Organic carbon and non-refractory aerosol over the remote Southeast Pacific: oceanic and combustion sources

L. M. Shank[1], S. Howell[1], A. D. Clarke[1], S. Freitag[1], V. Brekhovskikh[1], V. Kapustin[1], C. McNaughton[1], T. Campos[2], R. Wood[3]

[1]{Dept. of Oceanography, University of Hawaii , Honolulu, HI, USA}

[2]{National Center for Aerosol Research, Boulder, CO, USA}

[3]{Dept. of Atmospheric Sciences, University of Washington, Seattle, WA, USA}

Correspondence to: L. M. Shank (lshank@hawaii.edu)

Abstract

Submicron aerosol physical and chemical properties in remote marine air were measured from aircraft over the southeast Pacific during VOCALS-REx in 2008 and the north Pacific during IMPEX in 2006, and aboard a ship in the equatorial Pacific in 2009. A High Resolution – Particle Time of Flight Aerosol Mass Spectrometer (HR-ToF-AMS) measured non-refractory submicron aerosol composition during all campaigns. Sulfate (SO4) and organics (Org), during VOCALS and the cruise show lower absolute values than those reported for previous "clean air" studies. In the marine boundary layer, average concentrations for SO4 were 0.52 μg m $^{-3}$ for the VOCALS region and 0.85 μg m $^{-3}$ for the equatorial region while average Org concentrations were 0.10 and 0.07 μg m $^{-3}$, respectively. Campaign average Org/SO4 ratios were 0.19 (VOCALS) and 0.08 (equatorial Pacific), while previous studies report "clean marine" Org/SO4 ratios between 0.25 and 0.40, and in some cases as high as 3.5. CO and black carbon (BC) measurements over the southeast Pacific provided sensitive indicators of pollution, and were used to identify the least polluted air, which had average concentrations of SO4 and Org of 0.14 and 0.01 μg m^{-3} , respectively, with an average Org/SO4 of 0.10. Furthermore, under cleanest MBL conditions, identified by CO below 60 ppbv, we found a robust linear relationship between Org and combustion derived BC concentrations between 2 and 15 ng m^{-3}, suggesting little to no marine source of submicrometer Org to the atmosphere over the eastern South Pacific. This suggests that identification of Org in clean marine air may require a BC threshold below 4 ng m^{-3}, an order of magnitude lower than has been used in prior studies. Data from IMPEX was constrained to similar clean air criterion, and resulted in an average Org/SO4 ratio of 0.19.

1 Introduction

Aerosols play an important role in the radiative balance of earth's atmosphere, as they affect Earth's planetary albedo, thus climate, through the scattering of solar radiation (direct effect) and their ability to alter the lifetime and optical properties of clouds (indirect effect) (Charlson et al., 1987; Charlson et al., 1992; Twomey, 1974). In the marine boundary layer (MBL) over the remote ocean and far removed from anthropogenic influences, the ocean surface is a major source of aerosol mass and number. This includes the primary emission of sea-salt particles from wave breaking and bubble bursting, as well as gas to particle conversion of vapors emitted to the atmosphere from oceanic phytoplankton (i.e., dimethylsulfide (DMS))

(Andreae and Raemdonck, 1983; Grenfell et al., 1999). Another source of aerosols to the remote MBL is entrainment from the free troposphere (FT) (Clarke et al., 1998). Long range transport of pollution, as well as local sources of aerosols, can increase aerosol and cloud condensation nuclei (CCN) concentrations in these remote areas, thus potentially affecting the local albedo and cloud properties (Clarke et al., 2001; Clarke and Kapustin, 2010; Jaffe et al., 1999).

To quantify how human perturbations are altering aerosol concentrations, and ultimately how increased aerosol loadings affect global climate, it is essential to determine the physical and chemical properties of aerosol which constitute a clean marine atmosphere. Many studies have attempted to describe background conditions by taking marine aerosol measurements from land sites and ships (Allan et al., 2004; Andreae et al., 1999; Lohmann et al., 2005; Phinney et al., 2006; Quinn and Bates, 2003; Yoon et al., 2007). During these campaigns, various criteria for "clean" marine conditions were implemented, and included parameters such as clean sector wind direction (Andreae et al., 1999; Yoon et al., 2007), particle number concentration below a certain threshold, or Air Mass Back Trajectories (AMBTs) used to indicate air masses with no continental influence a certain number of days before collection took place (Allen et al., 2004; O'Dowd et al., 2004, Quinn and Bates, 2003).

The role of sea-salt aerosol and non-sea salt sulfates in climate forcing (Charlson et al., 1987; Shaw, 1983) have long motivated investigations of marine aerosol. However, as significant concentrations of organic carbon (OC) have been observed at sites believed to represent clean marine conditions (Hoffman and Duce, 1976; Kleefeld et al., 2002; Middlebrook et al., 1998; Novakov et al., 1997; Putaud et al., 2000), the possibility of an oceanic OC source to the fine aerosol mode has been under investigation. More recently, at Mace Head, Ireland, an oceanic sampling site in the North Atlantic, relatively large amounts of organic aerosol (up to 72 % of total aerosol mass) have been linked to increased biological production (O'Dowd et al., 2004; Spracklen et al., 2008), suggesting that biogenic emissions are an important source of both water-soluble and insoluble organic matter to the MBL. Both satellite-derived mean chlorophyll-a and trajectory-weighted chlorophyll-a concentrations have been correlated with OC concentrations in clean marine aerosols collected there. However, in other studies, only weak correlations between trajectory weighted chlorophyll-a and OC were found for aerosols collected at Amsterdam Island and no relationship between chlorophyll-a and OC was found for clean marine aerosols collected at the Azores (Spracklen et al., 2008). These studies used a combination and variety of parameters, such as AMBTs, wind direction, carbon monoxide (CO), and black carbon (BC) mass as criterion for establishing clean air cases. AMBTs indicating that air masses had spent at least four days advecting over the North Atlantic Ocean prior to sampling was the primary criterion for determining clean marine cases during the Mace Head study (O'Dowd et al., 2004; Spracklen et al., 2008; Yoon et al., 2007). Mean CO in these air masses was 130 ± 5 ppbv, a value taken as representative of background conditions in the remote Arctic and North Atlantic environment (Cavalli et al., 2004). Like CO, BC is derived from combustion, and therefore has primarily anthropogenic sources. BC concentrations for "clean" cases were around 40 ng m^{-3}.

However, unless aerosol from sources upwind have been effectively scavenged through boundary layer precipitation, these sites remain subject to potential influences from local and/or long range transport. Coastal sites can be subject to influence by higher levels of OC due to increased local ocean production, as well as terrestrial sources (Spracklen et al., 2008).

Here we present two studies conducted in the central and southeast Pacific Ocean that show significantly lower absolute and relative contributions of organics (Org) to the total submicron aerosol mass than previously reported. CO and BC had significantly lower concentrations then those found at the above mentioned coastal sites. Another campaign that took place over the North Pacific Ocean, showed similar low Org/SO4 ratios to those in the South Pacific, when constrained to CO and BC concentrations similar to those at Mace Head under their established clean criteria.

2 Methods

2.1 Field campaigns

Submicron aerosols were collected during two campaigns over the southeast and central Pacific shown in Fig. 1. The VAMOS Ocean-Cloud-Land-Study Regional Experiment (VOCALS-REx), took place in October/November 2008 out of Arica, Chile. The campaign involved 14 research flights aboard the National Center for Aerosol Research (NCAR) C-130, with three distinct flight patterns (Wood et al., 2010b). These included 1) flights along 20°S with 10 minute legs above-cloud, in-cloud and below cloud, 2) flights investigating pockets of open cells (POCs) in the stratocumulus deck (Wood et al., 2010a), and 3) southern pollution surveys to 30°S along the coast of Chile.

Submicron particles were also sampled in the MBL on board the NOAA ship R/V *Ka'imimoana* over the central Pacific during August/September 2009. The cruise originated in Hawaii and serviced Tropical Atmosphere Ocean (TAO) buoys along the 140°W and 125°W longitudes, from 8°N to 8°S.

The Intercontinental and Megacity Pollution Experiment (IMPEX) took place aboard the C-130 in April 2006, with flights from Seattle, WA over the Northeast Pacific Ocean.

2.2 Instrumentation

During the VOCALS and IMPEX campaigns, as well as the TAO cruise, non-refractory chemical composition of submicron aerosols was determined using an Aerodyne High Resolution Time of Flight Mass Spectrometer (HR-ToF-AMS). The HR-ToF-AMS uses an aerodynamic lens assembly to focus 35 nm - 1μm vacuum aerodynamic diameter particles onto a 600°C heated surface (Zhang et al., 2002; Zhang et al., 2004). Particles are evaporated off the heater, ionized by electron impaction (70 eV), and mass analyzed by ToF-MS. The AMS was typically operated in high-sensitivity mode (V-mode), though on the ship and occasionally during VOCALS, the instrument was operated in a high resolution mode (W-mode), that offers more detailed chemical composition of ion fragments. A detailed description of the instrument and its operation is given in Drewnick et al. (2005). Typical detection limits for one-minute averaged V-mode data have been reported as $< 0.04\ \mu g\ m^{-3}$ for all chemical species (SO4, Org, nitrate (NO3), and ammonium (NH4)) (DeCarlo et al., 2006). However, these detection limits were derived from ground-based experiments. Aircraft-based AMS measurements are typically 2-5 times higher due to higher background because the instrument has to be turned off between flights. Detection limits for our campaigns were calculated as twice the standard deviation of the species signal during a filter period. For example, during VOCALS the detection limit varied depending on the duration of AMS operation over a flight, and with lower detection limits reached after several hours. The lowest detection limit for one minute averaged Org was calculated to be $0.06\ \mu g\ m^{-3}$, while for SO4 it was $0.013\ \mu g\ m^{-3}$.

Processing of the AMS data was done using the standard AMS data analysis software (SQUIRREL v.1.48C and PIKA v.1.07B, Sueper, 2010) within Igor Pro 6 (Wavemetrics, Lake Oswego, OR). The frag table in SQUIRREL was adjusted to give zero Org mass concentrations during filter periods.

The collection efficiency (CE) of the AMS for the inorganic ions was estimated by comparing the molar ratio of NH4 to SO4 to determine the acidity of the aerosol. More acidic aerosols (i.e., lower NH4/SO4 molar ratio) are collected more efficiently than neutralized aerosol (Drewnick et al., 2003). The CE correction factor was determined by finding the NH4/SO4 over the desired collection time, and assuming CE varies linearly (from 50 to 100%) as the ratio of NH4/SO4 decreases from 1 to 0 (Matthew et al., 2008). Anytime the NH4/SO4 ratio is above 1, the CE is assumed to be 50%.

Among many other aerosol optical and physical measurements taken on board the C-130, particle concentrations were monitored with condensation nuclei (CN) counters (TSI 3010). Two CN counters were operated in parallel; one with an inlet heated to 360°C. Non-volatile CN (CNhot) refers to those particles which do not volatilize at 360°C, i.e., sea-salt and soot, the latter as a proxy for pollution. An Optical Particle Counter (OPC), LAS-X with modified electronics, was also operated using a heated inlet which cycled between non-heated, 150, 300, and 400°C, and yielded size distributions of the aerosol (Clarke, 1991). A long differential mobility analyzer (LDMA) model TSI 3934 with modified flow control, electronics, and data acquisition was used to acquire size distributions in the 10-500 nm range. Inversions were done according to Zhou et al., 2002. Also on board was a three-wavelength TSI nephelometer (model 3563). Continuously measured natural and anthropogenic trace gases included, sulfur dioxide (SO_2), CO, and dimethul sulfide (DMS). A single particle soot photometer (SP2) was also used to measure BC particle number and mass for sizes between about 0.11 - 0.5 µm (Schwarz et al., 2006, Stephens et al., 2003). Instrumentation aboard the *Ka'imimoana* included the AMS, CN counters (heated and unheated), nephelometer, and LDMA.

3 Results

As a test of AMS performance, submicron non-refractory AMS mass was compared to submicron aerosol volume determined from size distributions measured by the LDMA, assuming a particle density of 1.7 g cm^{-3} for dry sulfate. This provided an independent assessment of potential particle losses by the AMS. Fig. 2 shows a plot of AMS mass and LDMA mass for the VOCALS marine boundary layer (MBL) that yields a linear regression equation with a slope of 0.65, R^2=0.68, suggesting that the AMS was under sampling submicron aerosol compared to the LDMA ($LDMA_{before}$). However, the LDMA distributions can include refractory mass, (e.g., sea salt, dust, soot, and/or refractory Org) not detected by the AMS. Consequently, LDMA volumes were corrected for non-volatile mass determined independently by the OPC. The volatile mass from the OPC was calculated as the difference between the non-heated mass (M1) and the mass that volatilized at 450°C (M4) over the same size bins as the LDMA (~10-500 nm). The fraction of volatile mass (Vol) was then calculated using Vol = (M1 - M4)/M1. A histogram of the Vol fraction is shown in Fig. 2. The measured Vol fraction from the OPC was multiplied by the measured LDMA mass over the same time scale (approximately 90 seconds) in order to estimate only the volatile LDMA mass. The LDMA volatile mass was then compared with the AMS, and is plotted in Fig. 2 as red circles over the uncorrected data in grey. After this correction, the slope of the linear regression between the LDMA and AMS improved to 0.81, R^2=0.65, indicating better quantitative agreement with the non-refractory aerosol component. The comparison between LDMA, OPC, and AMS is not perfect, and is complicated by incommensurate timescales which make direct comparisons difficult. The AMS and OPC data are averaged over 90 s timescales in order to compare with the LDMA, and even then the AMS spends half the sampling time in a "blanking" mode. The LDMA size distributions represent a 20 s grab sample that is then scanned over a 90 s period. Selecting only periods of stable conditions might reduce noise, but would not affect the overall slope.

Table 1 shows the average concentrations for SO4, Org, NO3, and NH4 for VOCALS and TAO 2009, as well as average BC mass and CO for VOCALS. In addition, average values of these aerosol constituents and the average Org/SO4 ratio from several previous clean marine investigations (Fig 1) are shown for comparison. Our VOCALS data is averaged based on three different criteria. The first is simply campaign-averaged MBL, the second is the nominally clean MBL, with data restricted to BC mass less than 2 ng m^{-3} and CO less than 60 ppb, values representative of background conditions in the SEP, and the best direct comparison between clean cases in the SEP and the North Atlantic (Mace Head). Finally, our criteria for the natural MBL as determined during this study, and described in Sect. 4.1. Pie charts in Fig. 1 illustrate the relative composition of clean submicron non-refractory mass during VOCALS and TAO compared to findings from previous investigations.

Data from the TAO 2009 cruise had to be screened for ship contamination. Periods influenced by the ship's plume were removed from the AMS data based upon exceeding a criteria of 700 cm^{-3} for CNhot and 15 Mm^{-1} for submicron scattering values from the TSI nephelometer. Next, CNhot (1 Hz data) was smoothed with a 12-point median filter. The smoothed data was subtracted from the raw data in order to capture any rapid changes in the concentration possibly related to stack contamination. Any data point where the difference in raw and smoothed data, on a one second time scale, was greater than a concentration of 200 particles cm^{-3} was removed. After this screening the same CE scheme employed for the VOCALS data was applied. The resulting average concentration of SO4 was 0.85 μg m^{-3}, while Org was 0.07 μg m^{-3}. NH4 concentrations averaged 0.11 μg m^{-3}.

During the TAO cruise neither CO nor BC measurements were made, making it more difficult to identify air influenced by continental pollution. However, a plot of Org vs. SO4 for the entire cruise (100 minute averaged data), overlaid by VOCALS data (10 minute, or leg-averaged, data), shows a considerable fraction of the measurements lie on or near to a line with a slope ~0.1 (TAO and VOC, Fig. 3). VOCALS FT data (VOC FT), where the Org/SO4 is significantly higher, is also plotted and reveals the potential to increase MBL values of Org/SO4 through entrainment.

Time series of TAO cruise data for SO4, Org, NH4 and NO3 are shown in Fig. 4, along with the time series of Org/SO4. Fig. 4 also includes the cruise track with date labels, rain events, and wind direction indicated. The excursions from the average Org/SO4 ratio are pronounced along the easternmost leg of the cruise, along 125°W from 8°S to 5°N, where Org concentrations increase gradually from 0.07 μg m^{-3} at the southern end of the cruise track, to 0.17 μg m^{-3} near the equator. As the ship moved north after 15 Sep, and north of the Intertropical Convergence Zone (ITCZ), the Org/SO4 ratio decreased to values below 0.1, typical of those observed elsewhere during the cruise, while the absolute value of Org also decreased back to concentrations typical of the cruise average 0.07 μg m^{-3}. These excursions from the TAO cruise-average ratio of 0.08 are indicated by TAO* in Fig. 3.

The AMS was operated in both V and W modes during the cruise, cycling between the two modes every one and four minutes, respectively. When cycling between the two modes, ten-minute averages include only two minutes of V-mode data, compared to 10 minutes of data when operating solely in V-mode. Due to the condition of the AMS, we were able to operate the instrument only in V-mode after 10 Sep. Since the current study focuses on V-mode data exclusively, the data is therefore noisier before 10 Sep than after.

4 Discussion

4.1 Determination of clean air criteria in the SEP

Particulate species, such as BC and Org, can be scavenged from the atmosphere by precipitation but CO is not. CO is only slowly removed by reaction with OH with an e-folding time of about 1-2 months (Jaffe et al., 1997) in the tropics and over a year in high latitudes during the winter (Staudt et al., 2001). These properties provide us with useful tools for identifying combustion influences and for establishing clean marine criteria. Here they are also combined with AMBTs to establish a marine-source contribution of Org to the remote marine atmosphere.

Based on the varying relationships between Org vs BC and SO4 vs BC, as well as CO in the VOCALS MBL, which are plotted in Fig. 5, we established values of BC < 2 ng m^{-3} and CO < 60 ppb as our criteria for clean marine air. Fig. 5a shows Org vs BC and Fig. 5b shows the SO4 vs BC relationships for the FT and MBL, all colored by CO. Above cloud air in the FT often has higher concentrations of Org, BC, and CO than below cloud, but lower SO4 concentrations. Entrainment evident in this region (Bretherton et al., 2010) would therefore raise concentrations of Org and BC in the MBL while lowering SO4 by dilution. Furthermore, the range of relationships evident between OC and BC in the freet troposphere (FT) in Fig. 5a suggest the involvement of variable sources and aerosol removal processes.

Fig. 5c shows the strong relationship between Org and BC for BC values under 20 ng m^{-3} (half of the Mace Head "clean" criteria) and CO < 60 ppbv. The regression has an intercept of 0, and a R^2 value of 0.66, suggesting a significant linear relationship and a common anthropogenic source even for these low CO values. This is not true for the weak regression between SO4 and BC over this same range (Fig. 5d). Also evident is a residual and variable SO4 concentration when BC approaches our detection limit and CO is near the minimum of 50 ppb (dark blue). This is an expected result for clean background marine air, given SO4 has a known and well-documented oceanic source (Andreae and Raemdonck, 1983; Charlson et al., 1987,).

At low concentrations of CO (< 60 ppb) and for BC concentrations below 2 ng m^{-3} the variation in SO4 appears to represent the natural marine variability in SO4 (Fig. 5d), i.e., SO4 varies from 0.05-.5 µg m^{-3} (average 0.14 ± 0.11), while BC and CO stay nearly constant. SO4 and Org were further restricted to CO < 56.5 ppb and BC < 2 ng m^{-3} to more closely examine this low CO branch (dark blue) of the SO4 vs BC relationship. The relationship between SO4 and Org for this data is shown in Fig. 6. These values of Org and SO4, free of combustion influence, were then bin-averaged for every 0.05 increment of SO4, and are superimposed on the one-minute data from Fig. 5 with 1 σ error bars. A linear fit to the bin-averaged data suggests a relationship (R^2=0.75) between Org and SO4, with a slope of 0.08, possibly indicative of an oceanic source for this Org.

Under this clean criteria, designed to isolate marine sulfate aerosol (CO < 56.5 ppb and BC mass < 2 ng m^{-3}) Org constitutes only 8% of total submicron, non-refractory aerosol mass, while SO4 constitutes 87% of the total mass in the MBL. These results contrast with previous investigations of clean marine aerosols (Fig. 1) which find Org to make up 25-40% of the total submicron non-refractory mass, and even up to 77% in North Atlantic aerosols (O'Dowd and de Leeuw, 2007). The latter values can be compared to known polluted environments (i.e., in Fig. 1: Ace-Asia, NEAQS, and the VOCALS FT) where Org can comprise 25-70% of the total submicron mass.

Approximate slopes of the Org/SO4 ratio are drawn in Fig. 3, as visual representation of the relationships evident from various studies that all focused on clean marine aerosols: Trinidad Head (TH), Mace Head (MH), VOCALS Ron Brown (RB), Ace-Asia (AA), IMPEX (IMP) and Ocean Station Papa (OSP). The light blue triangle indicates the range of Org/SO4 ratios from various biomass burning studies: the Western Arctic (McNaughton et al., 2011), Siberia and Kazakhstan (Warneke et al., 2009), and western Africa (Capes et al., 2008). We note that the average value for MH (Org/SO4=3.5) is plotted off scale but the implied slope falls within the ranges of Org/SO4 ratios seen in these biomass burning studies.

4.2 Org enrichment during the TAO cruise

In order to explore the relation of the Org enhancement during the cruise (TAO* in Fig. 3) to possible ocean sources, eight-day composites of chlorophyll-a concentration were produced using SeaWIFS (Sea-viewing Wide Field-of-view- Sensor) Level 3 products provided by NASA/Goddard Space Flight Center (Ocean Color Web (http://oceancolor.gsfc.nasa.gov) accessed June 2010). Surface chlorophyll-a concentrations do not indicate a significant increase in biological production for corresponding aerosol measurements on the western boundary of the cruise track (Fig. 7a), and the eastern edge of the cruise (Fig. 7b, 11 Sep to 15 Sep). Maximum chlorophyll-a concentrations encountered within 3 days upwind of the ship track ranged from 0.2-0.3 mg m^{-3}, similar to concentrations found during periods of low biological activity in the O'Dowd et al., 2004 study. In contrast, during their periods of high biological activity, there was an approximate tenfold increase in chlorophyll-a concentrations that they associate with an enhancement of Org aerosol (from ~1 μg m^{-3} Org to ~5 μg m^{-3}).

Fifteen-day Air Mass Back Trajectories (AMBTs) were performed using the National Oceanic and Atmospheric Administration's (NOAA) Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model access via NOAA ARL READY website (http://www.arl.noaa.gov/ready/hysplit4.html). Isentropic trajectories were run at 4 altitudes (100 m, 1000 m, 1250 m, and 1500 m) using the GDAS meteorological dataset. The 100 m trajectory (red) origin was varied spatially by 1° north, south, east, and west, in order to capture spatial variability in the model. Within this spatial variation the trajectories were consistent for approximately the first 6 days of the AMBT, after which the 100 m trajectories tended to diverge. For simplicity, only one of the 100 m trajectories is displayed in Fig. 7. Several sets of trajectories were run, half during the peak of the Org/SO4 excursion on the eastern most edge of the cruise track, and half on the western edge of the cruise track, where Org/SO4 is close to the cruise-average 0.08 value. However, for clarity, only two sets of trajectories are plotted in Fig. 7. Altitude profiles for the AMBTs are shown in Fig. 7c and 7d.

AMBTs from one day, chosen to represent the western edge of the cruise track (3 Sep), indicate that influencing air masses have a) passed through the Inter-Tropical Convergence Zone (ITCZ), where convection and rainfall could have removed particulate matter, and b) spent the past 15 days over the ocean, with no indication of continental influence. The influence of ITCZ precipitation upon aerosol concentrations is clearly evident in Fig. 4 where they are reduced by up to a factor of four on 11 Sep and recover by 14 Sep. During this excursion the Org/SO4 ratio shows little change, indicating no preferential removal of either species. AMBTs during the peak in the Org/SO4 ratio from 13 Sep indicate that air masses have had possible continental influence in the past 15 days.

As previously noted for our VOCALS data, biomass burning in South America serves as a potential source of Org to the FT, and data from the Fire Locating and Modeling of Burning Emissions (FLAMBE' (http://www.nrlmry.navy.mil/flambe) accessed July 2010) indicates widespread fires in the Amazon at the beginning of Sep, approximately 1-2 weeks before sampling occurred (Fig. 7e). Levoglucosan is a chemical tracer for biomass burning, as it is formed during the pyrolysis of cellulose (Simoneit et al., 1998). Lee et al. (2010) found that the AMS peak at m/z 60, more specifically $C_2H_4O_2$, a fragment resulting from the breakdown of levoglucosan and other anhydrosugars, including mannosan, galactosan, arabinosan, and xylosan, is an even better indication of biomass burning than levoglucosan itself. Using the high resolution data analysis and elemental analysis package for the AMS (Aiken et al., 2008), $C_2H_4O_2$ was identified and quantified by averaging the cruise data over ~12 hour periods. Fig. 8 shows the $C_2H_4O_2$ concentration, along with 12-hour averaged Org/SO4 overlaying the 10 minute Org/SO4 from Fig. 4. Because the signal to noise level is higher for the $C_2H_4O_2$ peak, error bars (1σ) are shown as well. The elevated $C_2H_4O_2$ between 11 Sep and 20 Sep drops at the transition from southern hemisphere air to northern hemisphere air (Fig. 4) suggesting that the increased Org can be associated with an increase in the relative amount of levoglucosan, indicating a biomass burning source in the southern hemisphere that is not present in the northern hemisphere. Levoglucosan was also detected at a ground-site in Paposo Chile during VOCALS, a region upwind of the TAO cruise area (Chand et al., 2010).

The 12 hour averages of the elemental ratios H/C and O/C for this data are shown on a Van Krevelen plot (Heald et al., 2010) in Fig. 8 as well, and are colored by the Org/SO4 ratio. Heald et al. (2010) showed that a Van Krevelen diagram provides an indication of the amount of aging an aerosol has undergone, i.e., the longer an aerosol is in the atmosphere, the more oxidized it will become, and the H/C ratio will decrease while the O/C ratio will increase (Heald et al., 2010). Fig. 8 reveals the more aged aerosol during TAO to be generally associated with the higher Org/SO4 ratio, consistent with a non-local source for these aerosols. In contrast, values of Org/SO4 near 0.08 are associated with higher H/C, suggesting a more local, prehaps oceanic, source.

Although the AMBTs do not confirm a clear source of the rise in the Org/SO4 ratio along the eastern edge of the TAO cruise track, SeaWIFS imagery does not suggest the increased Org can be attributed to increased biological production. Transport in the FT appears reasonable as a potential source of Org to the central Pacific MBL, similar to what was observed during VOCALS, but unfortunately no above-cloud data is available during the TAO cruise. However, such transport in the FT over this equatorial region has been noted in other papers (Hsu et al., 1996; Kim and Newchurch, 1996).

4.3 Instrument bias

Recent studies have determined that there is an under sampling of Org by the AMS, which could bias our results to lower values. For example, Hawkins et al. (2010) found the AMS had a particularly low CE in the VOCALS region during the same campaign (sampling in the MBL from the R/V *Ron Brown*). The low CE was associated with Org found on submicron dust particles originating from South America. However, dust particles are of continental origin, therefore low CE values associated with Org on dust would not impact the results of this study.

Another possible source of error that might bias the absolute values of Org low is through application of CE correction values to the data. A "worst case" scenario would be for a completely externally mixed aerosol, where Org are collected with half the efficiency and the SO4 is not neutralized, and is therefore being collected with 100% efficiency. In this case, the CE scheme applied to our data would not account for the Org being under sampled (i.e., Org would not be properly multiplied by a correction factor of 2). However, a histogram of the CE values applied to the VOCALS campaign reveal that the CE lies between 0.5 and 0.7, 64% of the time. Therefore, if anything, Org values for VOCALS are more likely to be overestimated by using the CE correction factors. A third possibility for under sampling of Org by our AMS could be the inlet efficiency. Calibrations have shown that there are significant particle losses by our inlet at particle diameters greater than 600 nm, aerodynamic diameter. Hence, the potential for a significant Org fraction present on coarse sea-salt remains possible. However, plots of Org vs OPC coarse non-volatile mass (a sea-salt surrogate – as used in the discussion of Fig. 2) revealed no evidence of a trend.

There is also a significant distinction between primary and secondary organic aerosol, and what the AMS is able to sample. Recent studies have shown that much of the organic matter in marine aerosol is primary, emitted directly with sea-salt, rather than secondary, which forms from the oxidation of organic vapors. While sea-salt particles are typically too large for the AMS inlet, submicron particles are enriched in primary Org in the size range the AMS should measure (Keene et al., 2007). Our results are not consistent with studies such as Keene et al., 2007, which found significant amount of primary submicron Org aerosol, even over oligotrophic ocean. Their experiment involved bubbling zero air through seawater, where they measured aerosol in the same size range as the AMS, and found Org concentrations roughly an order of magnitude (~0.1 $\mu g\ m^{-3}$) greater then observed during

VOCALS and TAO. It is possible that primary Org emitted from the ocean surface are too refractory for the AMS to measure.

4.4 Sampling bias

Throughout VOCALS, dedicated intercomparison periods took place between sampling platforms. These consisted of level legs where aircraft and/or the R/V *Ron Brown* sampled the same air mass for a given amount of time, allowing direct comparison of instrument performance across platforms. More detailed descriptions of intercomparison periods can be found in Allen et al. (2010). Other aircraft involved in the campaign, and with an AMS on board, included the United Kingdom (UK) British Aerospace-146 (BAe-146), and the United States Department of Energy Gulfstream-1 (DoE-G1). AMS data across all platforms was found to contain no systematic sampling biases, and mean quantities from intercomparison runs agreed within one standard deviation (Allen et al., 2010). The comparison between the BAe-146 and C-130 AMS data showed agreement within 20% for the absolute values of Org and SO4, and showed less than 6% disagreement in the Org/SO4 ratio.

However, the agreement between the Ron Brown and C-130 AMS data during intercomparison periods was not as consistent. The AMS on board the Ron Brown was an Aerodyne Quadrupole AMS (Q-AMS), with significantly higher detection limits for Org (0.16 μg m^{-3}) than the ToF-AMS operated aboard the aircraft. Therefore, when intercomparisons were conducted during periods with Org concentrations near the detection limit of the Q-AMS, the discrepancies between platforms were worse than during periods of elevated Org concentrations. During the latter periods, comparison between the C-130 and Ron Brown AMS Org/SO4 ratio was within the expected uncertainties of the instruments.

Differences in the campaign Org/SO4 ratios between the C-130 and Ron Brown are shown in Fig. 9a and b as histograms of the ratio. Ron Brown AMS Org were reported as 0 for concentrations below their instrument's detection limit (< 0.16 μg m^{-3}), biasing average concentrations low. In order to decrease this bias, for the purpose of this comparison, Org concentrations below instrument detection limits were replaced with half of that detection limit (0.08 μg m^{-3}). For the unrestricted cases, i.e., no clean air selection criteria applied, the Ron Brown observed higher Org/SO4 ratios than the C-130. However, when CN is used as a clean air indicator, and is restricted to cases < 700 per cm^3 and < 350 per cm^3, the frequency distributions of Org/SO4 for the two platforms become more consistent. It should be noted that although CN is not as sensitive an indicator of pollution as the use of CO and BC, it was the only common measurement across the sampling platforms. This result suggests that during VOCALS, the Ron Brown was in contact with more continentally influenced air than the C-130, and therefore observed higher absolute and relative concentrations of Org throughout the campaign.

Fig. 9c shows the Org/SO4 histograms during VOCALS, but constrained to clean air cases using varying, and increasingly more restrictive, concentrations of BC and CO. These criteria yield narrower frequency distributions of Org/SO4, and also shifted to lower Org/SO4 values, than the more indirect index of pollution (CN). Histograms of Org/SO4 ratios for IMPEX are shown in Fig. 9d. The northern hemisphere is generally more polluted, and therefore CO and BC concentrations were not at the low levels observed in the Southeast Pacific. In an effort to duplicate the Mace Head clean air criteria, similar values of CO and BC were chosen to restrict the AMS data. The frequency distributions of the Org/SO4 ratio are similar to those observed in VOCALS, and indicate an average Org/SO4 ratio of about 0.16-0.20. Unfortunately, the clean IMPEX data suffers from poor statistics, as one of the main objectives of the campaign was to study pollution, and therefore few cases of clean air were measured. The clean Org/SO4 ratio that was observed is significantly lower than other clean air studies in the north Pacific (i.e., Allan et al., 2004; Phinney et al., 2006). This is due to the rapid responses of the SP2 and CO allowing for the stricter stratification of data into clean and polluted cases.

4.5 Implications for modeling studies

Modeling sea-spray aerosol, and the organic aerosol contribution to the global emission, has been the subject of recent studies (Langmann et al., 2008, O'Dowd et al., 2008, Vignati et al., 2010). Several relationships have been used to relate water insoluble organic mass fraction to surface chlorophyll-a concentrations upwind of the measurements. Some data used to establish these relationships can be found in O'Dowd et al. (2008), and are duplicated in Fig. 10. Modeling studies that employ these functions to extrapolate Org aerosol production globally often overestimate Org aerosol concentrations by a factor of 4 or 5 compared to observations (Lapina et al., in review, Westervelt et al., in review). However, the VOCALS, TAO, and IMPEX Org contributions to total submicron mass (6%, 7%, 18%, respectively) and monthly averaged chlorophyll-a concentrations (from SeaWIFS) in surface water upwind of these study areas, yield data points that lie well below the linear function found in O'Dowd et al. (2008), Langmann et al. (2008), and Vignati et al. (2010), and are also plotted in Fig. 10. However, our data are within the low percent Org mass (0-20%) , low chlorophyll-a (0.15-0.2 mg m^{-3}) regime of the O'Dowd (2008) data, suggesting a relationship that goes through the origin rather than having a significant intercept at zero chlorophyll-a. If one uses the slope from O'Dowd et al. (2008) but displaces it lower to pass through the origin it would encompass our VOCALS, TAO and IMPEX data as well as the lower envelope of points from Mace Head. This would suggest the higher ratios for Mace Head may reflect non-oceanic source of Org or uncertainties in effective chlorophyll-a. If this resulting relationship were assumed for models then the modeled Org mass for the mean global chlorophyll of 0.36 mg m^{-3} (Siegel et al., 2002) should drop from about 33.7% to 22.7%, a factor of 1.5.

5 Conclusion

Our measurements in air over the remote South Pacific during VOCALS revealed low Org concentration in marine aerosol with values that trended linearly with combustion derived BC mass concentrations down to values of BC < 2 ng m^{-3}. This is more than an order of magnitude lower than BC values of 40 ng m^{-3} used as a criteria for identifying clean marine air over the North Atlantic in some other studies (Cavalli et al., 2004; O'Dowd et al., 2004). This raises questions over the appropriate choice of a clean threshold for BC used to eliminate influences of combustion aerosol when characterizing background marine aerosol. During VOCALS, the linear relationship between BC mass and Org suggests that most, if not all, Org in this region is associated with biomass burning and pollution, and that the ocean in this remote region is not a significant source of Org to the marine atmosphere. The linear relationship between CO and BC at low concentrations of these species also suggests that absolute values of aerosol constituents aren't good enough to describe "background" conditions, unless the natural source greatly overwhelms the combustion source.

Relative concentrations of clean SO4 and Org during the TAO 2009 cruise and VOCALS campaign reveal that only a small percentage of submicron non-refractory aerosol mass is Org (~8 % for VOCALS, ~7 % for TAO). This is considerably lower than previous investigations where the Org/SO4 was found to be ~30-40% at other sites (Allan et al., 2004; Phinney et al., 2006), and as much as 72% of total submicron mass during periods of high biological activity at Mace Head (Cavalli et al., 2004; O'Dowd et al., 2004). Our results from the central and southeast Pacific suggest that these previous studies are not representative of large oceanic regions in general and may have been subjected to contamination from continental influences.

We were also able to compare with data from a completely separate campaign, which took place in the northern hemisphere, and also measured Org, SO4, BC, and CO. The findings were similar to VOCALS and TAO, where the mode Org/SO4 ratios decreased to smaller and smaller values as clean air criteria were restricted to lower BC and CO concentrations.

Although our results are for regions of lower productivity than some of these investigations, a recent study by Claeys et al. (2010) found Org mass contributes less than 10% to total submicron mass in aerosols collected at Amsterdam Island, with similar Org mass concentrations as seen during VOCALS and TAO. This was true even during periods of high biological production, demonstrating results that are in agreement with observations from this study.

Harmonizing these observations with the dependency of Org mass and chlorophyll-a reported for Mace Head may be possible by allowing the reported Mace Head slope for this relationship to pass through the origin. This would suggest a marine source that establishes the lower envelope of the Mace Head data points (Fig. 10). Such a relation will have the greatest relative impact for lower chlorophyll-a concentrations and should yield much improved consistency between measurements and models.

We believe the lower values from our studies can be attributed, at least in part, to collection taking place 1) in the southern hemisphere, where there is less population and landmass, 2) over a remote area of the ocean typically far removed from continental influence, and 3) over relatively unproductive ocean regions, therefore less primary and secondary organic aerosol. Hence, chemical pollution indicators, such as CO and BC, are at significantly lower concentrations in the southeast Pacific, providing lower thresholds with which to stratify data into clean and polluted cases and test for trends. Org and BC trended linearly (R2=0.66, y-intercept -0.003), suggesting that Org in VOCALS region is anthropogenically derived, and that the ocean surface is not a significant source of submicron, non-refractory Org. Much of the VOCALS SO4 concentrations also trended with BC, reflecting a combustion influence. However, others did not and revealed variability in SO4 between about 0.05 and 0.5 $\mu g\ m^{-3}$ when BC was at our detection limit of about 2 $ng\ m^{-3}$. At these low values of BC and CO, average SO4 values were $0.14 \pm 0.11\ \mu g\ m^{-3}$ and Org concentrations were $0.01 \pm 0.02\ \mu g\ m^{-3}$. Although BC measurements were not taken during TAO 2009, plots of Org vs SO4 suggest background conditions similar to those found in the MBL during VOCALS. Although we focus here on marine MBL aerosol, our data in the FT for VOCALS revealed elevated combustion aerosol aloft suggesting it must be considered as a potential source of Org to the MBL in remote regions.

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Table 1. Average submicron mass concentrations for major aerosol constituents from current and previous investigations of "clean" marine submicron aerosol[a]

Where	When	SO4	Org	NH4	NO3	BC	CO	Org/ SO4	Criteria[b]
North Pacific, Trindad Head, California[c]	Apr-May 02	0.93	0.38	0.2	0.09			0.41	2
North Pacific, Ocean Station Papa (50.0°N, 145.0°W)[d]	Jul 02	0.74	0.3	0.2	0.03			0.41	2
North Atlantic, Mace Head, Ireland[e]	Apr-Jun, Sep-Oct 02	0.26	0.91	0.1	0.02	20	130	3.5	1,2, 6
Ace-Asia, R/V Ron Brown[f]	Apr 02	0.25	0.31	0.07	<0.01			1.2	2
North Pacific, Seattle, Washington[g]	Apr 06	0.52	0.15	0.16	0.02			0.2	
Southeast Pacific, R/V Ron Brown[h]	Oct-Nov 08	0.9	0.3		<0.2			0.33	5,6
Southeast Pacific, VOCALS[i]	Oct-Nov 08	0.52	0.10	0.06	<0.01	10	60.4	0.19	3,4
clean MBL current study[j]		0.17	0.02	<0.01	<0.01	2.0	57.1	0.12	
natural MBL current study[k]		0.20	0.02	<0.01	<0.01	<1.0	56.8	0.10	
Central Pacific, TAO[i,l]	Aug-Sep 09	0.79	0.07	0.1	<0.01			0.08	6

[a] All concentrations are in μg m^{-3} except BC (ng m^{-3}) and CO (ppb)

[c]Allen et al., 2004; [d]Phinney et al., 2006; [e]Cavalli et al., 2004, [f]Quinn et al., 2004, [g]IMPEX*, [h]Hawkins et al., 2010, [i]Current study, [j]Data resticted to BC<0.005 µg m-3 , CO < 61 ppb, [k]Data resticted to BC<0.002 µg m-3 , CO < 56.5 ppb, lCN<700 cm-3

[b]Abbreviations for clean air criteria: 1=Clean air sector, 2=Air Mass Back Trajectories, 3=BC threshold, 4=CO threshold, 5=radon, 6=particle number concentration

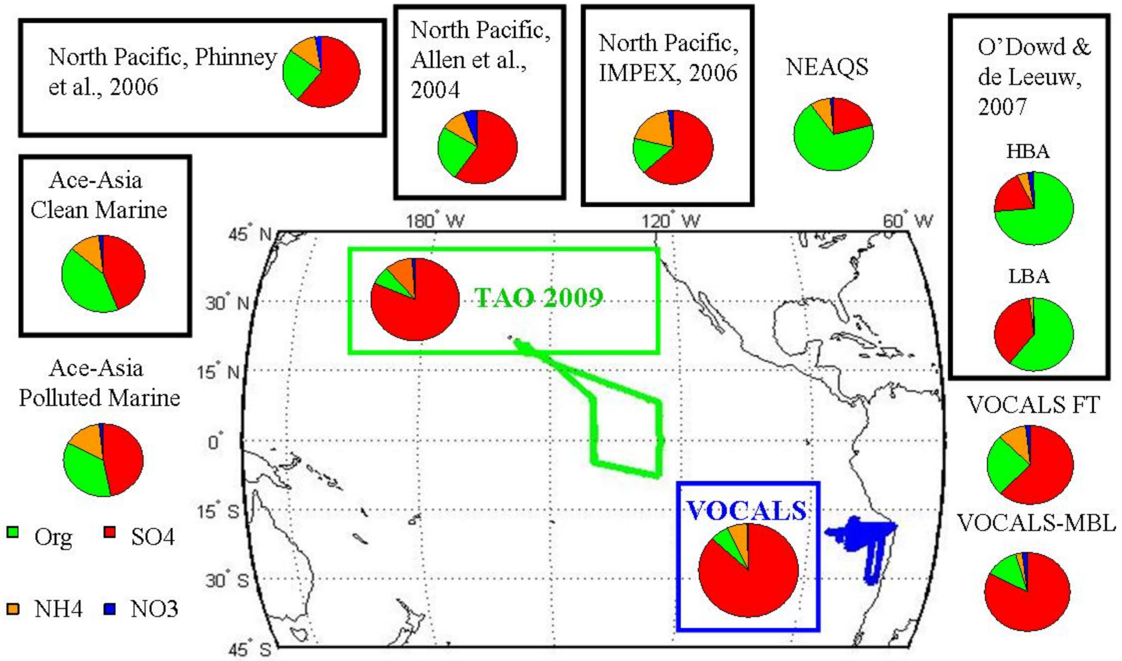

Figure 1. Study region for VOCALS (blue) and TAO 2009 cruise (green). Pie charts indicate relative contributions of submicron non-refractory species. All studies are of marine boundary layer aerosols, with the exception of the VOCALS Free Troposphere data (FT). Studies in bold boxes indicate those which focus on "clean" marine aerosol, (i.e., based upon various approaches to minimize continental influence). NEAQS=New England Air Quality Study, HBA=High Biological Activity, LBA=Low Biological Activity. Ace-Asia and NEAQS data adapted from Quinn and Bates, 2003.

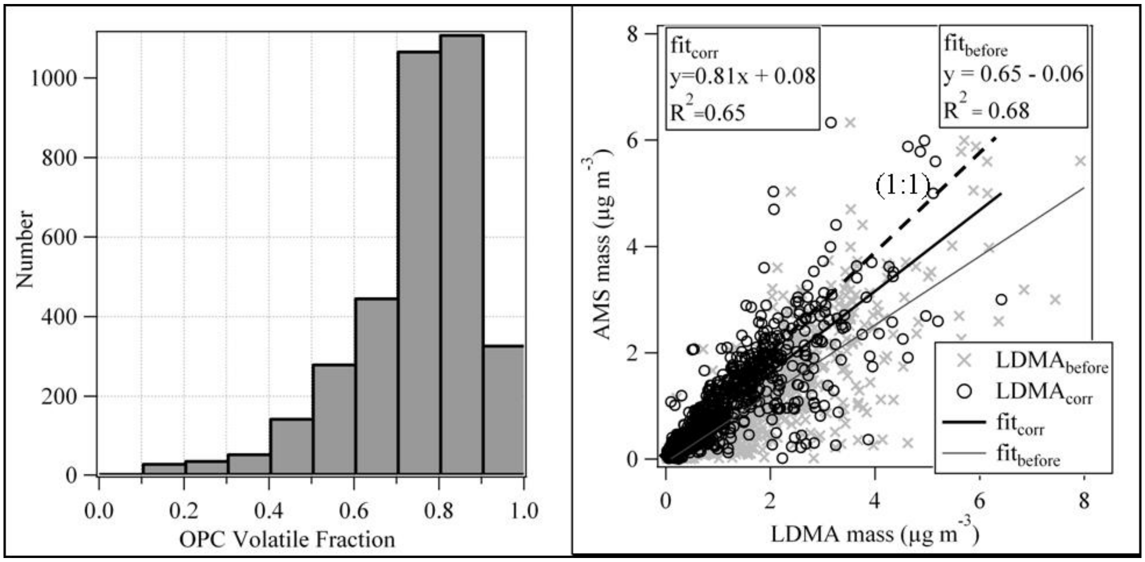

Figure 2. (Left) Histogram of the volatile fraction established from the OPC. (Right) Relationship between LDMA volatile mass and AMS mass for the VOCALS MBL before and after the non-volatile correction factor.

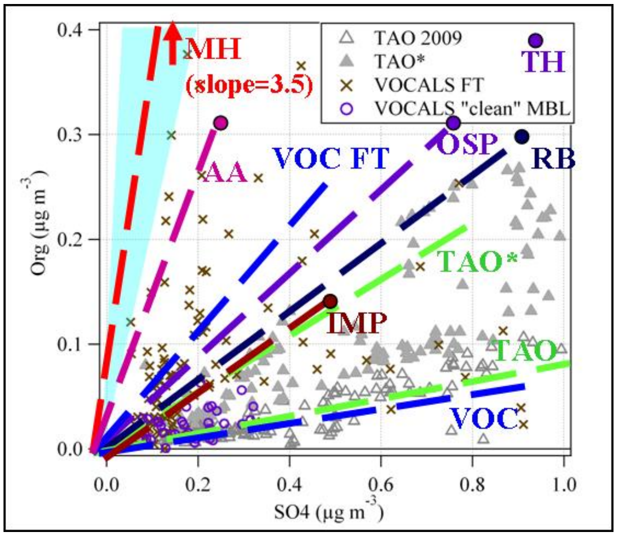

Figure 3. AMS organics (Org) versus sulfate (SO4) during TAO 2009 cruise, VOCALS "clean" MBL (VOC), and VOC FT. Also shown are approximate implicit slopes for the Org/SO4 relationship from Trinidad Head (TH), Mace Head (MH), Ace-Asia (AA), IMPEX (IMP), Ocean Station Papa (OSP), and VOCALS Ron Brown (RB). Average reported clean values are shown as circles, while the dashed lines indicate the implicit slope. Excursions from the TAO average Org/SO4 of 0.08 are indicated as TAO*. A range of biomass burning Org/SO4 ratios are indicated by the blue triangle.

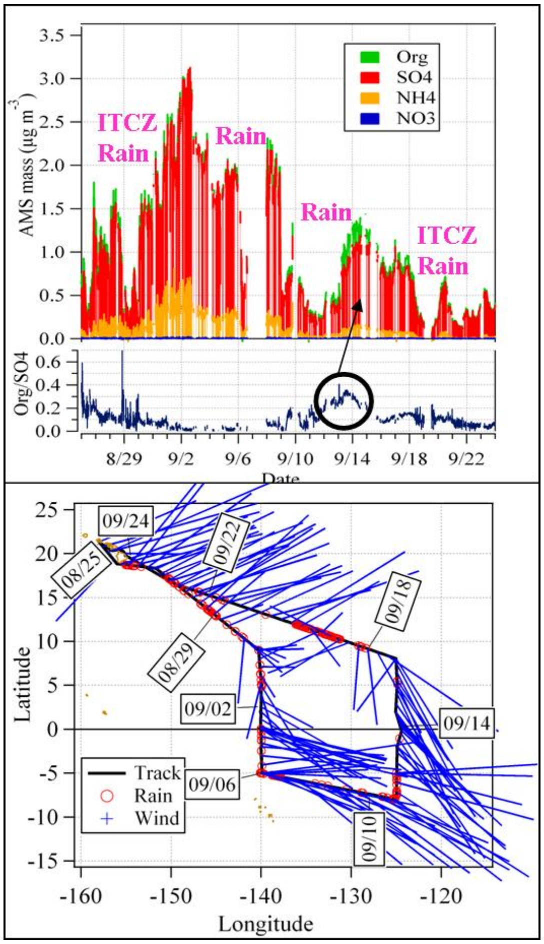

Figure 4. (Top) Time series of AMS Org, SO4, NH4, NO3 and Org/SO4 for TAO 2009 cruise. Dark circle and arrows indicate the increase in both Org/SO4 ratio and absolute Org values along the eastern leg of the cruise track. (Bottom) Cruise track with date tags, rain events, and wind direction.

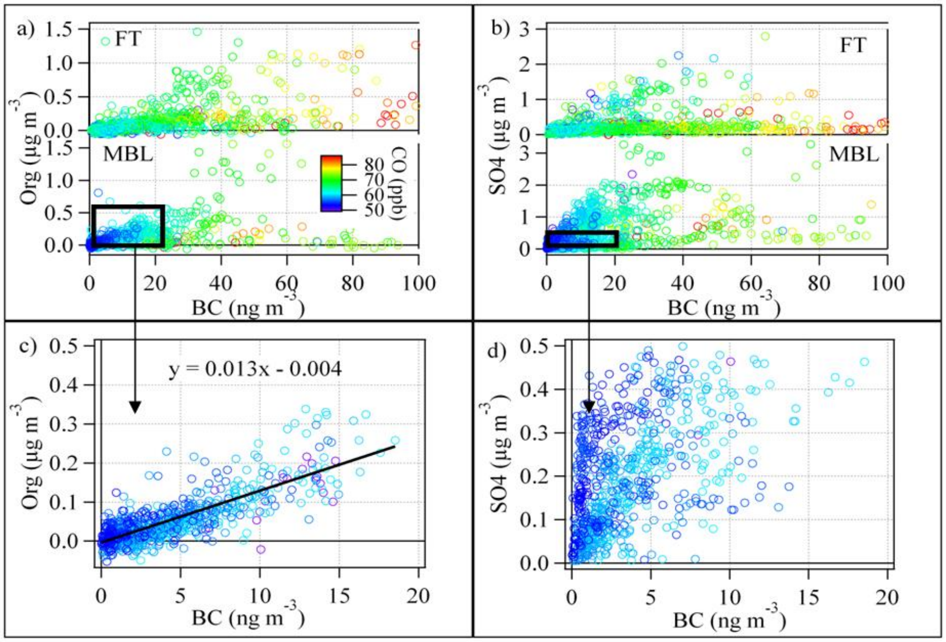

Figure 5. a) Org vs BC mass, colored by CO, both above (FT) and below (MBL) the inversion, b) Org vs BC mass, colored by CO, and c) Org and SO4 vs BC Mass under 0.02 µg m^{-3} and CO less than 61 ppb.

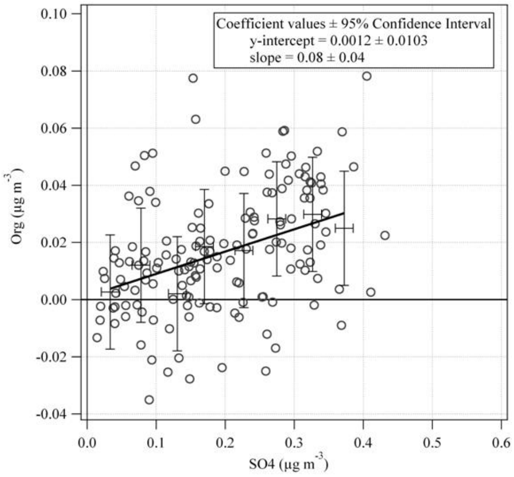

Figure 6. Natural Org vs. SO4, one minute and bin-averaged data.

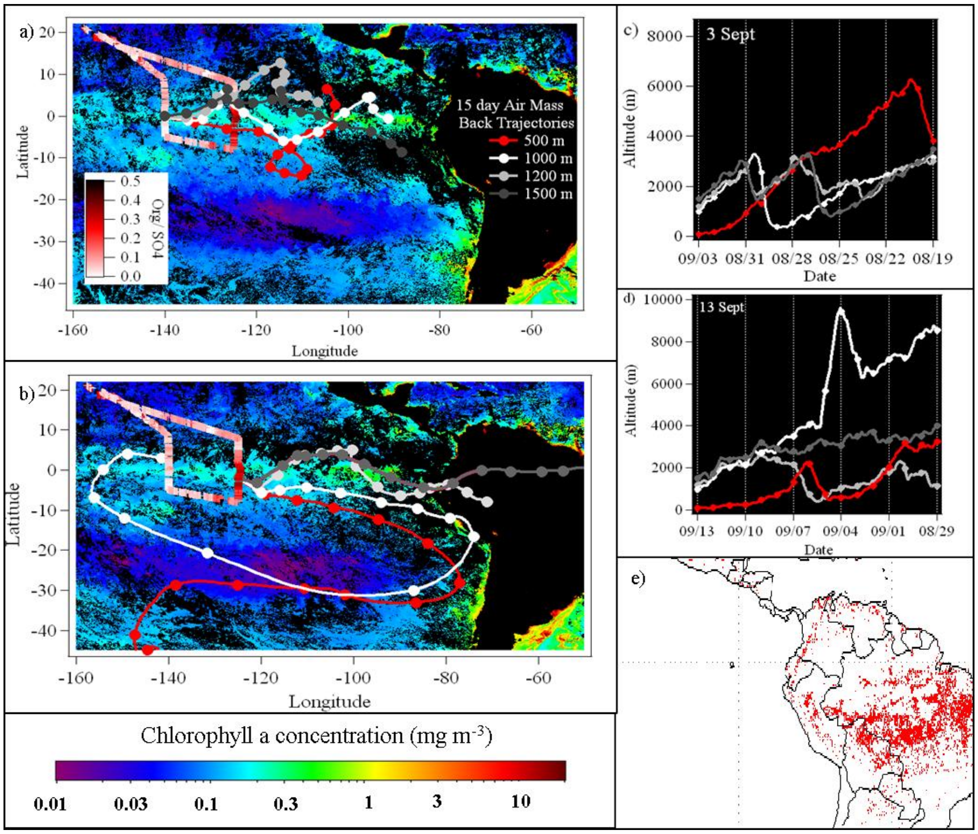

Figure 7. SeaWIFS chlorophyll-a 8 day composite for periods a) 29 Aug-5 Sep 2009 overlaid by AMBTs from 3 Sep 2009 and b) 6 Sep – 13 Sep 2009 overlaid by AMBTs from 13 Sep 2009. Cruise track is shown, colored by Org/SO4. AMBT altitude profiles are shown for c) 3 Sep 2009 and d) 13 Sep 2009. Panel e) biomass burning events from 1 Sep – 8 Sep 2009 (FLAMBE').

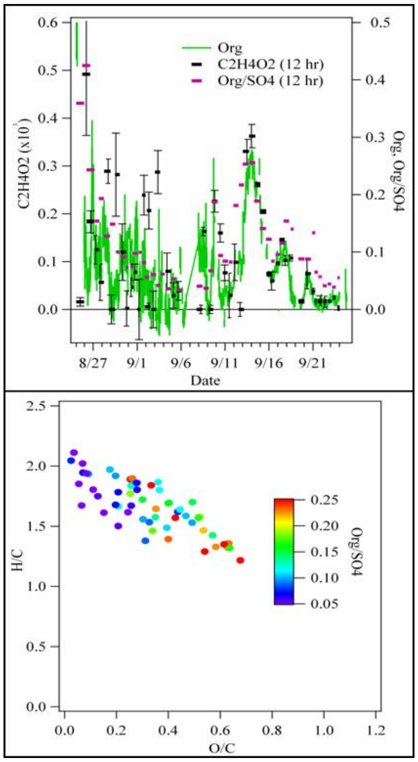

Figure 8. (Top) Time series of Org (10 min average), Org/SO4 (12 hr average), and C2H4O2 (12 hr). One sigma errors for the data are indicated. (Bottom) H/C vs O/C for the 12 hour averaged data (Van Krevelen plot).

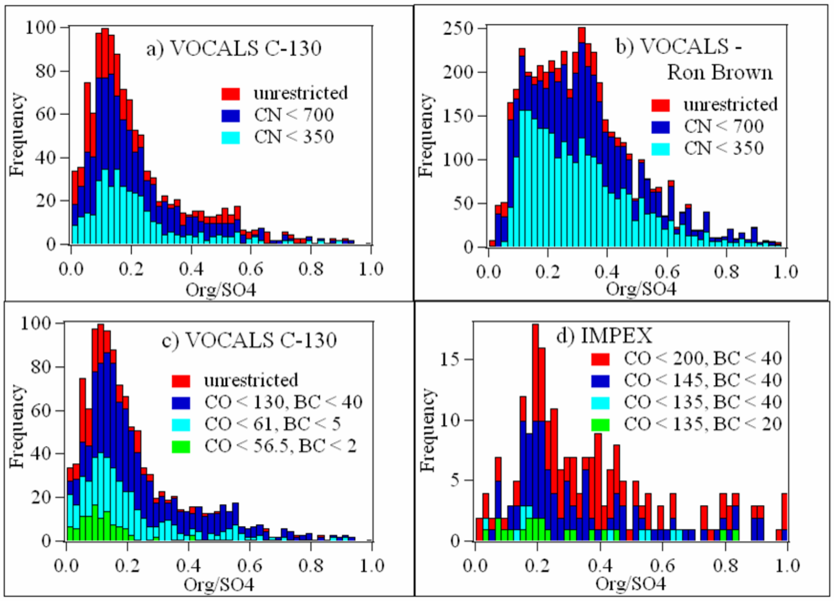

Figure 9. Histograms of Org/SO4 from different platforms and campaigns, restricted to varying clean air criteria. Units are as follows: CN (cm-3), CO (ppb), and BC (ng m^{-3}).

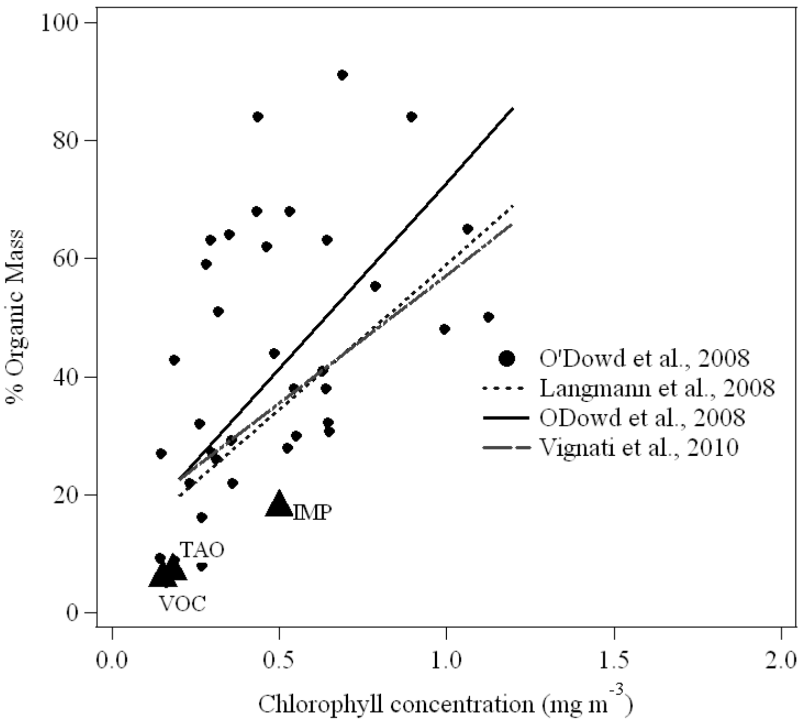

Figure 10. Organic-inorganic sea-spray source functions from recent studies (adapted from O'Dowd et al., 2008, Langmann et al., 2008, Vignati et al., 2008). Campaign averaged data from VOCALS, TAO, IMP are indicated by triangles.