

**Using single particle mass spectrometry and isotope
measurements to determine the contributions of ship emissions
to ambient PM in La Jolla, CA**

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Abstract

This document describes the results of several research projects partially funded by the California Air Resources Board to develop new analytical approaches that can be used for quantifying the contribution of ship emissions to the air quality of a coastal, urban area (San Diego). This objective has been addressed under separate funding contracts by two research groups based out of the University of California at San Diego.

The Thiemens group utilized isotopic measurements of aerosol nitrate and sulfate to search for and develop a proxy of the impact of ship emissions in the air. It was found that a signature of primary sulfate from ship emissions can be quantified using the isotopic composition of oxygen in aerosol particles < 1.5 micron.

Simultaneously, the Prather group collected ambient data over a seven week time period during fall 2006 on the Scripps Institution of Oceanography (SIO) pier using an aerosol time-of-flight mass spectrometer (ATOFMS), as well as particle size distribution and gas phase measurements. The data combined with back trajectory analysis demonstrated significant transport of emissions from the Los Angeles and Long Beach Port region to San Diego, with a strong component likely from ship emissions. A unique particle type with a mass spectral signature containing a strong vanadium signal as well as iron and nickel was identified and is hypothesized to be a good proxy for major ship traffic. This correlation explains previous findings of a significant background type during sampling at a freeway site in San Diego in 2004 and suggests ship pollution from the LA region can significantly impact the air quality in San Diego.

The combination of the analytical capabilities of both research groups is shown to have great potential for identifying and quantifying the contribution of ship exhaust in a coastal urban environment. In a future study, it is recommended real-time ATOFMS data be used as an instantaneous trigger for selective filter based sampling upon which isotope data can be acquired.

Executive Summary

Background

The impact of maritime vessel activities, presently and in the future, is expected to increase as international trade continues to increase. This increased vessel traffic in and out of port cities may have a significant impact on the air quality of these cities and those that surround them since commonly used fuels for these activities tend to be less refined and as a result enriched in sulfur, and heavy metals. This enrichment in turn produces gaseous and particulate sulfur emissions in the form of SO_2 (g) and SO_4^{2-} (s). In addition, combustion engines also produce significant quantities of black carbon particles, heavy metal particles, and NO_x (g). These products are well known pollutants in the atmosphere and the California Air Resources Board, which sponsored this research, is responsible for gathering and assessing the impact that these activities may have on the air quality of California. Quantifying the impact that maritime vessels have on the air quality of populated coastal regions poses analytical challenges because of the presence of other pollution sources in urban areas. This report details the significant progress made in addressing the challenge of quantifying the contribution that ship emissions have on the particulate matter levels in the San Diego region.

Methods

Collection of aerosol samples with daily or bi/weekly time resolution was done by the Thiemens group using a high-volume aerosol sampler and glass fiber filter sheets. This sampling used a multi-stage sampler for size resolved collections of these aerosol samples. The sampling of aerosols was primarily at the Scripps Pier in La Jolla, California, although samples of ship exhaust particulates donated by the California Air Resources Board were also analyzed during this study. Following collection, aerosol nitrate and sulfate were extracted from the filters and prepared for the isotopic analysis of the composition of oxygen using a pyrolysis technique and isotope ratio mass spectrometry (IRMS) of the product oxygen.

Individual aerosol particles were sampled in real-time using an aerosol time-of-flight mass spectrometer (ATOFMS) that measures both the aerodynamic size and chemical composition of each particle. Sampling took place in the CARB mobile lab developed by the Prather group at the Scripps Pier in La Jolla, CA. Co-located with the ATOFMS were instruments to measure the particle size distribution (aerodynamic particle sizer (APS) and scanning mobility particle sizer (SMPS)), particle mass and black carbon mass concentrations (tapered element oscillating microbalance (TEOM) and aethalometer), and gas phase concentrations (O_3 , CO , and NO_x). Additional ATOFMS data from a previous study in 2004 at a freeway location is also included in this analysis. To determine the origin of different air masses, back trajectories were calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectories (HYSPLIT) program developed by NOAA.

Results

Two complementary analytical techniques were utilized to observe the transport of emissions from ships and the other pollution sources from the vicinity of the Ports of Los Angeles and Long Beach. A technique for identifying and quantifying the contribution from ship emissions to the particulate environment of San Diego has been developed through the isotopic measurements of atmospheric sulfate. It is shown, through the analysis of ship exhaust particulate matter, that sulfate produced in the high-temperature combustion engines of ships has a unique isotopic composition in its oxygen atoms. This isotopic composition is also sufficiently distinct from the background that mixing between the oceanic (non-urban) air masses and air that is enriched in primary sulfate results in a measurable shift in the bulk isotopic composition of sulfate. Meteorological back trajectories and concurrent observations from the Prather group suggest that the primary sulfate sampled at La Jolla originated from ships, although other sources of particulate sulfate with the same isotopic composition as sulfate produced in ships cannot be ruled out at this time.

A unique class of particles likely resulting from ship emissions was identified during the measurement period at Scripps Pier. This class had a mass spectral fingerprint containing a strong vanadium signal as well as iron and nickel as observed by ATOFMS. This type was produced from the combustion of low grade diesel fuel (i.e. bunker fuel) that is enriched in metals and likely from ships or other residual fuel combustion sources. This link was reinforced by observing the temporal changes in vanadium particle counts, particle size distributions, HYSPLIT back trajectories, and ship traffic off the Southern California coast. The vanadium-type particles exhibited a strong correlation with elemental carbon (i.e. black carbon). Further, this particle type was one of the major contributors to the submicron size range of the ATOFMS (200 – 1000nm), especially during intense transport episodes. This study expands and supports previous findings of a background particle type observed during the 2004 San Diego Freeway Study that was not attributable to heavy duty diesel vehicles (HDDV) or light duty vehicles (LDV). It was noted during the 2004 study that the regional background during a period of strong influence by the ships from the LA/LB region that the PM levels overwhelmed those from the freeway being sampled even when we were sampling right alongside a major freeway in San Diego. Importantly, this study demonstrates how under periods with a certain meteorological influence, the contributions from the LA/LB harbor region can overwhelm local source contributions in San Diego.

The amount of primary sulfate from ships (docked in the Port of Los Angeles) or similar primary sulfate sources can be estimated by measuring the isotopic composition of submicron sized sulfate (SO_4) during periods of low to no urban influence (maritime air background) with days where back trajectory analysis and vanadium-type ATOFMS particle counts measured by the Prather group indicate the presence of polluted air from the Los Angeles region. As shown, the shift in the oxygen isotopic composition of the bulk aerosols can be used to quantitatively estimate the amount of particulate sulfate in the air.

Conclusions

The observed correlation between vanadium-type particles, ship monitoring records, increases in sulfate concentration, and isotopic analysis of aerosol sulfate in sub-micron and super-micron particles consistently point to the successful development of a new tracer for primary sulfate produced in ship exhaust, as well as a unique approach to determining the impact of ship emissions on atmospheric PM levels. We leave open the possibility that refinery exhaust or oil burning power plants may also produce primary sulfate with an identical oxygen isotopic signature, and therefore we recommend that targeted and time-triggered sampling of exhaust from both sources be done for comparison purposes in a future mobile lab study. The use of oxygen isotopes in submicron particles as a proxy for primary sulfate exhaust from ships is demonstrated. The results presented here indicate the strong potential for measuring the impact of ship traffic as a function of geographic location by measuring the isotopic composition of submicron sulfate in areas surrounding major ports and we recommend that such studies be undertaken. The combined study with the Prather group confirms a direct link between vanadium particles with a distinct mass spectral signature and ship emissions. Given the known link between vanadium and deleterious health effects, the results from this study suggest that the health implications of ship emissions need to be studied in depth.

Body of Report

A. Introduction and Background

The impact of ship emissions globally and on southern California are expected to increase substantially over the next fifty yearsⁱ. Of particular consequence are sulfate, soot, and heavy metal containing particles produced by the low grade residual fuel that ships burn. The consequences of atmospheric sulfate on the earth's environment are well known and documented. Sulfate aerosols are associated with a number of significant consequences that include: a poorly defined influence on radiative equilibrium, respiratory and cardio vascular hazards, acid deposition and the myriad of associated environmental consequences. These consequences are pervasive and include alterations of biodiversity, agricultural yield decreases, and destruction of materials, including buildings, highways and other structures. Each of these is of significance in the state of California.

One of the major remaining issues with regard to sulfate is the lack of high definition source identification. For example, source resolution is complicated in the western United States by long-range transport from Asia and China. Most recently, it has become quite clear that ship emissions may exert a potentially strong influence on sulphur cycling and radiative climate forcing over the ocean and coastal regionsⁱ. A primary reason for this importance is the relative sensitivity of regions, such as oceanic or coastal California, to air pollution. Sulfate in particular appears to be a significant agent in this regard, and anthropogenic emissions to the ocean and coastal regions could be an important climate and sulfur cycle perturbing agent. A report by Corbett et al.ⁱⁱ indicated that in some regions, sulfur emissions from ships might equal the natural oceanic sulfur flux from the ocean to the atmosphere. Of particular importance in the modeling efforts was the recognition that ship emissions in coastal California, and indeed a sizable fraction of the eastern Pacific, could make sizeable contributions of sulfur dioxide to the total SO₂ budget (as much as 80-100%)ⁱ. It has also been found that ship emissions account for 16% of sulfur from petroleum uses and 5% of sulfur emitted by fuel combustion sources. In addition, it is most important to recognize that ship emissions account for 14% of nitrogen emissionsⁱⁱ. Most studies to date have focused upon sulfate aerosols and the concomitant impact; it is quite possible that the perturbations to the nitrogen cycle are more severe, especially in light of the fact that the impact of nitrogen is more severe than that for sulfur. If such findings are indeed correct, then a re-evaluation of our understanding of the sulfur and nitrogen cycles in California, and indeed the western United States, is vitally needed.

There is yet another aspect that is particularly important for California. Corbett et al have discussed the longer range implications of sulfur, *viz a viz* the inland input of ship produced sulfur. It has been shown by Schwartz that ship emissions may contribute to pollution up to hundreds of kilometers inlandⁱⁱⁱ. With the lifetimes of both SO_x and NO_x, it is possible that, via the oxidative process, such influences could be noticeable 400 to 1200 km away. If such is the case, then measurements are clearly needed to quantify the true observed influence of ships on the sulfur and nitrogen cycles. In addition, not only do the sulfur and nitrogen burdens need to be quantified, but also the oxidative processes as these determine the size of aerosols that uptake and eventually transport these

emissions inland. Both nitrate and sulfate species have background concentrations in the atmosphere, making the resolution of the magnitude and atmospheric transformation processes non-trivial.

The damage caused by the input of atmospheric sulfate and nitrate to the environment remains one of the largest environmental threats globally and is particularly important to California. These particles destroy vegetation, damage water quality and impact human health. Furthermore, it is well known that biodiversity is particularly impacted by nitrates in California, and biologic extinctions have been widely noted. Although the sulfur cycle has been intensively studied, there remain significant and outstanding issues with respect to its budget and resolution. Nitrate is more problematic as there are not only gaps in our understanding of the budget, but it is also one of the only EPA top ten species that has been increasing in time. For California and its decision making bodies, this resolution is of particular importance given the pervasive nature of the inflicted damage to the state and the need for precise source identification as well as definition of transport phenomena. It has become increasingly apparent that emissions from ships may be of particular importance. Studies from the North Sea have revealed that ship stack emissions might contribute as much as the natural background in sulfate. Nitrates could be as large in the contribution but their contribution is at present unknown.

In addition to the emission of high levels of sulfur dioxide which ultimately lead to sulfate in aerosols, the introduction of transition metals such as vanadium, nickel, and iron into the atmosphere through ship emissions is also of great importance. The concentration of vanadium in residual oil is higher than all other transition metals, with nickel having the second highest.^{iv} The emission of these metals into the atmosphere has been observed previously in ambient observations^{v,vi}. Of particular importance is that particulate matter with vanadium has been shown to cause negative health effects^{vii}. Vanadium in particular has been shown to have its mass peak in the submicron size mode.^{viii} Considering the drastically smaller mass of individual of submicron particles, the number concentrations must be substantial since the mass of vanadium was similar to many other metals primarily in the supermicron. The metals discussed present unique challenges and need to be addressed to fully evaluate the overall impact of ship emissions on Southern California.

In a coastal state such as California, the contributions to sulfate, nitrate, and metals may be highly significant, particularly in cities with major ports such as San Diego, Los Angeles, and Oakland. California in fact may be one of the most impacted regions in the world, yet at present the contributions from maritime vessels are largely unknown. A quantitative resolution of ship emissions and their impact on air quality is therefore of high significance to the state and the Air Resources Board.

Quantification of ship derived sulfate and nitrate in urban coastal areas is not straightforward as there are multiple sources of sulfate and nitrate and their precursor pollutants (NO_x , SO_x) in the area. Therefore separating the contributions from ships is not easily done using concentration measurements alone. One of the main goals of both the Prather and Thiemens research components was to develop analytical methods for identifying and quantifying the contribution of ship emissions in coastal San Diego through measurements of particulate sulfate, nitrate, black carbon, and heavy metals. We describe the methods used by the Prather and Thiemens research groups in the next section.

B. Materials and Methods

Triple-oxygen Isotope Ratio Measurements and Oxidation

Recently developed stable isotope measurement techniques are ideally suited to address the issues of source strength, transport, and transformation. Field campaigns by the Thiemens group in the Indian Ocean Experiment^{ix}, ACE-ASIA (Korea), Trinidad Head, California^x, Nova Scotia, Alert (Arctic)^{xi}, and the South Pole^{xii} have established that triple-oxygen isotope measurements of aerosol nitrate and sulfate can be used to trace the oxidative pathways of these species. The power of the technique is derived from the observation that tropospheric ozone (O₃) is enriched in ¹⁷O and that this anomalous enrichment is passed on to atmospheric species that are oxidized by ozone. The systematic of the relative ratio of OH to O₃ oxidation in sulfate has been used to extract information regarding changes in the oxidation capacity of the atmosphere on time scales from less than a year, to 100,000 years^{xiii,xiv}. A major conceptual motivation for using isotopes of oxygen to track ship emissions is the possibility of detecting perturbations to the dominant oxidation pathways followed to make nitrate and sulfate in the polluted marine boundary layer.

High Volume Sample Collection

A 5-stage cascade laminar flow impactor was used to collect size-segregated aerosols on glass filter paper at the Scripps Pier in La Jolla, CA starting in late May 2005. A listing of the approximate aerosol size ranges collected by each stage is shown in Table 1. Typically, aerosol-filter samples were collected with 3.5 day durations, with the exception of the field campaign period between late August and early September 2006, where samples with high time resolutions (1 day vs. 3.5 days) were acquired¹. For each sample, a start and stop date was recorded, and an average air volumetric flow rate was recorded using a manometer attached to the motor pulling air through the assemblage of filter stages. After collection, these filters were processed for their chemical composition as follows:

- Slotted glass-fiber filters (stages 1-4) were placed in 50 mL centrifuge tubes and stored.
- The backup filter (stage 5) was folded and subsequently cut in half (5a,5b) and placed in two 50 mL centrifuge tubes.
- At the lab, these filters were hydrated with Millipore water (up to 30 mL) and sonicated for 1 hour using standard laboratory equipment.
- After sonication, the wet filter papers were placed in a syringe and plunged dry. The water with soluble aerosol components were collected in a separate centrifuge tube. The filter paper was rinsed with an additional 10 mL of millipore water and squeezed dry. Additional water was added until the level of the liquid reached 50 mL.

¹ This time period coincided with observations by the Prather group at this same location.

- The Cl^{-1} , NO_3^{-1} , and SO_4^{-2} concentrations in these samples were measured using an ion chromatograph with autosampler input module using 1 mL of the 50 mL sample volume and standard cation calibration techniques.

Table 1. High volume impactor-stage aerosol sizes. 50% cut-off size indicates that 50% of particles smaller than the indicated cut-off will pass through to the next stage. ^{xv}

Stage	50% cut-off (μm)	Approx. Range(μm)	ΔD
1	8.0	>6.0	
2	4	6.0-2.8	3.2
3	1.5	2.8-1.0	1.8
4	0.5	1.0-0.3	0.7
5	<0.5	0.3-0.001	0.3

Sample preparation for Isotopic Analysis

The UCSD Stable Isotopes Laboratory of the Thiemens Group has developed a combustion technique that ideally consumes about 3 and 6 micromoles of nitrate^{xvi} and sulfate^{xvii} respectively per isotopic measurement. This requirement is not strict, but is generally targeted to achieve analytical precisions of 0.01 % in the measurements of isotopic compositions using isotope ratio mass spectroscopy (IRMS) of the O_2 produced from the pyrolysis of AgNO_3 or Ag_2SO_4 . The ion chromatographic determinations of the ionic concentrations of NO_3^{-1} and SO_4^{-2} determined in each of the 5 stages (See section above) were used to prepare representative aliquots of the coarse (stages 1-3) and fine (stages 4,5) water soluble aerosols. This binning of fine and coarse aerosols was done primarily to satisfy the sample size requirement for analytical precision using IRMS.

Once an aliquot was prepared, the amount of carbon present in the sample was minimized to allow for efficient anion separation and subsequent combustion. Organics removal was achieved by filtering the samples through column filled with Polyvinylpyrrolidone (PVP), C18 resin (Alltech), and silica gel. Often this step was repeated to ensure that the amount of carbon was minimized in the sample. Following cleaning, Cl^{-} was removed from these samples with the use of a silver resin cartridge (IC-Ag) that is designed to selectively remove chlorine (and make AgCl). This is a necessary step that allows for the separation of up to ~ 20 micromoles of total anions using an ion chromatography system with a high capacity column. The separated anions were collected as HNO_3 and H_2SO_4 in 15 mL centrifuge tubes.

Conversion of HNO_3 to AgNO_3 and H_2SO_4 to Ag_2SO_4 (necessary for combustion) was achieved by adding Ag_2O in stoichiometric excess, sonicating for 1 hour, and acidifying the solution using a centrifuged vacuum dryer. This step can be summarized as:



The Ag^+ ions were then free to react to form AgNO_3 or Ag_2SO_4 with the anions nitrate and sulfate respectively. The excess Ag_2O was separated from the AgNO_3 or Ag_2SO_4 by rehydrating and centrifuging the sample followed by supernatant removal or filtration using a syringe filter. A final freeze dry was done (usually overnight) and the sample powders were loaded into Ag boats (AgNO_3) or quartz tubes (Ag_2SO_4) using small amounts of water to redissolve the nitrate and sulfate silver salts. Finally, the samples were dried down at $\sim 40^\circ\text{C}$ before combustion at 530°C (AgNO_3) or 1100°C (Ag_2SO_4). Combustion of these silver salts can be represented as:



The presence of significant quantities of carbon (organics) in the samples at this point can be problematic as the released O_2 can subsequently be converted entirely to CO_2 . Techniques for purifying samples were developed during this study to minimize their effect. The oxygen produced from combustion was separated from NO_2 or SO_2 using double cold traps (nitrate) or a gas chromatograph (sulfate).

Isotopic Analysis and Quantification

For the isotopic data that reported here, we will make use of the standard delta notation. All of the isotopic data reported were determined using isotope ratio mass-spectrometry (IRMS). Thus, the oxygen isotopic data reported here were determined from the following expression:

$$\delta^x\text{O} = \left[\frac{\left(\frac{x\text{O}}{^{16}\text{O}} \right)_{\text{sample}}}{\left(\frac{x\text{O}}{^{16}\text{O}} \right)_{\text{standard}}} - 1 \right] \times 1000$$

where $x=17$ and 18 . All of our numbers are reported with respect to the standard mean oceanic water (SMOW) standard and are expressed in parts per thousand or per mil (‰).

Excesses of oxygen ^{17}O , for a given $\delta^{18}\text{O}$, are quantified and expressed as:

$$\Delta^{17}\text{O} \cong \delta^{17}\text{O} - 0.52\delta^{18}\text{O}$$

When the isotopic composition of an oxygen bearing compound is such that $\Delta^{17}\text{O} = 0\text{‰}$, its composition is termed “mass-dependent”.

Backtrajectory Analysis of Concentration Data: Sources of Aerosol Nitrate and Sulfate Variability

Everyday experience suggests that the air quality in San Diego is highly variable. This impression is confirmed by the concentration of nitrate and sulfate in aerosols collected at the Scripps Pier. To what extent to ship emissions contribute to the

magnitude and variability? To what extent does the transport air pollutants from Los Angeles or other major urban areas contribute to this variability? To better understand these questions, the NOAA HYSPLIT was used to generate back-trajectories using the run daily utility in the PC (personal computer) distributed version. The results of these calculations were then accessed using a Matlab program that picks out the end points of these backtrajectories and assigns a vector corresponding to the distance and direction of the net displacement backtrajectory. These backtrajectories were run every 6 hours. As a consequence, a single calendar day has four backtrajectory vectors associated with it. For each of these back-trajectories, an urban index was assigned to encode how “urban” or “oceanic” the air-mass arriving at Scripps Pier was. Trajectories that originated from inland (San Diego) or from the greater Los Angeles area were assigned a value 1 while trajectories coming from oceanic endpoints were assigned a value of 0. For a given aerosol filter sampling period (which typically spanned 3.5 days), an average urban index for the collection periods was calculated. This encoding was chosen for simplicity and could certainly be easily refined in the future. However, this approach was sufficiently accurate enough to allow us to isolate samples with no urban influence (urban index = 0) as well as to assess the influence of air masses originating from the greater Los Angeles area. Figure 1 displays the backtrajectories used in determining the urban index assigned to samples collected during May 2005 and May 2006.

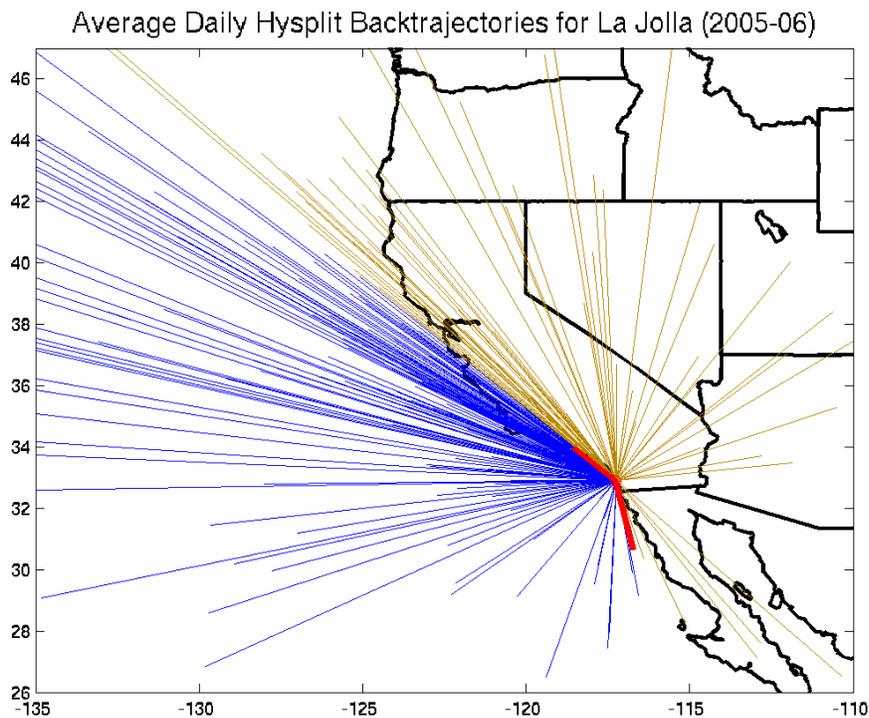


Figure 1: Average 72 hour backtrajectories (end-start) and their associated urban index (blue=0, brown=1) values. Red lines indicate the boundary of oceanic and urban sectors.

Ship Traffic Monitoring

Using outside funding (Dreyfus Foundation), an antenna capable of intercepting the Automated Identification System (AIS) radio bursts put out by major commercial and passenger ships in US waters, was acquired during the summer of 2006. This antenna was networked and the raw output streams have been logged continuously since then using a computer server at UCSD. The computer software for logging the raw data streams was written during the time period of this funding, and the antenna was acquired from outside funds (Dreyfus Postdoctoral Fellowship). The primary goal of this antenna was to monitor and log the names, sizes, speeds, and headings of cargo ships traveling off-shore from the Scripps Pier. These data files can be accessed in an automated manner using simple computer programs (i.e. Matlab). A map of intercepted ship transmissions during the month of September 2006, shown in Figure 2, reveals the locations of major ship traffic corridors in Southern California.

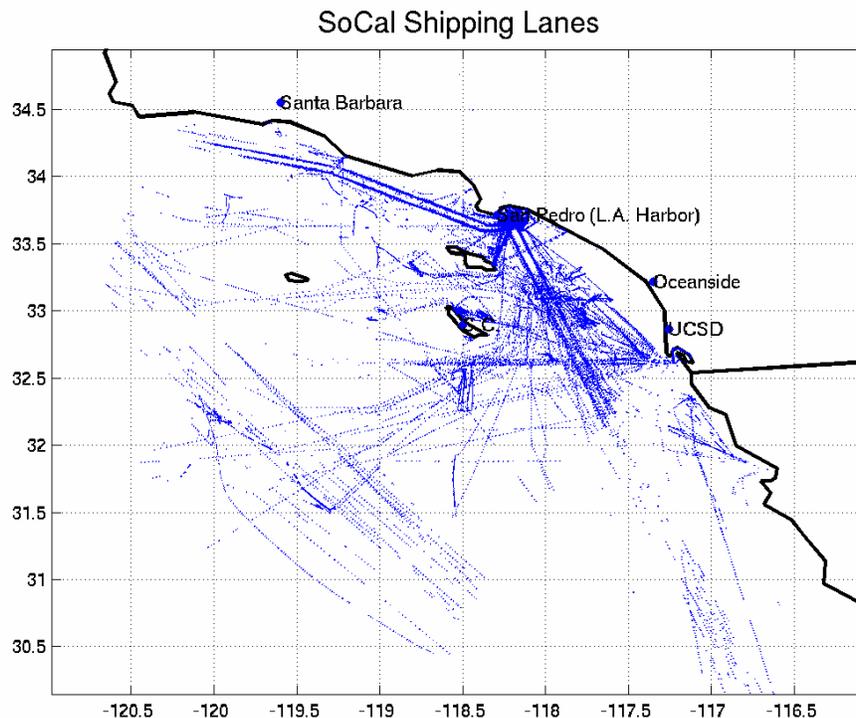


Figure 2: Location of individual ships as logged using a networked AIS VHF (Automated Identification System Very High Frequency) antenna. Raw data was decoded using C program and plot was generated using Matlab programming environment.

Prather Group Mobile Laboratory Sampling Information

The Prather Group mobile laboratory was located at the end of Scripps Pier from August 15, 2007 to October 10, 2007, during which measurements were made with a wide array of particle and gas phase instrumentation. Table 2 lists the instruments used, with measurement capabilities and dates of operation during the study.

Table 2. Instrumentation During Prather Group Sampling Period

Instrument	Measurement	Units	Sampling Interval	Sampling Period
Aerosol Time-of-Flight Mass Spectrometer (ATOFMS)	Size and Chemical Composition of Single Particles (200 - 3000nm)		Real-Time	August 17, 2006 - October 3, 2006
Aerodynamic Particle Sizer (APS) TSI Model 3321	Particle Number Concentration (0.5 – 20 µm)	#/cm ³	1 min	August 17, 2006 - October 10, 2006
Scanning Mobility Particle Sizer (SMPS) TSI Model 3936	Particle Number Concentration (10 – 600 nm)	#/cm ³	5 min	August 17, 2006 - October 10, 2006
Aethelometer Magee Scientific AE-3	Black Carbon Mass	ng/m ³	5 min	August 17, 2006 - October 10, 2006
Tapered Element Oscillating Microbalance (TEOM) R&P 1400a	PM2.5 Mass	ug/m ³	30 min	August 17, 2006 - October 3, 2006
Chemiluminescence NO-NO ₂ -NO _x Analyzer TEI Model 42C	NO & NO _x Concentrations	ppb	1 min	August 17, 2006 - October 10, 2006
UV Photometric O ₃ Analyzer TEI Model 49	Ozone Concentrations	ppb	1 min	August 17, 2006 - October 10, 2006
CO Analyzer Monitor Labs ML9830	Carbon Monoxide Concentrations	ppb	1 min	August 17, 2006 - October 10, 2006
Ultrafine Condensation Particle Counter TSI Model 3025	Number Concentration (3 – 3000nm)	#/cm ³	1 min	August 17, 2006 - September 18, 2006
Cloud Condensation Nuclei Counter	CCN Number Concentration	#/cm ³	1 sec	August 17, 2006 - October 3, 2006

The measurements during the San Diego Freeway Study were made adjacent to Interstate 5 on the UCSD campus from July 24, 2004 – August 2, 2004. Sampling included an ATOFMS in addition to similar peripheral (aethalometer, TEOM, NO_x, Ozone, CO, nephelometer, and UCPC).

Description of the Aerosol Time-of-Flight Mass Spectrometer

The aerosol time-of-flight mass spectrometer (ATOFMS), developed in the

Prather Group, measures the aerodynamic size and chemical composition of individual particles in real-time. The instrument is shown in Figure 3 and has been described in detail^{xviii}. Briefly, particles are introduced to the ATOFMS through a converging nozzle into a differentially pumped vacuum chamber during which the particles are accelerated to a terminal velocity. The particles then pass through two

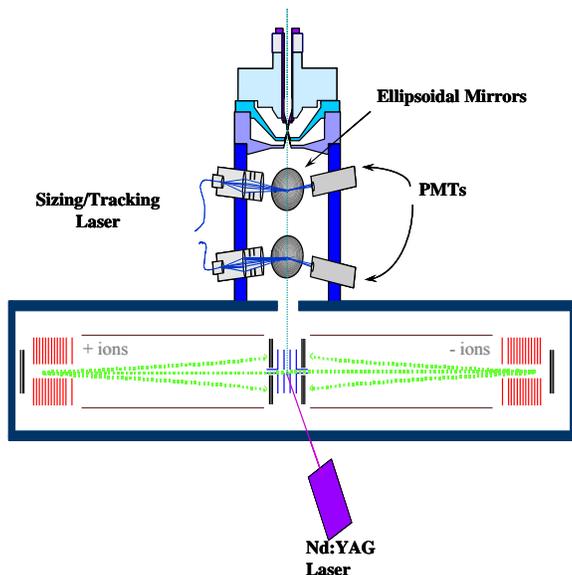


Figure 3: Schematic of the Aerosol Time-of-Flight Mass Spectrometer

continuous wave lasers (diode pumped Nd:YAG operating at 532nm) located 6 cm apart. The speed of the particles is then used to determine the aerodynamic size by calibration with polystyrene latex spheres of known aerodynamic size. Particles are then desorbed and ionized by a Q-switched Nd:YAG laser emitting at 266nm (1.2-1.4 mJ) that is triggered when the particle has entered the center of the mass spectrometer region. Both positive and negative polarity ions from the same particle are detected by the dual reflectron time-of-flight mass spectrometer. The ATOFMS can sample particles between 200 – 3000 nm and chemically analyzed particles at ~ 1-2 Hz during the study.

ATOFMS particle size and mass spectral information were imported into Matlab 6.5.1 (The MathWorks, Inc.) and analyzed utilizing YAADA 1.2 (www.yaada.org). Particles were grouped via two methods: 1) searches of mass spectral, aerodynamic size, and temporal features and 2) clustering via an adaptive resonance theory based neural network algorithm (ART-2a) at a vigilance factor of 0.8 and regrouped at 0.85^{xix}.

C. Results

Comparison Between Back Trajectories and Anion Concentrations

A simple examination of the anion concentrations and average urban index during a

particular collection sampling period reveals that the simple urban index and the concentration of anions in both the coarse (stages 1-3) and fine (stages 4-5) are correlated (See Figure 4 and 6). It is also clear that the amount of nitrate and sulfate in air masses arriving at Scripps Pier are highly variable and influenced by urban air pollution, although the amount of non-sea salt sulfate was not determined for this sample set. As discussed previously, direct information on ship traffic during the sampling periods shown was not available until the summer of 2006.

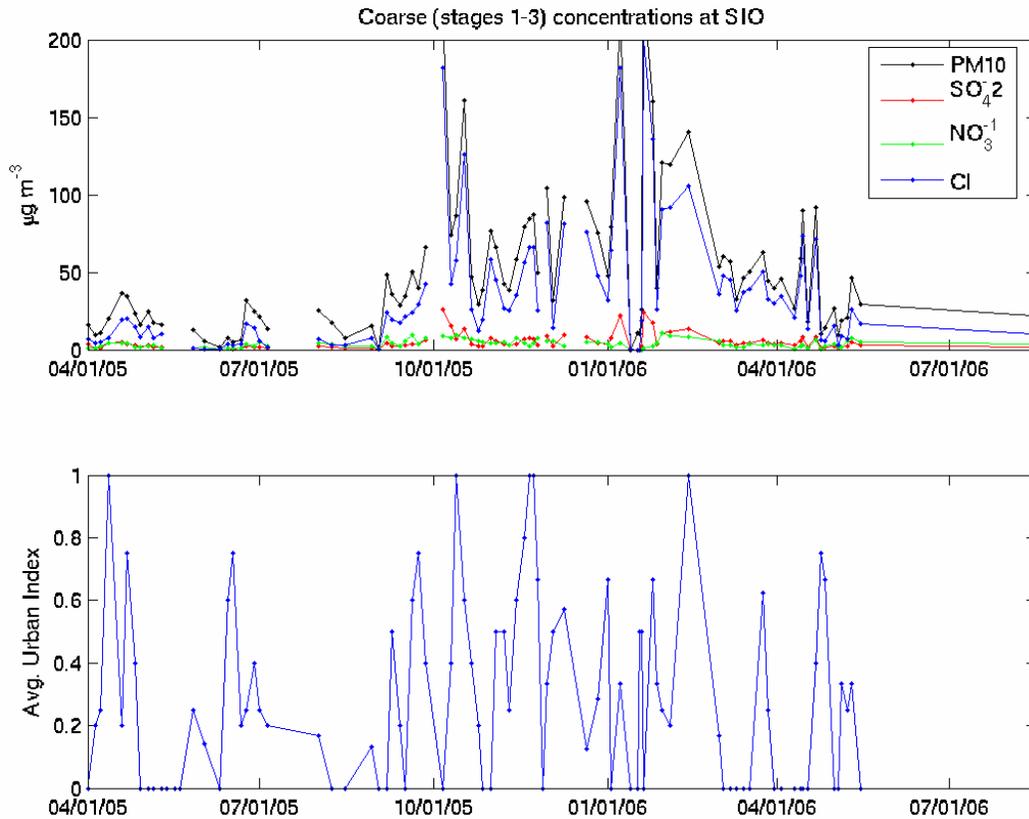


Figure 4: Concentration of Cl^{-1} , NO_3^{-1} , and SO_4^{-2} in aerosols vs. time and average urban index of these air masses.

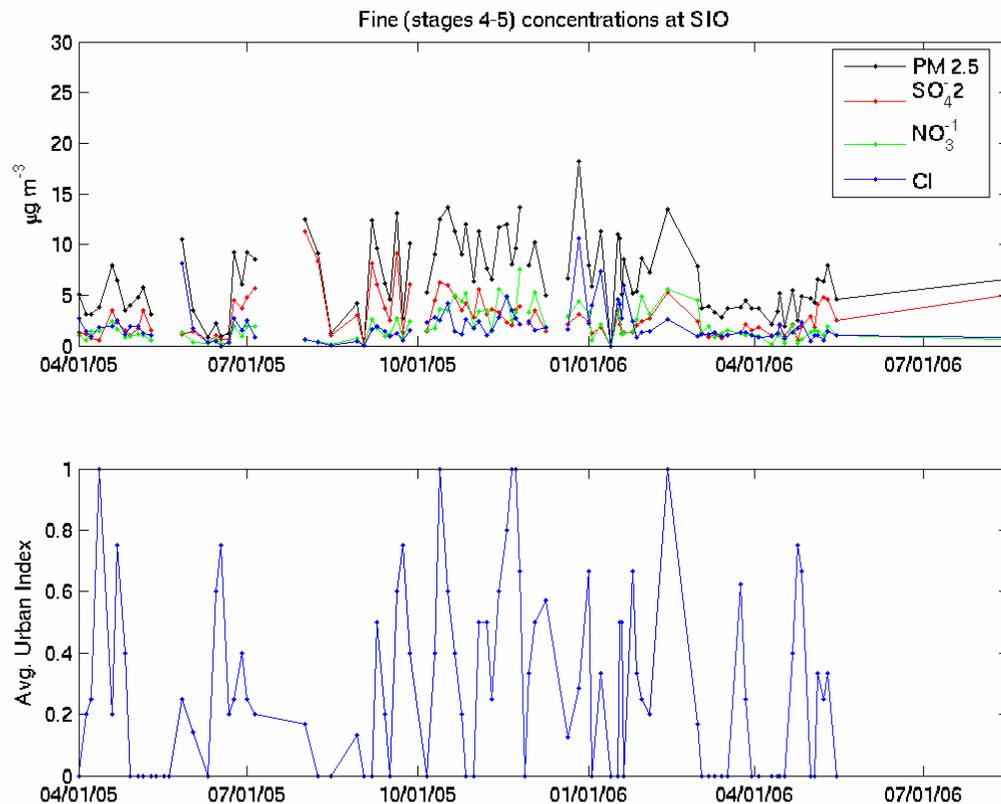


Figure 5: Concentration of anions in stages 4-5 at Scripps Pier.

Characterizing Urban and Oceanic Air Masses Using Oxygen Isotopes of Aerosol Nitrate

Due to the significant analytical effort involved in making a single isotope ratio measurement, an early phase of this project focused on selecting a limited number of samples. These were measured using the AgNO_3 and Ag_2SO_4 combustion techniques detailed previously. An examination of the nitrate aerosol data (through the Summer of 2006) reveals a systematic trend in the mass-independent composition ($\Delta^{17}\text{O}$) when aggregated vs. urban index. These results for the fine and coarse size fractions are shown in Figure 6 and Figure 7.

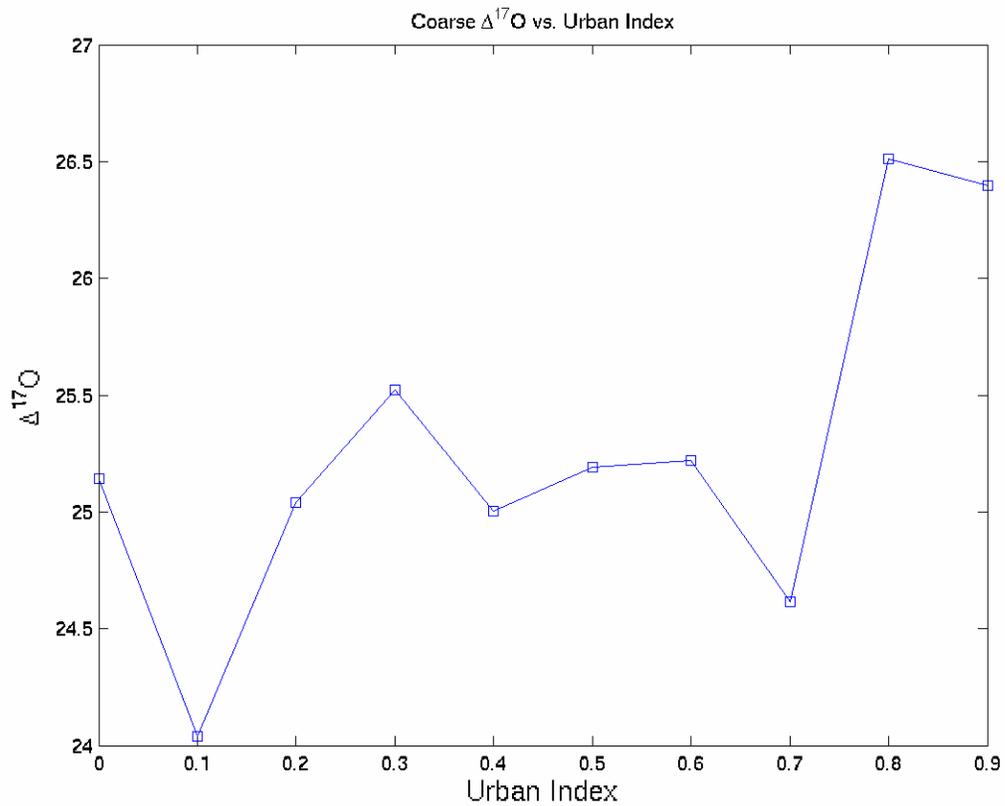


Figure 6: $\Delta^{17}\text{O}$ vs Urban Index in the coarse aerosol size fraction of aerosols collected at Scripps Pier. The $\Delta^{17}\text{O}$ of individual data points were binned (0-0.1, 0.1-0.2, etc.) and plotted as a function of corresponding urban index (shown for samples analyzed through Summer of 2006).

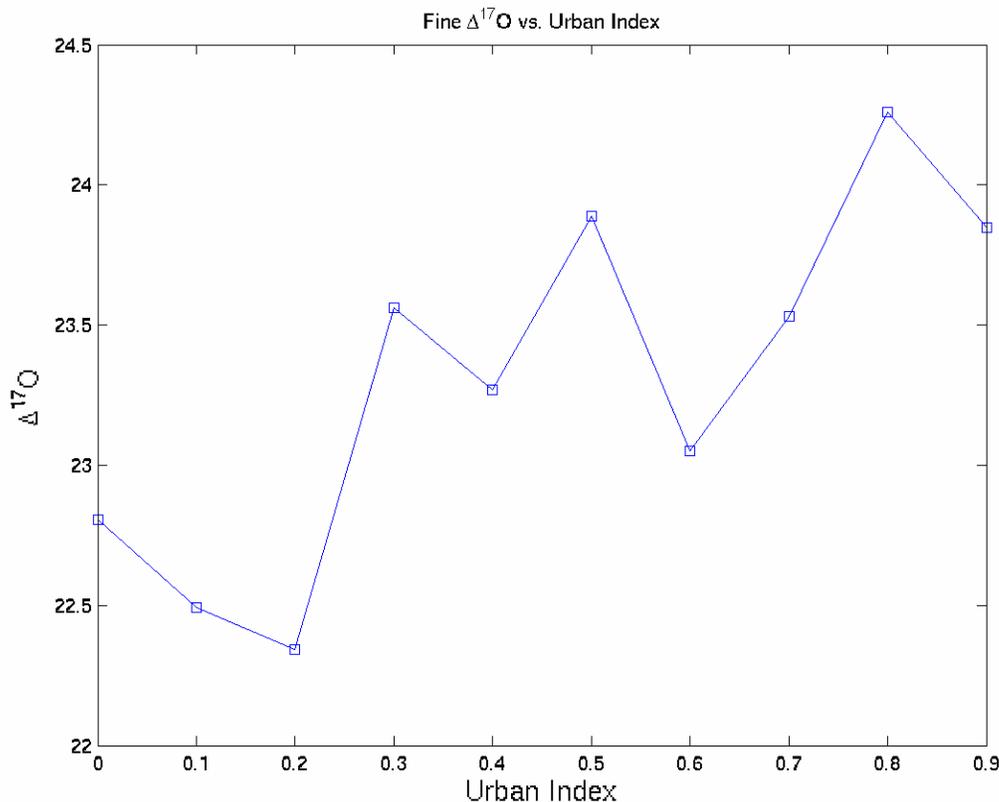


Figure 7: $\Delta^{17}\text{O}$ vs Urban Index for nitrate found in the fine aerosol size fraction. Note the stronger dependence compared to coarse aerosols.

There are two important things to note here. First, note the systematic upward trend versus urban index. This observation probably reflects the relative increase in the importance of the NO oxidation by O_3 in urban areas compared to clean marine air masses. Second, it is interesting that the isotopic composition of fine aerosols appears to respond more strongly than the coarse aerosol particles (shown in Figure 6), possibly reflecting the bias against transporting coarse aerosol particles that originate in the polluted air of Los Angeles.

There is considerable scatter in the data, but the trends are clear when plotted vs. urban index. What is not clear, at this point, is what role (if any) do ship NOx emissions have on the overall scatter in the data. We will discuss the implications of the data shown here in the conclusions section.

Oxygen Isotopes in Aerosol Sulfate at La Jolla, California (2005)

Measurements of oxygen isotopes in sulfate (SO_4^{-2}) were carried out in three phases. During the first, we focused on understanding the variation of the isotope ratios of oxygen. At this point, the work needed to measure oxygen isotope ratios using the combustion technique described earlier is similar to that needed for NO_3^{-1} . A summary

of our measurements of fine and coarse sulfate oxygen isotopes is shown in Figure 8. These measurements were taken on samples collected through the end of 2005.

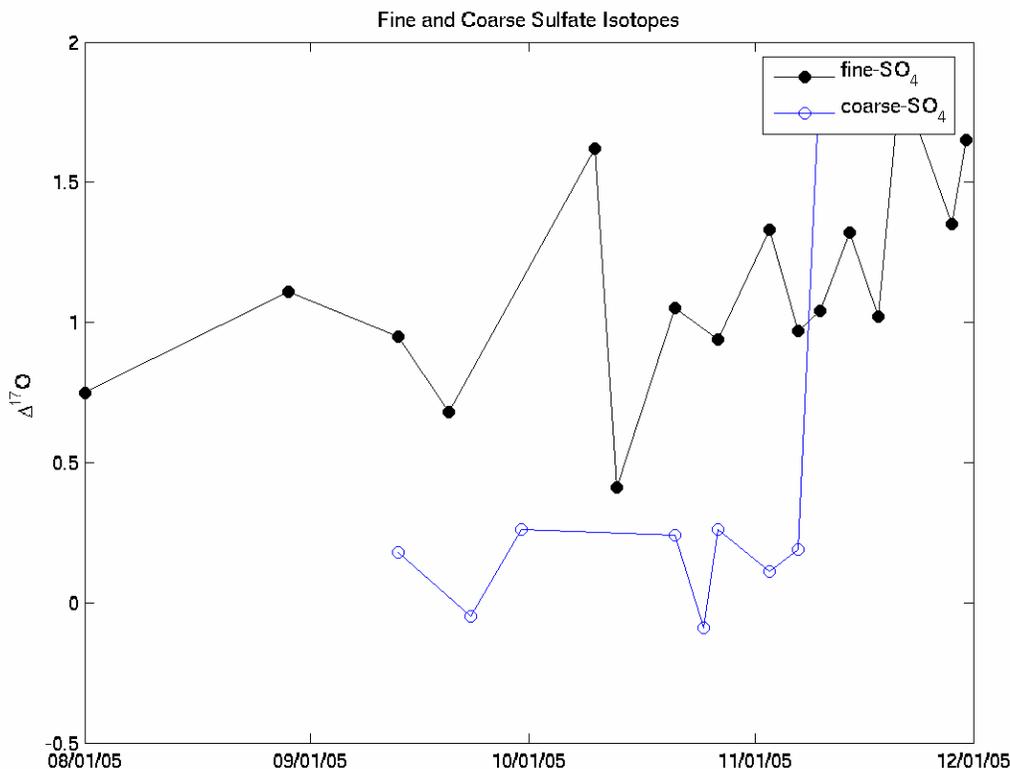


Figure 8: $\Delta^{17}\text{O}(\text{SO}_4)$ in fine and coarse aerosols. These measurements are bulk measurements and have not been corrected for sea-salt sulfate. This, in part, accounts for the systematically lower values for the coarse particles.

Oxygen Isotopes in Primary Sulfate from Ships and in Aerosol Sulfate at La Jolla, California (August-October, 2006)

During the Fall of 2006, the Thiemens and Prather groups carried out simultaneous collections/observations of aerosols at the Scripps Pier. Details of the Prather group observations are summarized elsewhere in this report. Ships are significant sources of particulate (primary) sulfate and, motivated by the possibility of resolving this influence in our measurements at the Scripps Pier, the ARB suggested and provided samples of primary sulfate sampled from the exhaust of a container ship (Sine Maersk, Post-Panamax Series S). A summary of these measurements is provided in Table 3. It is highly significant to note that the isotopic composition of primary sulfate from the Denmark ship has a strikingly similar composition to that of atmospheric oxygen. A repeat of the measurement yielded a similar value for the $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values of primary sulfate from the ship stack.

Table 3. Results of triple isotope measurements of primary sulfate from a marine vessel.

sample	$\delta^{18}\text{O}$ (‰)	$\delta^{17}\text{O}$ (‰)	$\Delta^{17}\text{O}$ (‰)
Denmark-AB65	20.01	10.41	0.04 ±0.1
Denmark-AB68	21.99	11.53	0.10 ±0.1
Denmark-AB81	21.20	11.12	0.09±0.1

The observation period, spanning from August 17-October 3, 2006, was marked by variable levels of air quality. During this period, aerosol samples were collected with 1.0 and 2.5 day time resolutions over weekdays and weekends respectively. A select number of these, chosen on the basis of high and low vanadium-type particle counts measured by the Prather Group, were processed for analytical IC and isotopic ratio determinations of their nitrate and sulfate fractions. Table 4 summarizes the concentration, size fraction, and oxygen isotopic composition of aerosol sulfate collected at the Scripps Pier during the August-October period. The measurement of sodium concentrations (a recent analytical addition to the laboratory-summer 2007) has allowed us to correct the isotopic measurements of our bulk fine and coarse size fractions for the contribution of sea-salt sulfate. This corrected data is presented in Table 5.

Table 4. Sample names, sampling periods, size fractions, sulfate and sodium concentrations, and triple-isotope values for aerosol sulfate. Samples with – have not been measured.

sample	start time	end time	size cut	[SO ₄] μmol. m ⁻³	[Na] μ mol. m ⁻³	SO ₄ ⁻ δ ¹⁸ O (‰)	SO ₄ ⁻ δ ¹⁷ O (‰)	SO ₄ ⁻ Δ ¹⁷ O (‰)
SIO060905-A	9/1/06	9/5/06	Coarse	0.05	0.25	-	-	-
SIO060905-B	9/2/06	9/6/06	Fine	0.05	0.07	10.56	6.37	0.88
SIO060907-A	9/6/06	9/7/06	Coarse	0.02	0.22	-	-	0.00
SIO060907-B	9/6/06	9/7/06	Fine	0.06	0.11	10.84	6.55	0.91
SIO060908-A	9/7/06	9/8/06	Coarse	0.02	0.16	10.94	6.31	0.62
SIO060908-B	9/7/06	9/8/06	Fine	0.05	0.11	13.32	7.92	0.99
SIO060911-A	9/8/06	9/11/06	Coarse	0.02	0.15	9.79	5.22	0.13
SIO060911-B	9/8/06	9/11/06	Fine	0.05	0.05	14.32	8.18	0.74
SIO060912-A	9/11/06	9/12/06	Coarse	0.02	0.23	10.83	6.04	0.41
SIO060912-B	9/11/06	9/12/06	Fine	0.07	0.12	13.93	7.80	0.56
SIO060913-A	9/12/06	9/13/06	Coarse	0.01	0.16	12.68	7.20	0.61
SIO060913-B	9/12/06	9/13/06	Fine	0.09	0.12	14.36	8.08	0.61
SIO060914-A	9/13/06	9/14/06	Coarse	0.02	0.20	12.88	7.38	0.68
SIO060914-B	9/13/06	9/14/06	Fine	0.05	0.00	11.02	6.56	0.83

Table 5. Sample names, sampling periods, size fractions, sulfate and sodium concentrations, and triple-isotope values for non-sea-salt sulfate (nss-SO₄) in these air masses. Samples with – have not been measured. Non-sea-salt sulfate concentrations were determined using the Na:SO₄ molar ratio of 0.0604 found in sea-water. The triple-isotopic composition of sea-salt SO₄ is assumed to be $\delta^{18}\text{O}=10$ and $\Delta^{17}\text{O}=0$.

sample	start time	end time	size cut	[SO ₄] μmol. m ⁻³	[Na] μmol. m ⁻³	nss-SO ₄ - $\delta^{18}\text{O}$ (‰)	nss-SO ₄ - $\delta^{17}\text{O}$ (‰)	nss-SO ₄ - $\Delta^{17}\text{O}$ (‰)
SIO060905-A	9/1/06	9/5/06	Coarse	0.05	0.25	-	-	-
SIO060905-B	9/2/06	9/6/06	Fine	0.05	0.07	10.62	6.48	0.96
SIO060907-A	9/6/06	9/7/06	Coarse	0.02	0.22	-	-	-
SIO060907-B	9/6/06	9/7/06	Fine	0.06	0.11	10.96	6.73	1.04
SIO060908-A	9/7/06	9/8/06	Coarse	0.02	0.16	12.20	7.79	1.45
SIO060908-B	9/7/06	9/8/06	Fine	0.05	0.11	13.86	8.36	1.16
SIO060911-A	9/8/06	9/11/06	Coarse	0.02	0.15	9.66	5.23	0.21
SIO060911-B	9/8/06	9/11/06	Fine	0.05	0.05	14.62	8.39	0.79
SIO060912-A	9/11/06	9/12/06	Coarse	0.02	0.23	11.97	7.19	0.97
SIO060912-B	9/11/06	9/12/06	Fine	0.07	0.12	14.40	8.11	0.62
SIO060913-A	9/12/06	9/13/06	Coarse	0.01	0.16	40.83	28.26	7.02
SIO060913-B	9/12/06	9/13/06	Fine	0.09	0.12	14.78	8.36	0.67
SIO060914-A	9/13/06	9/14/06	Coarse	0.02	0.20	19.61	12.46	2.27
SIO060914-B	9/13/06	9/14/06	Fine	0.05	0.00	11.02	6.57	0.84

Aerosol Time-of-Flight Mass Spectrometry Results from Scripps Institution of Oceanography Pier August – October 2006

During ATOFMS sampling at Scripps Pier a unique particle type was observed containing a strong vanadium signal as well as iron and nickel (Figure 9). This particle type is primarily in the submicron size range and contained elemental carbon (EC) and organic carbon (OC) markers. While EC and OC particles by themselves are a major fraction of particles produced in both light duty vehicles and heavy duty diesel vehicle emissions, vanadium is not a major fraction of the emissions from those sources. Most likely the vanadium particles are produced by the combustion of a less refined fuel having a higher metal content such as the bunker fuel often burned by ships.

The vanadium particle type is not only unique in its mass spectrum, but the size distribution is also unique and quite different compared to the other major submicron

classes (Figure 9 & **Error! Reference source not found.**). Figure 10 shows the size-resolved relative fractions of observed particle types over the whole study. It can be seen that the fraction of vanadium particles drops off considerably below 300nm, while elemental carbon with minor organic peaks (ECOC) and potassium-elemental carbon both maintain their fractional contribution down to 200 nm, the lower detection limit of the standard inlet ATOFMS. Both of these types track the vanadium type well in time suggesting a similar source.

Figure 10 lists the top submicron types during transport events, which account for roughly 75% of submicron particles during those times. Beyond the vanadium, elemental carbon, and potassium-elemental carbon described above, other types observed during these event were commonly observed in the submicron size range regardless of whether an event was occurring. They include ECOC with sulfate or both sulfate and nitrate (types 3&6), potassium-combustion (likely biomass burning) (type 4), and sea salt (type 5). Further analysis as part of a separate CARB grant will examine these submicron types further.

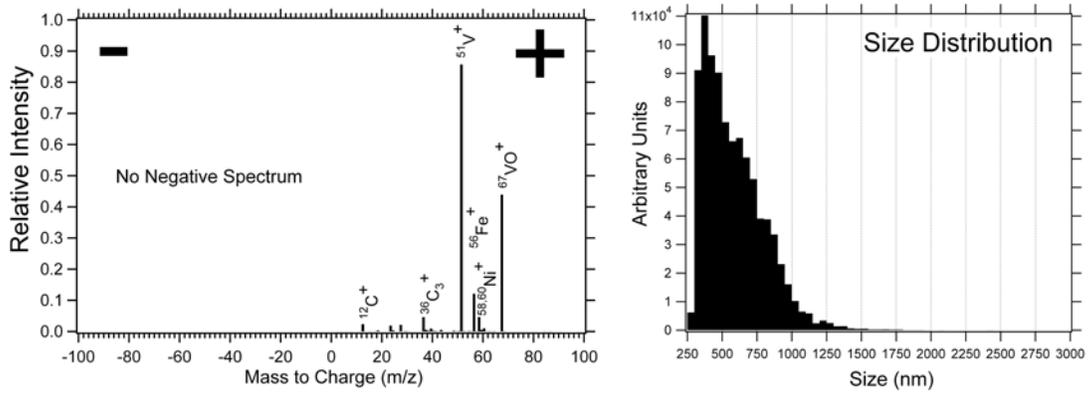
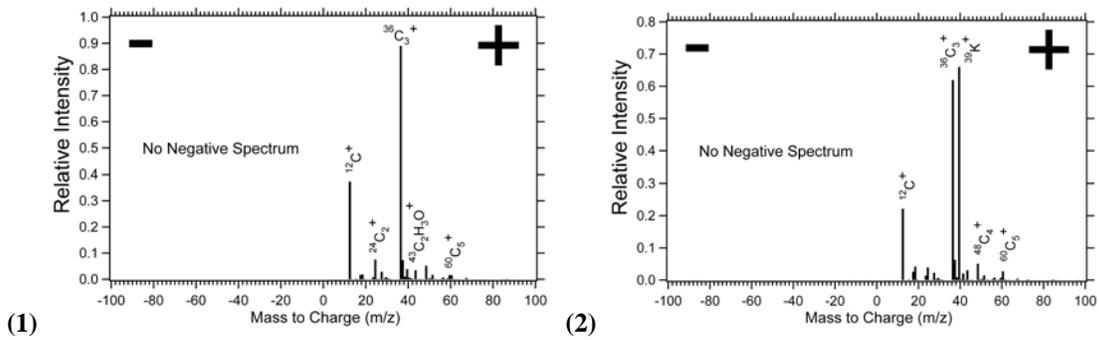


Figure 9: Mass spectral signature of the vanadium particle type (left) and the corresponding normalized size distribution (right).



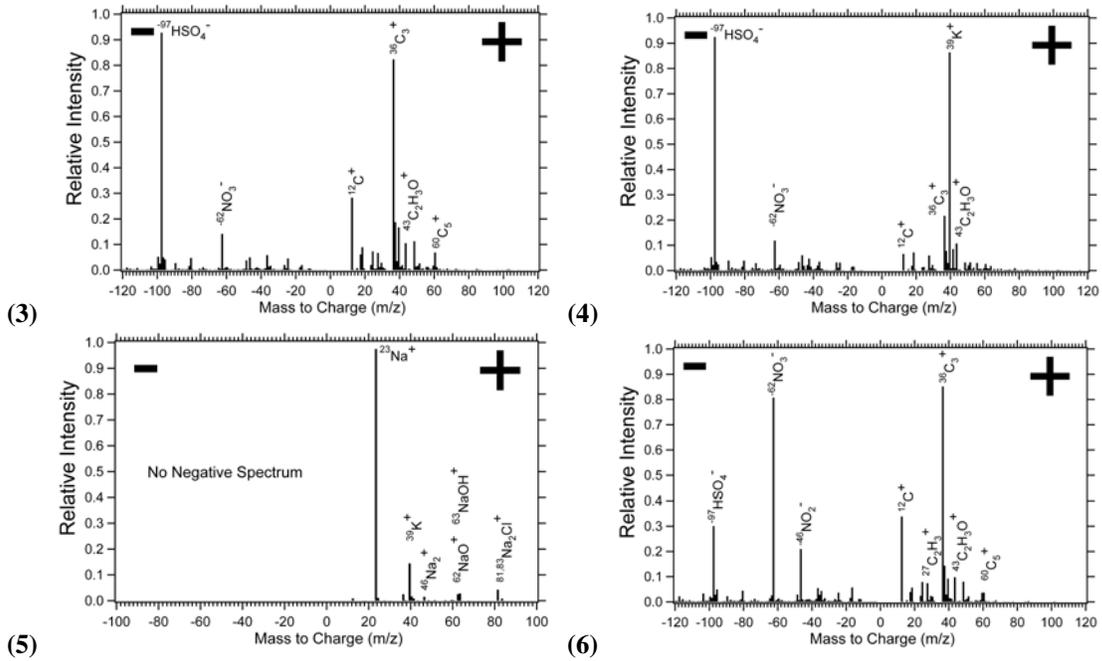


Figure 10: Mass spectra of the top particle types during submicron events (1) ECOC, no negatives, (2) Potassium-EC, no negatives, (3) ECOC, Sulfate, (4) Potassium-Combustion, Sulfate, (5) Sea Salt, no negatives, and (6) ECOC, Nitrate Sulfate

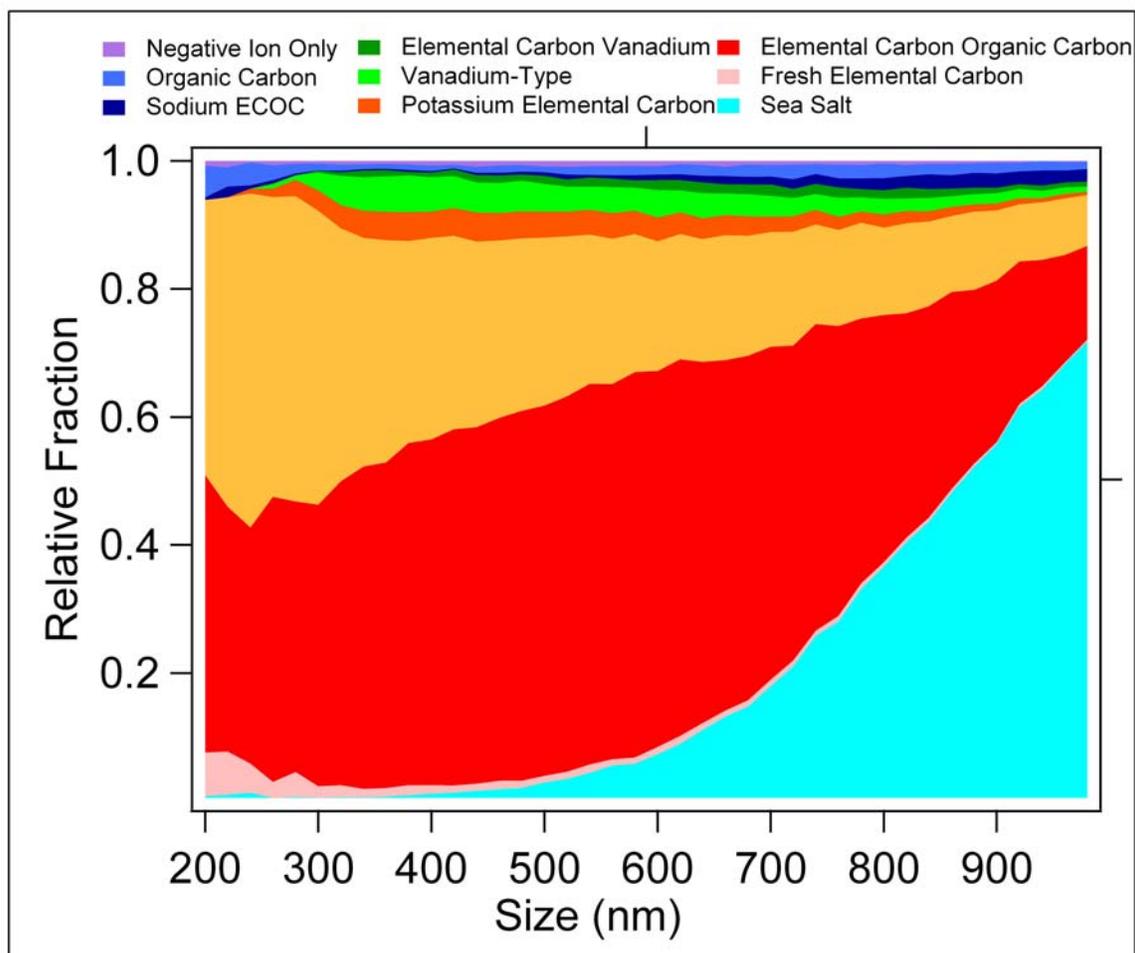


Figure 11: The relative fraction of the top 85% of submicron particle classes in 50 nm bins in the submicron size range. Vanadium can be seen to have a unique size profile when compared with the other major submicron classes.

The temporal fractions of particle types in the submicron size range over the entirety of the study are shown in Figure 12. It is important to note that the time series displays neither a constant contribution from one particle type nor any diurnal variations. The vanadium particle type has unique episodes with no obvious weekday/weekend trends. Time periods with a high fraction of sea salt particles had overall very low concentrations of particles in the submicron region and were generally cleaner time periods with winds mainly coming from over the ocean.

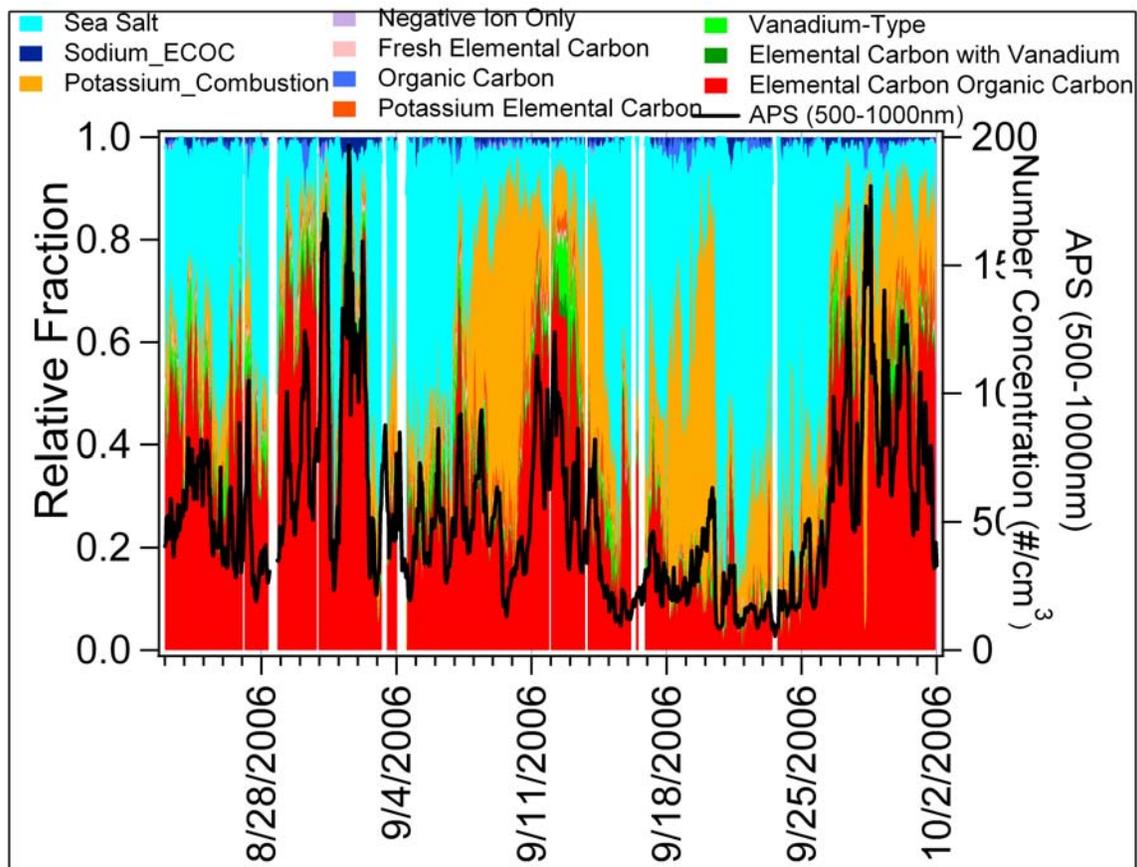


Figure 12: Plot of particle type percentage vs time in one hour bins. The black line is APS (500-1000nm) number concentration per hour.

The submicron APS counts, shown in Figure 12, correlate well with increases in the vanadium particle type fraction, with the exception of September 29th. Thus when the overall PM concentrations rose in the area, it was due to a source that produced significant vanadium particles. From this, we can conclude that ships in the region contribute to high pollution loadings in the San Diego region. **Error! Reference source not found.** shows the submicron APS counts (500-1000nm) vs. supermicron APS counts (1000 – 3000nm), with each point representing a one hour bin. During times when the submicron contributions are higher in proportion to the supermicron the vanadium counts tend to be higher, as indicated by the color and size of the markers.

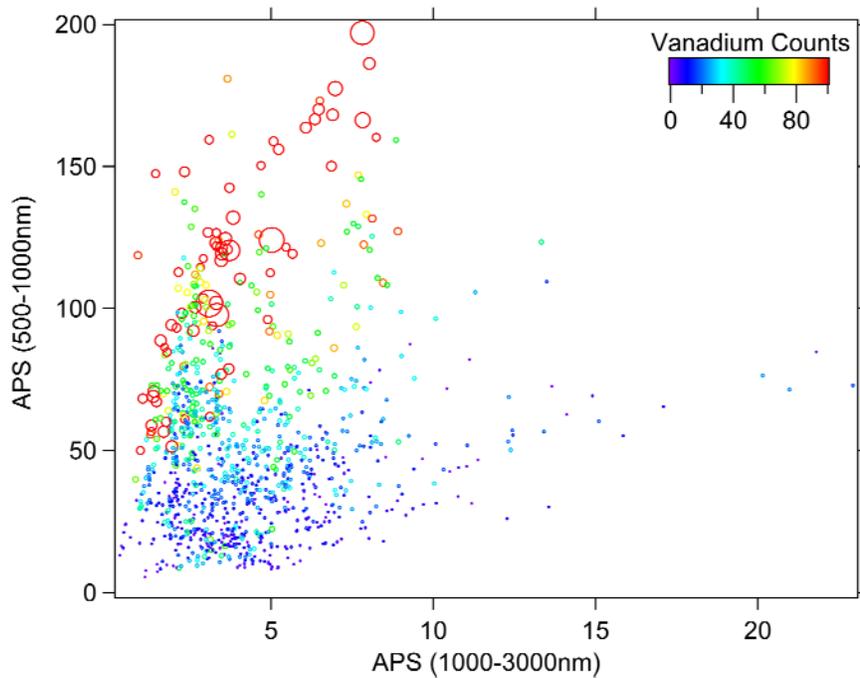


Figure 13: Correlation plot of submicron APS counts (500-1000nm) versus supermicron APS counts (1000-3000nm) for each hour of the study. The color and size of the points correspond to the number of vanadium counts for that hour.

The fraction of ECOC in Figure 12 often also increases during the same time periods when the fraction of vanadium particles increase. This correlation can be seen in Figure 14 which shows the time series of vanadium-type counts per hour and ECOC counts per hour. The direct correlation plot between vanadium and ECOC particles is shown in the inset and displays a high R^2 for ambient data of 0.6693. This correlation strongly suggests the source of the ECOC and vanadium particles is the likely same.

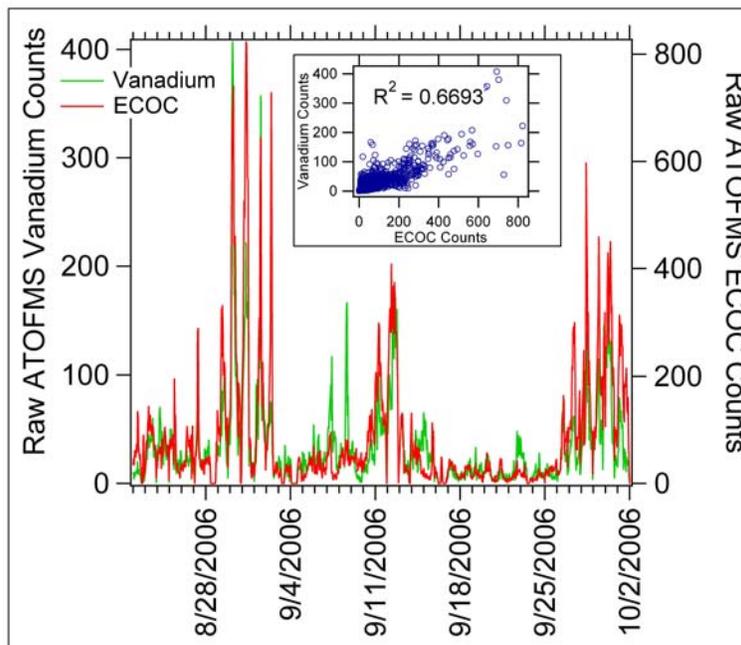


Figure 14: Time series data for both vanadium and EC particle types. The correlation plot of vanadium vs. EC is shown in the inset

A major contributor to ECOC particles in the atmosphere is diesel fuel combustion. This correlation between vanadium and ECOC is logical as most ships burn low grade diesel fuel. This indicates the highest pollution periods in San Diego (at the Scripps Pier during this study) were during periods with major ship influences.

D. Discussion

A plot of $\Delta^{17}\text{O}$ in the non-sea salt sulfate in fine and coarse particles vs. $\delta^{18}\text{O}$ is shown in Figure 16. Trend-lines for fine and coarse particles determined using a χ^2 minimization algorithm (written in Matlab) are also shown. The trend-lines for the coarse and fine aerosol sulfate fractions are distinct at a statistically significant level ($>3\sigma$). For reference we also plot the triple isotope composition of oxygen in nss-sulfate in the fine and coarse aerosols from a pristine coastal marine environment in Northern California^{xx}. The distinct slopes observed in fine and coarse aerosol nss-sulfate indicate that the sources and/or oxidative pathways of additional sulfate are isotopically distinct, with the mixing line of aerosol nss-sulfate in coarse aerosols consistent with ozone ($\delta^{18}\text{O} \sim 40-100\text{‰}$, $\Delta^{17}\text{O} \sim 30-35\text{‰}$) dominated oxidation of $\text{SO}_2(\text{aq})$ in sea-salt aerosols in this size fraction^{xxi}. The negative slope and intercept of the sulfate in fine aerosol particles differs significantly from those of the coarse particles.

Triple-oxygen isotope compositions and Oxidation Pathways

For a given background isotopic composition, departures in the concentration and isotopic composition of aerosol sulfate collected are attributed to contributions of primary sulfate and secondary sulfate from the oxidation of SO_2 . The pathway for oxidation determines the isotopic composition individual molecules of sulfate in an air mass, and the effects of transport modify the average composition of sulfate in an air mass over time.

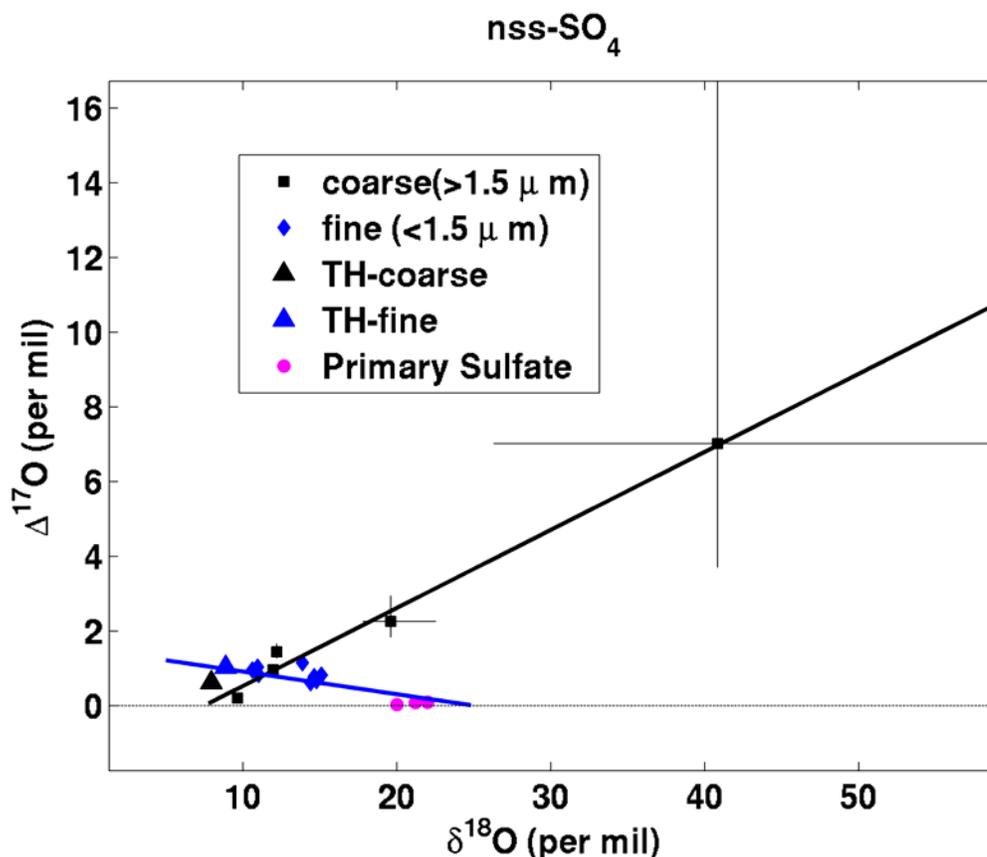
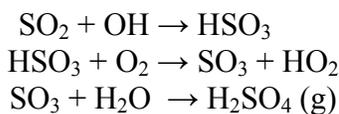


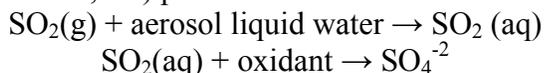
Figure 15: $\Delta^{17}\text{O}$ vs. $\delta^{18}\text{O}$ for fine and coarse aerosol non-sea-salt sulfate collected at Scripps Pier. Trend-lines for fine and coarse aerosol sulfate display distinct slopes and intercepts. The trend-line (solid black) for the coarse particles is consistent with the aqueous-phase oxidation of SO_2 by O_3 ($\Delta^{17}\text{O} > 0\text{‰}$) while the fine particle composition trends towards a mass-dependent ($\Delta^{17}\text{O} = 0\text{‰}$) primary sulfate.

In the case of sulfate, oxidation mechanisms can be divided into two general classes: homogenous and heterogeneous. In the homogenous oxidative pathway, OH participates as:



Given the rapid isotopic exchange rate between SO₂ and H₂O (vapor, $\delta^{18}\text{O} \sim 0\text{‰}$ -temperature dependent, $\Delta^{17}\text{O}=0\text{‰}$) as well as OH and H₂O in the atmosphere, all four of the oxygen atoms in SO₄ are essentially set by the composition of water vapor and OH ($\Delta^{17}\text{O}=0\text{‰}$) in the atmosphere. Thus, the homogenous oxidation pathway imparts a $\Delta^{17}\text{O}=0\text{‰}$ isotopic composition on aerosol sulfate molecules formed via this route.

In the heterogeneous pathway, aqueous phase reactions of the surface of existing aerosols (cloud droplets, sea-salt aerosols, etc) proceed as follows:



where “oxidant” is mainly either dissolved O₃ or H₂O₂. Other oxidants may also play a role in the aqueous phase oxidation of SO₂ in the atmosphere and these include metal catalyzed oxidation by atmospheric O₂ ($\delta^{18}\text{O} \sim 22\text{‰}$, $\Delta^{17}\text{O}=0\text{‰}$) or HO₂NO₂.

Our previous work at Trinidad Head, CA^x, regarding measurements of the oxygen isotopic composition of aerosol sulfate (and nitrate) in a clean-remote boundary layer shows small, but measurable, isotopic differences were found between fine and coarse aerosol sulfate. These measurements were done using a high-volume aerosol sampling and sample processing very similar to this study. Because of the relatively “clean” characteristics of Trinidad Head, we can think of this site and the oxygen isotopic composition of nitrate and sulfate as an indicator of the average background conditions in a “clean” marine boundary layer. It is interesting that the trend-lines seen in La Jolla (Figure 16) appear to correspond to those at Trinidad Head in $\delta^{18}\text{O}$ - $\Delta^{17}\text{O}$ space, namely that fine and coarse aerosol sulfate have oxygen isotopic compositions ($\delta^{18}\text{O}$ (fine-SO₄)= 8.89±1.1 ‰, $\Delta^{17}\text{O}$ (fine-SO₄)=1.03 ± 0.16 and $\delta^{18}\text{O}$ (coarse-SO₄)=7.95 ± 1.05 ‰, $\Delta^{17}\text{O}$ (coarse-SO₄)=0.63 ±0.17 ‰). These observations suggest that the triple-oxygen isotope composition of nss-sulfate in aerosols found at La Jolla is set by similar relative proportions of homogenous and heterogeneous oxidation of SO₂.

The upward trend line of aerosol sulfate found in coarse particle (toward ozone’s isotopic composition) indicate that a substantial fraction of non-sea-salt sulfate in coarse particles is derived from the oxidation of SO₂ by dissolved O₃ in sea-salt aerosols. We forego analysis of these data here to focus on fine aerosol sulfate.

Fine Aerosol Non-Sea Salt Sulfate and Ship Emissions

The isotopic composition of oxygen in nss-sulfate in remote marine air masses is determined by the relative strengths of OH- ($\delta^{18}\text{O} = \sim 0\text{‰}$, $\Delta^{17}\text{O} = 0\text{‰}$), H₂O₂ ($\delta^{18}\text{O} = 21.9\text{--}52.6\text{‰}$, $\Delta^{17}\text{O} = (1.4\text{--}2.4)\text{‰}$)^{xxii} and ozone ($\delta^{18}\text{O} = 81.6 \pm 6\text{‰}$, $\Delta^{17}\text{O} = 26.7 \pm 5\text{‰}$)^{xxiii} oxidation of SO₂ ($\Delta^{17}\text{O} = 0\text{‰}$)^{xxiv} and the associated $\delta^{18}\text{O}$ fractionations (equilibrium and/or kinetic) and $\Delta^{17}\text{O}$ compositions of these oxidants^{xxv}. Given the possible natural explanations for the trend lines seen in our data, it is interesting that the $\Delta^{17}\text{O}$ of sulfate in fine aerosols decreases for higher $\delta^{18}\text{O}$ values, indicating the influence of a distinct mass-dependent source of sulfate in the atmosphere of Southern California.

This trend is in marked contrast to the nss-sulfate found in coarse particles.

Considering the location of the sampling and the measured isotopic composition of primary sulfate from the ship stack (See Table 3), it is plausible that the fine aerosol trendline represents a mixing line between a background with a marine nss-sulfate like composition and that of primary sulfate from ship emissions in coastal San Diego and/or the greater Los Angeles area. The trendline in the coarse particles also indicate that oxidation of SO₂ by ozone in submicron sea-salt aerosols could potentially be a significant source of sulfate. We examine the relative role of the various oxidation pathways in the fine size fraction using a simple mixing model and mass balance. For simplicity, we assume that the measured triple-isotopic composition of aerosol sulfate is represented as a linear combination of fractions of sulfate that was formed similarly to the background nss-SO₄ in a remote marine environment, mass-dependent primary sulfate, and sulfate made from the oxidation of SO₂(aq.) by ozone. This general model can be expressed as follows:

$$\begin{aligned}\Delta^{17}\text{O}(\text{nss-SO}_4) &= \Delta^{17}\text{O}(\text{B})f_B + \Delta^{17}\text{O}(\text{P})f_P + \Delta^{17}\text{O}(\text{O}_3)f_{\text{O}_3} \\ \delta^{18}\text{O}(\text{nss-SO}_4) &= \delta^{18}\text{O}(\text{B})f_B + \delta^{18}\text{O}(\text{P})f_P + \delta^{18}\text{O}(\text{O}_3)f_{\text{O}_3} \\ 1 &= f_B + f_P + f_{\text{O}_3}\end{aligned}$$

where f_B , f_P , and f_{O_3} are the fractions of sulfate made with isotopic compositions matching the “background” oxidative conditions, primary sulfate, and ozone oxidation respectively. These relationships can be written in matrix form and solved f_B , f_P , and f_{O_3} , yielding the relative contributions of each. To obtain an upper limit to the contribution made by ships, we assume that ships contribute 100% to the mass-dependent primary sulfate source and therefore the primary sulfate end-member in this case is found at $\delta^{18}\text{O}(\text{P}) = 21\text{‰}$, $\Delta^{17}\text{O}(\text{P}) = 0\text{‰}$. A summary of the resulting estimates for ship primary sulfate are shown in **Table 6**. It is interesting to note that f_{O_3} in the fine aerosols is typically less than 0.02, with $f_B + f_P \sim 1$. The results are relatively insensitive to the isotopic composition of ozone in the atmosphere, indicating that ozone oxidation of SO₂ is very minor in this size range. These estimates represent an upper limit to the amount of primary sulfate contributed by ships in the region.

Table 6. Upper limits to the amounts of ship primary sulfate in coastal San Diego during September 1- September 14, 2006 assuming 100% of mass-dependent source of primary sulfate is from ships.

sample	start time	end time	[SO ₄] μg m ⁻³	[nss-SO ₄] μg m ⁻³	[SO ₄ (ships)] μg m ⁻³	% of nss- SO ₄ from ships (f _p)
SIO060901-B	8/29/06	9/1/06	8.53	8.18	4.00	49
SIO060905-B	9/2/06	9/6/06	4.61	4.20	0.58	14
SIO060907-B	9/6/06	9/7/06	5.34	4.69	0.70	15
SIO060908-B	9/7/06	9/8/06	4.56	3.93	1.32	33
SIO060911-B	9/8/06	9/11/06	4.56	4.27	1.97	46
SIO060912-B	9/11/06	9/12/06	6.54	5.84	2.79	48
SIO060913-B	9/12/06	9/13/06	8.19	7.48	3.70	49
SIO060914-B	9/13/06	9/14/06	4.33	4.31	0.83	19

There is the possibility that the observed influence of a mass-dependent source originates from either wholly or partly from land-based diesel engine exhaust. However, an examination of the triple-isotopic composition of oxygen in primary sulfate from diesel engines by Lee *et al.* (2002)^{xxvi} found that the $\delta^{18}\text{O}$ ranged from 5-7‰ and $\Delta^{17}\text{O}$ from -0.2 to 0.2‰. The $\delta^{18}\text{O}$ values of diesel engine primary sulfate are too low to satisfy the isotopic constraints of our data. If we treat the mass-dependent primary sulfate as a generic end-member, it can be easily shown that values of f_p less than 1 are obtained when the mass-dependent ($\Delta^{17}\text{O} = 0$ ‰) source of primary sulfate has a $\delta^{18}\text{O} > 13$ ‰. This end-member ($\delta^{18}\text{O}(\text{P}) = 13$ ‰, $\Delta^{17}\text{O}(\text{P}) = 0$ ‰) is equivalent to a mixture of diesel primary sulfate (61%) and ship primary sulfate (39%), and the results for f_p derived from this end-member composition constitute a lower limit to the amount of ship sulfate needed to explain the triple oxygen isotopic data. Table 7 summarizes the results of this analysis and Figure 16. graphically illustrates the necessity of having a mass-dependent sulfate end-member with relatively high $\delta^{18}\text{O}$ values to explain our triple-oxygen isotope data.

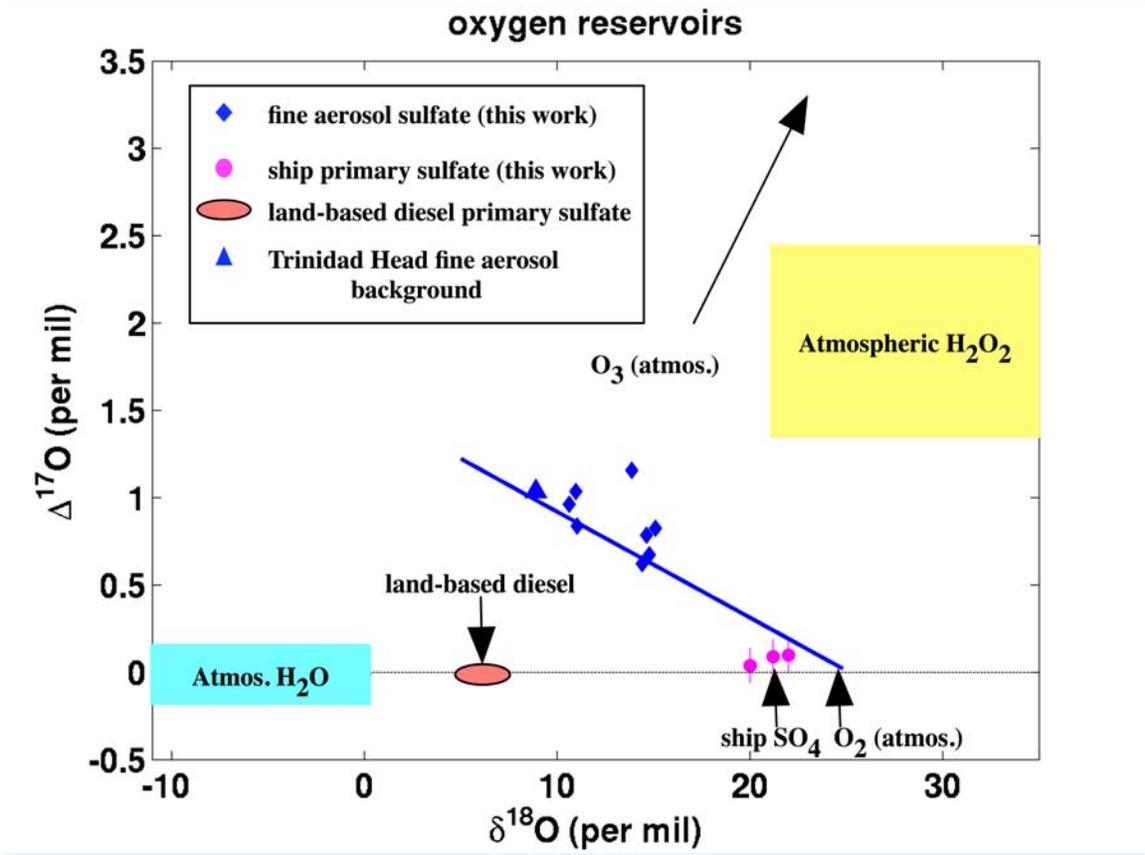


Figure 16: Natural and anthropogenic reservoirs of oxygen in the atmosphere plotted in triple oxygen isotope space.

sample	start time	end time	[SO ₄] μg m ⁻³	[nss-SO ₄] μg m ⁻³	[SO ₄ (ships)] μg m ⁻³	% of nss- SO ₄ from ships (f _p)
SIO060901-B	8/29/06	9/1/06	8.53	8.18	3.15	39
SIO060905-B	9/2/06	9/6/06	4.61	4.20	0.46	11
SIO060907-B	9/6/06	9/7/06	5.34	4.69	0.55	12
SIO060908-B	9/7/06	9/8/06	4.56	3.93	1.04	26
SIO060911-B	9/8/06	9/11/06	4.56	4.27	1.55	36
SIO060912-B	9/11/06	9/12/06	6.54	5.84	2.19	38
SIO060913-B	9/12/06	9/13/06	8.19	7.48	2.90	39
SIO060914-B	9/13/06	9/14/06	4.33	4.31	0.65	15

Table 7. Lower limits to the amount of primary ship sulfate in coastal San Diego assuming that ships contribute 39% of mass-dependent primary sulfate.

Elevated levels of certain metal ions (Mn²⁺, Fe³⁺) are known to catalyze the oxidation of aqueous SO₂ by O₂ and this oxidation pathway would also result in a mixing line with a very similar slope^{xxvii,xxviii} (See Figure 16**Error! Reference source not found.**). Given that isotopic composition of primary sulfate from ship samples we analyzed is so similar to that of atmospheric oxygen, we suggest that the oxidation of sulfur in marine diesel engines may result from the catalytic oxidation of S by atmospheric oxygen within ship engines. Studies of ship plumes indicate that most of their particulate emissions are submicron in size and have elevated levels of trace metals such as Ni, Zn, V, and Pb^{xxix,xxx}. At this time it is unclear whether these metals are capable of acting as catalysts, but this possibility should be explored. Future work will examine the potential role of metal-catalyzed oxidation of SO₂ in sub-micron sized aerosols using a combination isotopic and trace-metal analyses as well as laboratory experiments. The work we have presented strongly suggests that triple-isotope determinations of oxygen in sulfate from size segregated samples of the atmosphere have the potential of greatly clarifying our understanding of the local, regional, and global sulfur budgets, and the analytical tools we have presented provide a clear and simple way of quantifying the amount, or at the very least placing limits, to the amount of nss-sulfate contributed by marine vessel emissions in coastal urban environments.

Transport of Vanadium Particles from Long Beach

The vanadium particle type identified is indicative of low grade diesel combustion. Time periods when both vanadium and elemental carbon spike have HYSPLIT back trajectories that come from the vicinity of the Ports of Los Angeles and Long Beach. In Figure 17, the HYSPLIT data from one of the more intense ship influence episodes (September 1st, 2006) are plotted. For each hour with a high number of vanadium counts, the HYSPLIT analyses from three elevations are plotted (200m-red, 500m-green, and

1000m-blue). The points in dark blue are ships that radioed to shore during that time period and were recorded via the AIS that the Thiemens Group ran during the study. This plot shows that winds at all three elevations are coming from the vicinity of the Ports of Los Angeles and Long Beach.

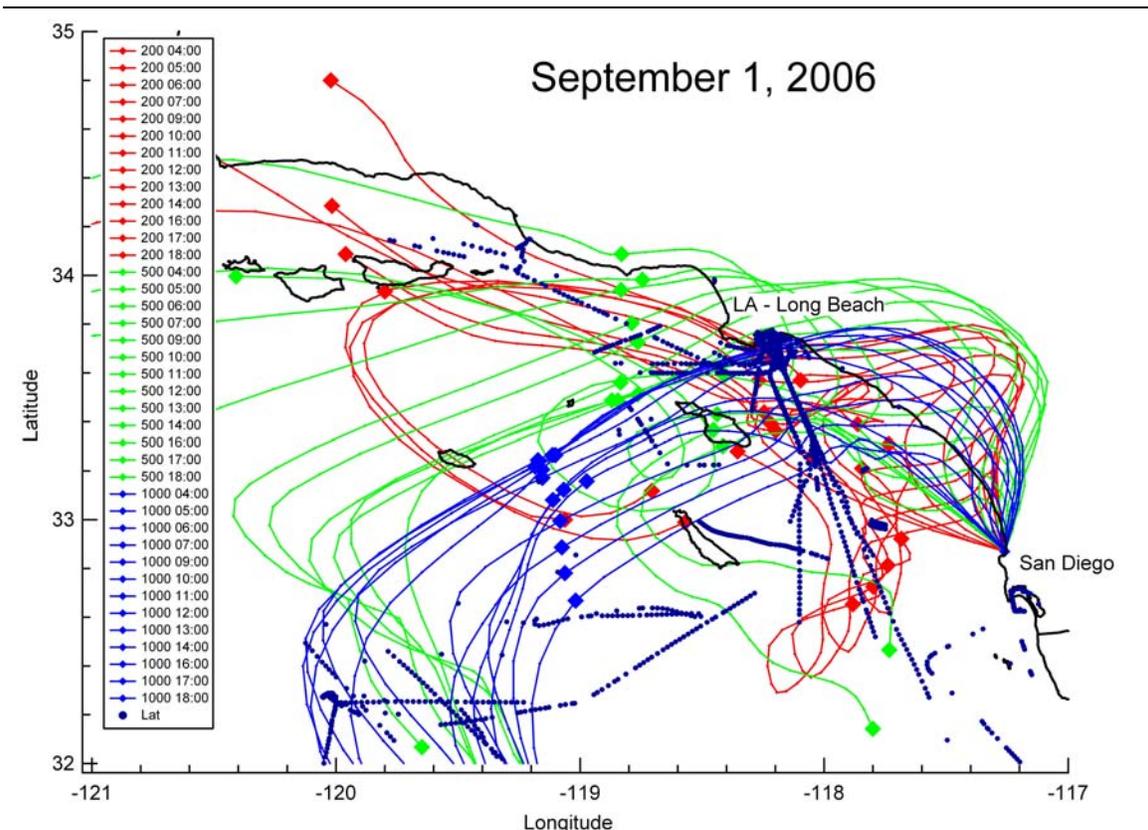


Figure 17: HYSPLIT pack trajectories at 3 elevations (200m – red, 500m – green, and 1000m – blue) during hours with high vanadium counts on September 1, 2006. The dark blue points are the latitude and longitude of ships that radioed in during the hour

Other Examples of the Vanadium Particle Type in San Diego

Similar mass spectral signatures for the vanadium particles measured in this study have been observed during previous studies with the ATOFMS. In 2004, a freeway study next to I-5 examined the overall impact of heavy versus light duty vehicles on air quality in San Diego. During a high pollution period vanadium particles constituted a significant portion of the background particles at both sites (next to the freeway and at a location ~ 1 mile towards the ocean). The signatures were identical to the signatures observed during the Scripps pier study conducted as part of this project. During both studies, the vanadium (and correlated EC) particles frequently did not have negative ion spectra. The lack of negative spectra has been shown to be an indicator of the amount of aging and

associated water uptake on particles. Thus more aged particles will have taken up more water and have a lower frequency of negative ion spectra. **Error! Reference source not found.** shows both the mass spectral signature and the time series data from this previous freeway study.^{xxxii}

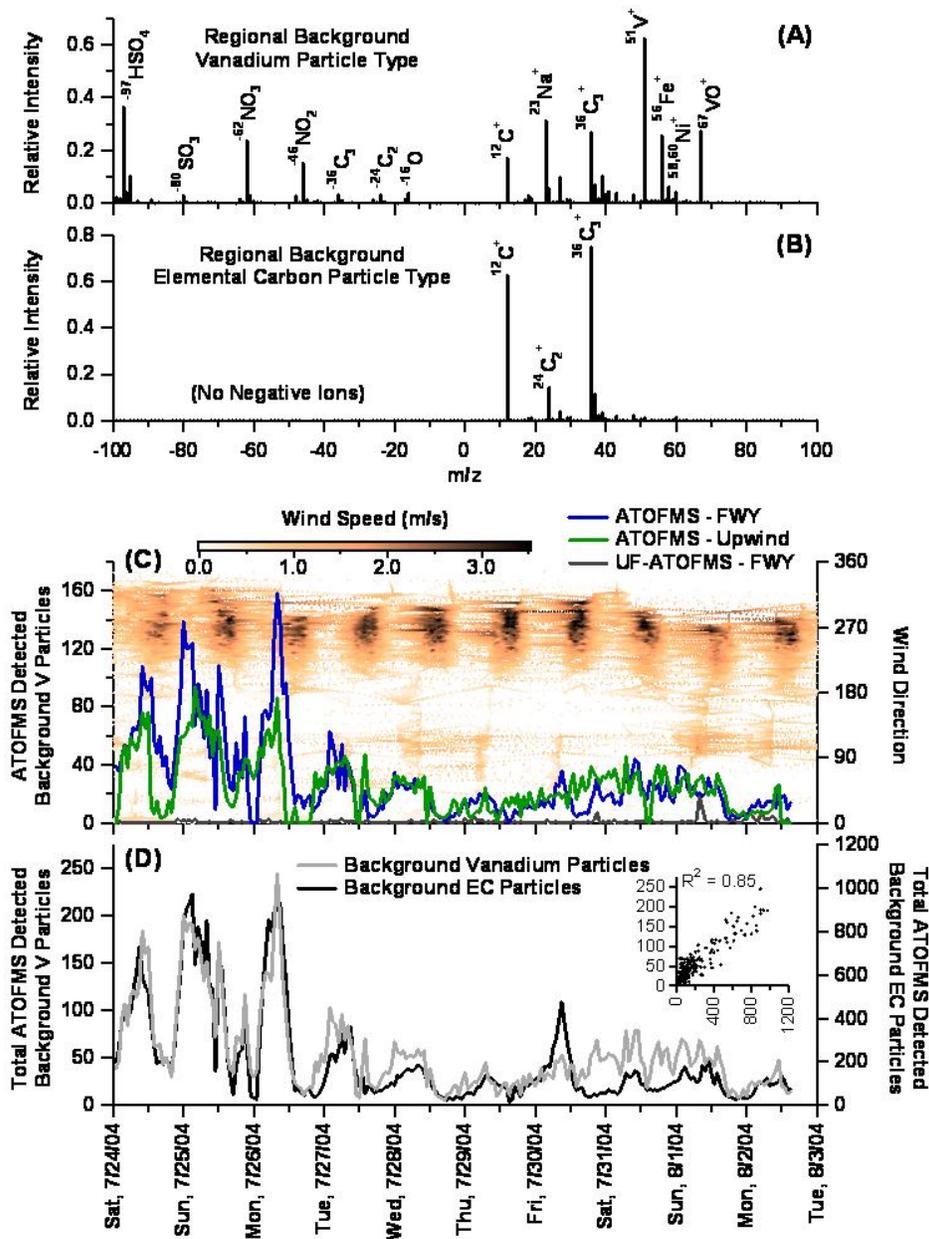


Figure 18: Positive and negative ion mass spectra for the regional background (A) vanadium and (B) EC particle types. (C) The temporal trends of the vanadium particle type detected with all three ATOFMS instruments compared to wind data. (D) Temporal (and correlation) of total background vanadium particles versus the total background EC particles for the three ATOFMS instruments.

The back trajectory of an air mass seems to be the best indicator of when the vanadium particle type will be observed. In Figure , the back trajectories for the time period when the vanadium particles were the most abundant during the freeway study corresponded to periods when the air mass passed over the LA/LB port regions. The particles were more abundant for both studies when the air mass moved quickly from the port region to the San Diego region diminishing time for particle losses or diffusion to occur. It is interesting to note that periods with major ship influences in San Diego also correspond to the overall highest concentrations periods observed. Even next to the freeway, the impact of the ship emissions and air pollution from the LA area overwhelm the concentrations of the particles being produced by vehicles on the nearby freeway. This demonstrates that even when sampling near a freeway, under certain circumstances contributions from other sources such as ships can be even higher than the freeway generated particles. As is seen during both the Scripps Pier Study and the Freeway Study during periods of transport to the San Diego region carbonaceous and heavy metal particles are a significant fraction of the submicron aerosol

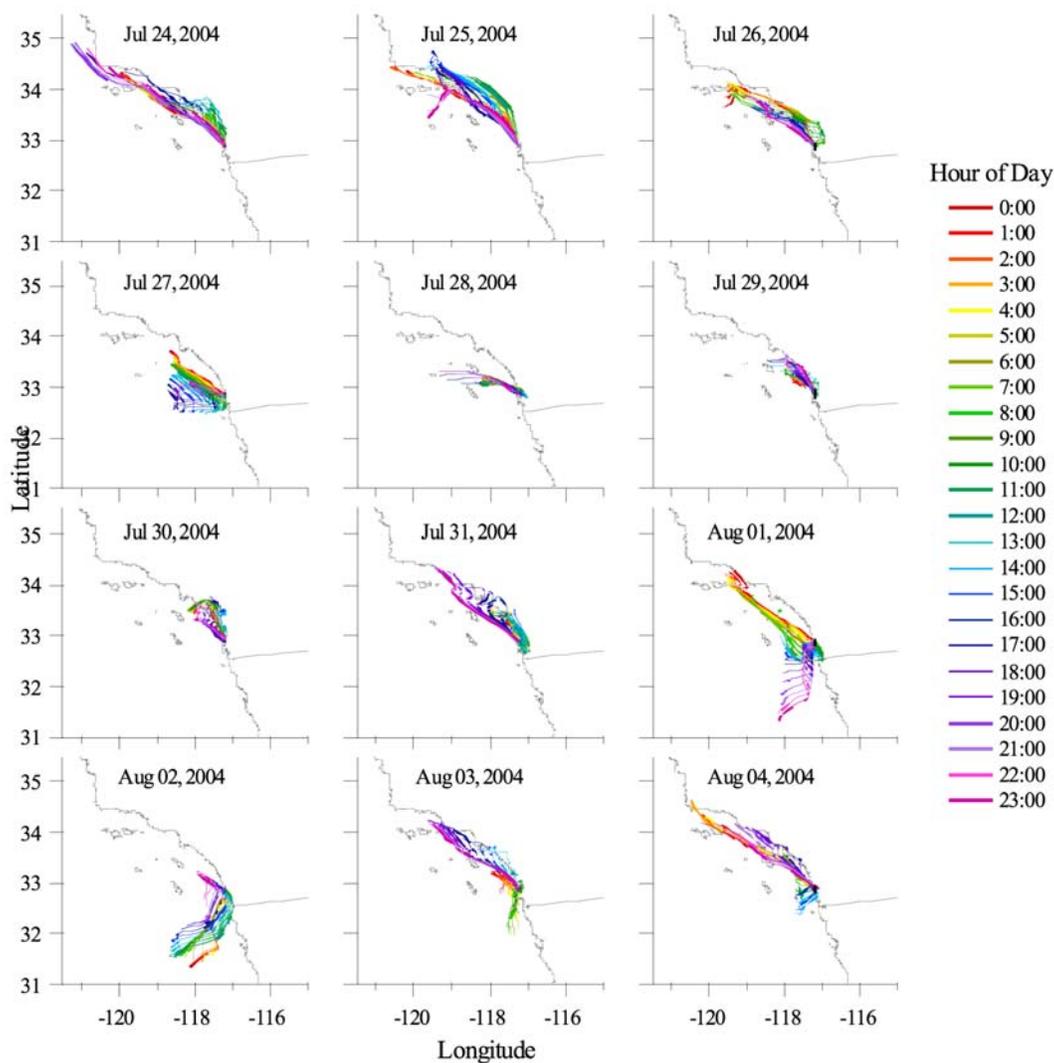


Figure 19: Backtrajectories of air masses arriving in San Diego for different portions of the Freeway Study. One can see that on the dates with the highest V and ECOC particle and overall PM concentrations (7/24 – 7/26), the air mass came from the Los Angeles - Long Beach Port vicinity directly to San Diego.

We examine the relationship between vanadium particle counts and the ship signatures in submicron sulfate in this section. Figure 19 plots the fraction of nss-SO₄ in submicron aerosol particles that is attributable to ship primary sulfate and counts of vanadium-type particles at Scripps during the August-October field campaign. The correlation is quite weak. This is most likely due to the long sampling times required for the isotopic analysis. The ATOFMS sees relatively rapid changes in the V and EC ship count data that become averaged out by the longer filter sampling times required. Also, uncertainties in the relationship between ATOFMS particle counts and ambient concentrations, in the correlation between vanadium and ship-sulfate at the point of

emission, and/or in the attribution of primary sulfate from ships using oxygen isotopes may all contribute to weaken the observed correlation. In Figure 20, we plot the maximum ATOFMS vanadium-type particle counts with the inferred concentration of nss-sulfate that we attribute to primary ship sulfate using oxygen isotopic measurements.

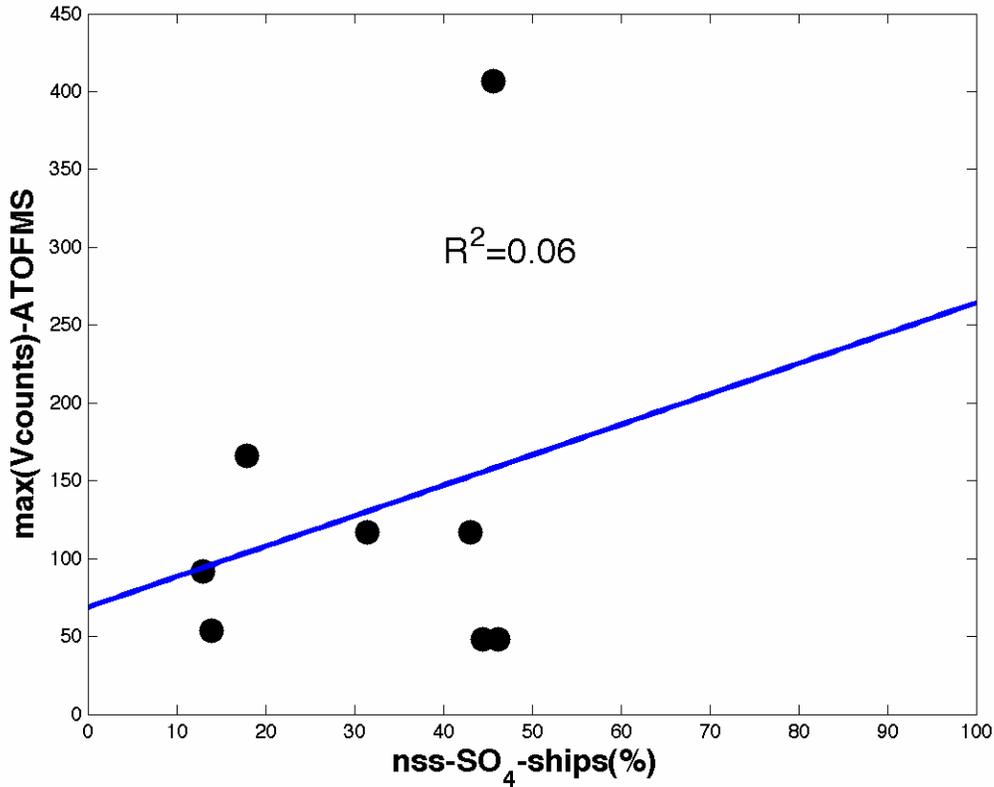


Figure 19: Maximum Vanadium-type particle counts (during high-vol sampling period) and % of nss-SO₄ from ship primary sulfate.

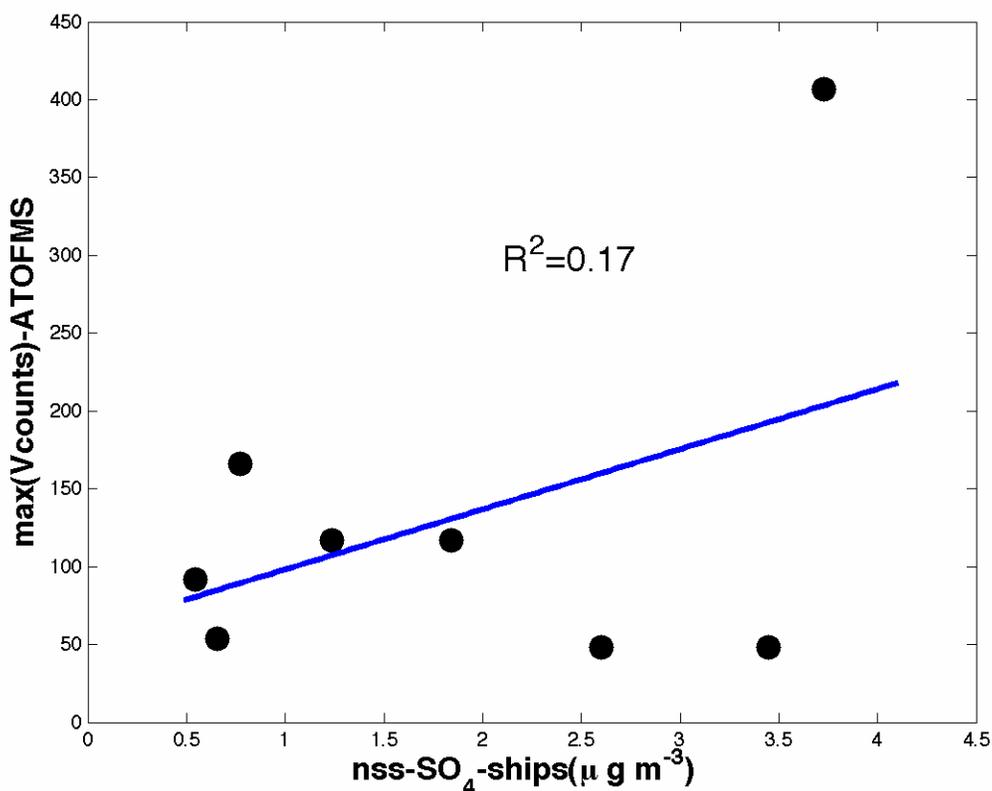


Figure 20: Maximum Vanadium-type particle counts (during high-vol sampling period) and concentration of nss-SO₄ attributable to ship primary sulfate.

When examined as a time series, the relationship between vanadium-type particle plumes and the amount of nss-SO₄ and the isotopic composition of the nss-SO₄ is more suggestive. The isotopic composition of sulfate appears to shift towards a more mass-dependent composition for days where there are 1) high vanadium counts and 2) higher sulfate concentrations in the submicron size range (See Figure 21). The shifts are not as apparent in the isotope data; again we attribute this to the longer sampling times required for the filters. These same shifts are also accompanied by higher $\delta^{18}\text{O}$ values as seen in Figure 22, consistent with ship primary sulfate as discussed in section. The reasons why the nss-SO₄ and vanadium count data are not linear at this time are most likely attributable to time resolution differences between the techniques. For this reason, in a future coastal study, we suggest using the ATOFMS V-counts to serve as a trigger for sampling on filters for targeted isotopic analysis. Ideally two filter samplers would collect high V- versus low V-count time periods. This would allow a direct comparison of the isotopic data with the unique ATOFMS ship signatures determined in this study.

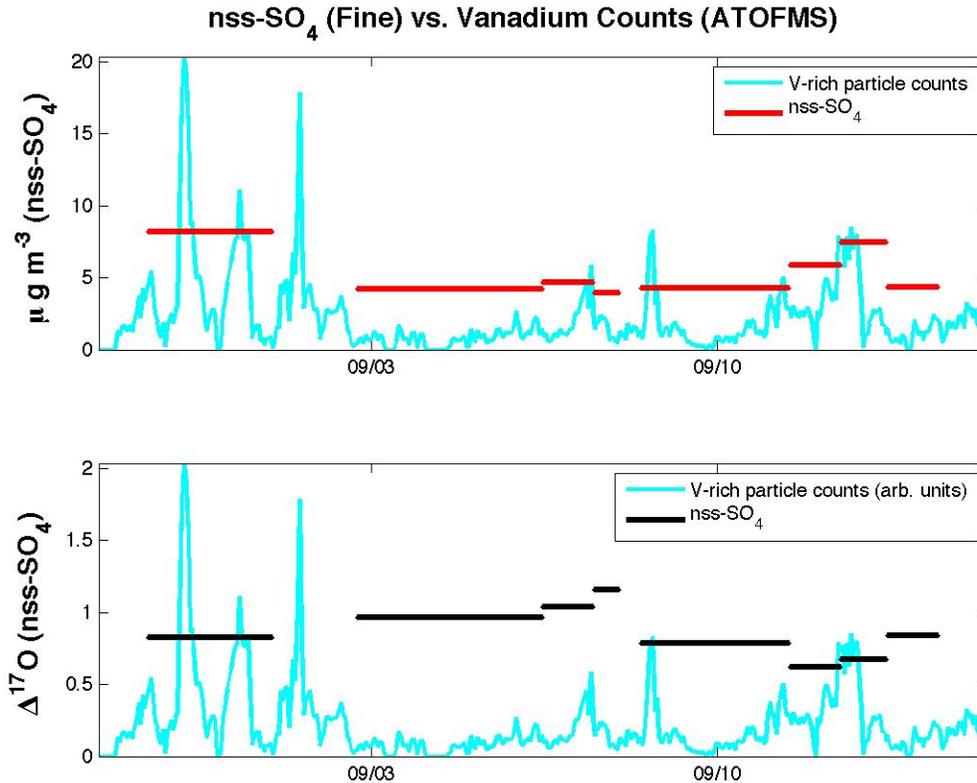


Figure 21. Upper plot is the average concentration of nss-SO₄ (fine) vs. time (red bars) together with the corresponding vanadium-rich particle counts (cyan). There appears to be a direct correspondence between changes in vanadium counts and amount of nss-SO₄. Lower plot shows the behavior of $\Delta^{17}\text{O}$ in aerosol sulfate (fine) vs. time. It is clear that “cleaner” or more oceanic air masses (low V), tend to give you higher $\Delta^{17}\text{O}$ values compared to the urban-polluted air. These trends are consistent with an input of mass-dependent sulfate ($\Delta^{17}\text{O}=0$) associated with these air masses. The corresponding $\delta^{18}\text{O}$ data are shown in Figure 22 .

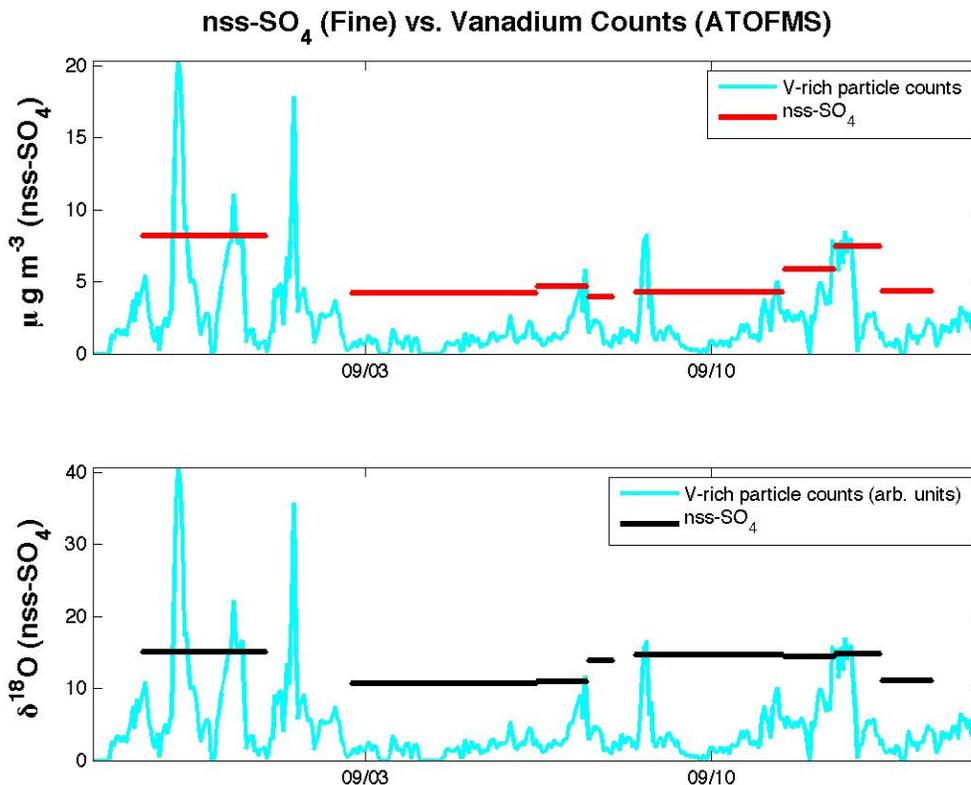


Figure 22. Upper plot same as Figure 21. Lower plot is of $\delta^{18}\text{O}$ for nss-SO₄ particles vs. time. Note that simultaneously higher $\delta^{18}\text{O}$ values and lower $\Delta^{17}\text{O}$ are the expected signature of ship primary sulfate in these air masses.

E. Summary and Conclusions

We have completed a pilot study on the use of a combination of stable isotope ratio measurements of aerosol nitrate and sulfate and ATOFMS single particle mass spectrometry data as a means of identifying the impact of ship emissions in the San Diego atmosphere. In particular, our focus on ship emissions required a more detailed understanding of the meteorology and variation of anion concentrations at La Jolla. We have performed back trajectory analysis to better understand the natural and anthropogenic source contributions to the aerosol in La Jolla. Based on these studies, and measurements of anion concentrations from size-segregated samples, we have quantitatively demonstrated that the air quality of coastal La Jolla is greatly influenced by local wind patterns and emissions from Los Angeles. In particular, the highest concentration PM days in La Jolla are directly correlated with the highest V levels, suggesting that ships are significantly impacting the air quality in this region of California.

To better understand the potential contribution of ship emissions, we developed a ship-tracking/logging computer system that has been logging ship traffic since the summer of

2006. This information has proven to be especially useful for examining high time resolution data, such as that acquired by ATOFMS (Prather Group), but may someday be used for quantifying NO_x emissions by ships passing off-shore from our sampling station. We will comment further on this point in the Recommendations section of this report.

We have measured the triple-isotopic composition of a select number of aerosol nitrate and sulfate samples collected at the Scripps Pier. Our study shows that the isotopic composition of aerosol nitrate at La Jolla is modulated by ozone rich urban air. These shifts are measurable. Chemical models of ship plumes perturb the oxidative conditions of the marine boundary layer. These shifts, given analytical techniques with enough time resolution (small sample size requirements), would be evident using measurements of the oxygen isotopic composition of aerosol nitrate. Aerosol nss-sulfate in these plumes may also carry signatures of ozone dominated oxidation of SO₂ emissions on sea-salt particles.

Our analysis of the composition of aerosol sulfate, binned in fine (<1.5 μm) and coarse (>1.5 μm) size modes indicates that distinct trend lines exist for these two size fractions. In the case of coarse particles, enhanced levels of ozone and SO₂ (aq) oxidation, probably on sea-salt aerosols, are evident in the plots of Δ¹⁷O vs. δ¹⁸O for this size fraction. In the case of sulfate found in fine particles, the trend-line indicates the influence of a significant primary sulfate source in the polluted marine boundary layer. These data are also consistent with trend lines seen in our other studies of aerosols in the Caribbean and Izana, in Northern Africa (unpublished data, in prep). The precise source of this additional primary sulfate needs to be further explored, although our initial measurements of primary sulfate emissions from a ship stack indicate that ships or ship-like sources contribute significant and quantifiable amounts of sulfate. We will also further probe the sulfate mixing state in the ATOFMS mass spectral data to see if further insight can be gained as to the main origin of these two forms of sulfate.

The ATOFMS and peripheral data have shown that vanadium particles with a specific mass spectral signature can serve as a unique tracer for particles produced by low grade diesel combustion, most likely ship emissions. The vanadium particle time series correlates strongly with the time series of elemental carbon suggesting a similar source. Diesel fuel combustion has been shown to be a significant contributor to ambient elemental carbon, which is a major component of ship plumes. The vanadium and elemental carbon particles were two of the major contributors to the submicron size range in the size range observed by the ATOFMS (200 – 1000 nm). Both vanadium and elemental carbon particles were frequently observed in the San Diego region during intense pollution episodes. The episodes did not follow a weekday/weekend pattern, but did tend to occur at the end of each month. These factors together suggest that the most likely source for these episodes is transport from the harbor region north of the SIO pier in LB/LA. The Scripps Pier was an ideal location to study the overall influence of ships as it is isolated from local sources, in particular during periods when the winds were coming from the ocean. The vanadium-type episodes occurred when the HYSPLIT back trajectories indicate that the air mass passed within the vicinity of the Ports of Long Beach and Los Angeles. This signature has been observed previously during other ATOFMS studies conducted in California, suggesting that ship emissions can represent a

significant contributor to high levels of air pollution in the Southern California region. Thus, when addressing the impact of primary sources on regional air quality, ship emissions must be considered as a major potential source.

F. Recommendations

The triple-isotope ratio determinations of aerosol nitrate and sulfate at the Scripps Pier display variations that are attributable to anthropogenic influences. These measurements indicate that ozone rich plumes in a marine boundary layer significantly influence the oxidative conditions and the measurement of oxygen isotopic compositions of nitrate in the marine boundary layer have the potential of clarifying the contribution of ships to nitrate in marine aerosols. These results also underscore the potential of tracking individual ship plumes with select high time resolution isotopic studies.

The second isotopic study (August-October 2006), with time-resolutions of one to three days, revealed highly variable concentration and triple-isotopic compositions in aerosol sulfate at the Scripps Pier. The isotopic composition of oxygen in submicron aerosol sulfate strongly suggests that triple-oxygen isotopic measurements record a signature of primary sulfate ship emissions. We therefore recommend that a geographic study of the triple-oxygen isotopic composition be made using an archive of filters, especially for the PM_{2.5} size range. Secondly, because it is possible that refinery sulfate emissions may have a similar isotopic signature to that of primary sulfate from ships, we recommend that direct sampling of these and other potentially significant primary sulfate sources in the Los Angeles/San Diego areas sources is urgently needed.

Assessing the impact of ship traffic traversing up and down the coast of San Diego is an ambitious and challenging task due to the non-linear nature of wind patterns and plume dispersion. Yet, as indicated by the AIS ship traffic logger, the amount of traffic, on the timescale of an hour or two, is highly variable. Thus, disturbances to the atmosphere caused by ship plumes may be resolved. Instrumentation with high time resolutions may be capable of identifying ship plumes (e.g. ATOFMS, CCN counters) in close to real-time. We recommend that funds be invested to study and develop proxies that are sensitive to individual ships and their plumes that originate from approximate 30 miles away.

The triple-isotope measurements presented are made using time-consuming instrumentation with limited time resolution. In recent years, however, there have been developments in analytical/geo-chemistry that are capable of measuring the oxygen (and nitrogen) isotopic composition of minute (~ 20 nanomoles of O vs ~ 2 micromoles) amounts of aerosol nitrate^{xxxii,xxxiii}. The funding and application of this technique, based on the use of denitrifying bacteria, to determine the isotopic composition of aerosol nitrate with ~ 1 hour time resolution could open the door for studying the NO_x-ozone system of individual ship plumes and thus better understand their impact on the air quality of coastal communities. Techniques such as laser fluorinations now exist that are capable of providing comparable time resolutions to measurements of aerosol sulfate (S

and O isotopes)^{xxxiv}. However, the use of these techniques is time consuming and can only be recommended for limited study of individual ship plumes.

The ATOFMS has identified a reliable vanadium-type particle signature for ship emissions. Thus, this unique signature can serve as a proxy for the presence of ship emissions on specific regions of California. The advantage of the single particle technique is that it can detect in real-time the impact of ship plumes. This ability has been greatly enhanced by the recent implementation of on-the-fly apportionment to the ATOFMS software suite. With these capabilities further studies that investigate the intensity and spatial variability of ship plume influenced air masses would aid greatly in gaining a detailed picture as to the overall impact of ship emissions on the Southern California region.

The implementation of regulations regarding the burning of cleaner fuel within 24 nautical miles of the California shoreline has been a step towards reducing the impact of ship emissions on Southern California. Assessing the effectiveness of this regulation is an important step towards fully addressing the impact of the ship emissions. At a recent, separate, CARB study the Prather Group at the Long Beach port, individual ship plumes were observed and these data are being examined now to determine whether the impact of the recent CARB regulation. Studies using the single particle capabilities of the ATOFMS on the emissions of different fuels both in a laboratory setting as well as with ambient sampling could make an important contribution to this assessment.

Given the ability of the isotopic technique to deconstruct sources of sulfate, and primary sulfate in particular, we suggest a study to map and document the historical impact of primary sulfate (and, by extension other pollutants) using archived filter paper samples at the Port of Los Angeles (or Port of San Diego). The Prather Group ATOFMS results also point to the value of developing sample extraction and analysis techniques for measuring trace metal concentrations in archived samples.

Finally, the results from this study suggest that it may be feasible to use the real-time data from the ATOFMS to selectively collect filter samples during periods with a significant ship influence based on V particle counts in the submicron size range. It is suggested that two samplers could be used to collect particles during periods with high V concentrations versus periods with low V concentrations. Focused filter analysis of the isotopes would yield major insight into how the isotopes change during these intensive sampling periods with known ship influences. These filters would also be used for in-vitro studies of the impacts of ships on health.

Further studies into the health effects of these ship polluted air masses will also be necessary to fully understand their specific health impacts. The increased toxicity of these transition metal laden particles could present unique threats to human health and must be further studied to mitigate the adverse effects they cause.

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Glossary

AIS	Automated Identification System
Ag	silver
Ag ⁺	silver ion
Ag ₂ SO ₄	silver sulfate
AgNO ₃	silver nitrate
AgCl	silver chloride
Ag ₂ O	silver oxide
ATOFMS	Aerosol Time-of-Flight Mass Spectrometry
Cl ⁻¹	Chlorine ion
C18	commercial (Alltech) resin cartridge for organics removal
CCN	Cloud Condensation Nuclei
CO ₂	Carbon dioxide
°C	degrees Celsius
δ ^x O	$\delta^x\text{O} = \left[\frac{\left(\frac{x\text{O}}{16\text{O}} \right)_{\text{sample}}}{\left(\frac{x\text{O}}{16\text{O}} \right)_{\text{standard}}} - 1 \right] \times 1000$ <p>where x={17,18} for ¹⁷O and ¹⁸O</p>
Δ ¹⁷ O	Δ ¹⁷ O ≅ δ ¹⁷ O - 0.52δ ¹⁸ O
EC	Elemental Carbon
Fe	Iron
Fe ³⁺	Iron ion

f_B	fraction of aerosol nss-sulfate formed with oxygen isotopic composition matching “background” oxidation pathways
f_P	fraction of aerosol nss-sulfate with mass-dependent ($\Delta^{17}\text{O} = 0\%$) isotopic composition
f_{O_3}	fraction of aerosol nss-sulfate formed from oxidation of SO_2 with ozone in aqueous phase.
H^+	Hydrogen ion
H_2O	Water
H_2O_2	Hydrogen Peroxide
H_2SO_4	Sulfuric acid
HNO_3	Nitric acid
IC	Ion Chromatography
IRMS	Isotope Ratio Mass Spectrometry
μg	microgram (10^{-6} grams)
μmole	micromole (10^{-6} moles)
μm	micrometer (10^{-6} meters)
Mn^{2+}	Manganese ion
mL	milliliter (10^{-3} liters)
m^3	cubic meter
NO	Nitric oxide
Ni	Nickel
NOAA	National Oceanic and Atmospheric Administration
NO_2	Nitrogen Dioxide
NO_x	Nitrogen oxide

NO_3^{-1}	Nitrate ion
nss-SO ₄	non-sea salt sulfate
¹⁶ O	isotope of oxygen with 8 protons and 8 neutrons
¹⁷ O	isotope of oxygen with 8 protons and 9 neutrons
¹⁸ O	isotope of oxygen with 8 protons and 10 neutrons
OH	Hydroxyl radical
OC	Organic Carbon
O ₂	molecular oxygen
O ₃	Ozone
‰	parts per thousand (per mil)
Pb	Lead
PVP	Polyvinylpyrrolidone
SO ₂	Sulfur Dioxide
SO _x	Sulfur oxide
SO ₄ ⁻²	Sulfate ion
V	Vanadium
VHF	Very High Frequency
Zn	Zinc