



Partnership for Air Transportation  
Noise and Emissions Reduction  
An FAA/NASA/Transport Canada-  
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# Use of Isotopic Measurement and Analysis Approach to Uniquely Relate Aircraft Emissions to Changes in Ambient Air Quality

**PARTNER Project 33 Final Report**

prepared by  
**Mark H. Thiemens**

June 2011

# **The Impact of Climate Policy on US Aviation**

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PARTNER-COE-2011-003

June 2011

This work is funded by the US Federal Aviation Administration Office of Environment and Energy under FAA Award Number: 07-C-NE-UMR, Amendment No. 008.

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**PARTNER Final Report**

**Project 33**  
**Isotopic Analysis of Airport Air Quality**

USE OF ISOTOPIC MEASUREMENT AND ANALYSIS APPROACH TO  
UNIQUELY RELATE AIRCRAFT EMISSIONS TO CHANGES IN  
AMBIENT AIR QUALITY

UNIVERSITY OF CALIFORNIA, SAN DIEGO

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- FAA Award Number 07-C-NE-UMR, Amendment No. 008
- Period of Performance July 1, 2009 through December 31, 2010

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## Executive Summary

Airports around the nation are considering expansion plans in order to meet increasing demand for aviation transport. There are increasing concerns, as well, about how and to what extent air pollutant emissions from airports contribute to local and regional air quality degradation and hence to negative impacts on human health and welfare. However, it is difficult to quantify the amount, transport, and secondary conversion processes of aircraft emissions, which usually comprise the bulk of airport-attributable emissions. This is due to four reasons:

1. Difficulty of determining the actual amounts of emissions from aircraft and characterizing the chemical speciation.
2. Difficulty of determining, at the particle level, the secondary chemical transformations that occur.
3. Difficulty in detection of the species and identification of the aircraft contribution in a region where air quality degradation is a consequence of emissions from multiple sources, both natural and anthropogenic.

For the project described in this report, the technique of stable isotopic measurements was utilized in an attempt to develop and assess the impact of aircraft emissions in a region. The theme was, “*Are the aircraft emissions recognizable at the isotopic level in a region and are they separable from other sulfates?*” To explore this theme, the project team performed three measurement campaigns at Los Angeles International Airport (LAX) to sample aerosol sulfate and characterize the isotopic composition of oxygen atoms in the sulfate particles. It was hoped that aerosol sulfate from jet engines would be shown to have a distinct isotopic character in comparison to sulfate from other sources such as diesel engines, aiding attribution of degraded air quality to jet aircraft sources.

The premise that the oxygen isotopic composition of aerosol sulfate could be used to define jet contributions to a region was ultimately not conclusively supported by the study presented in this report. It appears that at low humidity an isotopic anomaly is preferentially created, as observed in the first Aviation Alternative Fuels Experiment (AAFEX), thus identifying a jet aircraft engine. At the humidity of LAX however, the presence of excess water on the aerosol surfaces dilutes the anomaly. Hence, for assessment of the potential of the technique to be broadly applied, it is likely that only low-humidity areas would be capable of providing the signature, based upon the experiments conducted to-date. Furthermore, unexpectedly low sulfate concentrations were observed in the study, suggesting that jet engine exhaust SO<sub>2</sub> oxidation occurs further away from LAX and optimal sampling sites in future studies would need to be done at further distances. However, it is unlikely that increased distance between the source sulfur and the sampling monitors at LAX will show much isotopic anomaly in high humidity conditions (60+ %).

Conceptually, the potential remains for isotopic analysis to quantitatively address the contributions from aircraft jet engines to degraded air quality near airports. If future research is performed on this technique, an airport in a dry environment must be selected as an initial candidate so that the methods initially explored in this report can be retried. Monitors may need to be located further away from the airport environment so that engine SO<sub>2</sub> has more opportunity to become sulfate.

# Introduction

## *Intention of the Project*

Airports around the nation are considering expansion plans in order to meet increasing demand for aviation transport. On the other hand, there are increasing concerns about how and to what extent air pollutant emissions from airports contribute to local and regional air quality degradation and hence to overall potential health impacts. Additionally, airport operators and communities around the airport settings have consistently asked whether there are unique signatures associated with aircraft emissions that can distinctly relate them to incremental changes in ambient air quality. It is important to note that aircraft emissions within the landing-takeoff cycle account for most of the airport emissions.

Particulate matter (PM) has many negative impacts. PM impacts climate on local to global scales in both direct and indirect ways. Local and regional perturbations to climate and radiative forcing from PM perturb the hydrologic cycle and consequently the associated biodiversity and agriculture. Damage to buildings, roads and other structures are likewise well-known. Air quality and visibility are also characteristically denigrated due to the presence of PM. It is well established that particulate matter (PM) negatively contributes to human health and particularly to cardiovascular diseases and premature mortalities, with as many as 60,000 mortalities per year in the United States attributed to inhalation of PM from maritime shipping sources alone (Corbett et al., 2007). In the IPCC 2007 report (IPCC, 2007) and the IPCC separately evaluated special Report on Aviation and the Global Atmosphere (IPCC, 1999), aircraft were indicated to contribute both locally and globally to PM concentrations, especially concentrations of sulfate and nitrate.

Aircraft engines directly emit black carbon particles, referred to as primary PM. Aircraft  $\text{SO}_x$  and  $\text{NO}_x$  emissions are precursors to secondary (i.e. not directly emitted but instead arising from chemical reactions) pollutants such as ozone and secondary nitrate and sulfate PM. All aircraft engines produce PM precursor emissions and these emissions sensitively vary as a function of fuel type, operating condition, and ambient conditions. In particular, aircraft fuel is typically sulfur rich and consequently the formation of secondary sulfate PM particles of a range of particulate diameters readily occurs due to aircraft  $\text{SO}_x$  emissions. Thus PM is known to be emitted and secondarily produced by aircraft engines, but presently their contributions to degraded ambient air quality are inadequately characterized. Particular difficulty in assessing the true extent of a regional airport's impact upon a community and geographic locale resides in the difficulty in quantifying the amount, transport, and secondary conversion process of the emissions. At the most fundamental level, the problem in realizing these goals is a result of:

1. Difficulty of determining the actual amount of emission from the aircraft and characterizing the chemical speciation.
2. Difficulty of determining, at the particle level, the secondary chemical transformations that occur. This is an issue that challenges the state of art of chemical analysis in that the actual chemical speciation processes occur at the level of a single particle's surface. Analytically, this is a formidable process because of the number of molecules involved and the stringent analytical requirements.
3. Difficulty in detection of the species and identification of the aircraft contribution in a region where air quality degradation is a consequence of emissions from multiple sources, both natural and anthropogenic.

Separation from non-aircraft airport emission sources, such as auxiliary power units (APUs), ground support equipment (GSE), and mechanical sources is also particularly challenging. A major issue in the measurement approach to the three issues above is that aircraft emissions are not identifiable strictly by the measurement of pollutant concentration because of other non-aircraft sources, especially for sulfate and nitrate emissions. At present, quantification is imprecise and the measurement of only concentration does not permit strict assignment to individual sources. Measured aerosol species (both primary and secondary) in any given region of the country are likely to have two and in some cases four non-aircraft local sources. These molecular species are also highly reactive and chemically transform on surfaces, a process nearly impossible to identify by concentration measurements and extraordinarily difficult to model because of the imprecise state of art of the knowledge of physical chemical surface reactions; an issue not with modeling capability, but in fundamental chemistry.

On the modeling front, the Federal Aviation Administration's (FAA's) Emissions and Dispersion Modeling System (EDMS) has been used to develop aircraft and airport level emissions inventories. These emissions are then used in air quality simulations. Emissions from individual source types can be changed as an input to simulations in order to examine the influence of emissions on ambient air quality and attempt apportionment of degraded air quality to aircraft sources. However, there are significant inherent uncertainties in using both measurement and modeling approaches arising due to the interaction of air pollutants with the background air, non-linearity in the air pollutant interaction, interference from other source emissions types, meteorological variability, etc.

Given the totality of the concerns above, in order to achieve a goal of detailing the impact and character of aircraft emission at a specific airport and to expand and detail the consequence for a community, what is needed and presently missing is a new and unique measurement of a relevant, major aircraft emission species parameter that can be forensically utilized to specifically identify aircraft emissions, separate them from other sources, and to resolve their impact, magnitude and regional distribution. For the project described in this report, the new technique of stable isotopic measurements was utilized in an attempt to develop and assess the impact of aircraft emissions in a region. This method was intended to lead to better predictions of how increased air traffic may alter the environment of a region.

There are stable isotopes associated with each element present in the earth system. Isotopes of a specific element have the same atomic number (i.e. number of protons or electrons) but different atomic mass (numbers of protons + neutrons). For example, there are three stable isotopes of oxygen:  $^{16}\text{O}$ ,  $^{17}\text{O}$ , and  $^{18}\text{O}$ .  $^{16}\text{O}$  is the most abundant form of isotopic oxygen atom. Enrichment of these isotopes in the form of an element or a compound (e.g. particulate matter, ozone, etc.) depends upon the nature of their sources and also the chemical and physical processes to which these elements or compounds have been exposed. The measurement of these isotope ratios at state-of-the-art precision and accuracy, coupled with fundamental understanding of the physics and chemistry of their alteration processes, can provide a new forensic tool in delineating sources and transformational processes. The isotopic approach, especially using new measurement and physical chemical principles, is a state of the science advancement which has been extensively and successfully used to study atmospheric evolution of air pollutants and for budget (source and sink as well as associated variability in space and time) studies of various air pollutants present in the atmosphere. It has been applied to develop fingerprints of air pollutants associated with various mobile source emissions. For example, in a paper published by the

UCSD group in the Proceedings of the National Academy of Sciences researchers identified the regional impact of ships in the San Diego region, even with other sources in the region (Dominguez et al., 2008).

For the first time, the isotopic measurement approach was used during the Aviation Alternative Fuels Emissions Experiment (AAFEX) campaign in January 2009 to measure the isotopic fractionation in secondary sulfate and nitrate aerosols formed due to gaseous precursors released during combustion in an aircraft jet engine. This aerosol isotopic fractionation was measured as a function of distance and fuel type. The isotopic enrichments in aircraft-related particulate matter were found to be highly distinctive and unlike any measured at any location. This unique isotopic “fingerprint” in aircraft-related PM is caused by a combination of chemical processes during combustion under high temperatures and pressures. The uniqueness of this fingerprint in aircraft-related PM suggested that the isotopic analysis approach could be utilized to link aircraft emissions to airport community-scale variability in air quality. The high specificity of the new technique would be a significant advance in the ability to examine and determine contributions of a specific airport to a region. Using sampling during fall 2009, winter 2009, and spring 2010 at Los Angeles International Airport (LAX), the project described in this report evaluated and assessed the usage of the isotopic technique for fingerprinting aircraft jet engine activity in ambient sulfate in the region around an airport. The ability to simplify the collection procedures and the measurement throughput was also considered with the ultimate goal being the development of a technique that can be used at any given airport to identify aircraft emissions and their magnitude and spatial/temporal variation.

## ***Objectives***

The objectives of the project described in this report were to:

1. Use a coordinated aerosol sulfate sampling in the vicinity of LAX to measure the sulfate oxygen isotope ratio measurements. These measurements will be used to directly determine for the first time, the aircraft sulfate emissions in this region.
2. From the sampling network, determine the regional dispersion of the aircraft emissions and use the isotope ratios to distinguish from other sulfate sources that are overlain with the aircraft source.
3. Evaluate the seasonal character of the emissions.
4. Investigate and develop techniques for shorter-duration sampling and analysis for future, more extensive campaigns.

From the above objectives the impact of aircraft emissions may for the first time be directly determined. This would provide evidence of the efficacy of the isotopic technique and warrant further development and expansion of the technique to provide the best measurements to be used for future informed decision-making. The outcome of the research would be directly relevant to FAA and other stakeholders, such as community and regional planners. The analyses would aid in high-precision determinations of community exposure attributable to aircraft and other airport sources, a critical step for interpreting local community concerns and for designing future campaigns. The outcome would also facilitate and improve the ability of the FAA to make informed regional management decisions from the higher level of impact assessment. The work would also have direct applications in addressing regional health issues and their linkages to aircraft and in addressing major airport impacts.



### ***The AAFEX Campaign and Preliminary Technique Demonstration***

In the AAFEX campaign at Palmdale, CA, the UCSD laboratory employed the isotope technique to address the following question: ***Is there an aircraft emission fingerprint that may be unambiguously and quantitatively associated with their combustion process?***

Ideally this fingerprint would exist upon a major pollutant species so that the real impact may be determined more directly than by a minor species. Given that one aviation-related pollutant species of major interest is sulfate, the isotopic technique utilized entails oxygen isotope measurements of the sulfate species itself which renders the applicability as ideal. This is particularly powerful since concentration measurements alone are not distinctive or necessarily separable from other local or long range transported sources. One distinct advantage of the isotope technique is that it operates at the sub-molecular level, giving the lowest error and highest ability to distinguish various emissions sources. The technique also provides further insight into and resolution of secondary surface alteration processes.

In AAFEX it was directly observed that the sulfate produced due to jet aircraft engine activity is completely isotopically distinct from all other sulfate sources, both natural and anthropogenic. Measurements are shown in Figure 1. Based upon these measurements, the UCSD team was able to understand the physical chemical processes that are associated with the aircraft jet engine combustion process; this understanding is a critical component of development of the isotopic technique. These observations fully substantiate the original contention that stable isotope ratios of aircraft sulfate are an ideal marker that may quantitatively measure regional aircraft emissions and determine their distribution and variability, as a result of the highly unique nature of the aircraft jet engine combustion process.

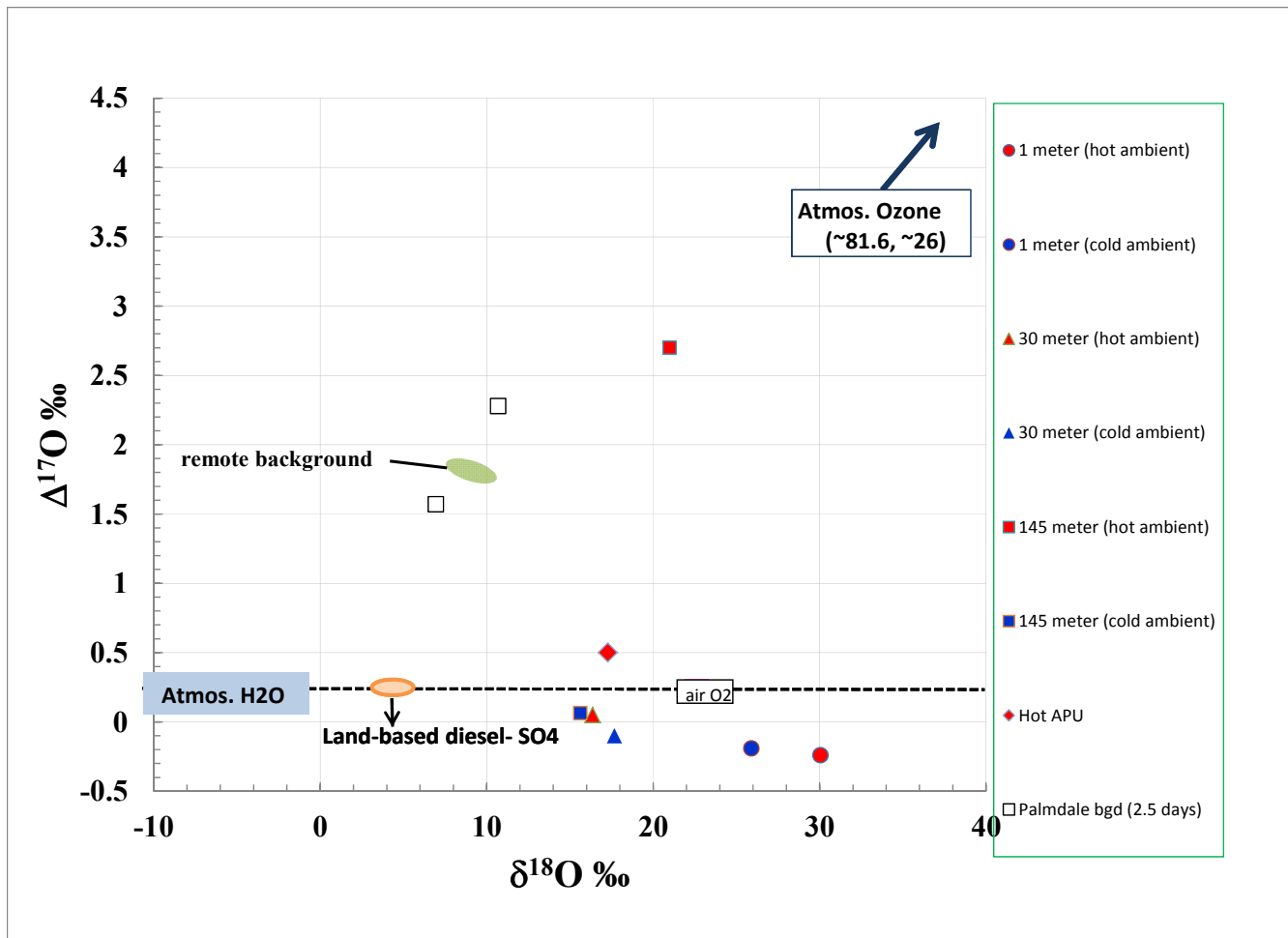


Figure 1: Isotope ratios measured in aircraft jet engine exhaust plume sulfate, at several distances from the nozzle and at hot and cold ambient temperatures. Values for Palmdale and marine backgrounds, atmospheric O<sub>3</sub>, H<sub>2</sub>O, and diesel SO<sub>4</sub> are also displayed.

# Project Overview

## *Sampling and analytical approach*

For this study the theme was, “*Are the aircraft emissions recognizable at the isotopic level in a region and are they separable from other sulfates?*” To explore this theme, sampling equipment was installed at four locations at LAX. The first site #1 was as close to jet emissions as feasible: at the east end of the south runway 25R at LAX, just behind the airfield’s southeast jet blast protection screen. The other sites were: #2 at the northwest edge of LAX close to incoming marine air during west wind conditions, #3 which was intended to have the direct jet emission about 1 km from the airport, and #4 just northeast of LAX terminal. These sites are shown in Figure 2. The distance of the sampling locations was intended to allow, based upon preliminary plume studies, evaluation and modeling of the data to determine regional impact; it was thought that if the sites were too remote from the airport, secondary meteorological and air mass admixture would confuse the measurements. The locations ultimately selected appeared at the time to be the best combination of source strength, transport, and secondary chemical analysis to address the proposed research questions in this project.

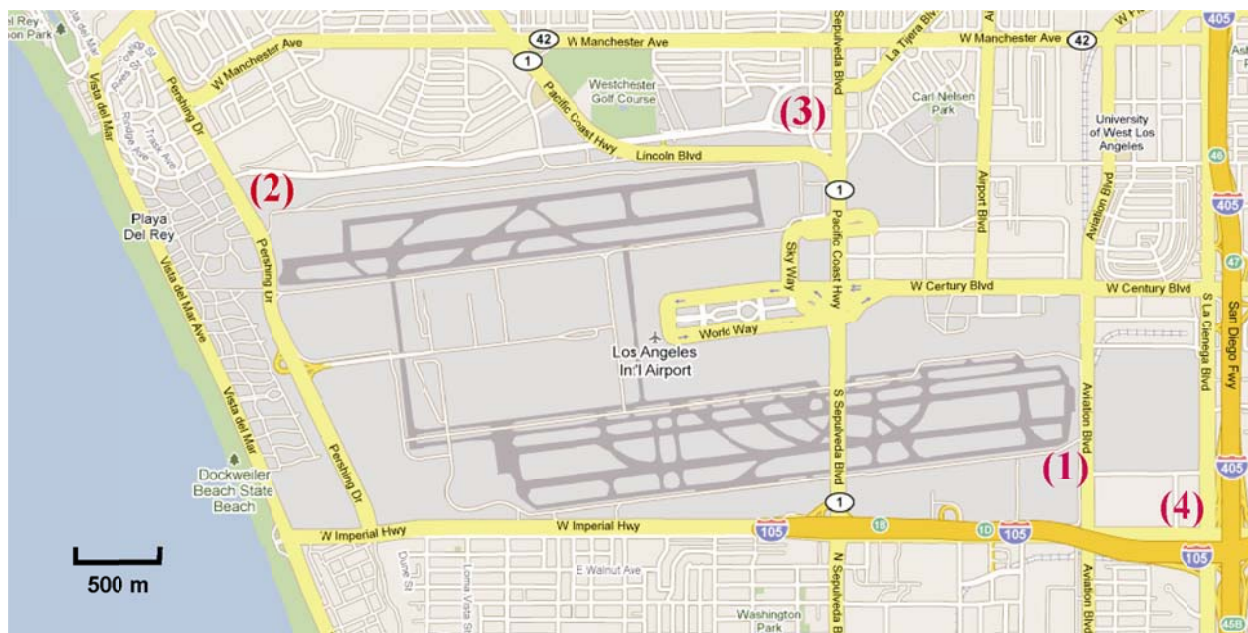


Figure 2: Map of the sampling sites used for this experiment.

This project executed three campaigns each of two weeks duration, with two aerosol samples per week, to evaluate at a regional level the degree of external isotopic identification of sulfate from jet aircraft. These sample periods were chosen to give more than ample sample and to damp out short time variability (which could be investigated in follow-on work to this project). Hi-volume cascade impactors (Hi Q Environmental, with air flow rates of  $40 \text{ feet}^3 \text{ min}^{-1}$ ) were used to collect aerosols on glass fiber filters, as was done during AAFEX. The four measurement sites gathered aerosol samples simultaneously, and each sample was collected over a period of two to three days. Once returned to UCSD, the samples were extracted, quantified, and analyzed for the sulfate, anion concentrations and the multi-oxygen isotopic composition of the sulfate. As was done for the AAFEX campaign, the isotope analyses were made on the smallest sulfate aerosol size fraction that was collected: less than 0.5

microns. As a further check on exogenous sources, a set of samples for radiogenic  $^{35}\text{S}$  was also measured, as  $^{35}\text{S}$  is an indicator of long-range transport to an area and an approximate chronometer of sulfate. It was felt that this general procedure would significantly address the objectives of this project.

During the course of the year's 3-campaign sampling effort, the project also intended to use sample aliquot to develop an experimental protocol appropriate for a much more extensive campaign where short-term time resolution would be used and consequently more samples would be analyzed. Another limit in such efforts is sample size and, based upon the UCSD team's measurement programs for polar ice, it was believed that in some regions an hour's time sampling is possible. It was proposed to test the time duration limits during the experiment described in this report.

Based upon the results obtained from AAFEX by the UCSD team, it is known that there is an isotopic evolution of the plume with space and time. When the UCSD team analyzed the isotopic characteristics of ship plumes (Dominguez et al., 2007), the team developed a time-evolutionary kinetic model for the chemistry and isotopes associated with nitrate. For the project described in this report, it was proposed to further develop this model to incorporate sulfate, which would have allowed a sophisticated approach in the actual interpretation of the acquired results. The results of the work were intended to be published in a suitable high profile journal, which is consistent with the publication record of the laboratory for the past three decades.

## Results

As proposed, sample collections for three seasonal campaigns Fall 2009, Winter 2010, and Spring 2010 were completed, with each campaign lasting two weeks and having filters switched out twice a week. Sulfate oxygen isotopes were measured for all campaigns for the smallest aerosol size fraction collected (less than 0.5 microns), as was done for the AAFEX campaign. The oxygen isotopic results for LAX are shown in Figure 3. The AAFEX results for JP8, a conventional jet fuel, are included in the figure for comparison.

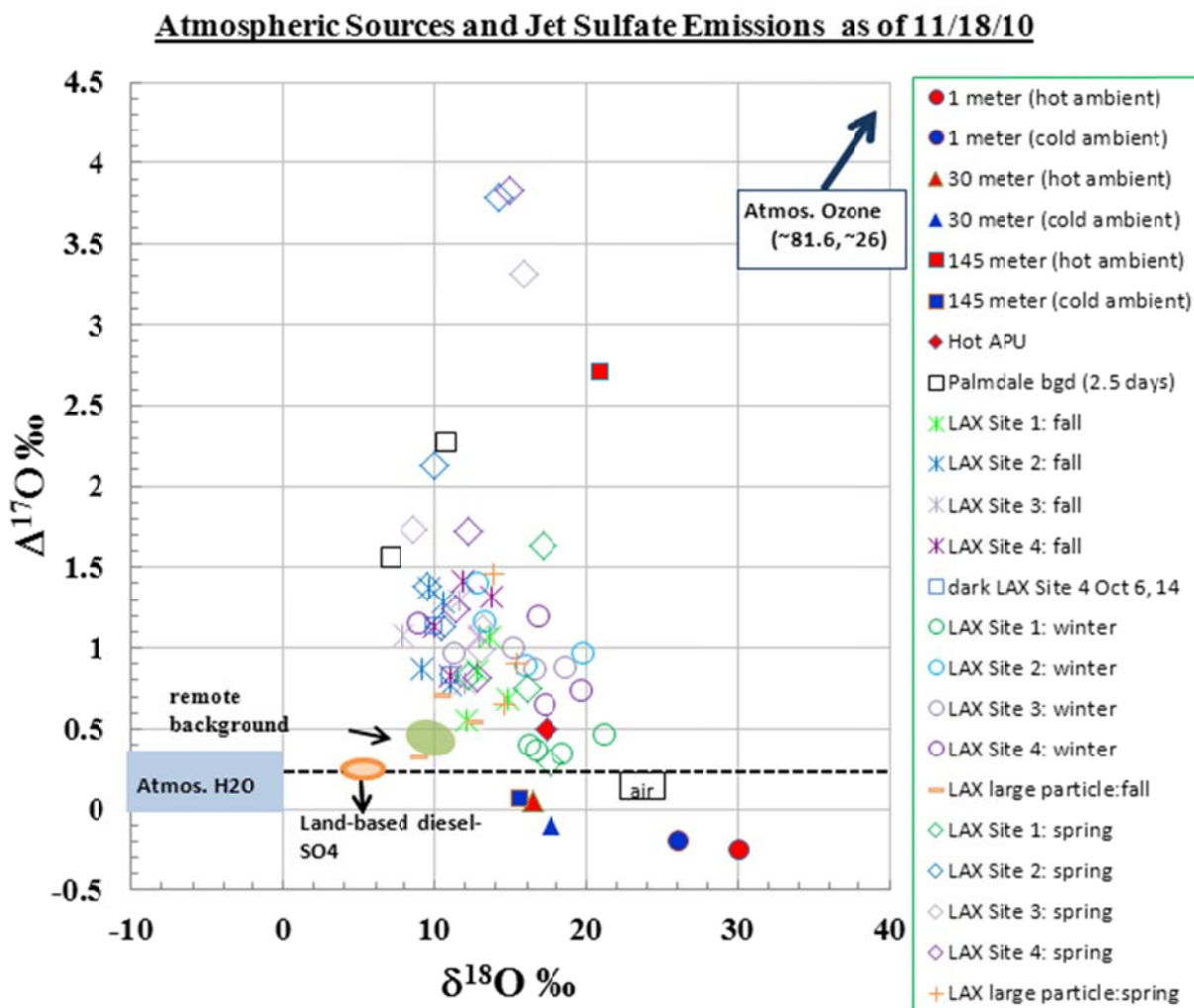


Figure 3: Results of the measurement campaigns.

The 25R runway site (site #1) for a given sampling period typically has greater enrichment in  $\Delta^{18}\text{O}$  and less enriched  $\Delta$  in the sulfate oxygen than the other three sites. This is consistent with initial findings in the AAFEX campaign at Palmdale, 2009, that jet aerosol sulfate emissions closest to the engine source were the most enriched in  $\Delta^{18}\text{O}$ , and most mass-dependent (near zero) in  $\Delta$  as shown in Figure 1, but it does not unambiguously identify the jet aircraft because the true intention of the isotopic technique is to distinguish aircraft sources via measurements further away from the runway (where plume evolution

would have already occurred). Of the three seasons, Spring 2010 shows the largest  $\Delta^{17}\text{O}$  values measured to date at LAX, the maximum being 3.8 per mil at site #4 from the period ending on March 12<sup>th</sup> 2010, which surpasses the conventional fuel (JP8) maximum of 2.7 per mil at AAFEX. The AAFEX campaign had the largest  $\Delta^{17}\text{O}$  jet engine sulfate yet measured at UCSD of 5.8 per mil in the Fischer Tropsch #1 fuel (at 145 meters approx. 55-70 degrees F ambient temp; see Figure 1). A similar  $\Delta^{17}\text{O}$  or greater was anticipated at LAX, but not realized in these sampling campaigns. The results obtained are essentially the same as measured at other coastal sites in California, and minimal isotopic evidence of the jet aircraft at LAX was observed, averaging 0.6 per mil less  $\Delta^{17}\text{O}$  (more mass-dependent) at site #1 (runway 25R) than at the other three sites.

Humidity has been examined in search of an explanation for the LAX  $\Delta^{17}\text{O}$  isotope variations in Spring 2010, the season with the largest range of sulfate oxygen isotopes. The relative average humidity at LAX was calculated from hourly measurements available on the weather website wunderground.com and then averaged for a given sampling period. For Spring 2010,  $\Delta^{17}\text{O}$  vs. average humidity has been plotted in Figure 4. This plot of Spring 2010 data shows a trend of **highest  $\Delta^{17}\text{O}$  with lowest average relative humidity**.

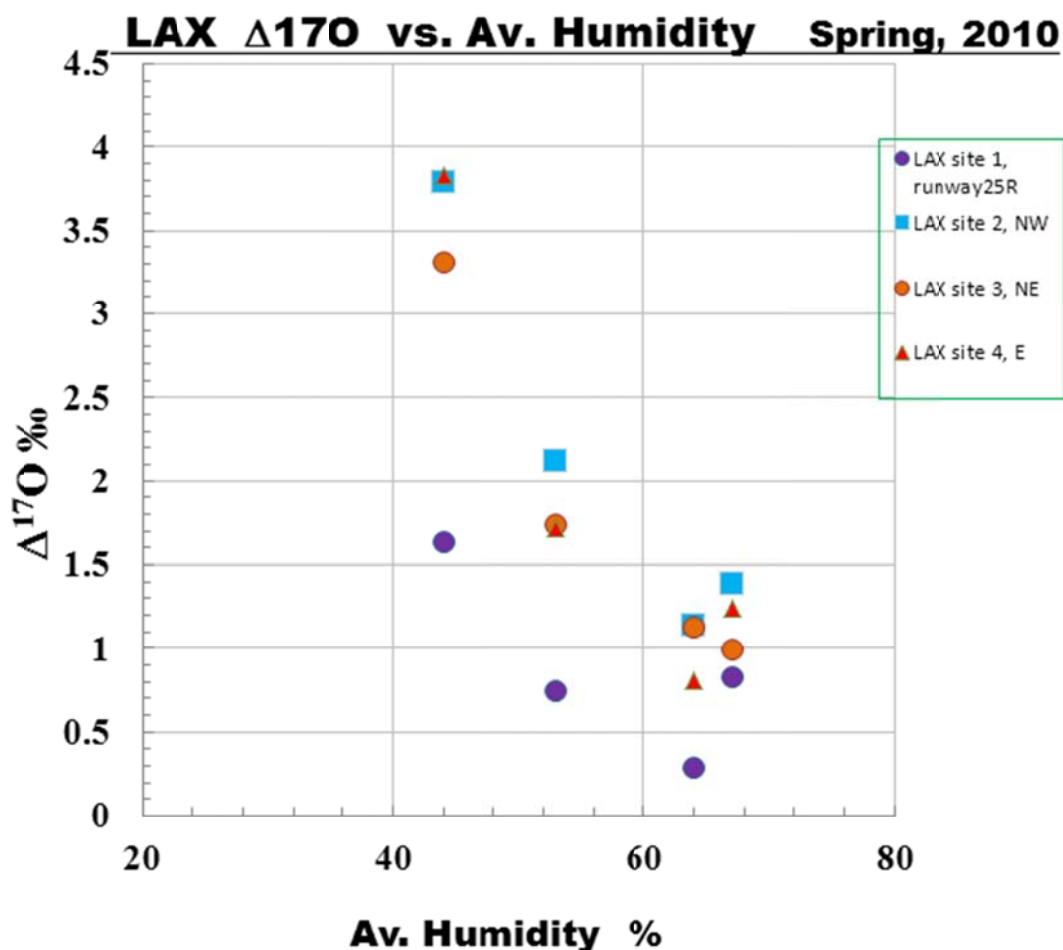


Figure 4: Average humidity at LAX during the Spring 2010 measurement campaign.

Each Spring 2010 sampling period was a half-week long, and the humidity can vary greatly at LAX. For example, the period ending March 12, 2010 (which has the highest measured  $\Delta^{17}\text{O}$  of 3.8 per mil measured at LAX site #4; see sites and map in Figure 1) has a minimum humidity of 28% and a maximum of 71%, for an hourly averaged humidity of 44%. For each of the four time periods in Spring 2010, the LAX site #1 always had the **smallest**  $\Delta^{17}\text{O}$  of the 4 sites, as expected from Palmdale results for a site closest to jet engine exhaust and resulting sulfate aerosols. Initial findings in the AAFEX campaign showed that jet aerosol sulfate emissions closest to the jet engine were the most mass-dependent (near zero) in  $\Delta^{17}\text{O}$  as well as the most enriched in  $\Delta^{18}\text{O}$ . The data may be explained by recent observations for chemistry on aerosol surfaces, published in the Proceedings of the National Academy of Sciences (Shaheen et al., 2010). In that work it was shown that for in situ carbonate formation, thin water films on surfaces along with ozone, catalyze formation of isotopically anomalous particles. In the work described in this report, it is believed that the results are consistent with everything that was analyzed. First, the AAFEX campaign, where the largest  $\Delta^{17}\text{O}$  effect was observed, is in an area of low humidity. At low humidity the effect of ozone is observable, and this is also consistent with the observation of a morning and night effect, where the low humidity during day provides a larger effect. At higher humidity the isotopic signature is erased, or diluted. At LAX the largest isotopic effect is observed at low humidity; however, given the coastal location these days are very limited.

After finding the trend from the Spring 2010 data of increased  $\Delta^{17}\text{O}$  isotopes with lower average humidity, the other two seasons Fall 2009 and Winter 2010 were then compared to the Spring 2010 results. Both Fall 2009 and Winter 2010 have a smaller range in  $\Delta^{17}\text{O}$  than found in Spring 2010. When the Fall 2009 data (diamonds in Figure 4, with higher average humidity and smaller  $\Delta^{17}\text{O}$ ) is added to Spring 2010 (squares + triangle) the trend of higher  $\Delta^{17}\text{O}$  as average humidity drops is still observable; see Figure 5. However, upon adding the Winter 2010 data as shown in the snowflakes shapes in Figure 6, the trend breaks down, possibly due to less photochemistry with the shorter daylight in winter and more cloud cover.

### **LAX Sulfate: $\Delta^{17}\text{O}$ vs. Av. Humidity (Fall + Spring 2010)**

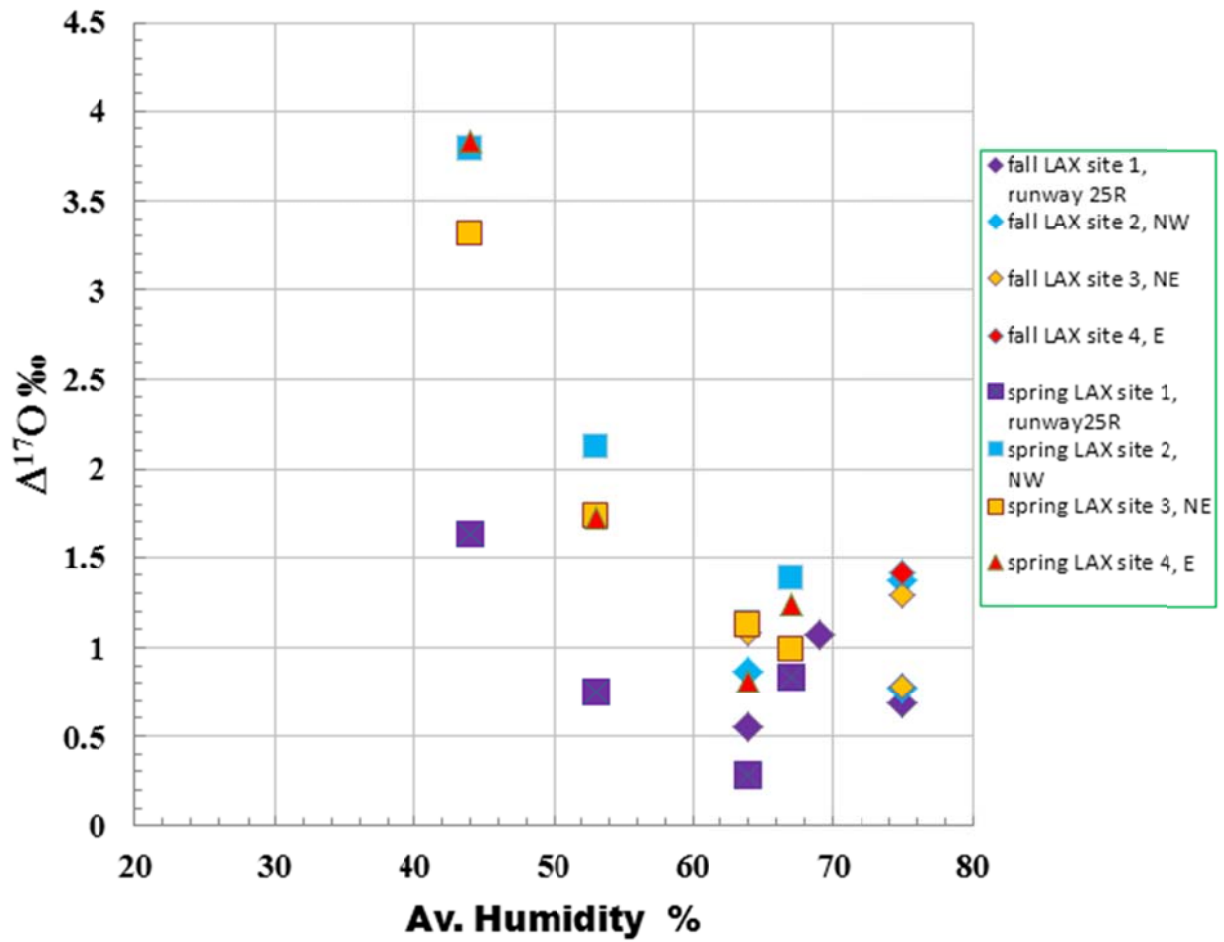


Figure 5: Humidity measurements for fall and spring campaigns.



**LAX Sulfate:  $\Delta^{17}\text{O}$  vs. Av. Humidity (Fall, Winter, Spring 2010)**

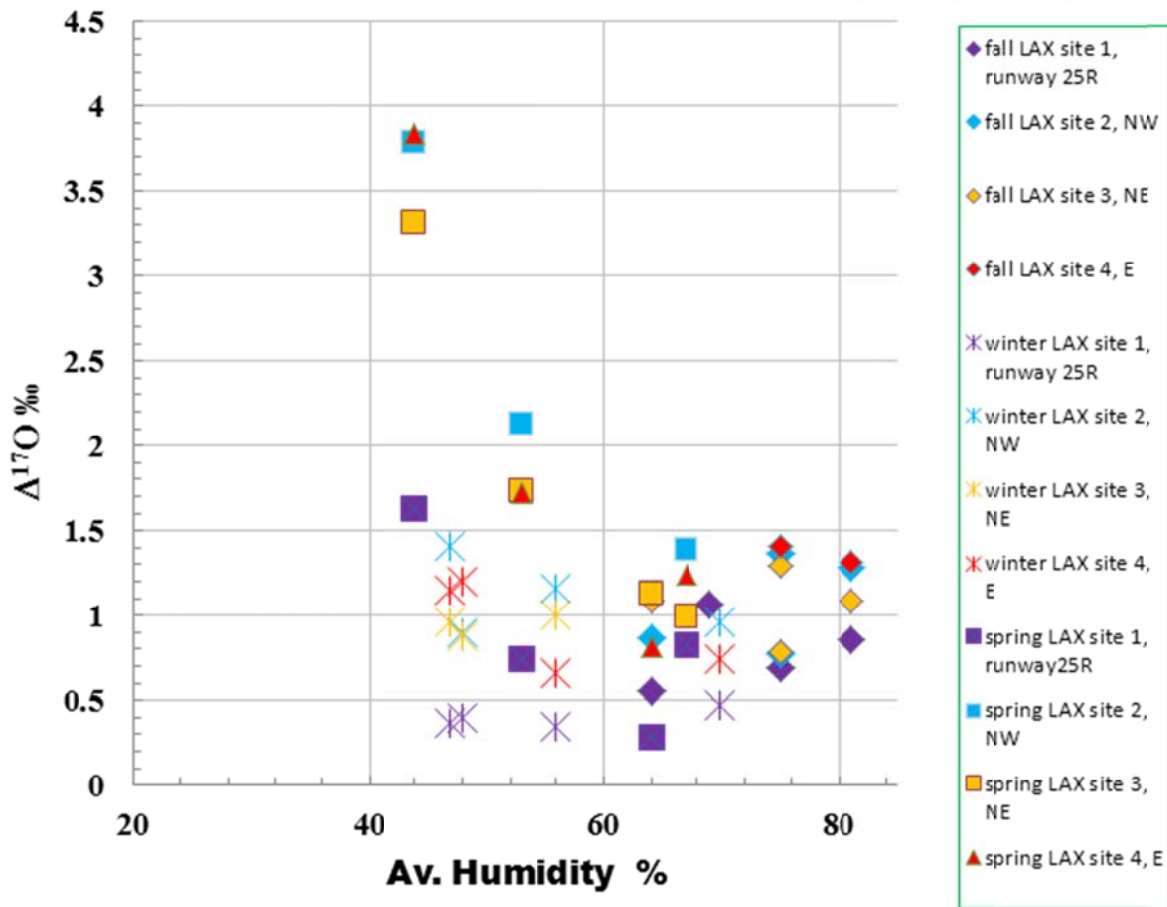


Figure 6: Humidity measurements for the fall, winter, and spring campaigns.

For the campaigns, emphasis was on isotopic analysis for the fine size fraction of aerosols less than one micron that is typically emitted from a jet engine. However, due to the smaller-than-expected isotopic anomaly at LAX and the surprisingly lower concentrations of sulfate than anticipated for a location of heavy jet traffic, the UCSD team theorized the possibility that there might be interesting, unexpected isotopic results in larger-size aerosols. Thus the team examined a subset of large-particle sulfate. The hi-vol cascade impactors allow for 5 different size fractions collecting at the same time on 5 separate filters as follows:

- Filter 1: largest particles, 7.2 down to 3.0 microns
- 2: 3.0 down to 1.5 microns
- 3: 1.5 down to 0.95 microns
- 4: 0.95 to 0.5 microns
- 5: below 0.5 microns (typically half of this larger filter is used)

All isotope sulfate data from LAX has size fractions components of 0.5 microns or less, except for the larger particles plotted as tan dashes in Figure 2. These tan dashes represent large particle samples from the Fall 2009 campaign, collected on October 23<sup>rd</sup>, 2009. Two of these samples (down to 3.0 microns)

measure close to marine sulfate  $\Delta^{18}\text{O} = 9$  to 10 per mil, with no significant jet engine sulfate component observable. The third sample (down to 0.95 microns) had  $\Delta^{18}\text{O} = 12.7$  per mil. Fall 2009 isotopes had a  $\Delta^{17}\text{O}$  of 1.4 per mil or less, compared to 3.8 per mil (0.5 microns) maximum for LAX in Spring 2010. Four larger particle measurements analyzed from Spring 2010 (collected on the date March 12<sup>th</sup>, 2010), had small  $\Delta^{17}\text{O}$  values ranging from 0.66 to 1.46 per mil; these are shown as tan crosses in the figure. The larger particles have lower  $\Delta^{17}\text{O}$  than the smaller particles, and thus do not reflect expected jet contributions for aircraft at LAX, but rather reflect normal background sulfate.

Data for LAX sample collections is tabulated in Appendix A. The size fractions are included in the sample names by including -1 through -5 to indicate the filter size. All anions (sulfate, chlorine, and nitrate) for the above large-particle size fractions 1 through 4 were run for October 23, 2009 (Fall campaign) and (Spring 2010 campaign: sampling date with largest  $\Delta^{17}\text{O}$ ).

As originally proposed, the project also measured a set of samples for radiogenic  $^{35}\text{S}$ , as it is indicator of long range transport to an area and an approximate chronometer of sulfate and aerosol age. The radioactivity is a marker of exogenous sulfate as it may only be produced in the stratosphere by cosmic ray bombardment of atmospheric argon; the same as for  $^{14}\text{C}$ .  $^{35}\text{S}$  measurements were made on the most recent sample set obtained, which was collected March 16, 2010 from LAX and shown in Table 1 below. A sample from the Scripps Institute of Oceanography in San Diego is also shown for comparison. The UCSD team finished and published a new protocol for the measurement of this radioactivity that for the first time has allowed for the analysis of samples of the size obtained here (Brothers et al., 2010).

**Table 1:  $^{35}\text{S}$  measurements made during this project, with a San Diego measurement shown for comparison.**

Sample Location	Date	$^{35}\text{S}$ Atoms/m <sup>3</sup>	$^{35}\text{S}$ Atoms/m <sup>3</sup> Error
Lax site #1 (runway)	3/16/2010	204.805	5.40
Lax site #2 (marine)	3/16/2010	237.630	5.28
Lax site #3 (northeast parking lot C)	3/16/2010	257.308	5.41
Lax site #4 (east parking lot C)	3/16/2010	302.725	5.88
San Diego: Scripps Institute of Oceanography	3/05/2010	450.932	7.53

The analysis of the LAX samples exhibits two observable factors:

1. The radioactivity is higher than expected. The team has routinely analyzed  $^{35}\text{S}$  radioactivity from a yearly collection at the Scripps Institution of Oceanography in San Diego, a site where the anticipated  $^{35}\text{S}$  activity should be approximately the same as at LAX. The lower and upper atmospheric dynamics are not significantly different, thus there is no reason to expect *a priori* the observed higher activities at LAX.
2. The activity varies significantly with radius of the particles. The observed variation far exceeds the analysis error (as published recently in the Proceedings of the National Academy of Sciences). Thus the variation is real and the only explanation is that the difference represents re-entrainment of sulfate aerosols that have been deposited on the runway/tarmac. Given that the half-life of  $^{35}\text{S}$  is 87.3 days, live aerosols deposited by dry deposition may be re-entrained and

collected and thus there would be short scale disturbances associated with daily, if not hourly jet traffic patterns, presumably during taxi procedures. As such then, the information obtained from the  $^{35}\text{S}$  measurements demonstrates that on the runway surfaces, re-entrainment of aerosol sulfate and other species such as nitrate and hydrocarbons may be significant, and built-up dry deposition on runways occurs as established by the radioactivity measurements.

## Conclusion

The premise that the oxygen isotopic composition of aerosol sulfate could be used to define jet contributions to a region is not conclusively supported by the present investigation. Based upon the most recent work by the UCSD group it appears that humidity is a major factor. At low humidity, the isotopic anomaly is preferentially created, as observed in the Palmdale experiments. At the humidity of LAX however, it is apparent that the presence of excess water on the aerosol surfaces dilutes the ozone carrier of the anomaly. Hence, for assessment of the potential of the technique to be broadly applied, it is likely that only low-humidity areas would be capable of providing the signature, based upon the experiments conducted to-date. Furthermore, the low sulfate concentrations observed in the study suggest that jet engine exhaust SO<sub>2</sub> oxidation occurs further away from LAX and optimal sampling sites in future studies would need to be done at further distances. However, it is unlikely that increased distance between the source sulfur and the sampling monitors at LAX will show much change in  $\Delta^{17}\text{O}$  in high humidity conditions (60+ %). The low-humidity nano-surface effect that led to the isotopic effect downwind during the AAFEX campaign in Palmdale has a low probability of occurring in a regime such as LAX, and the likeliness of occurrence at other sites is uncertain. In retrospect, an optimal site would have been a dry environment, and it is unlikely that modifying the LAX sampler configuration for the average weather conditions at LAX would have altered the results presented and discussed in this report.

Conceptually, the potential remains for isotopic analysis to quantitatively address the contributions from aircraft jet engines to degraded air quality near airports. If future research is performed on this technique, an airport in a dry environment must be selected as an initial candidate so that the methods initially explored in this report can be retried. As mentioned above, monitors may need to be located further away from the airport environment so that engine SO<sub>2</sub> has more opportunity to become sulfate. If results look promising, other airports in more humid environments could be studied so that the effect of humidity on the usage of the isotopic technique can be properly characterized.

### ***Publications/Presentation/Conferences***

Oral presentations:

- Project 33 presentation PARTNER meeting on October 22, 2009 at Atlanta, Georgia by Mark Thiemens
- Project 33 presentation for the 14th PARTNER Advisory Board meeting on March 24, 2010 at Chapel Hill, North Carolina, by Gerardo Dominguez
- Teleconferences: monthly (with FAA)
- Project 33 presentation for the 15th PARTNER Advisory Board meeting on October 20, 2010 at Atlanta, Georgia, by Christopher Sequeira

### ***Awards***

N/A

### ***Transition of Research Results***

N/A

### ***Plans for Next Period***

No immediate plans for sampling of sulfate aerosols at LAX are being considered, due to the strong marine influence and humidity on minimizing the  $\Delta$  isotopic composition at that location. In addition there are no immediate plans for sampling studies at any other sites due to the uncertainty of the technique and the inconclusive effects that humidity has on the results.

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# Appendix A: LAX Measurement Campaign Data

Table A-1: Fall 2009 measurements

Sample	Cl ( $\mu\text{mol}$ )	SO <sub>4</sub> ( $\mu\text{mol}$ )	NO <sub>3</sub> ( $\mu\text{mol}$ )	HI-VOL time (hours)	Total SCF	Air volume (m <sup>3</sup> )	Cl ( $\mu\text{mole}$ /m <sup>3</sup> )	NO <sub>3</sub> ( $\mu\text{mole}$ /m <sup>3</sup> )	SO <sub>4</sub> ( $\mu\text{mole}$ /m <sup>3</sup> )	$\delta^{18}\text{O}$ SO <sub>4</sub>	$\delta^{17}\text{O}$ SO <sub>4</sub>	$\Delta^{17}\text{O}$ SO <sub>4</sub>	Av. Rel. Hum- idity (%)	Min. Rel. Hum- idity (%)	Max. Rel. Hum- idity (%)
LAX1-SR-6Oct09-5A	22.5	37.4	29.5	99.2	236858.3	6702.27	0.0033	0.0044	0.0056	12.12	6.85	0.55	64	21	81
LAX2-PBSJ-6Oct09-5A	35.4	20.9	37.8	100.1	239292.5	6771.15	0.0052	0.0056	0.0031	9.17	5.64	0.87	64	21	81
LAX3-LOTB-6Oct09-5A	35.9	25.9	37.7	92.9	222175.8	6286.81	0.0057	0.0060	0.0041	7.88	5.17	1.08	64	21	81
LAX4-LOTB-DRK-6Oct09-5A	26.5	7.0	9.8	40.9	98771.3	2794.89	0.0095	0.0035	0.0025	10.03	6.34	1.13			
LAX1-25R-07Oct09-5A	22.9	7.7	4.5	21.1	50508.5	1429.22	0.0160	0.0031	0.0054	13.62	8.15	1.07	69	60	82
LAX2-PBSJ-14Oct09-5A	9.4	31.1	15.6	116.4	278337	7875.98	0.0012	0.0020	0.0039	11.08	6.91	0.77	75	56	100
LAX3-LOTB-14Oct09-5A	16.4	52.9	20.2	129.4	309199.2	8749.27	0.0019	0.0023	0.0060	11.97	7.01	0.79	75	56	100
LAX4-LOTB-DRK-14Oct09-5A	11.6	19.1	10.8	71.4	172548	4882.51	0.0024	0.0022	0.0039	11.05	6.58	0.83			
LAX1-25R-19Oct09-5A	6.8	77.7	27.6	118.7	263396.9	7453.22	0.0009	0.0037	0.0104	12.77	7.49	0.85	81	9	100
LAX2-PBSJ-19Oct09-5A	8.1	37.1	40.0	115.8	277001.4	7838.18	0.0010	0.0051	0.0047	10.64	6.81	1.28	81	9	100
LAX3-LOTB-19Oct09-5A	13.7	72.6	67.9	118.1	282015.9	7980.08	0.0017	0.0085	0.0091	12.96	7.82	1.08	81	9	100
LAX4-LOTB19Oct09-5A	17.0	6.4	18.4	22.0	53030.6	1500.58	0.0113	0.0122	0.0042	13.69	8.44	1.32	81	9	100
LAX1-25R-23Oct09-5A	16.2	34.9	42.6	95.0	227077.7	6425.51	0.0025	0.0066	0.0054	14.76	8.36	0.69	75	44	100
LAX2-PBSJ-23Oct09-5A	16.3	16.1	37.9	92.0	220013.7	6225.63	0.0026	0.0061	0.0026	9.69	6.41	1.37	75	44	100
LAX3-LOTB-23Oct09-5A	19.1	25.3	74.0	92.4	22.0834.8	6248.86	0.0031	0.0118	0.0040	11.58	7.31	1.29	75	44	100
LAX4-LOTB-23Oct09-5A	18.2	18.8	41.8	88.9	214700.8	6075.29	0.0030	0.0069	0.0031	11.89	7.59	1.41	75	44	100
LAX1-25R-23Oct09-1	145.3	17.5	22.2	95.0	227077.7	6425.51	0.0226	0.0034	0.0027	10.56	6.20	0.71	75	44	100
LAX1-25R-23Oct09-2	156.6	29.2	78.4	95.0	227077.7	6425.51	0.0244	0.0122	0.0045				75	44	100
LAX1-25R-23Oct09-3	40.8	11.7	56.5	95.0	227077.7	6425.51	0.0063	0.0088	0.0018				75	44	100
LAX1-25R-23Oct09-4	21.6	11.2	49.8	95.0	227077.7	6425.51	0.0034	0.0078	0.0017				75	44	100
LAX4-LOTB-23Oct09-1	200.7	13.3	35.0	88.9	214700.8	6075.29	0.0330	0.0058	0.0022	9.08	5.05	0.32	75	44	100
LAX4-LOTB-23Oct09-2	146.9	12.8	89.3	88.9	214700.8	6075.29	0.0242	0.0147	0.0021				75	44	100
LAX4-LOTB-23Oct09-3	40.7	8.1	61.8	88.9	214700.8	6075.29	0.0067	0.0102	0.0013	12.71	7.15	0.54	75	44	100
LAX4-LOTB-23Oct09-4	20.9	11.6	47.7	88.9	214700.8	6075.29	0.0034	0.0078	0.0019						

Table A-2: Winter 2009 measurements

Sample	Cl ( $\mu\text{mol}$ )	SO <sub>4</sub> ( $\mu\text{mol}$ )	NO <sub>3</sub> ( $\mu\text{mol}$ )	HI- VOL time (hours)	Total SCF	Air volume (m <sup>3</sup> )	Cl ( $\mu\text{mole}$ /m <sup>3</sup> )	NO <sub>3</sub> ( $\mu\text{mole}$ /m <sup>3</sup> )	SO <sub>4</sub> ( $\mu\text{mole}$ /m <sup>3</sup> )	$\delta^{18}\text{O}$ SO <sub>4</sub>	$\delta^{17}\text{O}$ SO <sub>4</sub>	$\Delta^{17}\text{O}$ SO <sub>4</sub>	Av. Rel. Hum- idity (%)	Min. Rel. Hum- idity (%)	Max. Rel. Hum- idity (%)
LAX1-25R-04Jan10-5A	11.4	32.4	35.1	119.7	287328.7	8130.41	0.0014	0.0043	0.0040	16.60	9.00	0.37	47	14	94
LAX2-PBSJ-04Jan10-5A	16.8	6.1	28.0	119.4	285599.6	8081.48	0.0021	0.0035	0.0008	12.74	8.03	1.41	47	14	94
LAX3-LOTC-04Jan10-5A	16.2	15.0	44.1	119.2	285004.9	8064.65	0.0020	0.0055	0.0019	11.23	6.80	0.96	47	14	94
LAX4-LOTB-04Jan10-5A	14.9	10.8	44.1	120.4	290670.4	8224.97	0.0018	0.0054	0.0013	9.01	5.84	1.15	47	14	94
LAX1-25R-07Jan10-5A	18.5	23.1	75.1	75.9	182133	5153.74	0.0036	0.0146	0.0045	16.14	8.79	0.40	48	13	81
LAX2-PBSJ-07Jan10-5A	20.7	7.2	60.3	72.3	172838.8	4890.74	0.0042	0.0123	0.0015	15.89	9.16	0.90	48	13	81
LAX3-LOTC-07Jan10-5A	24.0	13.5	120.3	75.2	179549.3	5080.63	0.0047	0.0237	0.0027	16.51	9.46	0.87	48	13	81
LAX4-LOTB-07Jan10-5A	19.5	10.8	65.8	76.2	184052	5208.04	0.0037	0.0126	0.0021	16.78	9.93	1.20	48	13	81
LAX1-25R-11Jan10-5A	13.0	32.2	50.9	91.6	219627.7	6214.71	0.0021	0.0082	0.0052	18.33	9.88	0.35	56	21	97
LAX2-PBSJ-11Jan10-5A	18.3	10.2	47.3	88.9	212421.2	6010.79	0.0030	0.0079	0.0017	13.27	8.06	1.16	56	21	97
LAX3-LOTC-11Jan10-5A	17.8	22.1	84.4	90.9	217220.3	6146.58	0.0029	0.0137	0.0036	15.12	8.86	1.00	56	21	97
LAX4-LOTB-11Jan10-5A	16.9	16.5	56.1	85.9	207500.4	5871.54	0.0029	0.0095	0.0028	17.19	9.59	0.66	56	21	97
LAX1-25R-14Jan10-5A	8.5	29.7	35.6	72.0	172857.5	4891.27	0.0017	0.0073	0.0061	21.20	11.49	0.47	70	23	100
LAX2-PBSJ-14Jan10-5A	10.6	13.0	26.2	71.5	171061.8	4840.46	0.0022	0.0054	0.0027	19.81	11.27	0.96	70	23	100
LAX3-LOTC-14Jan10-5A	11.2	22.9	91.9	71.9	171819.1	4861.89	0.0023	0.0189	0.0047	18.68	10.59	0.88	70	23	100
LAX4-LOTB-14Jan10-5A	8.9	22.4	30.5	76.4	184531.3	5221.60	0.0017	0.0058	0.0043	19.70	10.98	0.74	70	23	100



Table A-3: Spring 2010 measurements

Sample	Cl ( $\mu\text{mol}$ )	SO <sub>4</sub> ( $\mu\text{mol}$ )	NO <sub>3</sub> ( $\mu\text{mol}$ )	HI- VOL time (hour s)	Total SCF	Air volume (m <sup>3</sup> )	Cl ( $\mu\text{mole}/\text{m}^3$ )	NO <sub>3</sub> ( $\mu\text{mole}/\text{m}^3$ )	SO <sub>4</sub> ( $\mu\text{mole}/\text{m}^3$ )	$\delta^{18}\text{O}$ SO <sub>4</sub>	$\delta^{17}\text{O}$ SO <sub>4</sub>	$\Delta^{17}\text{O}$ SO <sub>4</sub>	Av. Rel. Hum- idity (%)	Min. Rel. Hum- idity (%)	Max. Rel. Hum- idity (%)
LAX1-25R-05Mar10-5A	17.6	26.9	17.6	71.6	171618.1	4856.20	0.0036	0.0036	0.0055	17.60	9.44	0.29	64	47	88
LAX2-PBSJ-05Mar10-5A	27.9	4.8	12.6	71.6	171279.9	4846.63	0.0057	0.0026	0.0010	10.50	6.60	1.14	64	47	88
LAX3-LOTC-05Mar10-5A	24.3	7.4	14.3	71.3	172212.8	4873.03	0.0050	0.0029	0.0015	13.18	7.98	1.13	64	47	88
LAX4-LOTB-05Mar10-5A	24.8	8.8	23.3	70.9	169644.2	4800.35	0.0052	0.0049	0.0018	12.74	7.44	0.81	64	47	88
LAX1-25R-09Mar10-5A	25.4	29.4	26.6	96.1	230591.3	6524.94	0.0039	0.0041	0.0045	12.17	7.16	0.83	67	34	88
LAX2-PBSJ-09Mar10-5A	21.7	14.6	20.7	94.2	225264.2	6374.20	0.0034	0.0033	0.0023	9.58	6.37	1.39	67	34	88
LAX3-LOTC-09Mar10-5A	23.4	14.9	23.1	95.9	231813.1	6559.51	0.0036	0.0035	0.0023	13.04	7.77	0.99	67	34	88
LAX4-LOTB-09Mar10-5A	16.3	22.4	35.3	100.2	239434.0	6775.16	0.0024	0.0052	0.0033	11.42	7.18	1.24	67	34	88
LAX1-25R-12Mar10-5A	31.6	27.4	29.8	71.4	171305.0	4847.34	0.0065	0.0062	0.0056	17.08	10.51	1.63	44	28	71
LAX2-PBSJ-12Mar10-5A	28.4	12.3	24.3	69.5	166038.3	4698.31	0.0061	0.0052	0.0026	14.18	11.16	3.79	44	28	71
LAX3-LOTC-12Mar10-5A	32.2	16.3	28.5	70.9	171180.0	4843.80	0.0066	0.0059	0.0034	15.88	11.57	3.31	44	28	71
LAX4-LOTB-12Mar10-5A	25.8	18.2	29.0	66.8	159473.8	4512.56	0.0057	0.0064	0.0040	14.89	11.57	3.83	44	28	71
LAX1-25R-12Mar10-1	77.2	7.5	8.3	71.4	171305.0	4847.34	0.0159	0.0017	0.0015				44	28	71
LAX1-25R-12Mar10-2	86.9	9.2	20.1	71.4	171305.0	4847.34	0.0179	0.0041	0.0019	15.34	8.87	0.90	44	28	71
LAX1-25R-12Mar10-3	36.7	6.2	20.3	71.4	171305.0	4847.34	0.0076	0.0042	0.0013				44	28	71
LAX1-25R-12Mar10-4	22.0	8.0	19.8	71.4	171305.0	4847.34	0.0045	0.0041	0.0016				44	28	71
LAX4-LOTB-12Mar10-1	142.8	10.7	12.6	66.8	159473.8	4512.56	0.0316	0.0028	0.0024				44	28	71
LAX4-LOTB-12Mar10-2	121.9	10.8	32.9	66.8	159473.8	4512.56	0.0270	0.0073	0.0024	14.56	8.17	0.66	44	28	71
LAX4-LOTB-12Mar10-3	40.6	5.9	25.3	66.8	159473.8	4512.56	0.0090	0.0056	0.0013	13.86	8.66	1.46	44	28	71
LAX4-LOTB-12Mar10-4	24.4	6.3	23.3	66.8	159473.8	4512.56	0.0054	0.0052	0.0014				44	28	71
LAX1-25R-16Mar10-5A	24.9	36.7	31.1	95.0	228137.3	6455.50	0.0039	0.0048	0.0057	16.00	9.07	0.75	53	19	83
LAX2-PBSJ-16Mar10-5A	24.5	12.4	26.8	93.2	223007.4	6310.34	0.0039	0.0042	0.0020	9.97	7.31	2.12	53	19	83
LAX3-LOTC-16Mar10-5A	26.2	16.4	37.0	95.3	230164.5	6512.86	0.0040	0.0057	0.0025	8.58	6.20	1.74	53	19	83
LAX4-LOTB-16Mar10-5A	22.1	23.1	49.7	95.1	227370.9	6433.81	0.0034	0.0077	0.0036	12.20	8.07	1.72	53	19	83