

On the Link Between Ocean Biota Emissions, Aerosol, and Maritime Clouds: Airborne, Ground, and Satellite Measurements off the Coast of California

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Abstract

Surface, airborne, and satellite measurements over the eastern Pacific Ocean off the coast of California during the period between 2005 and 2007 are used to explore the relationship between ocean chlorophyll A, aerosol, and marine clouds. Periods of enhanced chlorophyll A and wind speed are coincident with increases in particulate diethylamine and methanesulfonate concentrations. The measurements indicate that amines are a source of secondary organic aerosol in the marine atmosphere. Subsaturated aerosol hygroscopic growth measurements indicate that the organic component during periods of high chlorophyll A and wind speed exhibit considerable water-uptake ability. Increased average cloud condensation nucleus (CCN) activity during periods of increased chlorophyll A levels likely results from both size distribution and aerosol composition changes. The available data over the period of measurements indicate that the cloud microphysical response, as represented by either cloud droplet number concentration or cloud droplet effective radius, is likely influenced by a combination of atmospheric dynamics and aerosol perturbations during periods of high chlorophyll A concentrations.

Introduction

A physical relationship with potentially significant climatic implications that remains poorly understood is that between ocean ecology, aerosol, and clouds. Ocean biota emissions influence cloud condensation nucleus (CCN) properties, which in turn affect clouds through the following two so-called aerosol indirect effects: (1) for a fixed liquid water amount, more numerous sub-cloud aerosol result in more reflective clouds because of more abundant and smaller cloud droplets (Twomey, 1977); and (2) for more numerous and smaller cloud droplets, suppressed droplet collision-coalescence results in less precipitation and clouds with enhanced albedo (Albrecht, 1989). Marine stratocumulus clouds exert a strong net cooling effect globally owing to their persistent coverage over oceans, their high albedo compared to relatively dark ocean surfaces, and their close proximity to the surface. Stratocumulus clouds are especially abundant in subtropical subsidence regions, such as off the coast of California, where strong inversions exist at the boundary layer top.

Ocean biota emissions influence marine aerosol. Oceans are a source of particulate matter, particularly organic, via the following mechanisms: (1) primary emissions as a result of bubble bursting (Hoffman and Duce, 1976; Gershey, 1983; Blanchard, 1989; Tseng et al., 1992; Middlebrook et al., 1998; Martensson et al., 2003; Lewis and Schwartz, 2004; O'Dowd et al. 2004; Keene et al., 2007); (2) secondary formation via the oxidation of emitted volatile organic compounds (VOCs) followed by condensation onto pre-existing particles (O'Dowd and de Leeuw, 2007); (3) secondary formation by the partitioning of VOCs into cloud droplets, followed by aqueous-phase reactions to produce low-volatility organics that remain in the aerosol phase after droplet evaporation (Warneck, 2003; Crahan et al., 2004; Ervens et al., 2004; Yu et al., 2005; Sorooshian et al., 2006a, 2007a/b); and (4) new particle formation (Hegg et al., 1990; Covert et al., 1992; Leck and Bigg, 1999; Kazil et al., 2008). Recent measurements indicate that another pathway for organic aerosol formation is through aqueous-phase processing in deliquesced particles (Liggio et al., 2005; Volkamer et al., 2008; Corrigan et al., 2008; Hennigan et al., 2008).

Perhaps the most-documented example of the influence of ocean biota on aerosol involves ocean-emitted dimethylsulfide (DMS) undergoing oxidation to ultimately produce sulfate (Andreae and Raemdonck, 1983; Shaw, 1983; Charlson et al., 1987; Ayers and Cainey, 2007, and references therein). DMS can be emitted by phytoplankton directly, by the decomposition of dimethyl sulfoniopropionate, or by complex physiological and ecological interactions (e.g. Challenger and Simpson, 1948; Lovelock et al., 1972; Andreae, 1990; Leck et al., 1990). Facchini et al. (2008a) have also shown that biogenic emissions are a source of amines, specifically diethylamine (DEA) and dimethylamine (DMA), in marine aerosol via a gas-to-particle conversion mechanism. Meskhidze and Nenes (2006; hereinafter referred to as MN06) proposed a secondary organic aerosol (SOA) formation mechanism via the oxidation of ocean-emitted isoprene. Recent laboratory CCN experiments have shown that 2-methyltetrols, soluble isoprene oxidation products, can increase CCN levels in pristine marine atmospheres that are limited in CCN (Ekstrom et al., 2008). However, Arnold et al. (2008) suggested an oceanic isoprene source is insignificant in modulating marine aerosol abundances.

In addition to ocean-derived VOCs condensing onto pre-existing particles, organics can partition into cloud droplets and undergo aqueous-phase oxidation to

produce low-volatility organic species such as organic acids and oligomers. This is supported by similar spatial distributions between enhanced glyoxal levels and ocean chlorophyll (Fu et al., 2008); that study showed that there is a large marine source of dicarbonyls (e.g. glyoxal and methylglyoxal) missing in the GEOS-Chem global chemical transport model, which can be explained by marine biota emissions. Glyoxal, methylglyoxal, and glycolaldehyde, an aqueous-phase precursor to glyoxal (Perri et al., 2008), have been shown in laboratory studies to form low-volatility particulate organics after subsequent aqueous-phase oxidation (Carlton et al., 2007; Altieri et al., 2008; Perri et al., 2008). The aqueous-phase oxidation process presents another route by which marine biota emissions can influence aerosol properties.

The nature of primary biogenic particles remains poorly understood, owing to their diverse source mechanisms and the difficulty in their quantification (Andreae and Rosenfeld, 2008). Numerous studies have pointed to the importance of considering organic species in the surface microlayer of the ocean surface that can be lofted to the atmosphere in addition to sea salt (Riley, 1963; Blanchard 1964). Primary marine aerosol have been shown to be enriched with organics, especially water-insoluble species, in the submicron size range during periods of enhanced primary productivity (O'Dowd et al., 2004). The surface-active properties of such species can substantially affect the CCN activity of marine aerosol (e.g. Facchini et al., 1999). A body of work has specifically shown that ocean waters contain insoluble organic submicrometer particles that are typically joined into chains or aggregated balls, termed "marine microcolloids" (Wells and Goldberg, 1991, 1993; Benner et al., 1992; Wells, 1998; Bigg et al., 2004; Leck and Bigg, 2005a). The particles are connected by a gel-like material identified as marine exopolymer secretions (EPS) of algae and bacteria (Decho, 1990; Verdugo et al., 2004). It has been shown that a fraction of the EPS can spontaneously assemble into gels, and that these molecules exhibit high surface activity and strongly resist water loss (Chin et al., 1998). It was shown in the high Arctic that the CCN concentration was not governed by oxidation products of DMS, but by the concentration in the air of the small insoluble organic particles derived from the surface layer via bubble bursting, onto which acidic gases condense (Leck and Bigg, 2005b). They also showed that similar processes likely occur over all oceans (Leck and Bigg, 2008; Bigg and Leck, 2008). Although the importance of surface-active organic aerosols for pristine marine clouds has been demonstrated (Lohmann and Leck, 2005), consideration should be given to the complication that the gels of airborne marine aggregates can potentially collapse as a results of ultraviolet light exposure (Orellana and Verdugo, 2003), polymer hydrolysis by bacterial ectoenzymes (Verdugo et al., 2004), or acidification (Chin et al., 1998).

Clearly, significant uncertainty remains concerning the relative abundance of marine particulate matter (specifically organic) originating from biota emissions, the identity, transformation, and fates of those specific species, and the extent to which those species alter the physicochemical properties of particles. Since ocean emissions have been shown to modulate aerosol properties, it is of interest to evaluate if there are concomitant changes in cloud properties.

Recent work has studied the effect of phytoplankton blooms on cloud properties, via changes in CCN properties, using satellite remote sensing measurements (MN06; Miller and Yuter, 2008, hereinafter referred to as MY08). The methodology used in these two studies consisted of comparing cloud droplet effective radius (r_e) with levels of

chlorophyll A (chl A), the photosynthetic pigment in phytoplankton. These studies showed that r_e and chl A can be inversely proportional at a specific location and time frame; however, the correlation between r_e and chl A is sensitive to the methodology used, including the location studied, the time frame, and the use of threshold chl A levels to distinguish between bloom and non-bloom conditions (Meskhidze and Nenes, 2008).

The goal of our study is to further investigate the relationship between chl A, aerosol properties, and cloud microphysics using data from three measurement platforms (ground, aircraft, and satellite). The winds associated with the California current cause upwelling as surface water flows west, allowing nutrient-rich water to upwell, which results in frequent high chl A conditions. We investigate ocean-aerosol-cloud interactions in the marine atmosphere adjacent to the California coast. First, the spatial and temporal variation of chl A levels are presented off the coast of California. Then we evaluate whether enhanced chl A levels influence aerosol properties, and if so, by how much. Finally, we determine the extent to which cloud properties are affected during high chl A periods.

Experimental Methods

This study is based on data from three measurement platforms (airborne, ground, satellite) off the coast of California between 2005 and 2007. The space-borne satellite data are presented for the entire duration of 2005 – 2007, whereas the aircraft data are from July 2007, and the ground data are from June – September 2005. It is noted that July typically represents the month with the maximum stratocumulus coverage for this area (Warren et al., 1986).

Airborne Measurements

During July 2007, airborne measurements were made on board the Center for Interdisciplinary Remotely Piloted Aircraft Studies (CIRPAS) Twin Otter as part of the Marine Stratus/Stratocumulus Experiment (MASE II). We specifically report on measurements between July 12 – July 31 off the central coast of California (35.5 N, 37.0 N; 122.0 W, 123.5 W). The description of the instrument payload can be found in Table 1, and for a more detailed explanation of the instruments, the reader is referred to Hersey et al. (2009). Measurements were carried out to characterize aerosol and cloud properties.

Aerosol and cloud droplet size distribution data were obtained by a differential mobility analyzer (DMA) and forward scattering spectrometer probe (FSSP, PMS Inc., modified by DMT Inc.), respectively. Submicrometer water-soluble aerosol chemical composition (i.e. inorganics, organic acids, amines) was measured by a particle-into-liquid sampler coupled to ion chromatography (PILS-IC, Brechtel Mfg Inc.; Sorooshian et al., 2006b). A continuous flow thermal gradient cloud condensation nuclei counter (CCNc, Droplet Measurement Technologies Inc.; Roberts and Nenes, 2005; Lance et al., 2006) was used to quantify the number of particles that activate at supersaturations ranging from 0.1% to 0.6%. Subsaturated aerosol hygroscopicity measurements were provided by a differential aerosol sizing and hygroscopicity spectrometer probe (DASH-SP; Brechtel Mfg Inc.; Sorooshian et al., 2008b).

Ground Measurements

McComiskey et al. (2009) detail the suite of instruments deployed at the Department of Energy Atmospheric Radiation Measurement (ARM) Mobile Facility at Pt. Reyes, California (38.10 N; 122.96 W) from mid-March through mid-September in 2005. For this study, we present data only between June 27 - September 13. Table 1 describes the relevant instrumentation at the site. It is noted that r_e was calculated using measurements of liquid water path (LWP) and cloud optical depth (τ_d) with the following equation (Stephens, 1978):

$$r_e = 1.5 (LWP/\tau_d), \quad (1)$$

where LWP is in g m^{-2} and r_e is in μm . As shown by McComiskey et al. (2009), cloud drop number concentration (N_d) was derived from measurements of LWP and τ_d using the adiabatic assumption:

$$N_d = C(T,P) \tau_d^3 LWP^{-2.5}, \quad (2)$$

where $C(T,P)$ is a known function of cloud base temperature (T) and pressure (P).

In-situ aerosol data were obtained from the Aerosol Observation System (Sheridan et al., 2001; Delene and Ogren, 2002), into which air was sampled from a 30 m tower. We use aerosol index (AI), defined as the product of aerosol light scattering and the Ångström exponent (\hat{a}), as a CCN proxy. The Ångström exponent is related to the shape of the aerosol size distribution and is inversely related to average particle size. AI has been shown to correlate better with cloud properties and columnar aerosol concentrations as compared to aerosol optical depth (Nakajima et al., 2001). All ground-based data are interpolated to synchronize with the 20 s temporal resolution of the microwave radiometer (MWR), which is the source of the LWP measurement.

Satellite Remote Sensing Measurements

Table 1 summarizes the satellite data products that were used. Measurements of chl A are from the Sea-viewing Wide Field-of-view Sensor (Sea-WiFS) and cloud and aerosol measurements are obtained from the Moderate Resolution Imaging Spectroradiometer (MODIS) on both the AQUA and TERRA satellites. MODIS cloud data are used only when the cloud fraction exceeded 70%. Cloud fraction and r_e data are not inversely correlated, which would have indicated bias in r_e associated with broken clouds (Marshak et al., 2006).

We note that chl A is a measurement of phytoplankton biomass and it is not necessarily a proxy for primary production (Meredith et al., 2003). However, it has been shown that chl A and primary production are correlated in certain regions (Meredith et al., 2003; Korb and Whitehouse, 2004; Perry et al., 1989), and numerous other studies have used chl A as a proxy for identifying periods of low and high ocean biological activity (e.g. Andreae et al., 1994; O'Dowd et al., 2004; Ware and Thomson, 2005; MN06; Prakash and Ramesh, 2007; MY08; Facchini et al., 2008b). Therefore, we consider chl A as a proxy for phytoplankton biomass and also suggest that it may also

represent primary production (i.e. biota emissions), but that caution must be exercised in doing so.

Since recent work by MN06 and MY08 has used MODIS and Sea-WIFS data, it is important to compare the sampling statistics and overall methodology used here as compared to those studies, as these differences may have a bearing on the conclusions (Meskhidze and Nenes, 2008). Meskhidze and Nenes (2008) show that an accurate evaluation of the correlation between chl A and r_e should include all values of these parameters as opposed to assigning a threshold value for chl A to distinguish between bloom and non-bloom conditions. In this study, we use all data available (no thresholds) between 2005 – 2007, which coincides with locations and times when in-situ measurements are available off the coast of California. As discussed below, we perform this analysis for three regions (Figure 1), two of which coincide with measurement sites, and one farther west over the ocean that is removed from high chl A areas. The area of the spatial domains was chosen to be relatively small as compared to those in MN06 and MY08 to allow a close comparison with in-situ and surface measurements. Expanding the area of the spatial domains by up to a factor of four was found to have no bearing on the conclusions. The range of chl A levels in our regions of study are comparable to those of MN06 and MY08; however, the influence of ocean biota emissions on clouds does not scale linearly with chl A (Meskhidze and Nenes, 2008).

Although our choice of location for the remote sensing measurements is restricted by the availability of in-situ measurements, it is still important to consider the potential influence from non-biogenic sources (e.g. anthropogenic pollution and dust) in the region. Daily aerosol optical thickness (AOT) measurements at 0.55 μm from MODIS reveal that during the respective year of measurements in the domain of the three regions in Figure 1, average AOT levels were between 0.12 and 0.15 for 2005 - 2007. As a basis for comparison, globally-averaged AOT over cloud-free oceans was determined by Kaufman et al. (2005) to be 0.14 using two years of MODIS data, with an anthropogenic component amounting to 0.033. They also assumed a baseline level of 0.06 ± 0.01 to represent calm marine conditions. We note that exclusion of MODIS data on the few days with the highest AOT values (0.3 – 0.5) does not alter the conclusions drawn from the satellite measurements.

Results and Discussion

In order to evaluate the effect of ocean chl A on aerosol and cloud properties in the area of interest, all measurements during times influenced by fresh anthropogenic pollution have been removed from this analysis; these instances have been identified using back-trajectory data from the NOAA HYSPLIT model (Draxler and Rolph, 2003) and particle concentration data during the duration of the field measurements. Our screening procedure to remove dirty air masses from the analysis of the aircraft data resulted in noticeable differences in composition and hygroscopicity (see Hersey et al., 2009). For example, hygroscopicity was significantly suppressed in dirty air masses and sulfate levels in dirty and clear air masses were $\gtrsim 2 \mu\text{g}/\text{m}^3$ and $\lesssim 1 \mu\text{g}/\text{m}^3$, respectively. Approximately 10% and 34% of the data are removed for the period of the aircraft campaign (July 2007) and the overall study period (2005 – 2007), respectively. It is noted, however, that the background marine aerosol composition is still influenced by

aged ship emissions in the form of sulfate and organics (e.g. Capaldo et al., 1999). Our goal is to assess the effects of marine biota emissions on aerosol and clouds on top of the baseline aerosol conditions for the region. All measurements are also removed when there was evidence of a decoupled marine boundary layer, which was identified using vertical profiles of meteorological and particle concentration data. Conditions such as these would not favor an interaction of boundary layer aerosol and clouds, and would therefore obfuscate the analysis.

Temporal and Spatial Variation in Chl A

Figure 1 displays the average chl A levels between 2005 and 2007 off the US west coast. Labeled boxes correspond to the three spatial domains in which MODIS data are evaluated: (1) aircraft measurement region; (2) surface-based measurement region; and a (3) low chl A area farther off the coast. Figure 2 shows chl A levels between 2005 – 2007 for these three regions. Significantly higher chl A conditions exist adjacent to the California coast each year as compared to farther west off the coast. In addition, the chl A levels show significant variation during the time periods of the two field measurement programs, which allows us to examine the variation of aerosol and cloud measurements as a function of chl A.

Aircraft data from July 2007 are divided into three week-long periods in Table 2 that are synchronized with Sea-WiFS measurements. We examine three-day back-trajectories for the sampled air masses from each flight with respective chl A concentrations in those source regions to evaluate the level of aerosol exposure to potential ocean biota emissions prior to sampling. Marine boundary layer aerosol typically have a residence time of a few days prior to their removal primarily by wet deposition. Sampled air from the first week originated farther west over the Pacific Ocean. The second period consisted of air masses that usually originated farther west over the ocean, but with some air masses transported southward along the coast towards the end of that week. Air masses sampled during the final week were transported southward along the coast. Figure 3 shows typical back trajectories for the two scenarios. Chl A levels for the region farther west over the ocean were significantly lower and more stable ($0.24 \pm 0.05 \text{ mg/m}^3$; 32.0 N, 40.0 N; 122.0 W, 140.0 W) than those in the domain of the aircraft measurements (35.5 N, 37.0 N; 121.5 W, 123.5 W) and farther up the coast (35.0 N, 50.0 N; 121.5 W, 127.0 W). Chl A concentrations increased each successive week during the time of the aircraft study in the two latter regions (aircraft measurement domain: 1.01, 1.08, 3.58 mg/m^3 ; up the coast: 1.38, 1.69, 2.24 mg/m^3). The wind speed in the aircraft measurement domain was also highest during the third week, which is consistent with the lowest average sea-surface temperature, indicative of enhanced upwelling. Wind speed (<http://www.ndbc.noaa.gov/>) and upwelling index (<http://www.pfeg.noaa.gov/>), a measure of upwelling strength, were moderately correlated during these three periods ($r^2 = 0.40$); the correlation was similar ($r^2 = 0.42$) during the duration of the Pt. Reyes measurements in the summer of 2005. The data indicate that the air masses probed during the third period of aircraft flights experienced the most exposure to high chl A areas, followed in order by the second and first periods.

Ocean-Derived Biogenic Markers in Marine Aerosol

Aircraft measurements are used to investigate the relationship between ocean emissions and aerosol composition. The average concentrations of methanesulfonate (MSA), an oxidation product of DMS, and diethylamine (DEA) increase as a function of chl A, with a significant increase (more than a factor of two) simultaneous with the significant enhancement in chl A during the final time period in Table 2. The higher wind speed during the final period may have also resulted in peak concentrations of these species, especially MSA, since DMS levels have been associated with increased wind speed (e.g. Andreae et al., 1994). But we note that owing to the relatively long residence time of atmospheric aerosol, local DMS emissions are not necessarily correlated with particulate MSA. DEA and MSA are also not necessarily expected to exhibit a similar temporal trend during periods of high biological activity since MSA production is strongly associated with photochemical activity unlike amines (Facchini et al., 2008a). Although it has been shown that in specific regions and plankton ecological regimes (chl A < 0.25 mg/m³) that DMS concentrations in water exhibit the same trend as chl A (Andreae, 1985; Andreae et al., 1994), enhanced MSA levels are not expected to be a result of high chl A since diatoms (poor DMS emitters) are predominant in upwelling regions. The large standard deviations in MSA concentration on a weekly basis are possibly linked to complex physical and biological interactions that govern the production and breakdown of DMS in water.

Figure 4 shows that MSA and diethylamine are moderately correlated ($r^2 = 0.41$), and when detected simultaneously, MSA was on average 7.1 times more abundant. Both DEA and MSA exhibit their highest concentrations at altitudes less than 100 m over the ocean surface and then decay with increasing altitude in the boundary layer (Figure 4). These two species did not exhibit an increase in concentration in polluted air masses, specifically downwind of ships. These results are consistent with those of Facchini et al. (2008a) who showed that DEA and MSA are both enhanced in cleaner air masses. Since they measured significantly higher DEA concentrations during a period of high biological activity, this strongly suggests that the third week of our aircraft study was characterized by a higher amount of biota emissions, which is coincident with higher chl A levels and enhanced wind speeds. Facchini et al. (2008a) concluded that similar to ammonia and other reduced gases like DMS, that DEA may be a microbial turnover end product of labile organic matter (Gibb et al., 1999; Johnson et al., 2007).

Sulfate, ammonium, and organic acids (defined here as the sum of carboxylic acids with C₁ – C₉) do not exhibit a noticeable trend with chl A (Table 2). Although sulfate is an oxidation product of MSA, the two species are not highly correlated owing to background concentrations of sulfate likely from aged anthropogenic emissions. Organic acids, especially oxalate, tend to be more abundant in and above clouds, as compared to below clouds, due to a cloud processing mechanism, especially in the same sampling location as the current study (Crahan et al., 2004; Sorooshian et al., 2007). DEA likely condenses onto pre-existing particles partly because the average sub-cloud particle number concentration was similar during the three time periods (275 – 307 cm⁻³). These data are consistent with the conclusions drawn by Facchini et al. (2008a), who proposed that a gas-to-particle conversion process rather than a bubble bursting mechanism results in amine species partitioning to the aerosol phase. This latter hypothesis is supported by measurements of gaseous amines in the marine atmosphere (Vanneste et al., 1987).

Amines have been shown to form amine salts by acid–base chemistry with either sulfuric or nitric acid, and then condense onto existing particle surfaces (Murphy et al., 2007; Sorooshian et al., 2008a). As sulfate usually exceeds nitrate by more than an order of magnitude in this region, sulfuric acid is likely the acid reacting with the amine base.

At the peak of the chl A levels in July 2007, the cumulative mass concentration of MSA and DEA was approximately 14% that of sulfate. DEA and MSA were the only ocean biota tracers speciated in this study, but this does not preclude the possibility that other ocean-derived particulate components were present; these other species, potentially including primary biogenic emitted species, are hypothesized to have lower water-solubility since they could not be speciated using the PILS-IC technique. O’Dowd et al. (2004) showed that during bloom periods in North Atlantic waters, the organic fraction contributes ~ 63% to the submicrometer aerosol mass (~ 45% is water-insoluble and ~ 18% is water-soluble). They also showed that the organic fraction of the aerosol decreases to ~ 15% during periods of low ocean biological activity. Extrapolating their results to our study suggests that MSA and DEA constitute a minor proportion of the ocean-derived organic component and generally represent a conservative estimate of the effect of ocean biota emissions on marine aerosol composition and other associated properties (e.g. aerosol size distribution, CCN activity).

Does the Modified Composition Influence Aerosol Hygroscopicity?

We examine aerosol hygroscopic subsaturated growth factors ($GF = D_{p,wet}/D_{p,dry}$, where $D_{p,dry} = 0.2 \mu\text{m}$) to determine whether a modification of aerosol composition due to ocean emissions influences water-uptake. The selected dry particle diameter of $0.2 \mu\text{m}$ lies within the size range ($0.125 - 0.25 \mu\text{m}$) identified in a separate study in the Northern Atlantic where MSA and DEA reached significant mass concentrations (Facchini et al., 2008a). Table 2 shows an enhancement, from 1.52 ± 0.12 to 1.67 ± 0.05 , in the below-cloud growth factors at $\text{RH}_{\text{wet}} = 85\%$ ($\text{RH}_{\text{dry}} < 8\%$) for the last two time periods (no data are available from the first period). These growth factors and respective standard deviations are comparable to other measurements in the vicinity of clouds in the same geographic area (Hersey et al., 2008). It is noted that the growth factors ($\text{RH}_{\text{wet}} = 85\%$) for pure ammonium bisulfate and sulfuric acid, which were the two predominant forms of sulfate during these flights, are ~ 1.62 and ~ 1.91, respectively (Brechtel and Kreidenweis, 2000). Little variation existed between the second and third periods for the sub-cloud ammonium-to-sulfate molar ratios (0.70 ± 0.56 to 0.64 ± 0.45).

Using the hygroscopic closure method of Hersey et al. (2008) for MASE II measurements provides an estimate of the organic fraction growth factor needed to achieve perfect closure between the composition and growth factor measurements, assuming additive and independent water uptake by the individual aerosol components. Since the hygroscopic growth factors of organic acids, a class of organics with relatively high-water solubility, are considerably less than those of ammonium bisulfate and sulfuric acid at $\text{RH} = 85\%$ (Saxena et al., 1995; Hansson et al., 1998; Li et al., 1998; Ansari and Pandis, 2000; Cruz and Pandis, 2000; Peng et al., 2001; Prenni et al., 2001, 2003; Wise et al., 2003; Sorooshian et al., 2008b), it is expected that any addition of organic matter to acidic sulfate particles should suppress the overall hygroscopicity. For the second and third periods the calculated organic growth factors are 1.45 ± 0.37 and

1.35 ± 0.22 , respectively, which represent relatively high values for organics. Although the overall growth factor increased during the third period, the predicted organic growth factor decreased owing to a reduced organic volume fraction. An enhanced inorganic volume fraction relative to organics during the third period can potentially be explained by MSA producing hygroscopic sulfate components in the aerosol. The results indicate that the organic component of the marine aerosol during periods of high chl A, which contains a mixture of organics from ocean emissions and likely aged anthropogenic pollution (i.e. aged ship emissions), exhibits significant hygroscopicity.

Do Ocean Biota Emissions Enhance CCN Concentrations?

The average CCN concentration at $\sim 0.3\%$ supersaturation tended to increase each successive weeklong period, during which time the average total submicrometer particle number concentration did not change significantly (Table 2). The activated fraction of aerosol (ratio of CCN to total particle concentration) increased each successive period as well (0.24, 0.42, 0.46). Although the average CCN values exhibit an increasing trend as a function of chl A, we note that caution must be applied before extrapolating the results of this section owing to the considerable variability in the CCN measurement during the individual weeks. To evaluate the extent to which ocean emissions influence CCN activity, it is necessary to decouple effects associated with aerosol composition and size distribution. The sub-cloud dry aerosol size distributions exhibited variability on different days. A mode diameter usually existed between 20 – 50 nm and also between 80 – 170 nm (Table 2), the latter being more important with regard to droplet activation. Since the levels of measured biogenic aerosol markers were similar during the first two periods in the vicinity of the aircraft measurements, the increase in CCN concentration during the second week was likely due to size distribution effects. The larger sub-cloud mode size is significantly larger during the second week (166 ± 16 nm versus 98 ± 54 nm).

Since the size of the larger mode decreased from the second to third period, the increase in CCN activity during the third period is likely due to chemical effects. This is consistent with the enhancement in the subsaturated hygroscopic growth factor during the third period, which is coincident with higher DEA and MSA levels. Organics originating from ocean emissions can partition to the aerosol phase and influence CCN activity by adding solute and suppressing surface tension; these effects of organics on CCN activity have been discussed in previous work (Shulman et al., 1996; Li et al., 1998; Facchini et al., 1999; Nenes et al., 2002; Cavalli et al., 2004). It has been shown that surface tension decreases as a function of water-soluble organic carbon during bloom periods in the North Atlantic (Cavalli et al., 2004); these authors attributed the surface tension depression to organic species with both polar groups and aliphatic chains. Furthermore, the surface layer of seawater is enriched with surface-active organic matter, including previously mentioned microcolloids, fatty acids, humic substances, alcohols, and lipidic and proteinaceous material that have the potential to alter the surface tension behavior of particles (Lion and Leckie, 1981; Gershey, 1983; Wells and Goldberg, 1991, 1993; Benner et al., 1992, 1997; Chin et al., 1998; Mochida et al., 2002; Bigg et al., 2004; Cavalli et al., 2004; Verdugo et al., 2004; Bigg, 2007; Leck and Bigg, 2005a, 2005b, 2008).

Are CCN and Cloud Droplet Number Concentrations Correlated?

To evaluate the extent to which a link exists between ocean emissions and cloud properties via a modulation in CCN properties, we examine cloud droplet number concentrations (N_d) while simultaneously considering dynamical effects (Table 2). N_d increased during the third period ($130 \pm 47 \text{ cm}^{-3}$) as compared to the previous two ($104 \pm 56 \text{ cm}^{-3}$ and $99 \pm 28 \text{ cm}^{-3}$). Thus, the average N_d exhibited a noticeable enhancement coincident with the enhanced chl A levels during the third period. The third period was, however, also characterized by an overall increase in cloud liquid water content (LWC), cloud depth, wind speed, and turbulent kinetic energy (TKE), as represented by the square of the standard deviation of the cloud-base updraft velocity (σ_w^2); the values of these dynamical parameters were similar the first two periods (except wind speed), during which time the average N_d did not change considerably. To evaluate aerosol effects on N_d simultaneously with dynamic effects, we compare concentrations of CCN and N_d for all three periods. Average CCN levels increase each successive time period, while the average N_d increases only in the final week when cloud turbulence was higher. When isolating events with a relatively small range in CCN ($80 - 87 \text{ cm}^{-3}$), the correlation between TKE and N_d was $r^2 = 0.95$ ($n = 3$), while the correlation between CCN and N_d for events with a small range in TKE ($0.03 - 0.06$) was only $r^2 = 0.41$ ($n = 3$). These results suggest that although enhanced chl A, and presumably enhanced biota emissions, altered aerosol composition (i.e. enhanced DEA) and CCN concentrations, atmospheric dynamics were likely more important in influencing N_d . However, the relative contribution of aerosol effects during periods of enhanced chl A and dynamical effects on cloud microphysics is uncertain, especially owing to the large variabilities and limited measurements. These uncertainties motivate the subsequent investigation into the effect of chl A on cloud microphysics using remote sensing measurements.

Do Enhanced Ocean Biota Emissions Affect Cloud Droplet Effective Radius?

Remote sensing measurements of r_e from MODIS within the domain of the aircraft measurements, the surface-based measurements (discussed in detail below), and a low chl A area are evaluated. In order to isolate effects of an aerosol perturbation on clouds, the r_e data are stratified into *LWP* bins in accord with Twomey's (1977) approach. Data are only used for *LWP* between $50 - 150 \text{ g/m}^2$, to avoid measurements of thin or broken clouds ($< 50 \text{ g/m}^2$) and precipitating clouds ($> 150 \text{ g/m}^2$). Since there were relatively few MODIS measurements in each *LWP* bin during the duration of the field measurements, cumulative data from 2005 - 2007 are used.

Table 3 shows that although the correlation between chl A and r_e was typically weak, it was usually negative in the high chl A regions and positive in the low chl Area. The largest negative correlation was $r = -0.29$ ($n = 62$; *LWP* = $125 - 150 \text{ g/m}^2$) in the vicinity of the surface-based measurements. Further stratification of the r_e data at each *LWP* bin into additional bins of cloud top pressure does not result in a significant change in the overall correlations. Because the correlation between chl A and r_e is usually

negative in the high chl A regions (although weak), the data do not preclude the possibility that ocean emissions can lead to enhanced N_d and reduced r_e .

Surface-Based Measurements from Pt. Reyes, California

Finally, we examine the relationship between chl A, aerosol, and clouds at the surface-based site at Pt. Reyes. Owing to the closer proximity to clouds, surface-based remote sensing measurements are not prone to some of the measurement challenges of space-borne data. In addition, the ground site is adjacent to the coastline, which provides a different positional perspective compared to airborne measurements performed above the ocean.

In the analysis below, we evaluate how a quantity representing aerosol – cloud interactions varied as a function of time during the period of surface measurements. Using the methodology of McComiskey et al. (2009), we quantify aerosol-cloud interactions here as

$$ACI = \frac{d \ln N_d}{d \ln \alpha} \quad (0 < ACI < 1) \quad (3)$$

(Feingold et al., 2001), where α is an observed proxy for aerosol abundance ($\alpha = \text{CCN}$ in our case). An ACI value of unity indicates that all particles activate into droplets. It has been shown that ACI values are sensitive to variability in various aerosol properties (e.g. concentration, size distribution, chemistry) (Facchini et al., 1999; Feingold et al., 2001; Nenes et al., 2002; Lance et al., 2004; Dusek et al., 2006) and cloud dynamics (Leaitch et al., 1996; Feingold et al., 2003; Kim et al., 2008). With regard to aerosol properties, numerous studies have shown that droplet activation is more sensitive to size distribution rather than composition (Fitzgerald, 1974; Feingold, 2003; Ervens et al., 2005; Dusek et al., 2006).

Figure 5 displays the temporal evolution of the ACI measurements, other daily-averaged aerosol parameters (CCN and AI), and chl A. Chl A levels ranged between 0.36 – 7.02 mg/m^3 , consistent with the range measured during the aircraft measurements in July 2007. Chl A shows a weak correlation with both CCN concentration ($r^2 = 0.02$) and AI ($r^2 = 0.07$) during the period of the ground measurements. The lack of correlation with AI is consistent with the aircraft measurements, which show that particle concentrations exhibited no significant relationship with chl A. The lack of a correlation between chl A and CCN concentrations suggests that for the aerosol transported to the ground site, a sufficient change in composition and size distribution did not occur as a function of nearby chl A variations to influence the water-uptake properties. These results are in contrast to the aircraft measurements, and this may be attributed to how the measurements were performed (airborne over water versus on the ground adjacent to the coastline). It is possible that there was more continental influence near the ground-based site and that volatilization and chemical transformation may have altered the composition and size distribution of air parcels by the time they reached the ground site. The latter hypothesis is supported by the aircraft measurements that showed DEA decaying rapidly in concentration with increasing altitude above the ocean surface.

The average *ACI* value for aggregate Pt. Reyes data was found to be 0.48 ($n = 20,996$; $r^2 = 0.14$) (McComiskey et al., 2009). *LWP* and *ACI* were found to be inversely related for $LWP < 150 \text{ g/m}^2$, likely because enhanced droplet collision-coalescence (i.e. reduction in N_d) at higher *LWP* obscures *ACI* values associated with droplet activation. For $LWP > 150 \text{ g/m}^2$, *ACI* was highly variable and sometimes negative owing to the small range of α , presumably resulting from wet scavenging. *ACI* measurements are reported for only three days in this study because of the difficulty in achieving sufficient variability in aerosol abundance on other days to provide a robust calculation of *ACI*. For this reason, it is significantly more difficult to determine *ACI* values from satellite and aircraft measurements (McComiskey et al., 2009). The three *ACI* values as follows: 0.54 ($n = 1286$, $r^2 = 0.24$, $LWP = 80 \pm 17 \text{ g/m}^2$), 0.61 ($n = 423$, $r^2 = 0.22$, $LWP = 130 \pm 27 \text{ g/m}^2$), and 0.90 ($n = 657$, $r^2 = 0.54$, $LWP = 195 \pm 45 \text{ g/m}^2$). *ACI* is positively correlated with *LWP* ($r^2 = 0.93$), and the highest *ACI* value was coincident with the time period exhibiting the highest chl A concentration ($\sim 7 \text{ mg/m}^3$). Because the *ACI* analysis is based only on three data points, it is not possible to deduce any general causal links between *ACI* and ocean emissions with strong confidence, especially since no relationship was observed between chl A and CCN activity.

The correlation between chl A and ground-based measurements of r_e ranges from $r = -0.08 - 0.29$, and there is less statistical significance for these correlations as compared to the MODIS analysis. The correlation between N_d and chl A was negative for all *LWP* bins examined ($r = -0.11 - -0.37$). These data are in contrast to the MODIS data and do not provide conclusive evidence of the influence of ocean biota emissions on cloud microphysics, a result that may be at least partly due to a limited dataset. The Pt. Reyes measurements however provide a valuable snapshot of how a fixed measurement platform can be used to explore the ocean-aerosol-cloud relationship.

Conclusions

Airborne, ground, and satellite measurements have been used to evaluate the relationship between ocean chl A, aerosol, and clouds off the coast of California. A step-by-step analysis has been carried out to address the following: (1) did enhanced phytoplankton biomass, as identified by chl A concentrations, occur during the time frame of the airborne and ground field measurements? (2) do increases in chl A affect aerosol properties (composition, size distribution, hygroscopicity, CCN activity)? and (3) when holding dynamical parameters constant (e.g. *LWP*), do modulations in aerosol properties from increased chl A levels influence cloud microphysics?

Chl A data between 2005 – 2007 along the California coast exhibit significant fluctuations and periods of enhanced phytoplankton biomass, and potentially other ecological and physical interactions resulting in marine biota emissions. Furthermore, chl A levels in a spatial domain farther west off the California coast exhibited much lower concentrations (\sim an order of magnitude), thereby providing a control area. Aircraft measurements provide evidence that increased chl A levels influence aerosol composition. Enhanced chl A levels and wind speeds are coincident with higher particulate concentrations of DEA and MSA, the abundances of which were typically an order of magnitude less than that of sulfate. DEA is likely produced via the reaction of the gaseous amine and acidic sulfates. Subsaturated aerosol hygroscopicity data indicate

that the ocean-emitted organics are sufficiently hygroscopic that they do not significantly suppress the overall growth factor of the multicomponent marine aerosol. Average CCN concentrations increased as a function of chl A while total particle concentrations were relatively stable; it is argued that both chemical and size distribution effects led to enhanced CCN levels as a function of chl A. The increase in CCN did not, however, translate to enhanced N_d . The data show that dynamic factors, such as turbulent kinetic energy (σ_w), may be more important in governing N_d . But there are considerable variations and a limited number of CCN and N_d measurements and we cannot confidently quantify the relative contributions of dynamic and aerosol effects on cloud microphysical properties.

Measurements from a coastline ground site at Pt. Reyes exhibit a weak correlation between chl A and several properties including CCN concentration, AI , N_d , and r_e . Cloud r_e data, stratified by LWP , from MODIS on the AQUA and TERRA satellites were compared to chl A levels in the vicinity of the field measurements and a lower chl A area farther west. Although relatively weak, the correlation between chl A and r_e was usually negative in the high chl A areas and positive in the low chl A areas. An inverse relationship at constant LWP suggests that ocean biota activity results in more numerous and smaller cloud drops.

This work shows that cloud microphysical properties off the coast of California may be influenced by both dynamical factors (e.g. turbulence) and the modification of aerosol properties during periods of increased chl A and presumably greater biota emissions. The multi-platform dataset presented here does not provide overwhelming evidence for a causal link between ocean biota emissions and cloud microphysics owing to limited data, conflicting results between the ground-based and satellite remote sensing measurements for the relationship between chl A and r_e , and the relatively large variability observed during the period of the aircraft measurements for key parameters such as CCN and N_d . However, the results show that there is a clear link between ocean phytoplankton biomass and aerosol properties, including the presence of particulate DEA, and that the intriguing relationships between ocean emissions, aerosol, and clouds need to be further explored. In addition, future work should investigate the role of primary biogenic emissions such as marine microcolloids (e.g. Decho, 1990; Verdugo et al., 2004; Leck and Bigg, 2008; Bigg and Leck, 2008) in influencing cloud microphysics. To unravel such complexities and the extent to which there is a causal link between ocean biological productivity, aerosol, and maritime clouds, additional multi-platform measurements are desirable. Although attention has been placed here on the influence of marine biota activity on aerosol and clouds, another important issue to explore is the extent to which clouds influence marine biota activity by way of reflecting sunlight, thereby regulating photosynthesis.

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Table 1. Summary of relevant instrumentation from three measurement platforms.

Platform	Measurement Reported	Instrument
Airborne (CIRPAS Twin Otter); Time span = July 2007; Daily measurement time (UTC) = 16:00 - 20:00; Location = off the central California coast	Particle concentration ($D_p > 3$ nm)	Condensation particle counter (Model 3025, TSI Inc.)
	Cloud drop size distribution ($D_p = 2 - 46$ μm)	Forward scattering spectrometer probe (FSSP, PMS, modified by DMT Inc.)
	Aerosol size distribution ($D_p = 10 - 800$ nm)	Scanning differential mobility analyzer
	Cloud liquid water content	Gerber PVM-100 probe
	Cloud condensation nucleus (CCN) concentration (supersaturation = 0.29% - 0.32%)	CCN counter (DMT Inc.; Roberts and Nenes, 2005; Lance et al., 2006)
	Subsaturated hygroscopicity ($D_{p,dry} = 200$ nm, RH = 85%)	Differential aerosol sizing and hygroscopicity probe (DASH-SP) (Brechtel Mfg. Inc.; Sorooshian et al., 2008b)
	Water-soluble composition ($D_p < 1$ μm)	Particle-into-liquid sampler (PILS) (Brechtel Mfg. Inc.; Sorooshian et al., 2006b)
Ground (ARM Facility); Time span = June - September 2005; Daily measurement time (UTC) = 15:00 - 24:00; Location = Pt. Reyes, California	Cloud liquid water path	Microwave radiometer (MWR; Turner et al., 2007)
	Cloud optical depth	Two-channel narrow field-of-view radiometer (2NFOV; Chiu et al., 2006)
	Cloud drop effective radius	2NFOV/MWR
	Aerosol index (= total aerosol light scattering x Angstrom exponent; scattering data are from 550 nm)	Nephelometer (Model 3563, TSI Inc.)
	Cloud condensation nucleus (CCN) concentration (supersaturation = 0.55%)	CCN counter (DMT Inc.)
	Cloud drop number concentration	MWR/2NFOV
Space (satellite remote sensing); Time span = 2005 - 2007; Daily measurement time (UTC) = 18:20 - 19:50 (TERRA), 20:30 - 22:00 (AQUA)	Chlorophyll A concentration	Sea-viewing Wide Field-of-view Sensor (SeaWiFS) Level 3
	Cloud liquid water path, cloud drop effective radius, aerosol optical thickness	AQUA/TERRA MODIS Level 2 (Collection 5)

Table 2. Aircraft measurements over a three-week period during July 2007 off the central coast of California. Values in brackets represent standard deviations. (DEA = diethylamine; MSA = methanesulfonate; SST = sea surface temperature; N_d = cloud droplet number concentration; σ_w^2 = turbulent kinetic energy)

Date	Chlorophyll A (mg/m ³)	DEA (ng/m ³)	MSA (ng/m ³)	Organic acids (ng/m ³)	Sulfate (ng/m ³)	Particle concentration (#/cm ³)	Size distribution modes (nm)	CCN (0.29 - 0.32%) (#/cm ³)	Growth factor (RH = 85%)	N_d (#/cm ³)	LWC (g/m ³)	Cloud Depth (m)	σ_w^2	Wind Speed (m/s)
7/12 - 7/19	1.01	14 [2]	24 [18]	62 [106]	783 [594]	307 [239]	36 [28], 98 [54]	73 [27]	NA	104 [56]	0.15 [0.07]	205 [35]	0.06 [0.08]	7.3 [1.1]
7/20 - 7/27	1.08	17 [5]	27 [22]	46 [55]	533 [358]	275 [230]	47 [4], 166 [16]	116 [73]	1.52 [0.12]	99 [28]	0.15 [0.07]	214 [70]	0.08 [0.07]	9.9 [2.1]
7/28 - 8/4	3.58	35 [13]	56 [49]	68 [123]	641 [409]	301 [92]	45 [5], 134 [25]	137 [79]	1.67 [0.05]	130 [47]	0.20 [0.08]	358 [60]	0.16 [0.14]	12.6 [1.5]

Table 3. Correlation (r) between chl A and cloud effective radius for various LWP bins. Number of data points for each correlation calculation are shown in parentheses. Note: The bottom row shows the correlation between chl A and cloud droplet number concentration (N_d).

Time duration	Spatial domain	Measurement platform	LWP bins (g/m^2)			
			50 - 75	75 - 100	100 - 125	125 - 150
2005 - 2007	# 1 in Fig. 1 (Aircraft domain)	AQUA	-0.04 (64)	0.01 (104)	-0.21 (87)	-0.08 (85)
		TERRA	-0.12 (139)	-0.14 (165)	-0.13 (129)	-0.11 (71)
	# 2 in Fig. 1 (Ground site domain)	AQUA	0.11 (38)	0.1 (86)	-0.17 (101)	0.04 (78)
		TERRA	-0.25 (120)	-0.13 (157)	-0.24 (143)	-0.29 (62)
	# 3 in Fig. 1 (Low Chl A area)	AQUA	0.25 (41)	0.05 (135)	0.2 (138)	0.27 (93)
		TERRA	0.23 (140)	0.16 (242)	0.12 (205)	0.01 (101)
2005	Ground site	Surface	0.06 (19)	0.04 (22)	0.29 (21)	-0.08 (22)
2005	Ground site	Surface (Chl A vs N_d)	-0.11 (19)	-0.19 (22)	-0.37 (21)	-0.12 (22)

Figure Captions

Figure 1. Average Sea-WiFS chl A concentrations off the western United States coast between 2005 and 2007. Spatial domain 1 corresponds to the vicinity of the aircraft measurements off the central California coast, domain 2 is in the vicinity of the ground-based measurements at Pt. Reyes, and domain 3 represents a low chl A area farther west over the Pacific Ocean. Image courtesy of NASA's Giovanni (giovanni.gsfc.nasa.gov).

Figure 2. Time series of chl A concentration in the three spatial domains shown in Figure 1: (1) within the aircraft measurement spatial domain; (2) near the ground measurements by Pt. Reyes; and (3) in a low chl A area farther west over the Pacific Ocean. The shaded areas represent the periods when field measurements were carried out (domain 1 = July 2007, domain 2 = June – September 2005).

Figure 3. Typical back-trajectories for air masses originating in (a) more chl A-enriched areas farther north as compared to those that originate (b) farther west over the ocean where there are significantly lower chl A levels. The back-trajectory analysis is for altitudes up to 1 km, and the airborne measurements were usually performed below 500 m during the MASE II field study.

Figure 4. Relationship between particulate diethylamine (DEA) and methanesulfonate (MSA) in the marine boundary layer off the central California coast. Marker sizes are proportional to chl A concentration (range = 1.01 – 3.58 mg/m³). The highest concentrations of DEA and MSA exist at lower altitudes near the ocean surface and are coincident with higher chl A concentrations.

Figure 5. Temporal evolution of surface-based measurements of *ACI* (Eq. 3), CCN concentration, aerosol index (*AI*), and chl A concentration at Pt. Reyes, California.

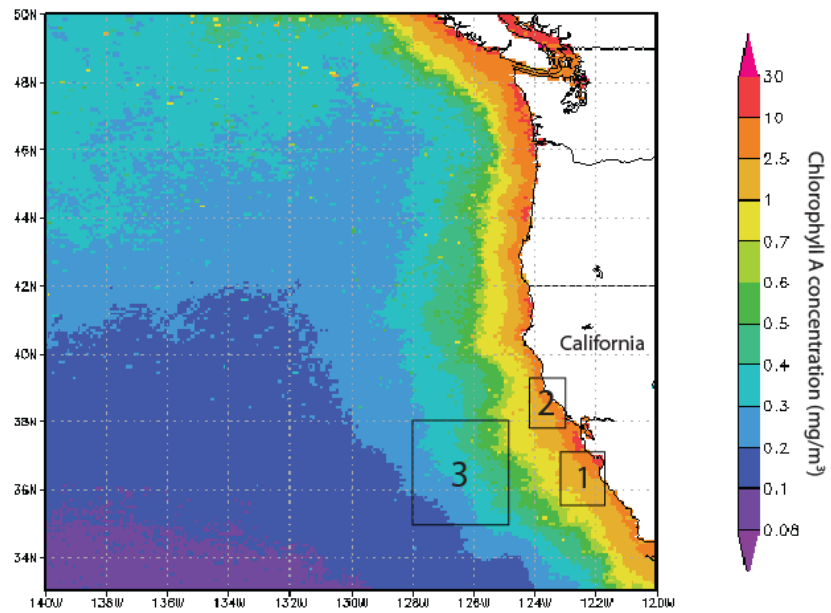


Figure 1.

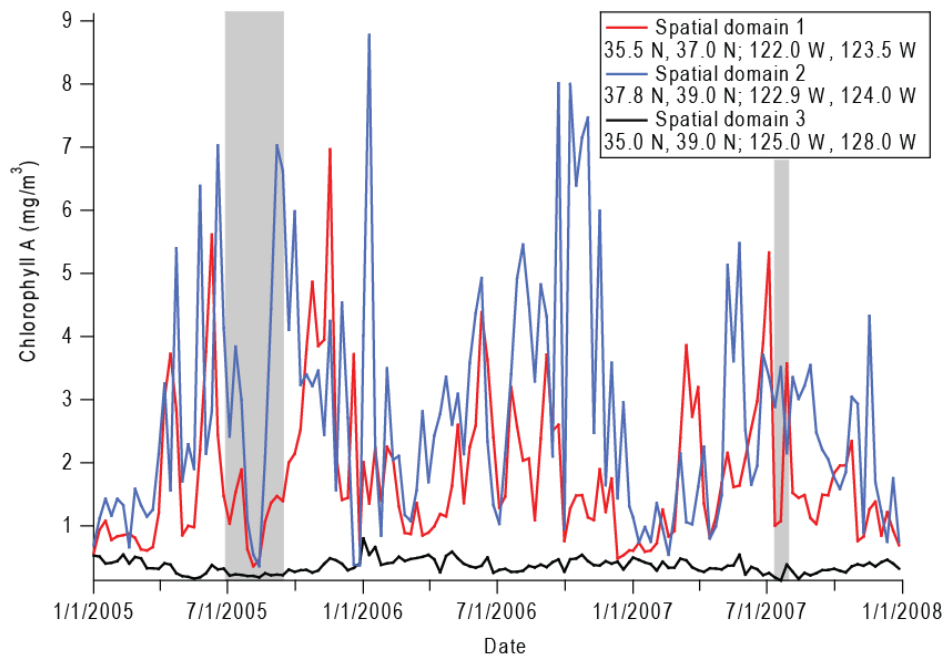


Figure 2.

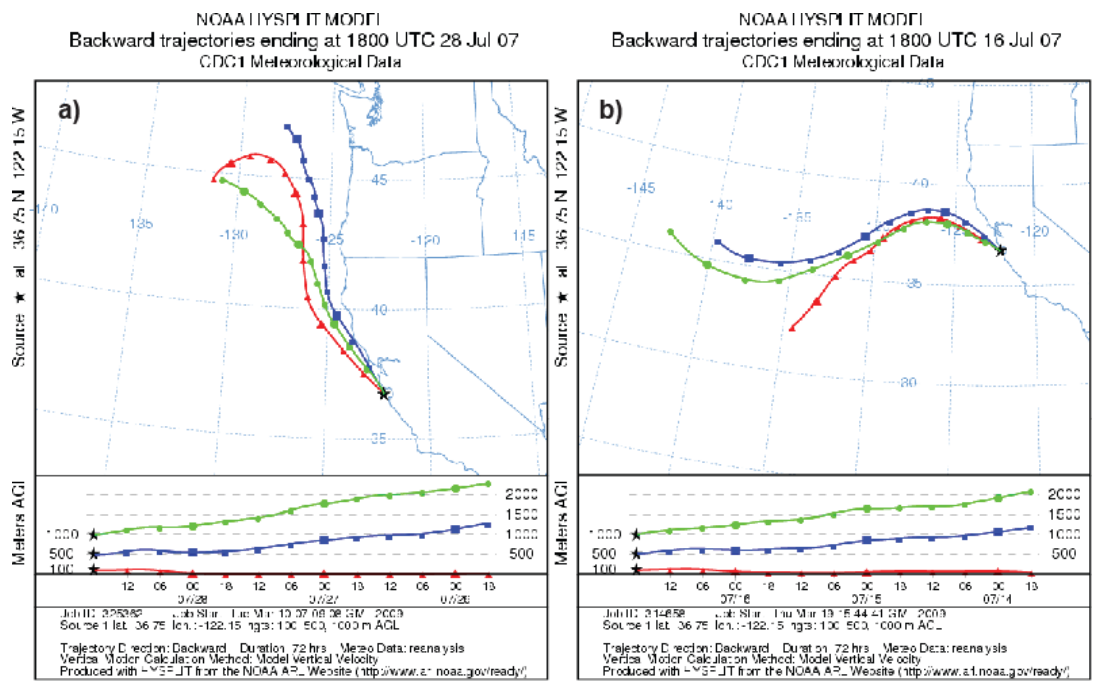


Figure 3.

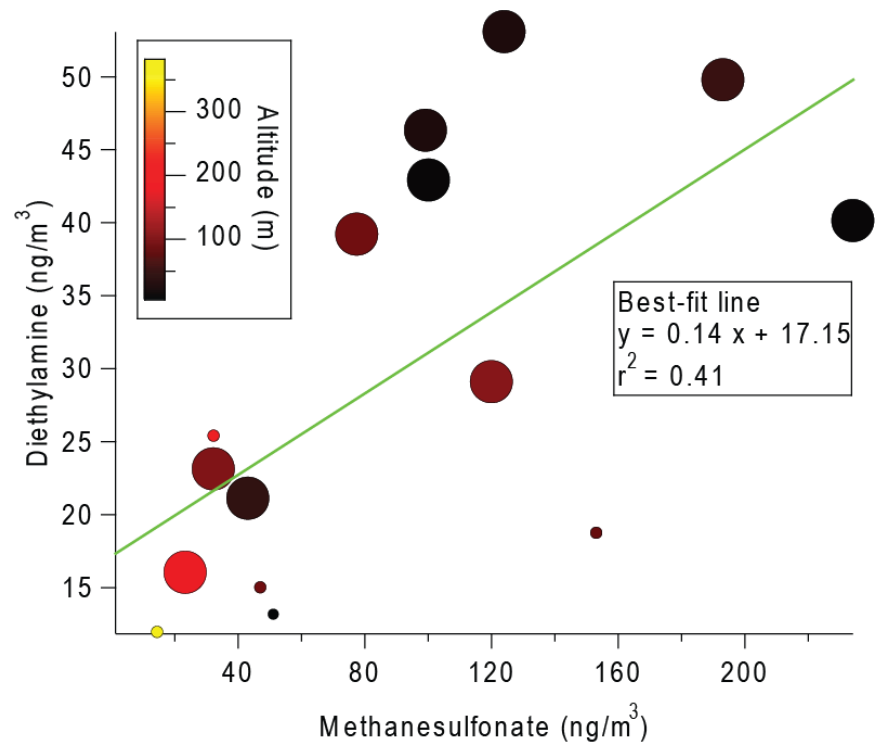


Figure 4.

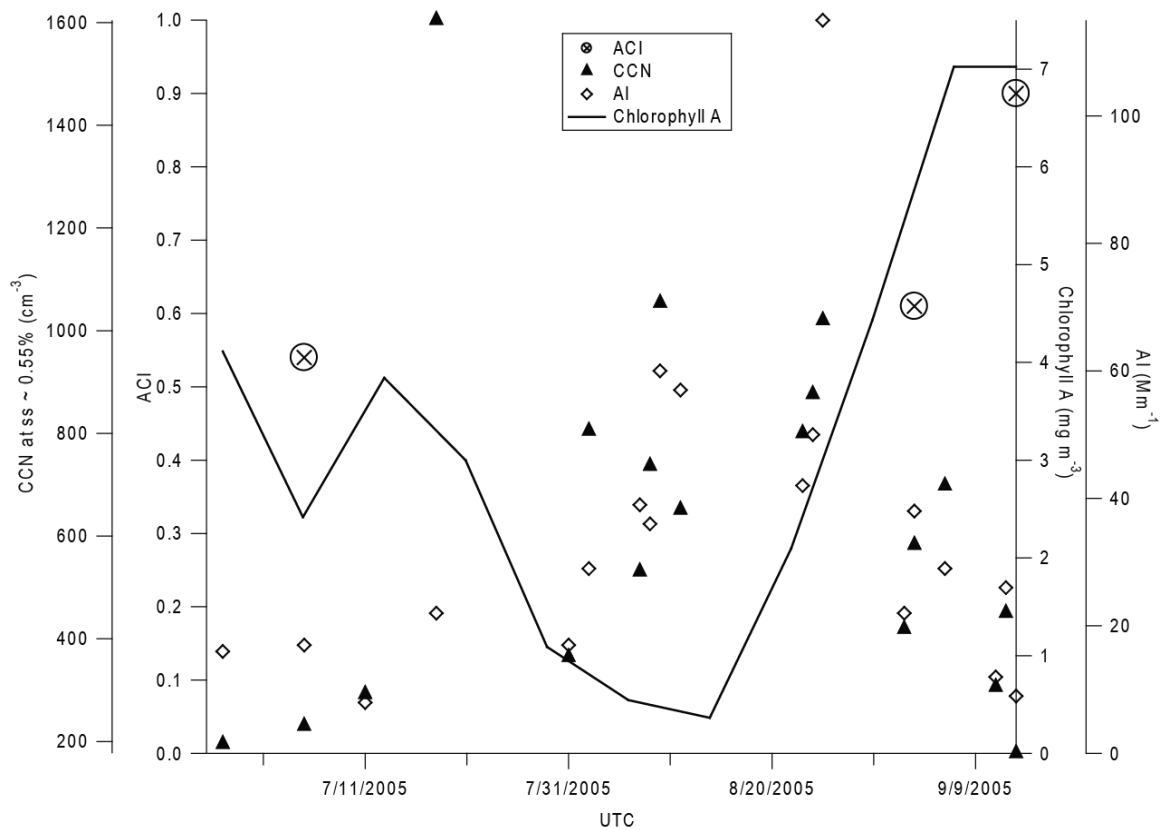


Figure 5.