diffusion in the gas phase, mass transfer at the particle interface, collision success rate of HNO<sub>3</sub> at the interface, and diffusion in the aqueous phase. Kinetics of the ensuing reactions within the SSA particle depend on processes such as substitution of chloride by nitrate and pH changes. The accommodation coefficient of HNO<sub>3</sub> onto SSA is high (0.5) until all Cl has been displaced into the gas phase as HCl<sub>(g)</sub>, at which time the accommodation coefficient decreases but continues to favor dissolution (Guimbaud et al, 2002). Displacement of halogens from small SSA particles has the potential to affect DMS oxidation through the activation of halogen chemistry (Figure 2, Equations 8-10). Comparison of nitrate mass with particle size (which is proportional to the square root of surface area) is a suitable method for exploring what controls the uptake and lifetime of this acidic gas.

Heterogeneous loss of SO<sub>2</sub> to hydrated SSA is an important term in the SO<sub>2</sub> budget in the cloud-free MBL. In this pathway to secondary sulfate, SO<sub>2</sub> is absorbed onto wet particles and oxidized by O<sub>3</sub> in the aqueous phase to SO<sub>4</sub><sup>2-</sup>. As with the uptake of nitric acid, this process acidifies particles, thus limiting the amount of further uptake of SO<sub>2</sub>. The rate-limiting steps of SO<sub>2</sub> heterogeneous loss limit the amount of coarse NSS as well as the size distribution of NSS. The mass of NSS formed on supermicron SSA may depend more heavily on either reaction volume (alkalinity) or available surface area. Quantifying the mechanisms constraining the NSS concentrations on large SSA will indicate how much the heterogeneous loss of SO<sub>2</sub> to SSA contributes to the removal of sulfur from the tropical MBL. In order to differentiate between particles with different properties, we measure the size distribution of marine aerosols using instruments that size and speciate particles. The size distribution function is important because it describes how the number, mass, and surface area of particulate matter is distributed over various particle sizes. Speciesspecific information in turn tells us about the residence time, composition, chemistry, and physical processes that occur over spatial and temporal scales of interest. Our chemically-speciated data can be used to resolve the coarse and fine mass fractions of components such as NSS and NO<sub>3</sub><sup>-</sup>. We can thus determine if a significant fraction of particulate sulfate is found on larger particles (15  $\mu$ m > D<sub>p</sub> > 0.8  $\mu$ m) rather than on smaller particles that presumably have different formation mechanisms.

#### Submicron aerosol

One of the big questions of this study is what fraction of emitted DMS becomes submicron sulfate aerosol, which can contribute to CCN number at low supersaturations and thereby possibly influence MBL cloud properties. In order to answer this question, it is necessary to consider our particulate data in the context of the complementary gasphase data. We need to approximate the contributions to the particulate sulfate burden made by homogeneous and heterogeneous processes in the remote MBL to quantify the DMS to fine sulfate oxidation path. Data from the small stages ( $0.8 \ \mu m > D_p > 0.08 \ \mu m$ ) of a cascade impactor will be used to explore the submicron size distributions of NSS and MS<sup>-</sup> aerosol and their relationships to altitude. To see how the structure of the marine troposphere affects fine NSS and its precursors, we shall examine whether there are concentration gradients between the boundary layer and the buffer layer. Comparisons of impactor fine sulfate mass from this project to those of a previous ground-based project located on Christmas Island will also serve to highlight differences between sampling strategies.

#### **Temporal Trends in NSS**

Of particular interest in this study is the change in NSS concentration throughout the day. Because the research flights were designed to be quasi-Lagrangian, the rate of change of NSS in the MBL relies on formation from  $SO_2$  oxidation, transport from the BuL, and removal due to dry deposition. We will explore the contributions from these terms to determine the sensitivity of the NSS concentration to MBL processes. The continuity expression for the time-dependent concentration of NSS becomes:

$$\frac{d[\mathrm{SO}_4^{2-}]}{dt} = F + \omega_e ([\mathrm{SO}_4^{2-}]_{\mathrm{BuL}} - [\mathrm{SO}_4^{2-}]_{\mathrm{BL}}) - \mathrm{V_d}[\mathrm{SO}_4^{2-}]_{\mathrm{BL}} - \mathrm{w}\frac{\mathrm{d}[\mathrm{SO}_4^{2-}]}{\mathrm{dx}}$$
(11)

Where  $[SO_4^{2-}]$  is the concentration of NSS, *F* is the formation rate of NSS,  $\omega_e$  is the entrainment velocity between the BL and BuL, V<sub>d</sub> is the dry deposition velocity, and the last term, w, describes advection of the aerosol into or from a given parcel of air. *F* includes formation from heterogeneous and homogeneous oxidation of SO<sub>2</sub>. The homogeneous rate results in sulfuric acid vapor that is either a precursor for new particles or condenses onto preexisting particles. An important parameter describing the relationship between the BL and BuL,  $\omega_e$  is the entrainment velocity (cm s<sup>-1</sup>). *F* can be estimated from the SO<sub>2</sub> budget as the mass of SO<sub>2</sub> lost to homogeneous and heterogeneous and magnitude of the transport terms relative to the formation term will determine the trend in NSS throughout the day. The dry deposition velocity term can be estimated from parameterizations given by Slinn and Slinn (1980)

and depends on the NSS size distribution. The advection term describes the addition or removal of NSS from the studied air parcel by horizontal transport in the presence of a concentration gradient along the mean wind. In this quasi-Lagrangian study, we assume that this term is zero.

The dry deposition velocity term in Equation 11 is notoriously difficult to measure, leaving models largely responsible for the estimation of this size-dependent particle removal parameter. Models proposed by authors like Slinn and Slinn (1980) and Ganzeveld et al. (1998) use mathematical methods to describe how the particle size distribution deposits to water surfaces at varying wind speeds and friction velocities. Models differ by an order of magnitude or more at some sizes (Lewis and Schwartz, 2004), illustrating the large uncertainties inherent in these estimations. This long-standing problem of quantifying aerosol dry deposition hinders our understanding of particulate and trace gas removal mechanisms. Most models can only agree for very large particles with  $D_p \ge 20 \ \mu m$  whose dry deposition velocities solely depend on gravitational sedimentation. Considerable uncertainties in coarse-mode dry deposition velocities can result in the assumed removal of either insignificant or large quantities of sulfur as NSS from the atmosphere to the ocean. In this study, we use the Slinn and Slinn (1980) parameterization to estimate  $V_d$ .

Aqueous-phase conversion of  $SO_2$  to NSS is the main mechanism (besides precipitation) responsible for modifying sizes of pre-existing CCN. There is considerable debate over the relative magnitudes of the two aqueous-phase NSS formation pathways (oxidation of  $SO_2$  in cloudwater vs. in SSA liquid water) for this reason. A crucial chemical property constraining the amount of NSS that can form on a given SSA particle

(or population of particles) is alkalinity. Some authors assume that SSA in the remote MBL starts with a pH close to that of seawater, about 8 (Chameides and Stelson, 1992). However, this alkalinity is quickly depleted with the uptake of acidic gases and the onset of S(VI) formation, limiting the potential of the O<sub>3</sub> pathway. The titration of large SSA particles and their residence time in the MBL will determine the amount of SO<sub>2</sub> they can sequester before depositing to the ocean surface.

The predominant removal mechanisms for NSS in the remote MBL include precipitation scavenging and dry deposition of particles to the ocean surface. Dilution through entrainment of cleaner free tropospheric air can also reduce MBL concentrations. For the flights being considered in this analysis, we assume there was a lack of appreciable precipitation activity within and upwind of the study site. Hence, we will investigate the size dependence of dry deposition and its importance to the effective lifetime of NSS. It is our aim to assess whether this removal process has a significant impact on the loss of NSS (and, by extension, SO<sub>2</sub>) compared to dilution from entrainment.

To evaluate the sources and sinks of NSS in the context of all sulfur fluxes, we will construct an NSS budget that incorporates Faloona et al.'s (2010) DMS and  $SO_2$  fluxes measured by eddy covariance for the PASE MBL as shown in the blue text of Figure 5. In the discussion, we will address the fluxes shown in red text as well as the completion of the sulfur budget.

#### Influence of non-local aerosol

Signatures of aerosol with continental origins were observed on many research flights. Long-range transport of biomass burning, mineral dust, and volcanogenic particles in the free troposphere has the ability to alter the biogeochemical cycles of environments thousands of miles away from the aerosol source (Andreae, 1983; Merrill et al., 1989; von Glasow et al., 2009). These foreign particles, as well as the trace gases associated with them, can introduce organics, soot, nitrate, sulfate, and alkalinity/acidity, and can significantly increase the aerosol number. Once entrained into the BuL and BL, this aerosol can decrease the lifetime of  $SO_2$  in the remote MBL; conversely, anthropogenic and volcanogenic SO<sub>2</sub> can significantly increase the amount of available atmospheric sulfur. Supermicron mineral dust acts as a site for condensation of gaseous sulfuric acid and can produce more NSS mass than SSA of comparable size due to the increased alkalinity supply available from the calcium associated with mineral dust (Andreae and Crutzen, 1997). Excess fine potassium and nitrate that accompany biomass burning smoke could potentially influence the chemical species and oxidation products found in the MBL. The fate of  $SO_2$  as put forth in the CLAW hypothesis is sensitive to the inclusion of biomass burning, mineral dust, and other non-local sources of aerosol number. Back-trajectories that aid in the identification of the aerosol source region will be used to determine the type of non-biogenic aerosol (biomass burning, mineral dust, or a combination) in addition to understanding why certain particulate species are enriched.

### CHAPTER 2

#### **EXPERIMENTAL**

Ambient samples of particulate species were collected from the National Science Foundation-owned C-130 aircraft (maintained by the National Center for Atmospheric Research (NCAR)) during the Pacific Atmospheric Sulfur Experiment (PASE) in August and September of 2007. The aircraft flew to the east of Christmas Island (Kiritimati; 157° W, 2° N), Republic of Kiribati, which is located in the equatorial Pacific upwelling regime. A multi-orifice impactor (MOI) (MSP Corp.) with six substrate stages and a filter stage allowed us to collect size-resolved ambient aerosol (Kline et al., 2004) at constant altitudes in the MBL, buffer layer, and free troposphere. An aerodynamic particle sizer (APS) sampled air from the inlet connected to the MOI for intercomparison. The inlet upstream of the MOI and APS, a low-turbulence inlet (LTI) (Huebert et al., 2004; Wilson et al., 2004), generated data along with the MOI flow controller that were used to correct apparent particle concentrations by size for enhancement by the LTI (above approximately  $0.5 \mu m$ ). Ancillary physical aerosol measurements used in this study were made by the Clarke group (UH). Supplemental gas-phase measurements were also available from various groups; SO<sub>2</sub> and DMS from Alan Bandy (Drexel); H<sub>2</sub>SO<sub>4</sub>, OH, and MSA from Lee Mauldin's group (NCAR); and CO and O<sub>3</sub> from Theresa Campos and Ilana Pollack (NCAR). Aircraft data, including position and meteorological parameters, were provided by NCAR's Research Aviation Facility (RAF).

The MSP Model 131 high-flow multi-orifice impactor stacks (MOI) were mounted in the aircraft and changed out for each new sample leg. These MSP Corp. impactors were designed for aircraft sampling. The original MOI was designed for automated sample changing with a manifold that distributed flow to 8 impactors in sequence. However, the manifold caused significant losses for large particles in a previous experiment (ACE-Asia), so it was eliminated for PASE in favor of impactor stacks that could be manually changed. Inlet tubing was large-diameter (1.7 - 2.5 cm in)diameter), had only smooth bends, and one "Y" to split air flow off to the APS. Volumetric air flow was maintained at 100 liters per minute (LPM) through the cascade impactors, which are designed to minimize the pressure drop between impaction stages. Aluminum foil was used as the collection medium (impaction substrates) as it minimizes particles loss from static electricity. 90 mm, 1 µm pore-size Gelman Zefluor Teflon filters were used as the backup stage. The nominal 50% cut sizes for the MOI are the following: stage 1: 10µm; stage 2: 5µm; stage 3: 1.4µm; stage 4: 0.8µm; stage 5: 0.44µm; stage 6: 0.25µm; filter: theoretically everything below the stage 6 cutoff. The geometric mean stage sizes were used for data plotting; therefore, MOI diameters are expressed as geometric mean diameter in microns, where geometric mean, m, of diameters p and q is calculated  $m = \sqrt{p \times q}$ . It is important to note that it is difficult to assign a single graphing size to the filter. We chose  $0.14 \,\mu m$ , which implies that very little mass is below 0.08 µm in diameter.

Assembly and disassembly of all MOI substrates and filters were carried out in a small makeshift laboratory on Christmas Island. Substrates and filters were placed in

individual plastic bags, sealed, and sent to Honolulu for analysis in our lab at the University of Hawaii in Manoa. Filters were wetted with 1 ml ethanol first, then extracted in 9 ml deionized (DI) water, whereas substrates were extracted in 10 ml of DI water and analyzed by ion chromatography (IC) using a Dionex AS11-HC analytical column for anions and a Dionex CS12A analytical column for cations. We analyzed for the following anions and cations:  $MS^{-}$ ,  $SO_{4}^{2-}$ ,  $Na^{+}$ ,  $CI^{-}$ ,  $NO_{3}^{-}$ ,  $NH_{4}^{+}$ ,  $Br^{-}$ ,  $Ca^{2+}$ ,  $C_{2}O_{4}^{2-}$ ,  $K^{+}$ , and  $Mg^{2+}$ . Nss-SO<sub>4</sub><sup>2-</sup> was then calculated as the excess sulfate resulting from the subtraction of the sulfate associated with sodium in bulk seawater. We chose not to use  $NH_{4}^{+}$  or  $K^{+}$  due to contamination on the backup filters. Analytical procedures are described in Huebert et al. (1998). Most MOI samples were exposed for approximately thirty minutes on constant altitude legs, most of which were within the MBL. One 10 s blank per flight was collected for the MOI while flying in the FT.

MOI data are expressed as ambient concentrations in ng X per standard m<sup>3</sup> (1013 mbar and 298K) or as ppt (moles X per 10<sup>12</sup> moles air), and are corrected for blanks and LTI enhancement. There was no need to correct for particle bounce due to the assumed properties of the marine aerosol being sampled (i.e. sticky, wet particles), which is supported by the relative humidity measured upstream of the APS, which did not drop below 50% RH in the MBL. Error bars account for uncertainties due to flow rates, blank corrections, and analytical uncertainties. Since ion ratios from any stage experience the same flow, they are free from that uncertainty. However, these uncertainties do not include the potential distortions of the distributions during sampling due to non-ideal inlet transfer lines or cutoffs. Because impactors tend to reduce evaporation and condensation

artifacts compared to filters, we assume that gas-phase artifacts are not a major source of error in this data.

The pressure drop associated with pulling air through an impactor will reduce the relative humidity, causing hydrated particles to shrink, although aerodynamic cooling within the jets can increase the relative humidity. This can considerably affect size distributions in impactors with large pressure drops, but the MOI has a large number of very small jets that reduce its pressure drop. Flow-induced relative humidity changes in the MOI should not perturb the size distributions (Fang et al., 1991).

Impactor samples were collected in the BL and BuL, but only once in the FT. Because sustained, level legs were rarely flown in the FT, we could not expose the MOI for a sufficient amount of time for the analytes to exceed our analytical uncertainty. Rapid profiles through this clean layer were not adequate for our integrated sampling. Except for one sample in RF08, the only aerosol information in the FT comes from the size distributions of the APS and Clarke group instruments.

An unidentified contaminant on the Teflon filters used in the MOI interfered with MS<sup>-</sup> during IC analysis and prevented us from quantifying the fine mode mass of this sulfur compound. During the 1994 experiment, MS<sup>-</sup> on the backup filter and smallest stage were undetectable or a negligibly small fraction of total MS<sup>-</sup>, so it is reasonable to assume that loss of the MOI filter data during PASE has little effect.

Non-sea-salt (excess) concentrations of inorganic ions were calculated from MOI data using the Na<sup>+</sup> fraction in bulk seawater. The assumptions inherent in these estimations are: 1) the reference species (Na<sup>+</sup>) originates exclusively from sea salt; 2) sea-salt constituents are not fractionated during or subsequent to the production of SSA
(Keene et al., 1986). NSS was calculated using a seawater  $SO_4^{2^-}/Na^+$  mass ratio of 0.251. Excess Cl<sup>-</sup> was calculated using a molar ratio of Cl<sup>-</sup>/Na<sup>+</sup> of 1.165. Excess  $Ca^{2^+}$  (xs  $Ca^{2^+}$ ) was calculated with a molar ratio of  $Ca^{2^+}/Na^+$  of 0.022. Excess  $Mg^{2^+}$  (xs  $Mg^{2^+}$ ) was calculated with a molar ratio of  $Mg^{2^+}/Na^+$  of 0.113.

# APS

The TSI 3321 aerodynamic particle sizer (APS) measures supermicron number distributions that we converted to volume and mass distributions by assuming humiditydependent diameters and densities for sea salt. Under this assumption, units of  $\mu$ m<sup>3</sup> cm<sup>-3</sup> are equivalent (not equal) to  $\mu$ g m<sup>-3</sup>. This instrument is capable of measuring aerodynamic particle diameters larger than 0.8  $\mu$ m, topping out at about 20  $\mu$ m, though the statistics are poor at such large sizes. No Stokes correction was applied to the data. The APS used in this study was downstream of the LTI in parallel with the MOI such that physical and chemical size distributions could be compared between the two instruments. APS size distributions were averaged over 15-second time scales then averaged over the duration of MOI samples. The APS is also very useful for surveying the large particle distribution of the free troposphere since legs suitable for MOI samples were not available.

An aerosol mass spectrometer (AMS) can be used to infer the submicron particulate chemistry. The long differential mobility analyzer (LDMA) was used in tandem with the APS to produce comprehensive size distributions at all altitudes. The Clarke group LDMA measured submicron aerosol size distributions spanning mobility diameters of 0.01 µm to roughly 0.5 µm on a time scale of approximately 85 seconds.

This combination of data was used to discern changes between the MBL, BuL, and FT mass distributions. Conversion of APS and LDMA diameters to geometric instead of aerodynamic and mobility diameters, respectively, was necessary in order to compare their mass distributions with those of the MOI. For spherical particles, the relationship between geometric and aerodynamic diameters is (Seinfeld and Pandis, 2006):

$$\frac{D_a}{D_g} = \sqrt{\frac{C_g \rho_p}{C_a \rho_o}} \tag{12}$$

Where  $C_g$  and  $C_a$  are the Cunningham slip correction factors for particles of geometric  $(D_g)$  and aerodynamic  $(D_a)$  diameter, respectively,  $\rho_p$  is particle density, and  $\rho_o$  is standard particle density (1 g cm<sup>-3</sup>). Because *C* hardly varies with diameter above 0.1  $\mu$ m,

$$D_g \approx \frac{D_a}{\sqrt{\rho_p}}$$
 (13)

Uncertainties in the APS and LDMA number concentrations lie near 5%, though the uncertainty increases dramatically at the limits of performance for these instruments.

## LTI

The low-turbulence inlet (LTI) developed at Denver University (Seebaugh et al., 1996; Huebert et al., 2004; Wilson et al., 2004) allowed us to properly measure the concentration of large particles with the MOI. The advantage of using this inlet is its predictable and well-characterized passing efficiency at high diameters (Huebert et al., 2004). Particle concentrations are distorted to some degree by all aircraft aerosol inlets due to the turbulence created within inlets during sampling. This efficiency changes with particle size and altitude. Particle composition also influences collection efficiency;

mineral dust tends to bounce while sea-salt tends to stick upon contact with a tubing wall. Thus, it is important to employ an inlet whose size-dependent passing efficiency can be modeled; the LTI makes this possible. Approximately 80% of incoming air is pulled through a porous stainless steel diffuser cone in the front of the LTI, while the remaining sample air, which should be relatively turbulence-free, passes through a bent tube and into the fuselage to be distributed to the MOI and APS. The LTI enhances large particles, making it necessary to correct the apparent MOI concentrations. Generally, it enhanced particles in the 0.7 - 1.4  $\mu$ m range by 3%, in the 1.4 - 5  $\mu$ m range by roughly 26%, and in the 5 - 10  $\mu$ m range by about 50%. See Table 1 for average enhancement factors per MOI stage in PASE.

Using mass flow and pressure data generated by the LTI in combination with mass flow data from the MOI, we calculated the enhancement factors at each MOI stage for each sample leg and applied them to the "raw" particulate concentrations measured by the IC. Enhancement factors were also calculated for each particle diameter measured by the APS and applied to the resulting volume distribution data. Equations used for these calculations and the resulting enhancement factors for MOI and APS diameters are displayed in the Appendix.

Because the relative humidity (RH) decreases once particles enter the LTI, we are not measuring aerosol at ambient RH in the MOI or APS. The RH sensor in the APS indicated 53% RH, whereas ambient RH was 80% in the MBL. As a result, ambient diameters for particles entering the MOI and APS are in reality larger, which will increase the LTI enhancement factors for coarse particles ( $D_p > 5 \mu m$ ) beyond the enhancement factors applied here. For the largest two MOI size cuts (10-15  $\mu m$  dry,

11.7-17.5  $\mu$ m wet; 5-10  $\mu$ m dry, 5.85-11.7  $\mu$ m wet), the enhancement factors would increase by ~10% and ~5%, respectively, which would decrease the masses on these stages by the same amount. We did not apply this correction to the MOI data since it would not significantly decrease the measured masses on the coarse mode, particularly in light of the barely-detectable NSS mass at these sizes.

Particle losses due to plumbing behind the LTI mainly affect particles with  $D_p > 1$  µm entering the MOI and APS. Calculations of the passing efficiencies for the plumbing downstream of the LTI appear in Huebert et al. (2004). Comparisons between models and lab measurements indicated that 8 µm and 6 µm particles experience the lowest tubing efficiencies, with losses potentially as large as ½ of the mass at 8µm and ⅓ of the mass at 6 µm. However, tubing used in PASE probably caused fewer particle losses than reported in Huebert et al. (2004) because of shorter tubes and fewer turns. The enhancement factors mentioned in the previous paragraph partially compensate for this reduction in mass.

The heating that occurs during the deceleration of air as it enters the LTI may cause evaporation of water from particles to some extent, adding to the uncertainty in our MOI measurements, particularly for small particles. However, this heating is only problematic if it drops the RH below the deliquescence point long enough to completely evaporate the water on the particle. We did not account for this effect in our calculations of LTI enhancement for large particles.

# **Flight patterns**

Fourteen research flights were flown within the area roughly covering 152-157° W, 0-2.5° N. On a typical research flight, the aircraft flew three "stacks" of legs that consisted of a low-MBL leg (~40m above the ocean), a mid-MBL leg (~300m), a top-MBL leg (~500m), and a buffer layer leg, which varied between 800m and 1200m, depending on the estimated height of the MBL (Figure 6). All but 2 flights were daytime flights, which generally took off at 0900 local and landed at approximately 1700. The 2 early morning flights (RF6 and RF13) that spanned sunrise took off at 0200 and landed at 1000 local time. Highly convective regions were avoided. BuL legs were usually just above cloud tops.

PASE observations reported in this study draw from the following set of research flights: 2, 3, 6-14. Research flight (RF) 1 was excluded because of sampling problems, RF04 had a different flight strategy, and the filters of RF5 were contaminated. Where appropriate, we excluded RF09 and RF10 due to failures in the aircraft data system.

Some spatial variability in SO<sub>2</sub> and DMS concentrations was encountered. However, some spatial inhomogeneity is expected in DMS source regions due to patchiness in phytoplankton habitat. For the most part, we can assume the research flights were quasi-Lagrangian as great care was taken to ensure that we followed the same parcel of air. At the beginning of the project, we intended to fly in circles that drifted with the wind, but contamination from aircraft exhaust forced us to modify this strategy. The aircraft flew in "V" or chevron shapes designed to move slowly upwind to avoid the problem of sampling our own exhaust. We flew in circles on one other flight, RF12, and flew chevrons for all other flights. The "V" patterns were made up of two 15 minute legs

connected by a 60° angle bisected by the mean wind (the prevailing BL winds during PASE were east-southeasterly with an average speed of 8 m s<sup>-1</sup>). The aircraft pattern remained nearly fixed in position while the air mass advected through the study region. Our sampling was thus somewhat Eulerian, but treating PASE as nearly Lagrangian is justified. An additional route at the end of some flights were flown through the apex of the "V"s in order to determine whether there was variability in DMS and SO<sub>2</sub> upwind that would indicate advective fluxes. This is further discussed in Conley et al. (2009).

# CHAPTER 3

# **RESULTS**

The 11 research flights considered in this study took place between August 10, 2007, and September 6, 2007, usually two days apart. Figure 7 illustrates the NSS concentration versus time as measured by the MOI impactors throughout the project (research flights 2, 3, 6-14). Each MOI NSS sample is plotted for each flight in order to display the agreement within a sampling period. For the most part, outliers can be attributed to altitude variations. We saw what appear to be episodic variations in the concentrations of NSS throughout PASE. Figure 7 shows day-to-day differences and intra-flight differences in NSS mass measured on each leg for each flight. Concentrations appear to remain somewhat constant within the period of about a week, perhaps a consequence of synoptic-scale weather patterns. There is more variation within the first few flights, which may reflect multiple NSS sources (e.g., pollution) or stronger temporal, meteorological, or altitude effects.

Near the middle of the project, we started seeing indications of continental influence on the air we sampled. Figure 8 shows the project time series of CO (ppbv) and particulate  $NO_3^-$  (ng m<sup>-3</sup>). Biomass burning is an important source of CO, especially in the Southern Hemisphere where CO is less concentrated than in the Northern Hemisphere.  $NO_3^-$  in the second half of the project varies with CO, suggesting a non-local source for this ion's precursor gas, HNO<sub>3</sub>.  $NO_3^-$  is excluded from three research flights as mentioned in the experimental section. A histogram (Figure 9) of total scattering at 550 nm from the Clarke group TSI nephelometer demonstrates the

proportional amount of time that the aircraft sampled aerosol (coarse and fine) mass in the remote marine FT above the trade wind inversion. Excluding values less than 2  $Mm^{-1}$ as instrument noise, this figure indicates that we encountered aerosol layers from longrange transport 20-30% of the little time in the FT. Rapid profiles into this layer lasted only ~15 min and occurred roughly 4 times per flight. All research flights except RF04 were included in this analysis.

The nitrate in PASE averaged 0.24  $\mu$ g m<sup>-3</sup> throughout the project, which is slightly higher than that observed in the equatorial Pacific (0.17  $\mu$ g m<sup>-3</sup>) by Savoie et al. (1989). An interesting trend in particulate NO<sub>3</sub><sup>-</sup> was observed by Prospero et al. (1985) on Fanning Island, an atoll in close proximity to Christmas Island. The time period spanning August and September saw BL nitrate levels that were elevated (0.3 – 0.4  $\mu$ g m<sup>-3</sup>) with respect to the rest of the year (0.18  $\mu$ g m<sup>-3</sup>). This is the same time of year that PASE went to the field. As the background nitrate concentration has been reported to be 0.11  $\mu$ g m<sup>-3</sup> for the remote BL of the tropical South Pacific Ocean (Savoie et al., 1989), PASE nitrate exceeds these background levels but agrees well with Liu et al. (1983) who observed 0.21  $\mu$ g m<sup>-3</sup> nitrate in the equatorial Pacific. Nitrate at Christmas Island in 1994 was very similar to PASE as measured by the MOUDIs; the 1994 intensive was also conducted during late July/early August.

Ions of acidic gases on the sea-salt mode have implications for titration of the SSA alkalinity. Figure 10 shows PASE project-average NSS, NO<sub>3</sub><sup>-</sup>, excess Cl<sup>-</sup>, MS<sup>-</sup>, and Na<sup>+</sup> % mass vs. size for boundary layer legs. NSS predominates on the fine mode while NO<sub>3</sub><sup>-</sup>, excess Cl<sup>-</sup>, and MS<sup>-</sup> primarily occur on the coarse sea-salt mode. Plotting % mass

instead of actual mass normalizes the ionic species of interest. Of the four ions, NSS has by far the smallest fraction of its mass on the coarse mode.

As a result of the pressure drop in aerosol sampling instruments, hygroscopic particles evaporate some of their water content. We corrected the APS mass distributions for this evaporation and the resulting reduction in SSA diameter and increase in density in Figure 11, which shows an MBL sample from a typical flight (RF03). Since the relative humidity sensor in the APS reported 53% RH, we corrected the observed SSA mass distribution back to ambient conditions in the MBL of 80% RH (blue line). The dry SSA mass distribution illustrates the amount of dry SSA mass that the MOI should measure (green dashed line), as coarse SSA will lose its water mass prior to collection in the MOI. Because the MOI and APS measured particles at the same RH (53%), their diameters agree closely.

To understand uptake of gases by SSA particles, we examine the MOI ion mass vs. APS total aerosol surface area in the MBL. Figure 12 shows the mass of NO<sub>3</sub><sup>-</sup> and NSS on coarse mode stages 1 (10-15  $\mu$ m), 2 (5-10  $\mu$ m), and 3 (1.4-5  $\mu$ m) of the MOI. It relates the amount of mass taken up on the coarse mode to the summed APS surface area at each coarse size range, which comes from the Figure 11 coarse surface area in ambient 80% relative humidity conditions. Sulfate and nitrate accumulation on supermicron sizes can be estimated as:

$$\frac{Surface Area}{Volume} \propto \frac{Ion}{Na^+}$$
(14)

Positive slopes in this plot indicate that gas uptake by SSA is area-limited while a negative slope would suggest that uptake is volume-limited. We used the same PASE

masses used to plot Figure 10. The error bars represent the standard error of the mean for these PASE-averaged masses.

Indications that cloud processing affected the PASE submicron size distributions attests to the important role of clouds in the PASE environment. LDMA number distributions for the BL and BuL of three flights are plotted in Figure 13. RF03 is a typical daytime flight, RF06 took off at night and landed after sunrise, and RF08 was a flight in which we noted pollution. The RF08 panel also includes the number distribution corresponding to the FT sample. PASE number concentrations (mean of 415 cm<sup>-3</sup>) exceed the typical range of remote marine aerosol number densities of 100-300 cm<sup>-3</sup> (Seinfeld and Pandis, 2006). The submicron population dominates the aerosol number. The Hoppel minimum, which is a gap in number distributions due to cloud processing (growth of particles as a result of in-cloud coalescence and solute condensation) in the remote atmosphere, appears in all distributions. The Hoppel minimum indicates the particle activation diameter at the supersaturation in marine cumulus clouds (Hoppel et al., 1990). This gap is almost always observed in remote marine conditions where CCN are a large fraction of the total aerosol population (Seinfeld and Pandis, 2006).

Observations of elevated CO and NO<sub>3</sub><sup>-</sup> (Figure 8) indicate continental influence, and elevated aerosol mass in the FT shown in Figure 14 confirms long-range transport of continental aerosol. A coincident MOI sample in the FT from one of these flights (RF08) allowed us to set an upper bound for NSS mass brought into the BuL from the FT. Figure 14 is a plot of LDMA and APS volume distributions in the FT for RF03, RF06, and RF08. RF03 is a typical clean flight whereas RF06 and RF08 exhibited some pollution in the FT, as shown by the enhanced fine and coarse mass. Representative legs

in the FT are the last FT leg of RF03, the last FT leg of RF06, and the midway FT leg of RF08.

The CO time series (Figure 8) indicated transport of trace gases from continents. Evidence of related SO<sub>2</sub> and CO layers in the FT implies a common distant origin. Figure 15 displays RF03 and RF08 profiles of DMS (pptv), SO<sub>2</sub> (pptv), and CO (ppbv) with inversion heights included. Again, RF03 typifies a clean flight while RF08, with its enhanced layers of CO and SO<sub>2</sub> aloft, represents a flight influenced by biomass burning pollution and possibly volcanic emissions.

Since the quantity of NSS formed on coarse SSA is a central focus of this study, we investigated whether coarse NSS exclusively associates with Na<sup>+</sup> (SSA) or whether it may associate with Ca<sup>2+</sup> (dust), which has greater alkalinity than SSA. Table 5 shows the average fraction of coarse NSS (NSS  $>_{1\mu m}$ /NSS<sub>total</sub> for each sample) along with the associated amounts of total Na<sup>+</sup> and Ca<sup>2+</sup> for the 1994 and PASE impactors. We segregated the flights by "less Ca<sup>2+</sup>", [Ca<sup>2+</sup>] < 0.25 µg m<sup>-3</sup>, and "more Ca<sup>2+</sup>", [Ca<sup>2+</sup>] > 0.25 µg m<sup>-3</sup>, in addition to including the project average values. This excess Ca<sup>2+</sup> may derive either from mineral dust transported from South America or from biogenic sources at the surface of the ocean (e.g., CaCO<sub>3</sub> phytoplankton casings).

#### PASE Sulfur vs. 1994 Sulfur

We use the 1994 Christmas Island experiment as a comparison to elucidate the relative importance of the mechanisms influencing particulate sulfur production in the equatorial Pacific during PASE. Contrasting meteorological conditions and atmospheric

species between the two years highlights the dominant factors influencing remote MBL aerosol populations.

One difference between the 1994 experiment and PASE is the difference in the El Niño/Southern Oscillation (ENSO) state. The 1994 experiment was conducted during a five-year ENSO warm phase, the 1990-1995 El Niño (Trenberth and Hoar, 1996). The outgoing longwave radiation (OLR) anomaly at Christmas Island is negative in an El Niño, reflecting enhanced tropical convection and cloudiness across the equatorial Pacific. This is coupled with unusually warm sea surface temperatures (SSTs) as indicated by positive SST anomalies. The easterly trade winds weaken, reducing equatorial upwelling. PASE, on the other hand, went to the field during the beginning of the 2007-2008 La Niña, an ENSO cold phase. The OLR anomaly is positive in a La Niña, reflecting a decrease in convective activity, which is suppressed by unusually cold SSTs and subsurface temperatures. Stronger easterly trade winds drive increased upwelling along the equator. Changes in central Pacific rainfall have been linked to the ENSO phase, with large amounts of rain falling during El Niño episodes and droughts during the La Niña episodes (Falkland and Woodroffe, 1997). Perturbations to the tightly-coupled ocean-atmosphere system have important biological, chemical, and physical consequences for this region.

Plots of hourly mean wind speed from 1994 indicate that speeds ranged from 2 to 7 m s<sup>-1</sup> during the experiment, suggesting an average wind speed of ~ 4.5 m s<sup>-1</sup>. Wind speeds in PASE ranged from 4.5 to 10 m s<sup>-1</sup> at 10 m and averaged ~8 m s<sup>-1</sup>. As expected, trade wind velocities were higher during the 2007 La Niña than during the 1994 El Niño. There are no accessible records of precipitation during the 1994 experiment. However,

archived data from the NOAA TAO (Tropical Atmosphere Ocean project) array indicates that the composite mean columnar precipitable water was greater in 1994 than PASE (>40 kg m<sup>-2</sup> in 1994 vs. <35 kg m<sup>-2</sup> in 2007; http://www.pmel.noaa.gov/tao/index.shtml). This is consistent with the extension of the equatorial dry-zone that occurs during La Niña years.

To estimate the precipitation conditions for the duration of the PASE study period, J. Merrill (URI) compiled Figures 16 and 17 from the TRMM (Tropical Rainfall Measuring Mission) satellite. Figure 16 illustrates the total accumulated rainfall for the month of August, 2007, within the region encompassing 15°N to 15°S and 130°W to 165°W. Roughly 30-50 mm of rain fell in the region directly east of Christmas Island, with 20 mm of this total having fallen in a single 40 min period prior to RF02 (08/10/2007). Figure 17 is a time plot of the total rainfall in August in the latitude band from 1°-2° North, showing how dry conditions were during PASE. Save for that single intense rainfall event, there was little (~10 mm) to no rainfall in the study region. However, this satellite is not capable of measuring drizzle or light rainfall, which was observed during several research flights.

Now that we have noted the relevant meteorological conditions for these two projects, the next set of figures focuses on comparisons between PASE and the 1994 Christmas Island experiment. Figure 18 demonstrates the observed and modeled DMS and SO<sub>2</sub> concentrations (in parts per trillion by volume, pptv) as measured in PASE along with the analogous DMS and SO<sub>2</sub> temporal patterns from the 1994 experiment (Bandy et al., 1996). The model utilized the observations as a guide to mimic diurnal patterns using first-order source and sink terms such as production, photochemical loss, and

entrainment. Modeled concentrations are the solid lines tracking the observations. Observed gas-phase concentrations from PASE were averaged every 2 hours for corresponding time-of-day bins from 10-second data for BL legs. Data were available for 24-hour cycles in 1994, whereas it is absent for an 8 or more hour window of time in the late evening/night during PASE. Note that the SO<sub>2</sub> curves nearly overlap while the precursor DMS is more than a factor of two higher in 1994 than 2007.

In 1994, DMS was twice that of PASE DMS, but SO<sub>2</sub> was the same. The connection between the ENSO state and emission of DMS has yet to be clarified, but the biological productivity may have responded differently to the meteorological conditions prevailing in 1994 and 2007. It is worth trying to understand the differences between the two projects to expose the primary factors causing such discrepancies in DMS and NSS concentrations in the same region. The ENSO state contributed to decreased cloud and minimal precipitation during PASE (Figures 16 and 17). A weak La Niña in the summer of 2007 led to cooler and, more importantly, dryer conditions upwind of the Christmas Island region. In contrast, 1994 was an El Niño year, characterized by warmer, wetter conditions.

Assuming no advection or DMS or SO<sub>2</sub> sources from the BuL, the change in SO<sub>2</sub> concentrations over time can be expressed:

$$\frac{d[SO_2]}{dt} = \gamma(k[DMS][OH]) - (\Sigma k_{losses}[oxidants] + V_d)[SO_2]$$
(15)

Where  $k_{Abs}$  is the second-order rate constant for the DMS-OH abstraction path,  $\Sigma k_{losses}[oxidants]$  represents all chemical loss including heterogeneous loss to cloud and aerosol and homogeneous oxidation to H<sub>2</sub>SO<sub>4(g)</sub>, and  $V_d$  is the SO<sub>2</sub> dry deposition velocity to the ocean surface. Assuming that  $SO_2$  is approximately in steady state in the remote BL over the timescale of an hour:

$$\frac{[SO_2]}{[DMS]} = \frac{\gamma(k_{DMS}[OH])}{\Sigma k_{SO_2 \ losses}[oxidants] + V_{d,SO_2}}$$
(16)

This ratio of  $SO_2$  to DMS is higher in PASE (0.56) than in 1994 (0.31). Figure 18 shows very different DMS results in PASE and 1994, leading us to consider Equation 16 for an explanation. Either a larger numerator or a smaller denominator in PASE can explain the observed differences.

Assuming the same conversion efficiency from DMS to SO<sub>2</sub> (an unchanging numerator on the right-hand-side of Equation 16), a smaller denominator during PASE would increase the [SO<sub>2</sub>]/[DMS] ratio, causing it to exceed 1994's ratio. Slower losses of SO<sub>2</sub> in PASE relative to 1994 could explain the equivalent SO<sub>2</sub> concentrations (Figure 18) for both years. One of the  $SO_2$  removal mechanisms, dry deposition, should actually have been slightly higher in 2007 due to higher winds. Hence, the other means of removing SO<sub>2</sub> from the troposphere, chemical destruction, must not have been as efficient in PASE. Observations in PASE of lower mean NSS concentrations (Table 2) are consistent with the hypothesis of reduced conversion of  $SO_2$  to acidic S(VI) species in PASE. With no OH information available from 1994, it is difficult to speculate about the difference in importance of the homogeneous loss of SO<sub>2</sub> between 1994 and 2007. As this pathway tends to be the least significant removal mechanism in the remote marine environment, it is not expected to change the removal of  $SO_2$  much in 2007 versus 1994. Nevertheless, greater OH in PASE possibly as a result of fewer clouds (La Niña) would increase the numerator of Equation 16, leading to increased SO<sub>2</sub> production and a higher [SO<sub>2</sub>]/[DMS] ratio.

Greater losses of SO<sub>2</sub> in 1994 are the converse of smaller losses in PASE. During model runs of the remote MBL sulfur cycle, von Glasow and Crutzen (2004) found that the SO<sub>2</sub> was an order of magnitude smaller in cloud runs than in cloud-free runs because of strong scavenging by cloud droplets, stressing the significant impact that multiphase cloud chemistry can have over the ocean. Greater NSS in 1994 (Table 2) could have resulted from greater cloud activity in 1994, translating to greater consumption of SO<sub>2</sub> in 1994, thus causing the 1994 SO<sub>2</sub> concentrations to be similar to the PASE SO<sub>2</sub>. The ENSO meteorology supports the concept of more active convection and influential cloud activity during the El Niño of 1994.

# CHAPTER 4 DISCUSSION

We sought to constrain the amount of NSS production that could result from each SO<sub>2</sub> oxidation pathway. The contributions from condensation of homogeneouslyproduced H<sub>2</sub>SO<sub>4</sub>, oxidation by H<sub>2</sub>O<sub>2</sub> in cloud, and oxidation of SO<sub>2</sub> by O<sub>3</sub> on SSA are important because their magnitudes control the effect that aerosol has on the albedo of clouds in the remote BL. However, because we could not directly measure the rate-ofchange for NSS, it is beyond our ability to provide temporal observations of production and removal rates. Whereas the gas-phase measurements used high time-resolution techniques (Figure 18), the airborne integrated particulate samplers and the limit of one flight per day were not well suited for examining temporal variations. We will thus focus on the relative importance of the various mechanisms for NSS growth and deposition via estimations of their rates and sulfur fluxes (Figure 5) based on data from a variety of instruments utilized during PASE.

#### **Oxidation of SO<sub>2</sub> in SSA Particles**

One of the main questions in this study is whether we can observe heterogeneous processing on sea salt aerosol that contributes NSS mass comparable in magnitude to cloud processing by  $H_2O_2$  and homogeneous  $SO_2$  oxidation by OH. The IPCC reports that sea salt is responsible for a "large fraction" of the NSS formation (IPCC 2007-AR4), based largely on Sievering et al.'s work. The implications of this are that much of the NSS is sequestered onto very large particles that dry deposit at rates of ~1 cm s<sup>-1</sup> or

larger, thereby limiting the albedo-enhancing capabilities of new NSS (Chameides and Stelson, 1992). The two primary assumptions allowing Sievering et al. to claim that significant removal of SO<sub>2</sub> from the MBL occurs on SSA are: 1) coarse-mode ( $D_p > 1.5$  µm) SSA can take up ~8 pptv SO<sub>2</sub> hr<sup>-1</sup> at an altitude of 150 m above sea level, and 2) at 10-15% cloud cover, cloud processing contributes <6% of the total NSS. We flew multiple legs per flight at 40 m above sea level and averaged 16 ppt coarse NSS for the project, whereas Sievering et al. reported 51 ppt coarse NSS in a region known to receive large amounts of Saharan dust (which is correlated with NSS and NO<sub>3</sub><sup>-</sup> mass, Savoie et al., 1989). As we will argue, we see a smaller amount of coarse NSS than Sievering et al.'s mechanism would produce even if we invoke dry deposition velocities that give us similar coarse-particle lifetimes against dry removal.

Faloona et al. (2010) assert that 57% of the total SO<sub>2</sub> loss in PASE is due to uptake by coarse SSA particles (Figure 5 and Table 3), which would form 58 ppt coarse NSS per day ( $1.6 \pm 1 \mu$ mol m<sup>-2</sup> day<sup>-1</sup>). Since we measured 16 ppt coarse NSS with the MOI, and since we can safely neglect wet deposition on the timescale of 3 days, dry deposition would need to remove 42 ppt (or 1.2 µmol m<sup>-2</sup> day<sup>-1</sup>) of their 58 ppt coarse NSS per day to match our observations. This large dry deposition flux (1.2 µmol m<sup>-2</sup> day<sup>-1</sup>) requires coarse dry deposition velocities (using [NSS] = 5 – 11 ng m<sup>-3</sup> on the first two MOI stages) that are a factor of 2 - 3 larger than those calculated using Slinn and Slinn (1980) depicted in Figure 19 (see Table 6 for the fluxes of the first two MOI stages and the Appendix for assumptions). The dry deposition velocities we used are already at the upper limit of most dry deposition models, so increasing them is not supported by theory (Lewis and Schwartz, 2004). This discrepancy led us to examine the DMS and  $SO_2$  fluxes calculated by Faloona et al. (2010) in order to explain why they had to remove such a large fraction of  $SO_2$  via SSA.

Taking the expressions for SO<sub>2</sub> production and loss in the MBL:

$$P_{SO_2} = \gamma(k_{OH+DMS}[OH][DMS])$$
(17)  
$$L_{SO_2} = \left(k_{OH+SO_2}[OH] + \left(\frac{1}{k_{mt}} + \frac{1}{k_{O_3}[O_3] + k_{H_2O_2}[H_2O_2]}\right)^{-1} + V_d\right)[SO_2]$$
$$-\omega \frac{d[SO_2]}{dz}$$
(18)

Where  $\gamma$  is the product yield of SO<sub>2</sub> from oxidation of DMS by OH in Equation 17. In Equation 18, the first term is the loss of SO<sub>2</sub> to homogeneous oxidation by OH, the second term expresses the heterogeneous loss of SO<sub>2</sub> to SSA, the third term is loss by dry deposition to the ocean surface, and the fourth term describes the upward transport of SO<sub>2</sub> to the BuL. The second loss term is a combination of the rate of mass transfer to SSA particles in series with the rates of Equations 3 and 4 for aqueous oxidation of SO<sub>2</sub>. Faloona et al. (2010) constrained each of these terms with the exception of the heterogeneous loss term in the MBL (Figure 5) using measurements of the DMS and SO<sub>2</sub> fluxes by eddy covariance.

As Equation 17 shows,  $\gamma$  determines the source of SO<sub>2</sub> to the MBL and, consequently, the total sink of SO<sub>2</sub> since Equations 17 and 18 must balance. In a survey of the literature, Faloona (2009) concluded that  $0.7 \pm 0.2$  is the best global value for  $\gamma$ . Physically,  $\gamma$  must be less than unity to allow for the observed non-SO<sub>2</sub> oxidation products such as DMSO, MSA and MS<sup>-</sup>. Yet Faloona et al. (2010) chose a  $\gamma$  of unity to force the SO<sub>2</sub> budgets from all daytime flights to include a positive sink for SO<sub>2</sub> on SSA particles. With the other SO<sub>2</sub> terms in their budget constrained (but not fixed) by measurements, Faloona et al. (2010) assigned the surplus SO<sub>2</sub> (from Equation 17) to heterogeneous oxidation in SSA (in Equation 18). As Table 4 shows, this residual is highly dependent upon the original SO<sub>2</sub> source, which derives from the choice of  $\gamma$ . Choosing the Faloona (2009) value for  $\gamma$  of 0.7 gives a flux of SO<sub>2</sub> to SSA of 0.73 µmol m<sup>-2</sup> day<sup>-1</sup>, which comprises 13-24% of NSS production. Once we factor in the dry deposition flux of the coarse mode (0 - 0.8 µmol m<sup>-2</sup> day<sup>-1</sup>), this new flux of SO<sub>2</sub> to coarse-mode SSA aligns well with our observations (Figure 10) as it generates a flux of 0.1 – 0.7 µmol m<sup>-2</sup> day<sup>-1</sup>, or 3-23% of NSS production (Figure 5).

In this treatment of the flux of SO<sub>2</sub> to aerosol, we have assumed that coarse-mode SSA is the sole recipient of the gaseous SO<sub>2</sub> budget residual. There is a possibility that there are additional mechanisms for coarse NSS production. A small portion of the DMS-derived coarse NSS may have been formed in cloud. Laj et al. (1997) observed cloud-produced sulfate associated with particles from 0.2 to 1.1  $\mu$ m dry diameter. A portion of homogeneously-produced vapor encounters and condenses on aerosol. Calculations indicate that radius controls H<sub>2</sub>SO<sub>4(g)</sub> mass transfer to particles, and when this flux is multiplied by a typical number distribution in the MBL, only ~15% of the H<sub>2</sub>SO<sub>4</sub> vapor flux goes to supermicron SSA particles while ~85% goes to submicron particles (Figure 20). The homogeneously-produced H<sub>2</sub>SO<sub>4</sub> contribution to the coarse mode is small.

We were able to use the PASE  $SO_2$  budget to constrain the coarse NSS production flux in the tropical MBL. In order to further assess the importance of the SSA mechanism, we investigate the processes controlling the uptake of  $SO_2$  onto coarse particles.

# NSS/Na<sup>+</sup>

To understand the factors controlling the uptake of SO<sub>2</sub> by large sea-salt particles, we compare the mass of NSS to the aerosol surface area (calculated from Figure 11) on the coarse impactor stages (Figure 12) and assume that SSA comprises the bulk of the surface area in the MBL. HNO<sub>3</sub> gas is also taken up by SSA and converted to particulate NO<sub>3</sub><sup>-</sup>. Mechanisms limiting the adsorption of these two species are related to surface area and volume effects of coarse particles. Figure 12 shows that NO<sub>3</sub><sup>-</sup>  $\propto$  surface area, indicating that the uptake of HNO<sub>3</sub> is area-limited (Savoie and Prospero, 1982). SO<sub>2</sub> uptake by SSA is weakly dependent on surface area, suggesting that adsorption of this acidic gas is not favored under these conditions.

2.6 µm geometric diameter (5 µm >  $D_p$  > 1.4 µm size range at 53% RH) is the peak of Na<sup>+</sup> mass and the stage where most of the SSA chemistry (e.g. gas uptake, removal) occurs in the BL. The NO<sub>3</sub><sup>-</sup>/Na<sup>+</sup> ratio (both mass and molar) exceeds the NSS/Na<sup>+</sup> ratio at this size, suggesting that uptake of SO<sub>2</sub> on most of the SSA mode is slower than for HNO<sub>3</sub>. Titration of sea-salt alkalinity by acidic gases, which ultimately depends on mass transfer efficiency and gas-phase concentrations, stands to limit the formation of NSS on large sea-salt particles (Chameides and Stelson, 1992). Indeed, highly soluble HNO<sub>3</sub> is very effectively scavenged by SSA (Keene et al., 1998). The slope of the NSS trend also suggests that a minimal amount of NSS is generated on particles larger than 5 µm.

Another possibility is that some of these anions (NSS and  $NO_3^-$ ) could have formed on other coarse mode particles, such as  $Ca^{2+}$  or  $Mg^{2+}$  in dust, or could be artifacts

of misplaced accumulation mode mass in our MOI. Soil particles can compete with SSA particles for acidic gases;  $NO_3^-$  and  $SO_4^{2-}$  form in or deposit on  $Ca^{2+}$ -rich aerosol from continents (Zhuang et al., 1999; Huebert et al., 2003; Bauer and Koch, 2005).

# % Coarse NSS

Using the MOUDI data from 1994, the fraction of total NSS on the coarse mode was calculated and compared to those from 2007 to shed light on which NSS formation pathway may have been more significant. As shown in Table 5, in relatively low-Ca<sup>2+</sup> conditions, represented by the 1994 data as well as the PASE research flights that had  $[Ca^{2+}] < 0.25 \ \mu g \ m^{-3}$ , the proportion of NSS on supermicron particles is small (6-7%). The PASE project-average coarse-mode NSS was  $11 \pm 5\%$ , including flights with nonlocal influence. Figure 10 displays the PASE-average NSS mass distribution showing a majority of fine NSS. Was most of the coarse NSS fraction formed on SSA via the heterogeneous O<sub>3</sub> oxidation pathway? With more than double the Na<sup>+</sup> concentrations relative to PASE (Table 5), the 1994 experiment seemingly had better conditions for NSS production on sea-salt particles, yet there was little coarse NSS (~6% of total NSS). The PASE samples with more  $Ca^{2+}$  (we chose  $[Ca^{2+}] > 0.25 \text{ µg m}^{-3}$  to be a marker of introduced alkalinity) exhibited higher fractions (14% and up to 23%) of supermicron NSS, providing evidence that either there was heterogeneous NSS formation occurring on dust particles in the PASE region (Li et al., 2006) or coarse sulfate was coming from long-range transport. Elevated coarse mass in the FT during the flight (RF06) with the highest Ca<sup>2+</sup> concentrations argues for some dust influence (Figure 14), particularly since  $Ca^{2+}$  increased with altitude during this flight. Alternatively, this calcium may have

come from biogenic sources in the ocean (Sievering et al., 2004) since winds were slightly stronger in some of these high- $Ca^{2+}$  flights. As is suggested by the factor of two difference in the coarse fraction of NSS between flights with more and less  $Ca^{2+}$ , the NSS on relatively  $Ca^{2+}$ -rich particles may be equivalent to the NSS formed on hydrated seasalt particles. It is not possible in this study to determine what type of internal mixture of SSA, mineral dust, and biomass burning aerosol was present. Further, we cannot distinguish sulfate derived from DMS from sulfate brought in via long-range transport or ship plume advection. However, we can place bounds on the supermicron vs. submicron NSS production rates. Throughout the project, we observed coarse NSS concentrations ranging from 3 to 55 ppt, with a median of 16 ppt.

O'Dowd et al. (1997) suggested that particles larger than 10  $\mu$ m contribute a large portion of the coarse NSS formed on unactivated SSA in the BL, and that due to their large size, these particles rapidly dry deposit to the ocean's surface, effectively removing much of the maritime SO<sub>2</sub>. We did not observe significant amounts of particles of such size in PASE: they were rarely detectable in the APS, the Forward Scattering Spectrometer Probe (FSSP), or the MOI. If such particles were common below our minimum altitude (40 m) and removed significant SO<sub>2</sub>, it would create a downward flux of SO<sub>2</sub> indistinguishable from dry deposition, which was measured. Hence, the computed SO<sub>2</sub> dry deposition flux accounts for this possibility.

## Alkalinity

Chameides and Stelson (1992) noted that the alkalinity of a sea-salt particle controls the amount of SO<sub>2</sub> that can be oxidized to  $SO_4^{2-}$  in that particle. Specifically, a

half-mole of NSS formation will theoretically balance a mole of alkalinity brought into the atmosphere in sea salt. An ambient sea-salt concentration of 10 µg m<sup>-3</sup> (drv) provides 0.75 neg m<sup>-3</sup> of SSA alkalinity and could support 0.75 neg m<sup>-3</sup> of NSS production on SSA in the MBL (Chameides and Stelson, 1992). This calculated alkalinity ignores the presence of other acidic gases, which the authors acknowledge will reduce the final NSS generated by the equivalent amount of other acids. If SSA alkalinity were linearly related to SSA mass concentration, we calculate that the PASE SSA burden (12  $\mu$ g m<sup>-3</sup> dav<sup>-1</sup>, assuming SSA builds up over 3 days) would supply a maximum of 0.9 neg m<sup>-3</sup> day<sup>-1</sup> alkalinity, which could support 0.9 neg m<sup>-3</sup> day<sup>-1</sup> NSS production on the smaller SSA sizes where the Na<sup>+</sup> concentrations are highest. Faloona et al.'s (2010) calculated flux of SO<sub>2</sub> to SSA (1.6  $\mu$ mol m<sup>-2</sup> day<sup>-1</sup> translating to ~1.3 neq m<sup>-3</sup> day<sup>-1</sup> NSS) is greater than the 0.9 neg m<sup>-3</sup> day<sup>-1</sup> starting alkalinity can support. Using  $\gamma = 0.7, 0.73$  µmol NSS m<sup>-2</sup> day<sup>-1</sup> or 0.6 neq m<sup>-3</sup> day<sup>-1</sup> NSS would form on SSA, which fits more reasonably with the available alkalinity. We measured an average of  $3.2 \text{ neg m}^{-3}$  of NO<sub>3</sub><sup>-</sup> on the coarse mode, which would more than titrate the alkalinity of SSA, preventing the generation of even 0.6 neq m<sup>-3</sup> NSS. Uptake of HCl would further limit the available alkalinity (Figure 10). Because we are calculating this based on the theoretical starting alkalinity, there could be a 30% error in these figures. However, their relative sizes emphasize that even fresh SSA alkalinity could not accommodate the observed mass of acidic ions (Figure 10) in addition to a large flux of SO<sub>2</sub>.

Distillation of Cl<sup>-</sup> from small particles to large particles rapidly acidifies the coarse mode ( $D_p > 1 \ \mu m$ ) and substantially lowers the pH of coarse SSA, titrating even the coarsest SSA. The PASE leg-average anion/cation equivalents ratio was 1.7,

signifying acidic aerosol. This assumes  $H^+$  is the unmeasured cation. This ratio averaged 1.3 for submicron aerosol and 1.9 for supermicron aerosol, reflecting the Cl<sup>-</sup> surpluses measured at larger sizes. This suggests that the coarse aerosol pH is well below the 7.5 to 8.4 range of seawater pH. Chameides and Stelson (1992) calculated that the rate of sulfate production via oxidation in SSA falls substantially below the production rates of other pathways at a pH of 5.5. The anion/cation ratios in flights RF07 and RF10 influenced by biomass burning (indicated by high CO) were much greater than unity (3.0 and 2.2, respectively), primarily on the supermicron mode (4.4 and 3.0, respectively) where significant excess Cl<sup>-</sup> was observed, suggesting that long-range transport of acidic gases can substantially lower the aerosol pH of the remote MBL. Cations that commonly associate with dust (Ca<sup>2+</sup>) impact the anion/cation ratio. In a flight influenced by dust (RF06), the anion/cation ratio (0.5) was well below the project average on both the coarse (0.6) and fine (0.4) modes.

The small portion of coarse NSS observed in PASE (11% of total NSS) argues that the Christmas Island MBL has a limited aqueous alkalinity flux that suppresses the NSS production potential on SSA, thus reducing the capacity of sea-salt particles as a sink for gaseous SO<sub>2</sub>. Uptake of other acidic gases such as HNO<sub>3</sub> and HCl by SSA reduces coarse-mode alkalinity and limits NSS production on an equivalents basis. Past observations have shown that the accumulation mode of marine aerosol is acidic since the majority of its mass is sulfate, while the coarse mode is slightly acidic (Keene and Savoie, 1998; Pszenny et al., 2003). With a long history over the eastern Pacific, the non-local fraction of the observed aerosol had ample time (>1 week) to age and acidify before subsiding into the BL over the study site. The acidic species introduced into the

marine environment (e.g.,  $NO_3^-$ , Figure 8) participate in cycling of trace species that tend to lower the pH of the local submicron population unless they were neutralized by ammonia or calcium from their source region. In this way, long-range transport (Figure 9) can greatly reduce the sink of SO<sub>2</sub> on SSA particles.

Our observations suggest that the SSA mechanism is neither the major SO<sub>2</sub> loss pathway nor the dominant NSS production route. We estimate that the flux of SO<sub>2</sub> to SSA is only 0.73  $\mu$ mol m<sup>-2</sup> day<sup>-1</sup> (using  $\gamma = 0.7$ ), roughly ½ Faloona et al.'s reported value. This flux is comparable to Faloona et al.'s calculated SO<sub>2</sub> dry deposition flux, 0.75  $\mu$ mol m<sup>-2</sup> day<sup>-1</sup>, suggesting that the SSA oxidation and dry removal mechanisms are equally important for SO<sub>2</sub>. We will subsequently discuss the dry removal of SSA particles to evaluate its importance as a sink for sulfur in the marine environment.

## **Dry Deposition of NSS**

The primary NSS removal mechanisms include dry deposition (which is only important for the large end of the coarse mode ( $D_p \ge 10 \ \mu m$ ) on a one-day timescale (Figure 19 and Table 6)), and dilution by entrainment of cleaner air from the free troposphere. Here we mainly focus on dry deposition of the coarse mode as others have hypothesized that it is a significant means of depositing NSS back to the ocean surface. We will assume that wet deposition is negligible on the timescale of 3 days to a week for the dry conditions of 2007 in which observations showed little or no precipitation (Figures 16 and 17). Using the parameterization of Slinn and Slinn (1980) for the dry deposition of sulfate as a function of particle diameter at a wind speed of 8 m s<sup>-1</sup> and a friction velocity of 0.3 m s<sup>-1</sup>, we generated Figure 19 and corresponding Table 6 for

deposition velocities pertinent to each MOI stage corrected for water uptake and diameter growth at ambient conditions (80% RH) but plotted with sampling diameter at 53% RH (see Appendix for assumptions used). As Table 6 shows, there is potential for a large dry deposition flux for aerosols with wet  $D_p \ge 12.5 \mu m$ , but this aerosol size bin represents only 0-2% of the total NSS mass. Particles with wet  $D_p \ge 6.3 \mu m$  have a lifetime against dry removal of a day, but this bin again potentially represents only 0-2% of the total NSS. Because NSS concentrations were very rarely above the uncertainty on the first two stages, the mass on these stages may range from 0 to 11 ng m<sup>-3</sup>, which is the minimum detection limit on these stages. The remainder of the size distribution except for the very fine particles will remain in the BL for days to weeks with respect to dry deposition. A maximum 4% portion of the total NSS (~15% of the coarse NSS) will dry deposit in less than a week, after which time wet deposition will begin to compete with dry deposition. The 1994 experiment conducted on Christmas Island provided evidence that the maximum possible dry deposition of NSS could not exceed 10-20% of observed loss (Huebert et al., 1996). On a timescale of days, dry removal of NSS is responsible for removing anywhere from 0-20% of total NSS, or 0-21% of the SO<sub>2</sub> (irrespective of SO<sub>2</sub>) dry deposition). The upper bound of this estimate depends, however, on our use of the uncertainty value for the NSS mass on the first two stages (Table 6). NSS above this uncertainty value was rarely observed outside of RF06, a flight included in the "more Ca<sup>2+</sup>, category in Table 5.

The calculated dry deposition flux for the coarse MOI size spectrum is 0 - 0.8  $\mu$ mol m<sup>-2</sup> day<sup>-1</sup> (Figure 5), though the upper bound signifies a quantity that was almost never measured. According to this estimation, dry deposition could reasonably remove

up to 67% of the coarse-mode NSS and 0-20% (up to 33% in the case of Figure 5) of the total NSS produced in a day. With regard to the original flux of SO<sub>2</sub> to coarse SSA calculated by Faloona et al. (2010) of 1.6  $\mu$ mol m<sup>-2</sup> day<sup>-1</sup> (Figure 5), we found that the dry deposition flux needs to be at least a factor of 3 larger, or 1.4  $\mu$ mol m<sup>-2</sup> day<sup>-1</sup>, to satisfy the hypothesis that rapid removal of large SSA particles removes a majority of NSS from SO<sub>2</sub>. A 2-3-fold (not possible) increase in coarse-mode dry deposition velocities would accomplish the 1.4  $\mu$ mol m<sup>-2</sup> day<sup>-1</sup> dry deposition flux necessary to achieve a 6-7% coarse NSS fraction and "scrub out" the fraction of SO<sub>2</sub> that Faloona et al. (2010) assign to the heterogeneous SSA oxidation pathway.

Our observations of  $NO_3^-$ , excess Cl<sup>-</sup>, and MS<sup>-</sup> (Figure 10) on supermicron particles in molar quantities exceeding NSS favor the arguments that little NSS production occurs on coarse SSA particles and that dry removal of large particles is not significant. Observed MS<sup>-</sup> on coarse SSA was 0.08 nmol m<sup>-3</sup> in PASE with a precursor gas-phase MSA concentration of  $3x10^{-3}$  nmol m<sup>-3</sup>. MSA's extremely high solubility predicts that it will primarily associate with hydrated particles in the humid boundary layer. However, such a large difference in concentration argues that the sea-salt mode has a lifetime of days in order to accumulate the observed amount of particulate MS<sup>-</sup> (Davis et al., 1999).

### Homogeneous Oxidation of SO<sub>2</sub>

OH homogeneously oxidizes  $SO_2$  to  $H_2SO_4$  vapor. Measurements of gas-phase sulfuric acid from Mauldin's chemical ionization mass spectrometer (CIMS) were averaged over the half-hour MOI samples and used to calculate the potential contribution

of condensed sulfuric acid vapor to the NSS mass observed. In environments near anthropogenic pollution sources, Bardouki et al. (2003) determined that condensational uptake of H<sub>2</sub>SO<sub>4</sub> represents a large portion of the NSS on sea salt particles. Despite our study site's great distance from anthropogenic pollution, we occasionally detected pollution layers characterized by elevated SO<sub>2</sub> or (what were hypothesized to be) aged ship plumes, so anthropogenic sources of excess sulfate should not be discounted (Dominguez et al., 2008). To compute the rate of homogeneous oxidation in the Christmas Island MBL, we estimated the flux of sulfuric acid vapor onto particles. By assuming that all H<sub>2</sub>SO<sub>4</sub> (g) originates via the OH + SO<sub>2</sub>  $\rightarrow$  H<sub>2</sub>SO<sub>4</sub> reaction (Reactions 5-7), that the acidic gas is in steady state with its precursor, and that the only sink for H<sub>2</sub>SO<sub>4</sub> is removal to the surface of aerosol, the rate of condensational uptake of H<sub>2</sub>SO<sub>4</sub> onto sea salt particles can be calculated:

$$k[\mathrm{SO}_2][\mathrm{OH}] = k_c[\mathrm{H}_2\mathrm{SO}_4] \tag{19}$$

We can express the homogenous production rate as:

$$P_{\text{homogeneous}} = \frac{\Delta NSS_{homo}}{\Delta t} = k[SO_2][OH]$$
(20)

Where *k* is  $8.5 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298K (DeMore et al., 1997). The highly timeresolved OH and SO<sub>2</sub> concentrations available from other groups were averaged over the corresponding MOI sample legs. Rates of H<sub>2</sub>SO<sub>4</sub>-derived NSS formation per time were thus calculated flight by flight to estimate its average hourly contribution to total NSS. The photochemical dependence of H<sub>2</sub>SO<sub>4</sub> formation is reflected in the temporal dependence of uptake of the gas onto SSA. Rates of condensation peak during the midday when the concentration of OH radicals is highest.

According to our calculations, the project average rate of NSS formation from sulfuric acid vapor uptake onto aerosol surface was  $0.9 \pm 0.3$  ppt hr<sup>-1</sup> or  $0.30 \pm 0.1$  umol  $m^{-2} dav^{-1}$ . If we assume a 3 day period as a minimum estimate for the lifetime of accumulation mode marine aerosol against washout (Chameides and Stelson, 1992), this can amount to approximately 30 ppt on average. 23% of the observed total NSS (145 ppt) could be coming from this source. Figure 5 displays Faloona et al.'s (2010) estimated daily flux of SO<sub>2</sub> $\rightarrow$ H<sub>2</sub>SO<sub>4</sub> as 0.25 ± 0.09 µmol m<sup>-2</sup> day<sup>-1</sup>, which is close to our estimation  $(0.30 \pm 0.1 \text{ }\mu\text{mol }\text{m}^{-2} \text{ }\text{dav}^{-1})$  and could comprise 5-7% of the daily NSS production flux. The small difference between these homogeneous oxidation estimates arises from use of a slightly different set of flights for averaging. Mass flux calculations (Figure 20) indicate that H<sub>2</sub>SO<sub>4</sub> vapor distributes by particle radius (Seinfeld and Pandis, 2006), and a typical number distribution in the MBL (Figure 1) indicates that ~15% of H<sub>2</sub>SO<sub>4</sub> mass adsorbs on supermicron SSA with the remaining ~85% condensing on submicron aerosol. This mechanism adds  $0.25 \ \mu mol \ m^{-2} \ day^{-1}$  to the daily fine-mode NSS production. Condensation of  $H_2SO_4$  on SSA could account for 0.04 µmol m<sup>-2</sup> day<sup>-1</sup> (10%) of the 0.39  $\mu$ mol m<sup>-2</sup> day<sup>-1</sup> coarse NSS observed in PASE (to the exclusion of the in-particle oxidation of SO<sub>2</sub>).

#### **In-Cloud Oxidation of SO<sub>2</sub>**

We took three approaches to estimating the amount of sulfate produced in cloud. The first involves rudimentary  $SO_2 \rightarrow SO_4^{2^-}$  chemical kinetic calculations based on project-average vapor-phase concentrations and general cloud parameters estimated for PASE. The second approach analyzes the measured proportion of DMS and SO<sub>2</sub> in individual cloud encounters to approximate the consumption of  $SO_2$  as a parcel of air passes through a cloud. The third approach builds upon MBL sulfur fluxes calculated by Faloona et al. (2010) by budgeting sulfur chemistry in the BuL and the transport of cloudproduced fine NSS to the MBL. These various methods for quantifying the role of clouds in PASE NSS production provide us with upper and lower limits for in-cloud  $SO_2$ oxidation.

Before addressing these approaches, we sought to establish whether cloudmodified aerosol was ubiquitous in the PASE MBL and whether SO<sub>2</sub> became depleted in the presence of cloud. The effect of cloud processing on the aerosol number distribution is evident in Figure 13, which displays bimodal distributions. Hoppel minima (Hoppel et al., 1986) observed between ~0.07 and 0.09  $\mu$ m signify that cloud processing has removed particles from the gap sizes and grown them using gas-phase species and coagulation into the optically-important 0.08 to 0.5  $\mu$ m size range. Observation of the Hoppel minimum in the BL and the BuL in all PASE flights suggests much of the NSS was formed in-cloud and there was extensive interaction between these two layers. The close resemblance of the LDMA number distributions in the BL and BuL indicate that most small particles in the BL had grown in clouds, which were confined to the BuL throughout PASE.

We plotted  $SO_2$  in the BuL vs. time (Figure 21) with liquid water content (LWC) as an indicator for cloud encounters. In the BuL, there is no  $SO_2$  loss from dry deposition to the surface. Hence, any decrease in the  $SO_2$  concentrations in this layer must be attributed to either scavenging by cloud droplets or mixing with a lower- $SO_2$  airmass. In this typical daytime flight (RF03), we observed large LWC increases (cloud penetrations)

correlating with significant decreases of  $SO_2$  as shown in Figure 21a. Figure 21b shows the LWC and  $SO_2$  from RF14, a flight influenced by cloud rolls. Figure 21 presents a strong argument for sustained production of NSS in the cloud-containing BuL. We hypothesize that clouds are a significant mechanism for the transfer of mass in the remote BL: they are potentially responsible for a large portion of NSS production and the movement of air between the BL and the BuL.

The primary aqueous-phase reactions governing in-cloud oxidation of SO<sub>2</sub> are:

$$S(IV) + H_2O_2 \to S(VI) + H_2O \qquad k_{298} = 7.5 \times 10^7 \qquad (3)$$
$$S(IV) + O_3 \to S(VI) + O_2 \qquad k_{298} = 3.7 \times 10^5 \qquad (4)$$

Reaction 3 is rapid and essentially pH-independent over the pH range of atmospheric interest, but reaction 4 is highly pH-dependent, only becoming faster than reaction 3 at pH>5.5 (Seinfeld and Pandis, 2006). It is unimportant in cloudwater as its pH is usually 5.6 or less (Chameides and Stelson, 1992). As the  $H_2O_{2(g)}$  was approximately 1 ppbv and  $O_3$  ranged from 13 to 19 ppbv throughout PASE, there was stoichiometrically-sufficient oxidant to heterogeneously oxidize <0.1 ppbv of SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup> in cloud droplets.

BuL clouds cycle BL air through the BuL. How often would BL air enter the BuL and become a cloud? Our method for approximating cloud cover relied on the down-welling UV irradiance for sample legs flown at the top of the MBL just below the clouds. We assumed that rapid, significant decreases in UV were due to cloud above the aircraft. The first panel of Figure 22 illustrates the result of a 300-point median filter applied to UV irradiance to find baseline UV irradiance (UVsmooth) throughout each flight. A ratio of UV/UVsmooth < 1 presumably indicates the aircraft is below cloud, though we chose a slightly lower threshold ratio of 0.96 for cloudiness based on a histogram of ratios (Figure 22b) for PASE flights. We chose sample legs flown midday at the top of the boundary layer so that the angle of the sun did not bias the classification process for overhead clouds. The cumulative probability (Figure 22c) at UV/UVsmooth = 0.96 for each flight is the % cloud cover for that flight. For example, RF03 (Figure 22) experienced 16% cloud cover. The PASE project-average cloud cover was also 16%.

To calculate the turnover time for MBL air's passage through the cloud layer, we averaged the vertical wind velocities below cloud bounded by the UV/UVsmooth<0.96 criterion. The PASE average updraft velocity under cloud was  $0.12 \text{ m s}^{-1}$ . With an average BL height of 600 m, a parcel of air takes roughly 83 min to reach the cloudy BuL from the ocean's surface. In 24 hours, an air parcel could make 3 cycles (0.16 x 1440 min day<sup>-1</sup>/83 min) through the BuL, assuming that the air's ascent occurs below cloud, which covers 16% of the sample area. Descent occurs in the cloud-free regions.

Analysis of GOES (Geostationary Operational Environmental Satellite) images and videos recorded by the aircraft's forward-looking camera helped to ground-truth our cloud cover estimation for the study region in the majority of flights. In some cases, larger clusters of trade cumulus appear in the GOES images upwind of the flight region. Comparing our calculations for individual flights against the videos recorded by the forward-looking camera mounted at the front of the aircraft gave us a kind of sanity check to ensure that the aircraft did in fact fly below cloud for approximately 1/6 of the time on upper-BL legs.

## Approach 1: Chemical Kinetic Theory

For our first approach to computing cloud oxidation rates, we used Reactions 3 and 4 to estimate the amount of  $SO_2$  that a single cloud encounter could oxidize. By assuming that the aqueous-phase concentrations of H<sub>2</sub>O<sub>2</sub> and SO<sub>2</sub> were controlled by their respective gas-phase concentrations, we obtained dissolved species concentrations using Henry's Law constants. We use the assumption of equilibrium between gas-phase and aqueous-phase species. (This ignores mass transfer, so this is an upper limit.) We assume that a parcel spends about 7 min in a cloud (~500 m deep with mean updraft velocity of 1.2 m s<sup>-1</sup>) and that it has the PASE average LWC of 0.45 g m<sup>-3</sup> (during cloud encounters) with a conservative cloud-water pH of 4.5 (neglecting pH change over the course of the reaction). This simplistic calculation fails to describe the horizontal spreading of air once entrained in cloud, but many clouds in PASE were small and optically-thin, suggesting that a given parcel's transit time through them was relatively short as were the total lifetimes of these small cumulus clouds. Using the mean  $[SO_2]$  (50 pptv),  $[H_2O_{2(g)}]$  (1 ppbv), and  $[O_{3(g)}]$  (13 ppbv), we calculated that ~50 ± 30% of the original SO<sub>2</sub> (or S(IV)) would be consumed to yield NSS in a single cloud encounter when taking into account both Reactions 3 and 4. At higher pH and LWC, these reactions become more rapid (especially Reaction 4) with the potential of depleting the  $SO_2$  stock in a single pass. However, there are other factors to account for such as the reaction's self-limiting pH changes as sulfate is formed, entrainment of new air into the cloud, mass transfer rates, and mixing processes.

#### Approach 2: Gas-Phase Observation

The observations of SO<sub>2</sub> decreases and DMS peaks in cloud are the basis of our second approach (no coherent changes in ozone were observed). We surveyed flights with multiple BuL legs and identified cloud passes such as those presented in Figure 21 where sudden increases in LWC match with drops in SO<sub>2</sub>. Coinciding with these sharp drops in SO<sub>2</sub> concentration, DMS usually peaked sharply during these encounters, indicating the transport of BL air to the BuL via strong updrafts under and within cloud. Assuming that the fractional mixing of SO<sub>2</sub> in the BL with SO<sub>2</sub> in the BuL is equivalent to the mixing that DMS exhibits between these two layers, we used the following equation to calculate the amount of SO<sub>2</sub> that we expect in the BuL:

$$[DMS]_{peak} = x[DMS]_{BL} + (1-x)[DMS]_{BuL}$$
(19)

We first applied Equation 19 to the DMS peaks during cloud encounters in order to solve for *x*, which essentially accounts for the dilution of each species as it ascends through the cloud into the BuL. We then solved for the amount of SO<sub>2</sub> that we expect in each cloud pass. The difference between the actual measured SO<sub>2</sub> and the expected SO<sub>2</sub> in the cloud encounter represents the amount of SO<sub>2</sub> oxidized as a parcel of air passes through a cloud. Because there is variability amongst cloud-type and microstructure, we present a summary (Table 7) of these calculations for PASE flights with cloud-level legs where this method was appropriate. This table displays the calculated SO<sub>2</sub> loss per cloud pass (which we assume results in a molar equivalent of NSS) and percent of SO<sub>2</sub> consumed per cloud pass. Most of these flights were daytime flights, though one flight with a nighttime takeoff (RF13) demonstrated that cloud processing continues to occur at night when there is less SO<sub>2</sub> and ample H<sub>2</sub>O<sub>2</sub>. On average, rising air parcels lost ~50% of their  $SO_2$  to chemical reaction in cloud, with a range of 20-80%. This  $50 \pm 30\%$   $SO_2$  loss to aqueous-phase oxidation in cloud agrees well with the 50%  $SO_2$  loss estimated in our first-approach assessment of this pathway.

As we previously estimated, BL air cycles through cloud ~3 times per day, though other estimates have been higher. The net transport of SO<sub>2</sub> to the BuL measured by eddy covariance (Faloona et al., 2010) suggests that the majority of SO<sub>2</sub> vented to the BuL is consumed in clouds and does not reenter the BL as SO<sub>2</sub>. Clouds processing an average BuL SO<sub>2</sub> concentration of 34 pptv could produce 17-18 ppt of accumulation-mode NSS per cycle (with a 50% consumption of SO<sub>2</sub> per cloud cycle) and  $50 \pm 15$  ppt day<sup>-1</sup>. During the 1994 Christmas Island experiment, Clarke et al. (1996) estimated that clouds could grow 55ppt NSS per day based on a separate approach comparing diurnal variations in accumulation-mode mass and ozone concentrations. These authors also estimated an aerosol lifetime of ~4 days. If we assume an aerosol lifetime of 3 days, cloud processing could produce 153-162 ppt, which is very close to the 145 ppt average NSS observed in the PASE troposphere.

## Approach 3: SO<sub>2</sub> Flux Budgets

Faloona et al. (2010) calculated DMS and SO<sub>2</sub> fluxes to construct an overall budget for PASE sulfur chemistry (Figure 5). Using these MBL fluxes for our third approach to estimating cloud processing, we added the eddy-covariance-measured SO<sub>2</sub> and NSS fluxes into the BuL from the BL and FT, which allowed us to constrain the flux of NSS transported to the BL. As Figure 5 shows, a net 0.2  $\mu$ mol m<sup>-2</sup> day<sup>-1</sup> of MBL SO<sub>2</sub> is transported into the BuL. To address the chemistry occurring in the BuL, we
developed Figure 23 using Figure 5 as a foundation. The net 0.9  $\mu$ mol DMS m<sup>-2</sup> day<sup>-1</sup> venting into the BuL will be mostly oxidized ( $\gamma = 0.7$ ) to NSS, resulting in 0.8  $\mu$ mol SO<sub>2</sub> m<sup>-2</sup> day<sup>-1</sup> entering the BuL from MBL sources. SO<sub>2</sub> in the FT was typically 25 pptv, but during some polluted flights, the median was ~45 pptv. We treated the SO<sub>2</sub> entraining at 3-4 mm s<sup>-1</sup> into the BuL as a range of these values, giving us 0.3 – 0.6  $\mu$ mol SO<sub>2</sub> m<sup>-2</sup> day<sup>-1</sup> entering the BuL from FT sources (Figure 23). MBL and FT sources combine to yield 1.1 – 1.4  $\mu$ mol SO<sub>2</sub> m<sup>-2</sup> day<sup>-1</sup>, which clouds must then oxidize to produce 1.1 – 1.4  $\mu$ mol NSS m<sup>-2</sup> day<sup>-1</sup> (the BL $\rightarrow$ BuL eddy covariance fluxes were net, meaning they accounted for any DMS or SO<sub>2</sub> moving back into the BL). We assume that in-cloud oxidation solely produced the fine NSS exported to the MBL from the BuL, with the exception of the NSS entrained into the BuL from the FT.

Because we are not evaluating changes in concentration across the inversions separating the tropospheric layers, we report fluxes of sulfur mass moving from one reservoir to another without the necessity of accounting for the movement of clean air that accompanies these fluxes. We acknowledge that divergence occurs when transporting air masses across these boundaries and that divergence will move mass out of the MBL and BuL. We identify divergence as another possible loss mechanism for NSS but cannot quantify it. Presumably all sulfur forms will be lost proportionally by divergence, so it should not change our conclusions about relative NSS production rates by the three mechanisms.

In a 600 m BL, this  $1.1 - 1.4 \mu mol NSS m^{-2} day^{-1}$  translates to 40 - 51 ppt NSS day<sup>-1</sup> from SO<sub>2</sub> oxidation in cloud, which is consistent with the findings of the first two approaches (~50 ppt NSS day<sup>-1</sup>). Following from our observations,  $0.3 - 0.6 \mu mol m^{-2}$ 

day<sup>-1</sup> of this flux entrained from the FT as SO<sub>2</sub>. This BuL $\rightarrow$ BL flux then increases to a range of 1.9 - 4.2 µmol NSS m<sup>-2</sup> day<sup>-1</sup> entraining into the BL when we account for the NSS subsiding from the FT to the BuL. Accounting for the extra NSS coming from the FT, 50 – 175 ppt day<sup>-1</sup> may be entering the BL from above. Cloud-regulated production of NSS thus consumed 33-46% of the total SO<sub>2</sub> source and produced 45-80% of the NSS burden in the tropical atmosphere (Table 3). Table 3 shows the primary fluxes and the percentage that flux represents of the total SO<sub>2</sub> source flux, which might be a combination of MBL, BuL, and FT SO<sub>2</sub>.

The 50  $\pm$  15 ppt NSS day<sup>-1</sup> in-cloud production rate from our first two approaches converts to  $1.4 - 1.5 \mu mol NSS m^{-2} day^{-1}$  in a 600 m MBL and closely aligns with our budget-derived NSS rate of  $1.1 - 1.4 \mu mol NSS m^{-2} day^{-1}$  obtained from our third approach to estimating conversion of SO<sub>2</sub> to  $SO_4^{2-}$  in clouds. This in-cloud NSS production flux comprises 33-90% of the fine NSS cycling into the MBL from above (the remainder is NSS from the FT) and consumes 33-46% of the total PASE SO<sub>2</sub> source (Table 3). Our calculated in-cloud formation rates imply that cloud uptake is not only a large sink for SO<sub>2</sub> but also the dominant NSS formation pathway in the Christmas Island environment. O'Dowd et al. (1997) argue that 85% of the NSS production can be explained by cloud processing. In certain conditions, it may be possible that an even greater fraction of sulfate formation in the remote troposphere originates from multiphase chemistry in clouds. Non-precipitating trade wind cumulus that populated the study region are capable of hosting numerous cycles between aerosol (as CCN) and cloud droplets, analogous to the condensation-evaporation cycling of water in the atmosphere (ten Brink et al., 1987). If NSS particles are not removed by wet deposition via

precipitating cloud, the consequent increase in number of these cycles would significantly increase the accumulation mode NSS mass in the MBL.

#### **Entrainment:**

In 1994, the nighttime decrease in NSS concentrations was attributed to an entrainment velocity of  $5.0 \pm 2.0$  mm s<sup>-1</sup> (Huebert et al., 1996), which is capable of diluting concentrations by 30% in a 600 m MBL in a day if the entraining air does not contain NSS. Wood et al. (2003) report an entrainment velocity in the equatorial Pacific of  $4.8 \pm 1.0$  mm s<sup>-1</sup>, similar to that of Huebert et al. (1996). Entrainment from the FT is capable of either bringing mass into the lower tropospheric layers or diluting the concentrations in these layers. Because PASE was located in a region of large-scale subsidence, FT air sinks into the BuL regardless of any concentration gradient. In the subtropical remote marine environment, Raes (1995) found FT-MBL exchange to be an important mechanism for controlling CN and CCN in the MBL. Whether this process significantly affects the NSS in the MBL by reducing or enhancing concentrations remains an important question.

#### Non-Local Air in the Remote MBL

When observing the atmospheric processes of a particular region (i.e. the tropical Pacific), it is essential to establish the fraction of aerosol that is locally-generated. As mentioned earlier, we saw pollution during certain research flights, indicating occasional long-range transport of aerosol precursors. To complete the NSS budget, we approximated the amount of  $SO_2$  and NSS entraining into the PASE BuL from the FT, as

depicted in Figure 23. The PASE FT had markers of mineral dust (APS coarse mass (Figure 14) coupled with MOI excess Ca<sup>2+</sup> and Mg<sup>2+</sup>; nephelometer total scattering (Figure 9)), and anthropogenic pollution (enhanced layers of SO<sub>2</sub> and CO (Figure 15; Figure 8)), and perhaps volcanogenic aerosol (excess Cl<sup>-</sup> (Figure 10) and SO<sub>2</sub>). The meteorology of the La Niña ENSO state caused a deficiency of clouds and precipitation (Figures 16 and 17) combined with slightly cooler conditions and increased probability of long-range transport from South America (Figure 24), relative to 1994.

On various flights, we observed layers of enhanced SO<sub>2</sub> associated with enhanced CO (an indicator for biomass burning, also see Figure 8) in the FT. Figure 15 illustrates a comparison between a clean flight (RF03) and a polluted flight (RF08). Any mass found in the FT must not be from local sources because subsidence prevails in this region. The average PASE background SO<sub>2</sub> in the FT during cleaner flights is 20-25 pptv, but we encountered layers of 45 pptv in RF08 and 102 pptv in RF14. The range of values for the FT NSS flux (Figure 23) reflects this variability in SO<sub>2</sub> concentrations aloft. On polluted flights, we also measured enhanced fine and coarse mass in the FT with the LDMA and APS (Figure 14). In the case of RF08, we observed excess  $Ca^{2+}$  and excess  $Mg^{2+}$  with the MOI in the FT, suggesting that mineral dust was present.

The ambient aerosol sampled in PASE was a mixture of sea salt, some mineral dust, carbonaceous aerosol, and other products of heterogeneous processes such as chloride, sulfate, and nitrate, which affect the chemistry and CCN concentration of the MBL. Influence from aerosol generated in South America has been observed in this region previously during the PEM-Tropics-B airborne experiment; air originating from the northern areas of this continent also exhibited the strongest pollution signature

compared to air from Australia and southern Africa (Maloney et al., 2001). Large-scale surveys of Amazonian aerosol conducted by aircraft (Artaxo et al., 1998) have revealed soil dust, natural biogenic material, and organic matter in biomass burning aerosol. Influences from non-local aerosol at Christmas Island could include alteration of wet scavenging rates (by changing hygroscopicity) and the ability to nucleate cloud droplets. Through pH modification, non-local aerosol also affects the uptake of SO<sub>2</sub> on sea salt by depleting the local alkalinity supply. However, biomass burning and dust aerosol carry with them enrichments of inorganic species such as sulfate and nitrate that vary according to their sources (Echalar et al., 1995; Kline et al., 2004), making it very difficult (with our paucity of FT legs) to separate the sulfate produced in the remote marine environment from the sulfate transported there from fires or pollution. Biogeochemical cycles and chemical budgets of species such as NSS in the marine BL are subject to considerable alteration when dust or anthropogenic aerosol is present.

We found chloride enrichments in all flights, indicating mixtures of dust, BBA, and SSA. Cl<sup>-</sup> enrichments were calculated using the seawater molar ratio of Cl<sup>-</sup> to Na<sup>+</sup> (1.165); any ratio exceeding 1 is an enrichment, and those below 1 are deficits. Very large chloride enhancements ( $1.6 \pm 0.1$ ) on large particles were observed on multiple flights, though it was sometimes difficult to quantify them due to the small loadings on the large MOI stages coupled with a higher detection limit for sodium than for chloride, particularly on stages 1 and 2. Large particles tend to be enriched in Cl<sup>-</sup>, while the smaller stages with measureable sea salt lack Cl<sup>-</sup> because they lose it as they are acidified by uptake of SO<sub>2</sub> and HNO<sub>3</sub> (McInnes et al., 1994).

When confined to flights without enhanced CO (a biomass burning indicator), the mean Cl enhancement decreases to 1.2, which is within the uncertainty of 1.0. On the other hand, flights with enhanced CO concentrations exhibited Cl enrichments at an average of 2.1. It is certain that Cl alters the chemistry of the MBL by reducing aerosol pH and affecting the end products of DMS oxidation (von Glasow et al., 2002; von Glasow and Crutzen, 2004).

It is likely that aerosol was transported from South America. Back trajectories of winds aloft were traced back to this region (Figure 24). The state of the southern oscillation in the late summer of 2007 (La Niña), strengthened easterly trade winds, creating optimal conditions for long-range transport from this continent. Satellite images from CALIPSO reveal thick aerosol layers over South America as well as plumes of aerosol in the FT very close to our study site (Figures 25 and 26). Furthermore, the PASE timeframe is the primary fire season in the Amazon Basin (Holben et al., 1996). Volcanic emissions are also a plausible source of atmospheric Cl. Transport of air from South America may include transport of gaseous and particulate species emitted by active volcanoes.

According to MOI analyses, mass distributions, CO, and SO<sub>2</sub> profiles (e.g. Figure 15), there is evidence in PASE of periodic occurrences of continental or anthropogenic influence, so we cannot classify the air composition as strictly originating from the remote marine environment. Due to the presence of dust and combustion aerosol from long-range transport, the S chemistry was not exclusively controlled by local sources. We attempted to estimate the influx of NSS from the FT to constrain the outside influence on the tropical Pacific.

#### **Summary of PASE NSS production**

MBL

We constructed an overall budget for PASE sulfur chemistry (Figure 23) by building upon Faloona et al.'s (2010) eddy-covariance-measured MBL DMS and SO2 fluxes (Figure 5). Their estimated total SO<sub>2</sub> production was  $2.8 \pm 1.4 \mu mol m^{-2} dav^{-1}$ from oxidation of DMS by OH (Table 3). Of this source,  $0.75 \pm 0.33 \mu mol m^{-2} day^{-1} dry$ deposited to the ocean surface and  $0.2 \pm 0.16 \,\mu\text{mol}\,\text{m}^{-2}\,\text{day}^{-1}$  vented into the BuL, leaving 1.8  $\mu$ mol m<sup>-2</sup> day<sup>-1</sup> of SO<sub>2</sub> in the MBL that is either homogeneously oxidized by OH or taken up by coarse SSA. Measurements of [OH] and [SO<sub>2</sub>] allowed for the constraint of the homogeneous oxidation to  $0.25 \pm 0.09 \ \mu mol \ m^{-2} \ day^{-1}$  (nearly the same as our  $3.0 \pm$ 1.0  $\mu$ mol m<sup>-2</sup> day<sup>-1</sup> for this term), which then left a flux of  $1.6 \pm 1.0 \mu$ mol SO<sub>2</sub> m<sup>-2</sup> day<sup>-1</sup> for condensation on SSA. As this last residual term relied heavily upon Faloona et al.'s (2010) assumed value for  $\gamma$  (Table 6), we believe that this heterogeneous flux is an overestimate. Our coarse NSS (6-12% of total NSS) observations, coarse NO<sub>3</sub><sup>-</sup> observations, and dry deposition velocity calculations support a reduced coarse NSS production of  $0.73 \pm 1.0$  µmol coarse NSS m<sup>-2</sup> day<sup>-1</sup> using a  $\gamma$  of 0.7. This more widely reported value for  $\gamma$  (Faloona 2009) reduces the SO<sub>2</sub> source from 2.75 ± 1.4  $\mu$ mol m<sup>-2</sup> day<sup>-1</sup> to  $1.93 \pm 1.4 \ \mu mol \ m^{-2} \ day^{-1}$  (Table 3).

Regarding NSS production in the MBL, homogeneous oxidation of SO<sub>2</sub> to  $H_2SO_{4(g)}$  followed by condensation on mostly submicron aerosol (0.3 µmol m<sup>-2</sup> day<sup>-1</sup>) corresponds to 10-12% of the daily SO<sub>2</sub> consumption (Table 3) and 6-10% of the daily NSS production with FT sources and 16% of total NSS without FT sources. Conversion of SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup> by O<sub>3</sub> oxidation in SSA particles (0.7 µmol m<sup>-2</sup> day<sup>-1</sup>, inferred from the

BL-inferred SO<sub>2</sub> residual) represents 13-24% of the daily NSS production (38% without FT sources) and 23-28% of the daily SO<sub>2</sub> sink.

BuL

Faloona et al. (2010) measured  $0.2 \pm 0.16 \mu$ mol m<sup>-2</sup> day<sup>-1</sup> of MBL SO<sub>2</sub> and  $0.9 \pm 0.6 \mu$ mol m<sup>-2</sup> day<sup>-1</sup> of DMS is being transported into the BuL. We assume that 70% of the DMS vented into the BuL is oxidized to SO<sub>2</sub>, resulting in a total of 0.8 µmol SO<sub>2</sub> m<sup>-2</sup> day<sup>-1</sup> entering the BuL from MBL sources (Figure 5). All of this must re-enter the BL as NSS. We treated the SO<sub>2</sub> entraining at 3-4 mm s<sup>-1</sup> into the BuL from the FT as a range of values (clean vs. polluted), giving us  $0.3 - 0.6 \mu$ mol SO<sub>2</sub> m<sup>-2</sup> day<sup>-1</sup> entering the BuL from FT sources (Figure 23). MBL and FT sources combine to yield  $1.1 - 1.4 \mu$ mol SO<sub>2</sub> m<sup>-2</sup> day<sup>-1</sup>, which clouds then oxidize to produce  $1.1 - 1.4 \mu$ mol NSS m<sup>-2</sup> day<sup>-1</sup>. From a range of NSS observations in the FT, we add  $0.8 - 2.8 \mu$ mol m<sup>-2</sup> day<sup>-1</sup> FT NSS to the NSS produced in the BuL by cloud processing  $(1.1 - 1.4 \mu$ mol NSS m<sup>-2</sup> day<sup>-1</sup>), resulting in a total of a  $1.9 - 4.2 \mu$ mol NSS m<sup>-2</sup> day<sup>-1</sup> source to the MBL that is presumed to be predominantly submicron (see Table 3).

In the case of Figure 23 where we only consider MBL and BuL sulfur fluxes, incloud oxidation produces 0.8  $\mu$ mol m<sup>-2</sup> day<sup>-1</sup> NSS, which consumes 33% of the daily SO<sub>2</sub> (Table 3) and produces 44% of the daily NSS.

When we include FT sources per Figure 23, oxidation of SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup> by H<sub>2</sub>O<sub>2</sub> in cloud droplets represents  $1.1 - 1.4 \mu mol m^{-2} day^{-1}$  of NSS production, making up 27-45% of the total NSS yield and 33-46% of the total SO<sub>2</sub> sink. We attribute a 26-42% portion of this NSS generated in cloud to the 0.3-0.6  $\mu mol m^{-2} day^{-1}$  SO<sub>2</sub> flux from the FT, which

represents 11-19% of the daily total SO<sub>2</sub> (Table 3). Depending on the composition of the FT, we estimate that  $0.8 - 2.8 \ \mu mol NSS \ m^{-2} \ day^{-1}$  entrained into the BuL from the FT, assuming an entrainment rate of 3-4 mm s<sup>-1</sup>. When long-range transport brings pollution to the lower FT at Christmas Island, the FT source of NSS could surpass cloud processing as the dominant NSS source. We estimate that subsiding NSS mass from the FT is responsible for 28-54% of the NSS burden.

Overall, NSS production in the MBL comprises only 19-34% of the total daily NSS production flux when FT sources of sulfur are considered. The BuL exports the remaining 66-81% of NSS to the MBL when a portion of the BuL NSS flux originates in the FT. Depending on the strength of the sulfur source in the FT, in-cloud oxidation and quite possibly the influx of sulfate from the FT are the most important NSS production mechanisms in this environment under the conditions prevalent in PASE. If we neglect contributions from the FT, the MBL mechanisms of NSS formation involving uptake of sulfur gases to SSA account for 40% of the total NSS production per day and 40% of the SO<sub>2</sub> consumption (28% for the uptake of SO<sub>2</sub> by SSA mechanism alone). At the upper limit of our dry deposition flux, this scenario would produce the observed coarse NSS mass-fraction, but it can only generate 45% of the measured daily NSS burden. The budgets that include the FT, on the other hand, are capable of explaining the 4.0  $\mu$ mol m<sup>-2</sup> day<sup>-1</sup> NSS that we observed in PASE. As our small-concentration-FT scenario yields 2.9  $\mu$ mol m<sup>-2</sup> day<sup>-1</sup> and our high-concentration-FT scenario yields 5.2  $\mu$ mol m<sup>-2</sup> day<sup>-1</sup>, our results indicate that an FT source in the middle of our range of estimates can satisfy our observations.

# **CHAPTER 5**

# **CONCLUSIONS**

We estimated the portions of the NSS production flux in the equatorial Pacific contributed by condensation of homogeneously-produced  $H_2SO_4$ , oxidation of  $SO_2$  by  $H_2O_2$  in cloud, oxidation of  $SO_2$  by  $O_3$  on SSA, and entrainment from the FT because their magnitudes constrain the aerosol (NSS and SSA) direct and indirect effects on the radiative balance of the remote BL. We also estimated the NSS removal by dry deposition for our treatment of the NSS budget in a non-precipitating, 16% cloud-cover marine atmosphere.

#### Homogeneous oxidation of SO<sub>2</sub>

We calculated that conversion of SO<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub> vapor followed by uptake onto aerosol surface area was responsible for a maximum of  $0.9 \pm 0.3$  ppt hr<sup>-1</sup> or  $0.3 \pm 0.1$ µmol NSS m<sup>-2</sup> day<sup>-1</sup>. This mechanism may account for ~20% of the NSS burden assuming an aerosol lifetime of 3 days. Our estimated flux is very similar to the homogeneous oxidation flux calculated by Faloona et al. (2010) of  $0.25 \pm 0.09$  µmol m<sup>-2</sup> day<sup>-1</sup>, which corresponds to 5-8% of the total PASE NSS production. Onto which particles sizes does this vapor condense? If H<sub>2</sub>SO<sub>4</sub> adsorbs with particle radius, then roughly 15% of it will associate with the coarse mode, leaving the possibility that a small portion of the measured coarse NSS formed via uptake of H<sub>2</sub>SO<sub>4</sub> by SSA.

#### **In-Cloud oxidation of SO<sub>2</sub>**

Producing  $1.1 - 1.4 \mu mol NSS m^{-2} day^{-1}$ , in-cloud oxidation of SO<sub>2</sub> corresponded to the largest single pathway for secondary sulfate production below the trade wind inversion in the equatorial Pacific. This flux was calculated three ways: from gas-phase observation, chemical kinetic theory, and SO<sub>2</sub> flux budgets, all of which agreed closely. Our estimations were also very similar to the Clarke et al. (1996) 55 ppt per day in-cloud growth inferred from ground-based measurements of accumulation-mode mass (0.07 um < D<sub>p</sub> < 0.3 um) and O<sub>3</sub> fluctuations at Christmas Island. We found that ~50% of SO<sub>2</sub> is consumed in a single cloud pass using two consistent approaches. We determined that 16% cover of non-precipitating clouds in the BuL is capable of recycling MBL air an average of 3 times per day, scavenging particles and gases vented up from the BL and subsiding from the FT. The PASE setting would be considered clear-sky conditions with moderate wind speeds, in which the SSA mechanism is thought by some authors (Sievering et al., 1991; Mari et al., 1999; Faloona et al., 2010) to prevail; however, we conclude that clouds are at least as large as any other mechanism of MBL particulate sulfate production even with <20% cloud cover. Of the total NSS production flux, oxidation of SO<sub>2</sub> in clouds represents 27-44%, which is the largest local NSS source in the MBL-BuL. If only DMS-derived SO<sub>2</sub> is considered, in-cloud oxidation consumes 33% of SO<sub>2</sub> and, if non-local sources are included, 46% of the total SO<sub>2</sub> is made in the MBL and imported from the FT.

#### **Oxidation of SO<sub>2</sub> in SSA Particles**

Authors such as Garciullo et al. (1999) contend that oxidation of  $SO_2$  in cloud and oxidation in SSA liquid water are the principal pathways for NSS formation in the remote marine environment. We did not find strong evidence to suggest that NSS production is dominated by the conversion of  $SO_2$  by  $O_3$  in sea-salt particles since only 11% of the NSS mass was associated with the coarse mode. The supermicron NSS fraction increases in flights containing indicators of non-local influence, a phenomenon which Li-Jones and Prospero (1998) have also observed in the Atlantic during Saharan dust episodes.

If  $\gamma = 0.7$ , MBL coarse NSS production from the SSA-O<sub>3</sub> mechanism was 0.73 µmol NSS m<sup>-2</sup> day<sup>-1</sup>. At 13-24% of the total NSS production flux, conversion of SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup> in SSA particles is about 1/2 the rate of heterogeneous conversion in clouds. When there is no input from the FT, this mechanism produces 38% of the total NSS in the MBL, making it indistinguishable from the in-cloud oxidation mechanism; however, the sulfur budget necessitates entrainment of FT sulfur in order to explain the observed daily NSS concentrations. Further studies are needed to evaluate the origin of coarse-mode NSS and its importance in the remote environment.

It has been proposed that very large and alkaline SSA particles that are so shortlived as to not be measurable are effectively sequestering large quantities of SO<sub>2</sub>. However, there is no evidence from the MOI, APS, or FSSP that such particles existed in the PASE environment. Furthermore, 0-2% of the NSS mass was associated with the largest MOI stage (15  $\mu$ m wet diameter), 0-2% on the stage below (9  $\mu$ m wet diameter), and 5% on the primary sea-salt stage (3.3  $\mu$ m wet diameter), yet there are significant portions of MS<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and Cl<sup>-</sup> observed on the coarse stages. Molar quantities of excess Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> exceeding those of NSS on the sea-salt mode would have acidified the coarse mode, practically shutting down the in-particle production of sulfate.

# **Dry Deposition of NSS**

In accordance with the model proposed by Slinn and Slinn (1980) and undetectably small [NSS] on particles  $> 6.5 \mu m$  wet diameter, we found that dry deposition can remove 0 - 0.8  $\mu$ mol m<sup>-2</sup> day<sup>-1</sup> of coarse NSS formed in sea-salt particles. If we assume that all the undetectable NSS on coarse stages was right at the MDL, dry deposition could be the primary removal mechanism for supermicron aerosol. Dry deposition of sea-salt particles could remove a maximum of 24% of SO<sub>2</sub> generated from DMS oxidation locally in the MBL per day (in the absence of non-local SO<sub>2</sub> entrained from the FT). However, if those un-measurable coarse NSS concentrations were zero, dry deposition of SSA would remove an insignificant portion of sulfur. Measurement uncertainties continue to hamper aerosol chemistry budgeting. Our coarse-mode dry deposition velocities were very similar to those used by Sievering et al. (1991) and Chameides and Stelson (1992) and were at the upper limit of dry deposition velocities given by most models (Lewis and Schwartz, 2004), so our estimation of dry removal is not responsible for the discrepancies between our findings and those of Faloona et al. (2010) concerning the amount of NSS formed on large SSA particles. Our results diminish the role of sea-salt particles in removing  $SO_2$  from the MBL in PASE from that claimed by some authors (Sievering et al., 1991; Luria et al., 1991; Suhre et al., 1995; Mari et., 1999; Faloona et al., 2010). Most of these studies derive their conclusions about heterogeneous SO<sub>2</sub> chemistry in SSA from models and poorly-described coarse/fine

measurements made in continentally-influenced environments (e.g., North Atlantic). We emphasize the need for constraining theory with high-quality, size-segregated observation when evaluating heterogeneous sulfur chemistry.

## Wet deposition

During wetter El Niño phases, wet deposition would presumably have removed a large fraction of both the coarse and fine particulate NSS mass, both at Christmas Island and farther upwind. Though TRMM satellites recorded very little rainfall, we did observe precipitating cloud on various flights, suggesting that minor removal by wet scavenging was likely. If rainfall occurs on a timescale of 3 days, wet deposition would out-compete dry deposition as a removal mechanism for aerosols below 6.5 µm diameter. In our daily NSS budget, dry deposition dominates coarse aerosol removal primarily due to the fact that we cannot quantify wet deposition and have little evidence for it during PASE.

# Entrainment

As Christmas Island lies in a region of large-scale subsidence, dilution by entrainment from the FT is one mechanism responsible for reducing the absolute NSS concentrations in the tropical Pacific lower troposphere. The unidirectional transport of FT air into the BuL represents a process by which BuL and MBL NSS concentrations are diluted in clean flights and enhanced in polluted flights. This complicated movement of air begs further study as to the degree of impact that it has on the MBL.

# FT SO<sub>2</sub> and NSS

Some SO<sub>2</sub> profiles that penetrated into the FT revealed pollution layers aloft (associated with increased concentrations of CO and CCN) on certain flights. We also observed NSS in the FT that was either imported from a distant source region or formed by multiphase reactions during transport. We accounted for the import of this mass in our budget of NSS chemistry by allowing a range of FT SO<sub>2</sub> and NSS to enter the BuL. This range of sulfur concentrations was representative of the conditions encountered in PASE, which were heterogeneous both in space and time. FT→BuL SO<sub>2</sub> fluxes ranged from 0.3 – 0.6 µmol m<sup>-2</sup> day<sup>-1</sup> and FT→BuL NSS fluxes ranged from 0.8 – 2.8 µmol m<sup>-2</sup> day<sup>-1</sup>. Of total BL NSS, FT NSS was a 28-54% portion and NSS generated in the BuL was 27-38%, demonstrating that pollution can compete with or even overshadow local NSS production. Once entrained into the BuL, we assumed that in-cloud oxidation converted FT SO<sub>2</sub> to NSS, which then combines with the FT NSS to comprise 38-65% of the total NSS production flux in the PASE atmosphere. Mass transported from the FT can significantly impact the sulfur burden even in the remote Pacific MBL.

Savoie et al. (1989) found that up to 60% of the NSS at Barbados was associated with mineral dust and that this NSS fraction was likely derived from anthropogenic sources rather than local soil composition in the Sahara. The high incidence of detection of pollution in PASE (~50% of 14 research flights) suggests that long-range transport of continental gases and particulate matter is common even in the isolated tropical Pacific, especially in dry subsidence regions.

# Non-Local Aerosol

The particulate CI<sup>-</sup> excesses that we saw in PASE were surprisingly large. As this ion is primarily associated with supermicron particles, it certainly limited the pH-dependent reaction between SO<sub>2</sub> and O<sub>3</sub> in large SSA particles. They quickly lose their alkalinity during multiphase chemistry with acid gases. Inorganic gas-phase Cl and Br radicals oxidize DMS, are taken up by deliquesced SSA, and react with tropospheric O<sub>3</sub> (Sander et al., 2003). Complex heterogeneous chemistry (surface reactions, reactions occurring in the bulk medium of aerosols, involving NOx, sulfur oxides, O<sub>3</sub>, organics, sunlight, clouds) may be taking place in the FT and in the lower troposphere along the latitude band stretching across the equatorial Pacific from South America. The consequence of this is that long-range transport of acids may deplete the alkalinity of the local system, especially when there is little precipitation to scavenge them. Further investigation is needed to characterize the spatial and temporal distribution of this climatically-important material that interacts with solar and thermal radiation and participates in geochemical cycling between land, air, and ocean.

#### **Implications for the Equatorial Pacific Remote MBL**

Our results strongly suggest that cloud processing, conversion of SO<sub>2</sub> in SSA, and when relevant, import of non-local sulfur (SO<sub>2</sub> and NSS) from the FT are of nearly equal importance as sources of NSS in the tropical remote MBL. During periods with little FT influence, heterogeneous loss of SO<sub>2</sub> to SSA may consume an amount of DMS-derived SO<sub>2</sub> comparable to in-cloud oxidation. For NSS production, uptake of SO<sub>2</sub> onto SSA and its subsequent conversion to coarse NSS yields (13-24%) of the daily NSS production

flux. Other mechanisms for coarse-mode NSS formation (e.g., NSS-SSA association facilitated by cloud processes) may be responsible for some of this NSS production that we attribute to SSA pathway. For the SO<sub>2</sub> budget, heterogeneous loss to SSA (23-28%) is roughly equal in importance to the dry deposition of SO<sub>2</sub> (24-30%) as a removal mechanism. On days with extensive entrainment of pollution from the FT, up to 65% of the daily NSS source may derive from continental SO<sub>2</sub> and NSS, potentially overshadowing any single NSS production mechanism in the tropical MBL DMS oxidation regime. Moreover, the upper bound on our FT sulfur flux estimate (3.4 µmol  $m^{-2}$  day<sup>-1</sup>) is comparable to the PASE DMS flux from the ocean (3.65 µmol  $m^{-2}$  day<sup>-1</sup>), of which 50% (1.8 µmol  $m^{-2}$  day<sup>-1</sup>) becomes NSS. Long-range transport may bring more NSS mass (0.8 – 2.8 µmol  $m^{-2}$  day<sup>-1</sup>) than can be produced by local DMS oxidation in the remote MBL. As the FT source estimates demonstrate, contributions of sulfur from the FT are highly variable and must be incorporated into the sulfur budget to properly treat the spectrum of conditions observed in a pollution-sensitive region.

What is the fate of biogenic DMS in the marine atmosphere? We based our analyses on budgetary approaches that began with sulfur gas fluxes measured using eddy covariance. (All the following numbers are project averages, in units of  $\mu$ mol m<sup>2</sup> day<sup>-1</sup>, followed by the standard deviation over all flights (not analytical uncertainties). Exceptions are percentages, %D representing percentage of the original DMS flux.) Of the 3.6 ± 1.5 DMS emission flux, about 1.9 ± 1.4 is converted to SO<sub>2</sub>. Of this, 0.8 ± 0.3 is dry-deposited to the ocean's surface. Homogeneous oxidation by OH converts 0.3 ± 0.1 into (mostly fine) NSS. Chemical loss in the MBL (presumably to SSA) is 0.7 ± 0.5.

The balance of DMS and SO<sub>2</sub> is oxidized in cloud before returning to the MBL as  $0.8 \pm 0.6$  (mostly fine) NSS.

Thus, of the original emitted DMS, dry deposition is 22%D; homogeneous oxidation by OH is 8%D; in-cloud oxidation by  $H_2O_2$  is 22%D; conversion on SSA by  $O_3$ is 19%D; and the 29%D balance is converted to other products of DMS oxidation. The rates of dry deposition, in-cloud oxidation, and oxidation on sea-salt are statistically indistinguishable from one another. Dry deposition of large SSA could conceivably remove as much as 22%D (if NSS on every coarse impactor stage was right at our minimum detection limit), but the rapid decrease of NSS toward larger sizes argues against this. PASE's La Niña conditions no doubt reduced cloudiness and in-cloud oxidation of SO<sub>2</sub>.

In the PASE environment, no one mechanism dominated the removal of DMS oxidation products. The variability of these mechanisms from flight to flight was, however, very large.

What controls the sulfate aerosol size distribution in the remote marine atmosphere? DMS is not the only source of sulfur; entrainment of SO<sub>2</sub> and NSS from the FT is also significant. During PASE the FT provided from 30 - 100%D, with no loss to organic S products. Other airborne programs have identified intense FT pollution layers from every continent but Antarctica. Thus, LRT can provide as little as  $\frac{1}{3}$  or up to >1x the NSS to the MBL as DMS does. Acids brought in by LRT probably reduced coarse aerosol pH, thus reducing SO<sub>2</sub> uptake by SSA.

Even in the middle of the Pacific, continental sources can dominate the MBL sulfur budget. The stronger trade winds and reduced upwind rainfall from La Niña probably increased the magnitude of this LRT term.

Our measured NSS size distributions found 88% of the NSS to be submicron, seemingly in conflict with Faloona et al. (2010), who argue that the vast majority of SO<sub>2</sub> is oxidized on SSA. The large FT source of (ultimately fine-mode) NSS to the products of DMS oxidation could be one explanation. Another is the rapid deposition of very large SSA containing NSS; the size distributions tend to argue against this. It is clear, however, that continental sources play a significant role in maintaining the large NSS accumulation mode.

**Table 1.** PASE LTI enhancement factors calculated for the MOI stages. MOI concentrations were divided by these enhancement factors to correct the particulate results. Cut and plot sizes are in geometric diameter at 53% RH sampling conditions. See experimental section for description and Appendix for enhancement factor equations.

Cut Size	<b>Plot Size</b>	Enhancement
μm	μm	Factor
10.00	12	2.05
5.00	7.1	1.33
1.40	2.6	1.08
0.80	1.1	1.02
0.44	0.59	1.01
0.25	0.33	1.00
Filter	0.14	1.00

**Table 2**. Particle-phase (ppt) and gas-phase (pptv) sulfur measured at Christmas Island (Kiritimati) during a 1994 intensive and PASE (2007). Both experiments were conducted during the same time of year (August-September). The 1994 intensive was a ground-based experiment while PASE was an aircraft experiment.

	1994	PASE
particulate	ppt	ppt
MS	10	7
NSS	218	145
MS7/NSS	0.05	0.05
gas-phase	pptv	pptv
SO <sub>2</sub>	45	39
DMS	147	70
SO <sub>2</sub> /DMS	0.31	0.56

**Table 3**. Summary of PASE sulfur fluxes (illustrated in Figures 5 and 23) calculated in Faloona et al. (2010) and this study. Percentages next to fluxes are the % of the total  $SO_2$  formation (including  $SO_2$  from DMS oxidation in the MBL and BuL as well as  $SO_2$  entraining from the FT) in each budget.

flux in $\mu$ mol m <sup>-2</sup> day <sup>-1</sup>	Faloona et al. (2010)	no FT	<b>This Study</b> small FT source	large FT source
MBL DMS source	3.75	3.75	3.75	3.75
MBL SO <sub>2</sub> source	2.75	1.9 (76%)	1.9 (68%)	1.9 (61%)
FT SO <sub>2</sub> source	-	-	0.3 (11%)	0.6 (19%)
FT NSS source	-	-	0.8	2.8
DMS upflux	0.9	0.9	0.9	0.9
BuL SO <sub>2</sub> source	-	0.6 (24%)	0.6 (21%)	0.6 (19%)
Total SO₂ source	2.75	2.5	2.8	3.1
SO <sub>2</sub> upflux	0.2 (7%)	0.2 (8%)	0.2 (7%)	0.2 (6%)
SO <sub>2</sub> dry dep	0.75 (27%)	0.75 (30%)	0.75 (27%)	0.75 (24%)
SO <sub>2</sub> homogeneous	0.25 (9%)	0.3 (12%)	0.3 (11%)	0.3 (10%)
$SO_2$ uptake by SSA	1.6 (58%)	0.7 (28%)	0.7 (25%)	0.7 (23%)
SO <sub>2</sub> oxidized in cloud	-	0.8 (33%)	1.1 (40%)	1.4 (46%)
NSS re-entrained	-	0.8 (33%)	1.9	4.2
Σcoarse NSS formation	1.6 (58%)	0.8 (31%)	0.8 (28%)	0.8 (25%)
$\Sigma$ fine NSS formation	-	1.1 (43%)	2.2	4.5
$\Sigma$ total NSS formation		1.8	2.9	5.2

**Table 4.** Resulting yields of SO<sub>2</sub> from DMS oxidation, depending on the choice of  $\gamma$ , for which a range of values (0.7 ± 0.2) is given. SO<sub>2</sub> yield and loss to sea-salt aerosol for  $\gamma = 1$  are the sulfur flux values reported in Faloona et al. (2010).

	μn	_	
	SO <sub>2</sub>		% SO₂ loss
γ	yield	SO <sub>2</sub> loss to SSA	to SSA
1	2.75	1.6	58
0.9	2.48	1.28	52
0.8	2.20	1.00	45
0.7	1.93	0.73	38
0.6	1.65	0.45	27
0.5	1.38	0.18	13

$$P_{SO_2} = \gamma(k_{OH+DMS}[OH][DMS])$$
(16)

**Table 5**. Comparison of 1994 and 2007 impactor species during episodes more or less influenced by introduced alkalinity, which may be due to dust or biogenic particles. "Less  $Ca^{2+}$ " includes research flights with average  $[Ca^{2+}] < 0.25 \ \mu g \ m^{-3}$ , and "more  $Ca^{2+}$ " includes flights with average  $[Ca^{2+}] > 0.25 \ \mu g \ m^{-3}$ .

	% NSS	Na <sup>+</sup>	Ca <sup>2+</sup>
	>1 µm	µg m⁻³	μg m⁻³
1994	6	4.8	0.15
PASE: less Ca <sup>2+</sup>	7	2.2	0.16
PASE: more Ca <sup>2+</sup>	14	1.5	0.37
PASE: project average	11	1.8	0.25

**Table 6**. Dry deposition velocities (V<sub>d</sub>) at each MOI stage calculated from the model described in Slinn and Slinn (1980), 8 m s<sup>-1</sup> wind speed, 0.3 m s<sup>-1</sup> friction velocity. MOI diameters were sampled at 53% RH, so wet diameters corresponding to 80% RH were calculated. V<sub>d</sub> values for the wet diameter range between the MOI cutoff sizes were averaged and are shown for each plot size. Lifetimes against dry removal ( $\tau_d$ ) were calculated assuming a 600 m BL, a typical height for PASE. Percent of the total NSS mass contributed by each stage for an average sample is also shown. Because NSS concentrations were very rarely above the uncertainty on the first two stages, the mass on these stages may range from 0 to 11 ng m<sup>-3</sup>, which is the analytical uncertainty on these stages.

D <sub>p</sub> (53%RH)	D <sub>p</sub> (80%RH)	V <sub>d</sub>	$ au_d$	NSS	F <sub>dry dep</sub>
μm	μm	cm s⁻¹	days	% mass <sub>tot</sub>	µmol NSS m <sup>-2</sup> day <sup>-1</sup>
12	15	7.1	0.1	1.7	0.7
7.1	8.9	1.1	1	1.7	0.1
2.6	3.3	0.020	35	4	0.005
1.1	1.4	0.035	20	5	0.01
0.59	0.74	0.050	14	10	0.03
0.33	0.41	0.085	8	30	0.1
0.14	0.18	0.19	4	50	0.5

				Actual in cloud			$SO_2$ ox per	
		Full leg a	average	pass		Expected	pass	
		avg	avg	DMS	SO <sub>2</sub>			
		DMS	SO <sub>2</sub>	(max)	(min)	SO <sub>2</sub> (calc)	SO₂(rea	cted)
Flight	Туре	pptv	pptv	pptv	pptv	pptv	pptv	%
2	BL1	66	50					
2	BuL2	19.5	19	38	13	31	18	59
2	BuL2	19.5	19	34	14	29	15	51
2	BuL2	19.5	19	35	19	29	10	35
2	BL2	44	57					
2	BuL3	13	23	23	28	34	6	18
2	BL3	38	54					
2	BuL	15	24	25	13	37	24	65
3	BL2	65	53					
3	BuL2	23.5	47	40	22	49	27	55
3	BL3	50	67					
3	BuL3	7	35	35	20	56	36	64
3	BuL3	7	35	29	20	51	31	61
3	BuL3	7	35	29	24	51	27	53
8	BL1	67	33					
8	BuL1	20	34	38	21	34	13	38
8	BL2	52	43.5					
8	BuL2	11	41	26	28	42	14	33
8	BL3	40	48					
8	BuL3	16	35	21	29	38	9	23
8	BuL3	16	35	32	8	44	36	82
13	BL2	121	26					
13	BuL2	61	27	88	17	27	10	36
14	BL2	91	75					
14	BuL3	51	53	71	40	64	24	38
14	BuL3	51	53	75	33	66	33	50
14	BuL3	51	53	59	21	57	36	63
14	BuL3	51	53	59	26	57	31	55

**Table 7**. Summary of DMS and  $SO_2$  in flights with unambiguous cloud encounters. Calculations of  $SO_2$  consumed per cloud encounter are included as are the DMS and  $SO_2$  in previous BL legs.

mean: 22

49%

**Table 8**. PASE MOI particulate sulfur species, divided between the BL and BuL. There are fewer submicron than supermicron samples in the boundary layer due to the probable contamination of the filters from RF06. We also lack filter data for MS<sup>-</sup>, and thus there are larger uncertainties in these numbers. We estimated the portion of MS<sup>-</sup> on the filter from the 1994 Christmas Island experiment, as described in the experimental section.

Boundary Layer					
ng m⁻³	Ν	Mean	Median	Range	Uncertainty
NSS (<1 μm)	58	564	583	162 – 824	44
NSS (1-15 μm)	67	72	52	0 – 259	33
MS <sup>-</sup> (<1 μm)*	58	8	8	2 - 13	18
MS <sup>-</sup> (1-15 μm)	67	18	18	10 - 28	3
Buffer Layer					
ng m <sup>-3</sup>	Ν	Mean	Median	Range	Uncertainty
NSS (<1 μm)	17	547	596	193 – 853	45
NSS (1-15 μm)	17	80	77	9 – 257	22
MS <sup>-</sup> (<1 μm)*	17	7	8	0 - 12	18
MS <sup>-</sup> (1-15 μm)	17	13	14	0 - 23	3

\*submicron MS<sup>-</sup> does not include filter MS<sup>-</sup>; however, 1994 MS<sup>-</sup> size distributions indicate that filter MS<sup>-</sup> is negligible



**Figure 1.** Number, surface area, and volume size distributions from the LDMA and APS for the PASE marine boundary layer. Diameters correspond to ambient sampling conditions. These size distributions are from a typical flight (RF12).



**Figure 2**. Simplified DMS reaction scheme showing the addition and abstraction pathways. Blue signifies aqueous-phase compounds, which can be found in hydrated aerosol or cloud droplets. Black signifies gas-phase sulfur species. Adapted from Zhu et al. (2006).



Figure 3. Schematic diagram of sulfur gas-aerosol-cloud processes in the marine troposphere. Dotted lines show uptake of of gaseous species. The heterogeneous  $SO_2$  pathways reresenting conversion of  $SO_2$  to non-sea-salt sulfate (NSS) are highlighted in gold.



**Figure 4**. Vertical profiles of potential temperature, vertical wind velocity, and water mixing ratio for a typical PASE flight (RF03). Potential temperature profile is labeled with the tropospheric layers as determined by S. Conley (Conley et al., 2009). The variability in vertical wind velocity demarcates the well-mixed layers.



**Figure 5.** PASE sulfur fluxes ( $\mu$ mol m<sup>-2</sup> day<sup>-1</sup>) in the marine boundary layer and buffer layer. Values in blue text denote fluxes calculated by Faloona et al. (2010). Fluxes denoted by red text represent our calculations. In this illustration, NSS signifies submicron NSS and 'NSS on SSA' signifies NSS associated with supermicron sea-salt particles. This diagram presents a survey of the conditions encountered in the PASE MBL rather than a project average.



**Figure 6**. Typical flight track for PASE. This single stack of 30-minute legs from RF03 shows the flight strategy used to sample various altitudes with the NCAR C-130 in the marine boundary layer and buffer layer. Each constant-altitude leg was flown in a "V" pattern pictured here.



**Figure 7**. PASE MOI non-sea-salt-sulfate (NSS) concentration time series from August to September of 2007. Samples from the lowest BL legs (<100 m) are the red open circles, samples from the middle to upper BL (>100 m) are the solid blue triangles, and samples from the BuL are the green x's. Each research flight is labeled. Note that some flights have been omitted, as explained in the experimental section.



**Figure 8**. PASE CO and MOI NO<sub>3</sub><sup>-</sup> concentration time series from August to September of 2007. All 14 research flights are labeled. Particulate NO<sub>3</sub><sup>-</sup> is not available for certain research flights for reasons discussed in the experimental section.



**Figure 9**. Histogram of total scattering at 550 nm during PASE FT profiles from the Clarke group nephelometer. Profiles into the FT occurred roughly 4 times per flight. Trade wind inversion heights were obtained from Conley et al. (2009). All research flights except RF04 are included. These are 1-second samples.


**Figure 10**. PASE project-average NSS,  $NO_3^-$ , excess Cl<sup>-</sup>, and MS<sup>-</sup> % mass per MOI geometric mean mass diameters at 53% RH. Mass distributions were averaged from all BL legs in each flight. MS<sup>-</sup> on the filter is an estimate (see experimental section).



**Figure 11**. Coarse-mode SSA mass distributions from the APS as measured (53% RH), and calculated for dry and typical ambient conditions (80% RH) compared to MOI [Na<sup>+</sup>] + [CI<sup>-</sup>] using MOI cut sizes at 53% RH. This plot shows a representative sample in the MBL of RF03. APS relative humidity sensor recorded ~ 53% RH in the MBL. MOI cut sizes correspond to APS diameters at the sampling RH, and MOI SSA mass proxy agrees well with APS dry mass. Perfect agreement between the APS and MOI would have the area under the green dashed (MOI) line equal the red (dry APS) line, but have the peak location at the same diameter as the black (APS sampling RH) line. The high values for the largest MOI stage are a combination of a graphing artifact and possible large particle settling losses during the relatively slow transport to the APS.



**Figure 12**. Excess MOI PASE-average coarse anions compared to APS surface area per MOI geometric mean mass diameter at ambient 80% RH. Coarse MOI stages 1 (12.5-20  $\mu$ m), 2 (6.3-12.5  $\mu$ m), and 3 (1.8-6.3  $\mu$ m) are plotted. NO<sub>3</sub><sup>-</sup> is known to preferentially adsorb according to greater surface area, which is reinforced by this plot. NSS on the two largest size bins (MOI stages) only rarely exceeded the minimum detection limit, so values (5 ng m<sup>-3</sup>) of half the minimum detection limit (11 ng m<sup>-3</sup>) were used to plot these coarse sizes.



**Figure 13.** BL and BuL number distributions at 53% RH from the LDMA and APS for RF03 (daytime flight), RF06 (nighttime flight), and RF08 (polluted flight with FT sample). Hoppel minima at ~0.08  $\mu$ m diameter in BL and BuL samples signify processing by cloud.



**Figure 14**. Comparison of FT APS and LDMA volume distributions for RF03, RF06, and RF08. RF06 and RF08 exhibited the highest concentrations of aerosol volume observed in the FT throughout PASE. The MOI sample corresponding to the depicted RF08 FT leg exhibited excess  $Ca^{2+}$  and  $Mg^{2+}$  in the coarse size range.



**Figure 15**. RF03 and RF08 DMS, SO<sub>2</sub>, and CO profiles. Inversion heights per S. Conley are included. RF03 is a typical clean flight and RF08 is a flight where pollution layers were observed. RF08 shows enhanced SO<sub>2</sub> and CO above the trade wind inversion. Note that throughout its profile, CO is  $\sim$ 10 ppbv higher in RF08 than RF03.



**Figure 16**. Accumulated rainfall (mm) for August 2007 estimated from the TRMM (Tropical Rainfall Measuring Mission) satellite. Christmas Island is the white spot at the center of the star. 30-60 mm of rain fell upwind of the island during the first month of PASE, with 20 mm falling in one 40 min period on 08/09/2007. Less than 15 mm of rain fell over a large area of the fetch upwind of the island. Courtesy of John Merrill.



**Figure 17**. Total rainfall for the 1°-2° North latitude band near Christmas Island during August, 2007, measured by the TRMM satellite. There was little or no rainfall in the PASE study region. The August 8-10 period reflects an intense rain event that lasted ~3hr on Christmas Island and occurred before RF02. Courtesy of John Merrill.



Figure 18. 1994 and PASE (2007) DMS and  $SO_2$  diurnal cycles in the BL. Points represent observations while lines represent models. Gas-phase PASE concentrations were measured on 10-second time scales with the airborne APIMS and averaged for every two hours. 1994 data measured from the ground at Christmas Island are shown for each half-hour.



**Figure 19.** Dry deposition velocities (right axis) by particle diameter calculated from Slinn and Slinn (1980) and taken from Ganzeveld et al. (1998) alongside mean PASE RF03 BL NSS MOI mass distribution (left axis). Dry deposition velocities calculated from Slinn and Slinn (1980) were calculated using wet diameters (80% RH) for the MOI size cuts. There is an order of magnitude uncertainty in the modeled dry deposition velocities shown here.



**Figure 20.** Flux of  $H_2SO_{4(g)}$  to particles in the MBL using Seinfeld and Pandis (2006). Adsorption of this vapor is controlled by particle diameter in the continuum regime. The majority of sulfuric acid vapor will condense on the accumulation mode.



**Figure 21.** Liquid water content (left blue axis) and SO<sub>2</sub> (right red axis) for (a) RF03 (08/13/2007) BuL leg 3 and (b) RF14 (09/06/2007) BuL leg 1. DMS and SO<sub>2</sub> were averaged for 10-second intervals. Note the drops in SO<sub>2</sub> during cloud encounters.



**Figure 22.** Panel a) displays UV irradiance (from the top) and UVsmooth (filtered with a 300-point median filter) during a midday sample leg flown at the top of the BL just under the cloud layer in RF03. We performed this analysis for all daytime PASE flights with upper BL legs. Times are UTC (local noon is near 2200 UTC). Sudden drops in UV indicate passage beneath clouds. Downwelling UV is often enhanced near cloud edge as the side of the cloud scatters light towards the sensor. Panel b) gives a histogram of UV/UVsmooth. Panel c) shows the cumulative distribution function (CDF) of the ratio UV/UVsmooth, which relates UV irradiance below the smoothed value to the presence of cloud overhead. Based on the histograms of the daytime PASE flights, we chose UV/UVsmooth values below 0.96 to represent cloudiness. The corresponding cumulative probability at this threshold is the % cloud cover for each respective flight.



**Figure 23**. PASE sulfur fluxes ( $\mu$ mol m<sup>-2</sup> day<sup>-1</sup>) in the marine boundary layer, buffer layer, and free troposphere. This budget includes BuL chemistry, in-cloud oxidation, and entrainment of continental SO<sub>2</sub> and NSS into the BuL-MBL. Values in blue text denote fluxes calculated by Faloona et al. (2010). Fluxes in black text represent our calculations. In this illustration, NSS signifies submicron NSS and 'NSS on SSA' signifies NSS associated with supermicron sea-salt particles.



**Figure 24**. HYSPLIT back trajectories originating at the RF06 study site on 08/20/2007 for three different times. Take-off was at 1200. Three altitudes are plotted for each time. The 10-day estimated back trajectories originate over the continent of South America. Uncertainties for a 10-day back trajectory are potentially as large as half of the distance in any direction.



Vertical Feature Mask Begin UTC: 2007-08-25 06:07:44.8281 End UTC: 2007-08-25 06:21:13.4751 Version: 2.01 Image Date: 02/23/2008



**Figure 25.** Interpreted images from the Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observation (CALIPSO) satellite (b). The upper (a) panel shows the path that the satellite took (in blue) in order to generate the image in (b). Horizontal axes are annotated with latitude and longitude (both in degree). Orange depicts aerosol, which can be seen in the free troposphere in these images. Thick aerosol layers are located over the Amazon Basin during biomass burning season in this figure. Image courtesy of NASA. CALIPSO products are archived and distributed through the Atmospheric Science Data Center (ASDC). Vaughan et al. (2004) expound upon the details about CALIPSO retrieval algorithms and data products.



Vertical Feature Mask Begin UTC: 2007-09-04 11:40:24.9331 End UTC: 2007-09-04 11:53:53.5811 Version: 2.01 Image Date: 02/25/2008



**Figure 26.** Interpreted images from the Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observation (CALIPSO) satellite (b). The upper (a) panel shows the path that the satellite took (in blue) in order to generate the image in (b). Horizontal axes are annotated with latitude and longitude (both in degree). Orange depicts aerosol, which can be seen in the free troposphere in these images. An aerosol layer or "stream" is shown in the free troposphere in the latitude band of the study site ( $2^{\circ}$ -  $3.4^{\circ}$ N,  $155^{\circ}$ - $154^{\circ}$ W) on RF13 (9/4/2007, starting at 1200 UTC), and we presume this stream extends to the study site. Note that the time of this image is very close to the beginning of the flight. The aerosol layer is ~4° east of the study site. Image courtesy of NASA.

# **APPENDIX A**

# Low Turbulence Inlet (LTI) Enhancement Factor Calculations for PASE

The following calculations provided by Dr. James Charles Wilson (University of Denver)

Enhancement Factor (EF) = ratio of particles/unit mass of air of a given size at the exit of the diffuser to the particles/unit mass of air in the ambient atmosphere

- PX: Pitot static pressure
- DPX: Pitot dynamic pressure
- P1: Diffuser entrance static pressure (measured directly)
- Po: Ambient stagnation pressure

$$P_o = PX + DPX$$

1) Determine ambient Mach number, M, which is the ratio of the local velocity to the local speed of sound

$$M = \sqrt{5 * \left[ \left(\frac{P_o}{PX}\right)^2 - 1 \right]}$$

2) Calculate diffuser entrance (throat) Mach number, M<sub>1</sub>

$$M_1 = \sqrt{5 * \left[ \left(\frac{P_o}{P_1}\right)^2 - 1 \right]}$$
$$\frac{P}{P_o} = \left[ 1 + \frac{M^2}{5} \right]^{-7/2}$$
$$\frac{T}{T_o} = \left[ 1 + \frac{M^2}{5} \right]^{-1}$$

3) Calculate stagnation density,  $\rho_0$ 

$$P_o = \rho_o R T_o$$
$$R = 287 \text{ m}^{-2} \text{s}^{-2} \text{K}^{-1} \text{ for air}$$

4) Determine the density,  $\rho_1$ , and the speed of sound,  $a_1$ , in the LTI throat from the stagnation conditions and Mach number in the throat,  $M_1$ 

$$\frac{\rho_1}{\rho_o} = \left(1 + \left[\frac{M_1^2}{5}\right]\right)^{-5/2} = \left(\frac{P_1}{P_o}\right)^{1/1.4}$$
$$\frac{a_1}{a_o} = \left(1 + \left[\frac{M_1^2}{5}\right]\right)^{-1/2} = \left(\frac{P_1}{P_o}\right)^{1/7}$$

5) Calculate LTI mass flow,  $\dot{M}$ 

$$\dot{M} = \rho_1 \times M_1 \times a_1 \times \pi \times \frac{d^2}{4}$$
  
d: throat diameter = 1.118\*10<sup>-2</sup> m

6) Determine mass flow in the sample stream from experimental data

mass flow in sample stream = experimental sample flow (MOI + APS in PASE)

suction mass flow = total mass flow into inlet - sample mass flow

7) Calculate enhancement factors

$$EF = 1.01 + m \times St_t$$

$$m = -1.171 \times R^3 + 1.5103 \times R^2 - 0.7709 \times R + 0.2426$$

$$R = \frac{\text{mass flow exiting the rear of the diffuser}}{\text{total mass flow}}$$

$$St_t = \left(\frac{\rho_p \times D_p^2 \times Cc \times V_t}{9 \times \mu \times d}\right)$$

 $\rho_{\text{p}}$  is particle density, assumed to be 1000 kg m  $^{-3}$ 

 $D_p$  is particle diameter in  $\mu m$ 

Cc is Cunningham slip correction (assumed to be 1 for particles with significant enhancements)

 $V_t$  is the throat velocity in m s<sup>-1</sup> (throat Mach (M<sub>1</sub>) x local speed of sound, a<sub>1</sub>)

 $\mu$  is the throat viscosity in Pa\*s (calculated from the throat temperature)

$$\mu = 1.708 \times 10^{-5} \left(\frac{T}{273.15}\right)^{1.5} \left(\frac{393.396}{T + 120.246}\right)$$

d is the throat diameter and equals  $1.118*10^{-2}$  m

Diameter	RF02	RF03	RF04	RF05	RF06	RF07	RF08	RF09	RF10	RF11	RF12	RF13	RF14	Mean	Std Dev
μm	EF														
0.54	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	5.1E-05
0.97	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.6E-04
1.98	1.04	1.04	1.04	1.04	1.04	1.04	1.04	1.04	1.04	1.04	1.04	1.04	1.04	1.04	5.8E-04
2.64	1.07	1.07	1.07	1.07	1.07	1.07	1.07	1.07	1.07	1.07	1.07	1.07	1.07	1.07	1.1E-03
3.52	1.11	1.11	1.12	1.11	1.11	1.11	1.12	1.11	1.11	1.11	1.11	1.11	1.11	1.11	1.9E-03
5.05	1.22	1.22	1.23	1.22	1.22	1.22	1.23	1.22	1.22	1.22	1.23	1.22	1.22	1.22	3.9E-03
5.42	1.25	1.25	1.26	1.25	1.25	1.26	1.26	1.25	1.25	1.25	1.26	1.26	1.25	1.26	4.5E-03
6.73	1.38	1.38	1.40	1.38	1.39	1.39	1.40	1.38	1.39	1.39	1.39	1.39	1.38	1.39	7.0E-03
7.77	1.51	1.51	1.52	1.50	1.51	1.52	1.53	1.51	1.51	1.51	1.52	1.52	1.50	1.51	9.3E-03
8.98	1.67	1.67	1.70	1.67	1.68	1.69	1.71	1.68	1.68	1.68	1.69	1.69	1.67	1.68	1.2E-02
9.65	1.77	1.77	1.80	1.77	1.78	1.79	1.81	1.78	1.78	1.78	1.80	1.79	1.77	1.79	1.4E-02
10.37	1.89	1.89	1.93	1.89	1.90	1.92	1.94	1.90	1.90	1.90	1.92	1.92	1.89	1.91	1.7E-02
11.97	2.18	2.18	2.23	2.18	2.20	2.22	2.25	2.19	2.20	2.20	2.22	2.22	2.18	2.20	2.2E-02
12.86	2.37	2.37	2.42	2.36	2.38	2.41	2.44	2.38	2.39	2.38	2.41	2.41	2.36	2.39	2.5E-02
13.82	2.58	2.58	2.64	2.57	2.59	2.62	2.66	2.59	2.60	2.60	2.62	2.62	2.57	2.60	2.9E-02
14.86	2.82	2.82	2.89	2.81	2.84	2.87	2.92	2.83	2.84	2.84	2.87	2.87	2.81	2.85	3.4E-02
15.96	3.10	3.10	3.18	3.09	3.12	3.16	3.21	3.11	3.13	3.13	3.16	3.16	3.09	3.13	3.9E-02
17.15	3.42	3.42	3.52	3.41	3.45	3.49	3.56	3.44	3.46	3.45	3.49	3.49	3.41	3.46	4.5E-02
18.44	3.79	3.79	3.91	3.78	3.82	3.88	3.95	3.81	3.84	3.83	3.88	3.88	3.78	3.84	5.2E-02
19.81	4.23	4.23	4.35	4.21	4.26	4.32	4.40	4.25	4.27	4.27	4.32	4.32	4.21	4.28	6.0E-02

**Table 1.** Average PASE APS enhancement factors (EF) by particle diameter. Calculated for 53% RH diameters inside APS. See experimental section.

### **APPENDIX B**

# Particle Dry Deposition Velocity Equations from Slinn and Slinn (1980)

Overall dry deposition velocity ( $V_d$ ) given in Slinn and Slinn (1980), is represented by the inverse of the overall transfer resistance, Vd-1, which is the sum of transfer resistances in series:

$$\frac{1}{V_d} = \frac{1}{k_c} + \frac{1}{k_D} - \frac{\nu_g(a_d)}{k_c k_D}$$

 $k_{C}^{-1}$  = resistance in the constant flux layer, where

$$k_C = k'_C + \nu_g(a_d)$$

 $k_D^{-1}$  = resistance in the constant flux layer, where

$$k_D = k'_D + \nu_g(a_w)$$

Subscripts:

- *C* constant flux layer
- *D* deposition layer
- d dry
- w wet
- h evaluated at z = h
  - 1) Gravitational settling velocities,  $v_g$ , determined from Seinfeld and Pandis (2006)

$$v_g = \frac{\rho_p \times D_p^2 \times g \times Cc}{18 \times u}$$

 $\rho_p$  is particle density, assumed to be 1180 kg m<sup>-3</sup> for wet sea-salt aerosol and 2200 kg m<sup>-3</sup> for dry sea-salt aerosol

D<sub>p</sub> is particle diameter in m

g is the acceleration of gravity, 9.8 m s<sup>-2</sup>

 $\mu$  is the viscosity of ambient air; 1.8\*10<sup>-5</sup> kg m<sup>-1</sup> s<sup>-1</sup> at T = 298 K and P = 1 atm (Seinfeld and Pandis, 2006)

Cc is Cunningham slip correction

$$Cc = 1 + \frac{2\lambda}{D_p} \left[ 1.257 + .4 \times exp\left(-\frac{1.1D_p}{2\lambda}\right) \right]$$
$$\lambda = \frac{\mu}{P\sqrt{2 \times M_0/\pi RT}}$$

P is pressure in Pascals; assumed to be 101,325 Pa  $M_0$  is the mean molecular weight of air; 0.02897 kg mol<sup>-1</sup> R is the universal gas constant; 8.314 J K<sup>-1</sup> mol<sup>-1</sup> T is ambient temperature in Kelvins; assumed to be 298 K

2) Transport across the constant flux layer:

$$k'_{C} = \frac{1}{(1-\kappa)} \frac{u_{*}^{2}}{\bar{u}_{h}} = \frac{1}{(1-\kappa)} C_{D} \bar{u}_{h}$$

κ is von Karman's constant; 0.4

 $\bar{u}_h$  is the mean wind speed at the reference height; assumed to be 8 m s<sup>-1</sup>

 $u_*$  is the friction velocity; assumed to be 0.3 m s<sup>-1</sup>

 $C_D$  is the drag coefficient;  $u_*^2 / \bar{u}_h^2$ ; assumed to be 1.406\*10<sup>-3</sup>

3) Transport across the deposition layer:

$$k'_{D} = -\alpha \dot{m}'' + \frac{1}{\kappa} C_{D} \bar{u}_{h} [Sc^{-1/2} + 10^{-2/St}]$$
  
\alpha is 10<sup>3</sup> cm s<sup>-1</sup>/(1 g cm<sup>-2</sup> s<sup>-1</sup>)

 $\dot{m}$ " is the rate of water evaporation (assumed negligible for particles greater than 1 µm, so left out of our calculations since diffusiophoresis will not affect the coarse-mode velocities)

Sc is the Schmidt number

$$Sc = v/D$$

v is the kinematic viscosity of air; assumed to be  $1.568*10^{-5}$  m<sup>2</sup> s<sup>-1</sup>

D is the particle's Brownian diffusivity in air

$$D = \frac{kTCc}{3\pi\mu D_p}$$

*k* is Boltzmann's constant;  $1.38*10^{-23}$  J K<sup>-1</sup>

St is the Stokes number

$$St = \frac{v_g(a_w)u_*^2}{gv}$$

These calculations determined the shape for the dry deposition velocity curve. In order to ensure that our dry deposition velocities did not disagree with the upper limit of models (shown in Lewis and Schwartz, 2004), especially at the controversial large end of the particle size spectrum, we multiplied our dry deposition velocities by a factor of ten. We adjusted the MOI diameter cut sizes for their ambient RH (80%) equivalent, then averaged the wet diameter dry deposition velocities over that size range. These are reported in Table 6 and plotted in Figure 19.

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