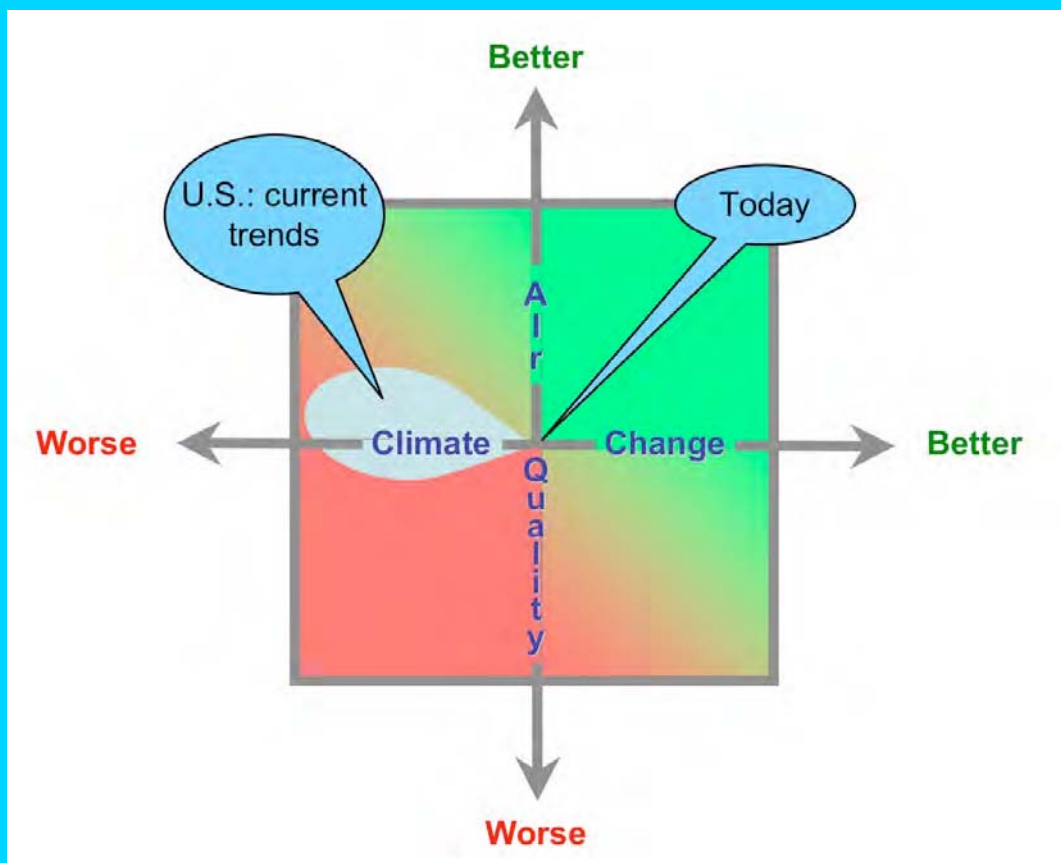




2010 CalNex Science and Implementation Plan

Science to Support Decisions



Research at the Nexus of Air Quality and Climate Change

6 October 2008

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Cover Figure: Schematic diagram of the trade-offs between the implications for regional air quality and global climate change of new policies for management of the atmosphere. The gray ellipse approximately represents the direction of current trends in the U.S

Air Quality and Climate Change: Tradeoffs Facing Decision Makers

The challenge of properly managing our atmospheric resources is complex, because management strategies must simultaneously deal with two interrelated concerns: air quality and climate change. These strategies must also effectively meet society's need for energy generation and demand for goods and services. The management of air quality is focused on limiting the levels of harmful pollutants and air toxics, as well as improving atmospheric visibility and reducing acidic deposition to ecosystems. These air quality issues are usually considered from local to regional scales, although it is becoming clear that there are important global scale influences. The mitigation of climate change effects requires controlling greenhouse gas emissions and reducing other radiative forcing agents. Climate change is usually considered from a global perspective, but strong regional differences are expected in the impacts of climate change. The goal of the CalNex 2010 program is to study the important issues at the nexus of the air quality and climate change problems, and to provide scientific information regarding the trade-offs faced by decision makers when addressing these two inter-related issues.

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Although separate programs are in place to research and manage both air quality and climate change effects, these problems are not separate and in fact are intimately connected. These connections arise because in many cases the agents of concern are the same, and in many cases the sources of the agents are the same or intimately connected. Figure 1.1 shows the radiative forcing factors in the global climate system as summarized by the Intergovernmental Panel on Climate Change; many of these factors are also important from air quality considerations. For example, surface ozone is both an air pollutant and a greenhouse gas. Also, aerosols not only have significant climate impacts, but they also constitute particulate matter (PM), an important air pollutant, are responsible for visibility degradation, and are important agents in acidic deposition. In many cases, efforts to address one of these issues can be beneficial to the other, but in other cases policies addressing one issue can have unintended detrimental impacts on the other.

Although separate programs are in place to research and manage air quality and climate change effects, these problems are not separate and in fact are intimately connected.

The complex roles that ozone and aerosols play in the atmosphere provide examples of such trade-offs. Reductions in the emissions of nitrogen oxides (NO_x) and/or volatile organic compounds (VOCs) to reduce ozone formation for improved air quality, also ameliorate climate impacts from ozone and VOCs. However, efforts to reduce emissions of PM and its precursors (SO_2 , NO_x , VOCs, ammonia) for air quality improvement can lead to a further warming effect on the climate, because scattering of sunlight by aerosols masks as much as 50% of the present warming effect of greenhouse gases [Ramanathan *et al.*, 2001]. Policy decisions also must recognize that some climate change impacts have a strong regional dependence, and not simply a uniform global impact. Where aerosol loadings are high, as in many of the populated areas of the globe, the regional cooling effects of aerosols can be much greater than the global averages

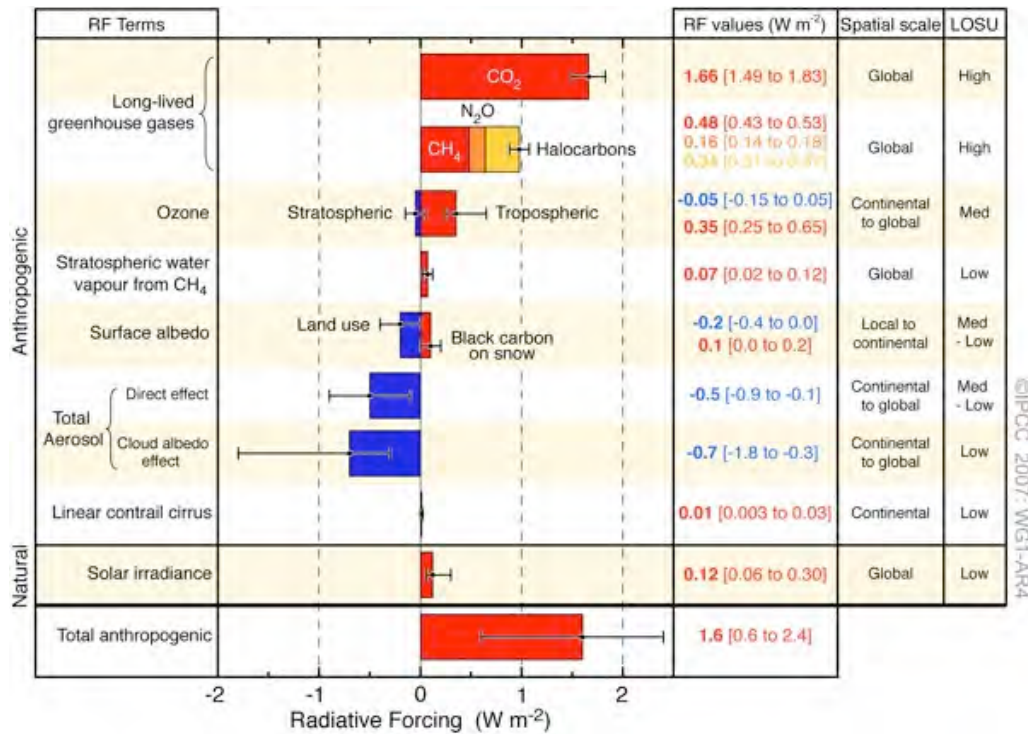


Figure 1.1: Radiative forcing factors in the Earth's climate system according to the 4th Assessment Report by Working Group 1 of the Intergovernmental Panel on Climate Change (IPCC).

that are usually discussed [Ramanathan *et al.*, 2007]. Aerosols also play a complex role in climate interactions with the water cycle. Enhanced aerosol levels potentially can lead to decreases in the rainfall and snow pack in critical regions, such as the Sierra Nevada Mountains.

The Cover Figure of this document illustrates, in a qualitative manner, the trade-offs faced by decision makers between the implications of new environmental policies for air quality on the one hand and climate change on the other hand. The center of the graph represents where we are in the U.S. today, given the current air quality and levels of radiative forcing factors as in Fig. 1. Movement away from the center of the graph represents the effects of projected changes in industrial and urban emissions in response to growth, technology change and/or emission management strategies. Such changes would affect both air quality (upward if the effect is positive, downward if negative) and climate change (to the right if the effect is positive, to the left if negative). Clearly, the goal is to make decisions that have beneficial effects for both problems (i.e. win-win strategies that move us into the upper-right quadrant of the figure), and certainly avoid lose-lose strategies that move us into the lower-left quadrant. However, some of the possible emission control strategies will likely have positive effects on regional air quality and negative effects on global climate change (movement into the top-left quadrant), or vice versa (movement into the bottom-right quadrant).

The projected effect of current emission trends in the U.S. is approximately indicated by the gray ellipse in the Cover Figure. Over the past decades in the U.S., emissions reductions implemented for vehicles and point sources have significantly improved air quality in most metropolitan areas, while accelerating emissions of greenhouse gases have increased the net radiative forcing of the climate system. Overall, from 1990 to 2005, total emissions of CO₂ in

the US are estimated to have increased by 20% (from 5062 to 6090 Tg per year) [EPA, 2007]. In recent years

Current trends indicate slowing improvement in air quality in the U.S., along with accelerating increases in greenhouse gas

improvement in air quality in most regions of the U.S. has slowed. For example, Fig. 1.2 shows the trends in regional ozone levels in California. Therefore, as represented by the gray ellipse, recent current trends imply a shift of the state of the atmosphere primarily toward the left of the Cover Figure, i.e. toward worsening climate change impacts with only modest improvement in air quality. This slow improvement in air quality is represented by a small displacement of the ellipse into the upper-left quadrant. The uncertainty of the projections is represented by the width of ellipse, which indicates the possibility of worsening air quality as increasing population and demand for goods and services may reverse current emission decreases. The challenge for the future is to adopt new policies that slow the increase in radiative forcing and increase the current rate of improvement in air quality. These policy decisions must recognize that the climate change impacts may have a strong regional dependence, and not simply a uniform global impact. The goal of CalNex 2010 is to develop the science needed to support such decisions for the State of California.

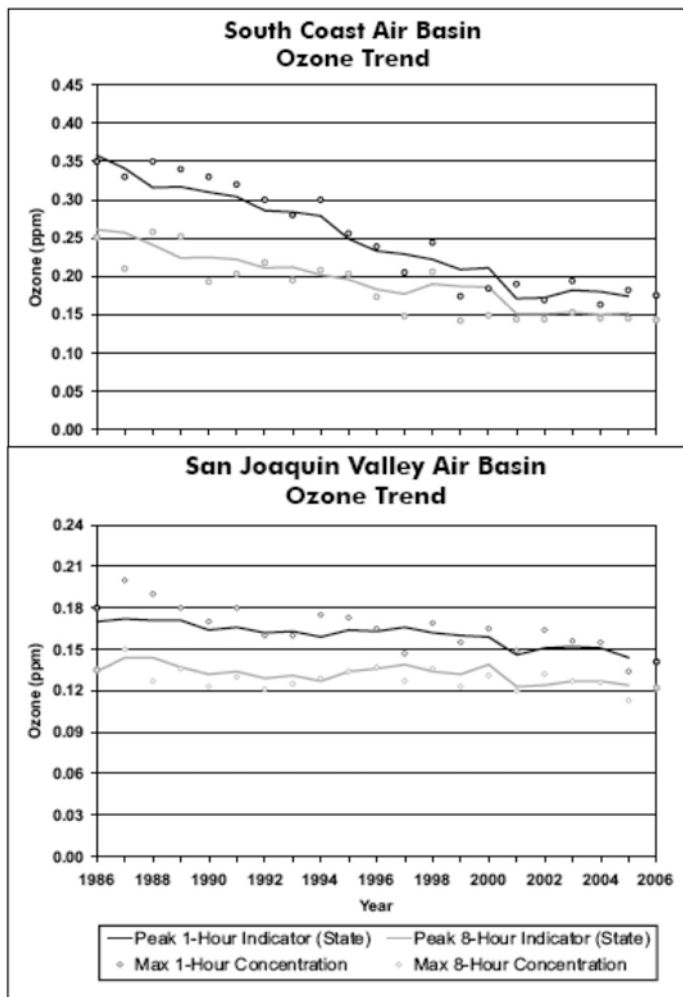


Figure 1.2: Trends in regional air quality over the past decade in two California air basins as represented by four metrics of maximum measured ozone concentrations [CARB, 2007].

In the CalNex 2010 study outlined here, NOAA researchers will study several issues at the heart of the coupled air quality and climate change problems. The State of California has been chosen as the site for this first case study. California has well-documented air quality problems and faces the difficult task of managing them with an increasing population and demand for goods and services. In addition, California has taken the lead in the Nation's effort to address global climate change and has proposed an ambitious program to control the

California has well documented air quality problems and has proposed an ambitious program to control the emissions of greenhouse gases in the State.

emissions of greenhouse gases in the State. Thus, California is particularly interested in finding the most effective way to simultaneously manage the two challenges of air quality and climate change. In other words: how can the emissions of greenhouse gases, aerosols, other air pollutants and their precursors be reduced, such that benefits are maximized for both air quality and climate change? Characterization of the regional effects of climate change in California will also be of particular interest: What benefits will the people of California receive as a result of climate change mitigation? In the CalNex Study, NOAA researchers will lead a major multi-institutional intensive field program in California in 2010 focusing on the science that couples the air quality and climate change issues facing this State. In addition, many of the Nation's experts in air quality and climate change research reside in California, and their involvement in the field study will enhance the program and improve the communication of the scientific findings to the Nation's and State's decision makers.

2. Research at the Nexus of Air Quality and Climate Change

In the development of policies to effectively address the combined air quality–climate change system a great many interrelated issues must be considered. This section discusses several of those issues, primarily as illustrations of the relationships between air quality and climate change that must be considered. The implications for possible emission control strategies will be discussed in terms of the decision diagram introduced in the cover figure.

2.1 Emission Inventories for GHG, aerosols, and precursors

California has led the nation by implementing an aggressive climate change program. The California Global Warming Solutions Act of 2006 (Assembly Bill 32) requires that the California Air Resources Board (CARB) determine the statewide 1990 greenhouse gas (GHG) emissions level as a statewide emissions limit to be achieved by 2020. Reaching this limit corresponds to about a 30% decrease from the projections of emissions in a business-as-usual scenario. CARB also has responsibility for maintaining the Statewide GHG emissions inventory as a means of tracking progress toward reaching the 2020 goal.

The emission inventory work required for California’s climate change program will provide significant challenges. Figure 2.1 summarizes a GHG emission inventory recently developed for California. The accuracy of that inventory total and the relative contributions of the separate categories requires further assessment.

Extrapolating the inventory to 1990 and maintaining an accurate inventory in future years will require further work. This work will require the collaborative efforts of modelers, who develop bottom-up inventories, and experimentalists, who provide top-down assessments of the inventories through measurements of the ambient concentrations of the emitted species. The Nation’s experience in the development of emission inventories for the criteria pollutants has demonstrated that it is not possible to develop accurate emission inventories without such collaboration [e.g. *NARSTO*, 2005; *Parrish*, 2006].

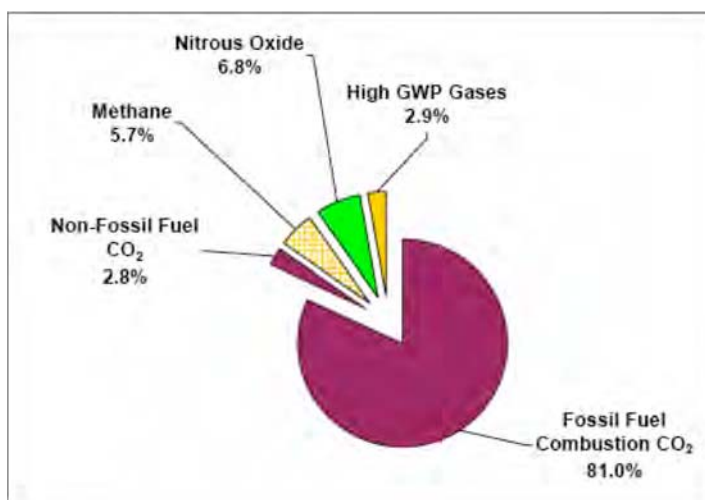
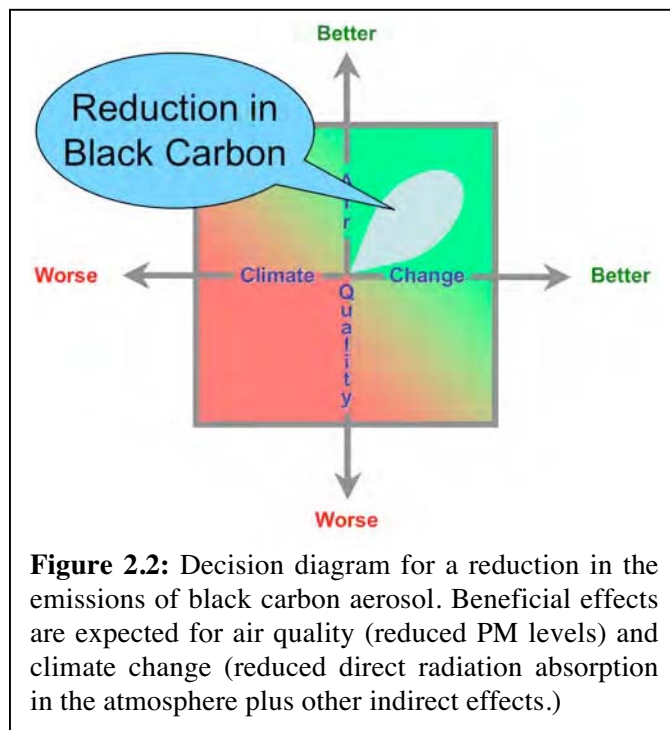


Figure 2.1: Estimated 2004 GHG emissions in California in CO₂-equivalent units (*Bemis and Allen*, 2005). The emissions totaled 492 Tg CO₂-equivalent.

Assessment for GHG emission inventories and for criteria pollutant emission inventories will complement each other. For example, airborne platforms can simultaneously measure both categories of emissions in a single transect downwind of common sources. Further, CO₂, the most important GHG, is copiously emitted from the combustion sources that emit criteria pollutants, and thus serves as a convenient tracer of the transported emission plume. During CalNex 2010 full advantage will be taken of this complementarity.

2.2 Particulate Matter: Black Carbon

One clear example of a “win-win” control strategy is reduction in emissions of light-absorbing or black carbon aerosol. This material is emitted with widely varying emission factors from a variety of combustion processes, including heavy-duty diesel engines and biomass burning. It is a component of PM that is suspected to be particularly important in the negative health effects associated with aerosols, and thus constitutes an important air quality issue. It also acts as a warming agent in the atmosphere due to its light-absorbing properties, and thus constitutes an equally important climate change issue. Control of black carbon is important from both perspectives, as illustrated in Figure 2.2.



2.3 Reduction of non-CO₂ Greenhouse Gas Emissions

The non-CO₂ greenhouse gases methane (CH₄), nitrous oxide (N₂O), halocarbons (CFCs and HCFCs) and tropospheric ozone (O₃) together account for about 1.33 W m⁻² of radiative forcing, which is only slightly smaller than the contribution from CO₂ (1.66 W m⁻²). This comparison with confidence limits is illustrated in Fig. 2.3. A significant reduction in greenhouse gas emissions can therefore be achieved by focusing on the non-CO₂ gases. However, the scientific understanding of the sources of these gases is far from complete, in particular on regional scales. In addition, the atmospheric lifetimes of non-CO₂ GHGs must be considered to assess the impact that a reduction in the emissions could have. For example, ozone has a lifetime on the order of weeks: reductions in the emissions of its precursors would have an immediate impact on ozone levels in the troposphere. Nitrous oxide, on the other hand, has a lifetime of more than 100 years: emissions reductions will only pay off in terms of reduced radiative forcing on the order of decades.

The growth rate in global methane concentration has decreased over the last few years, but the reasons for this decrease are largely unknown [Dlugokencky *et al.*, 2003]. A resumption of methane increases in the future can therefore not

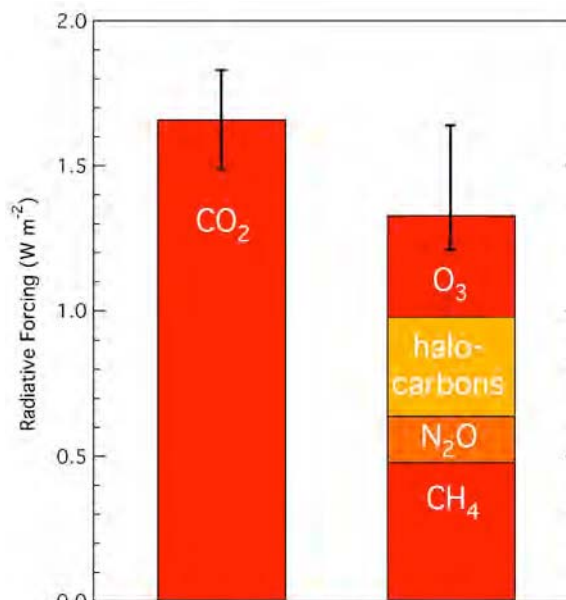
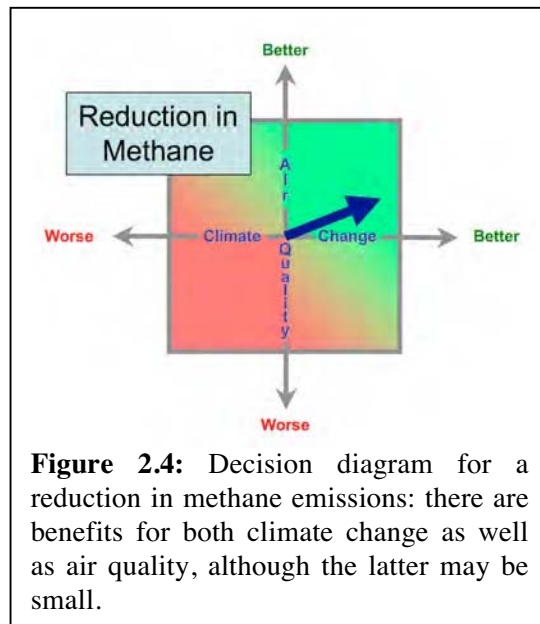


Figure 2.3: Comparison of the radiative forcing factors of CO₂ and the non-CO₂ greenhouse gases. These values are taken from Fig. 1.1.

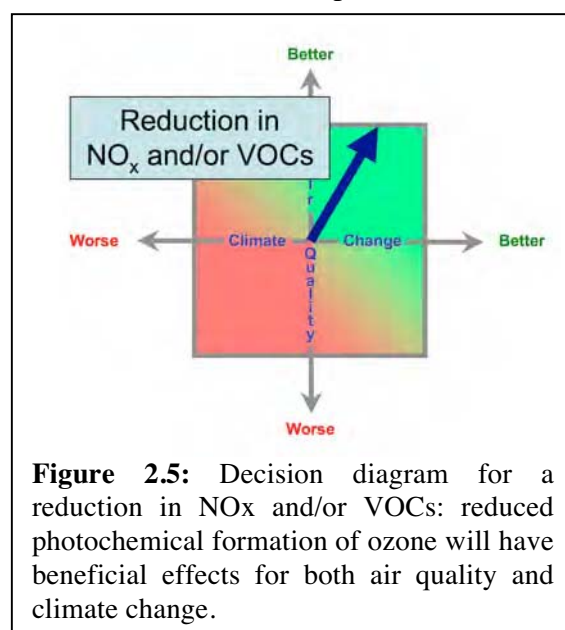
be ruled out. Methane plays an important role in the chemistry of hydroxyl (OH) radicals and ozone. Reductions in the levels of methane were suggested to have beneficial, albeit small effects on global air quality [West *et al.*, 2007]. However, possible effects on the oxidizing capacity of the atmosphere, i.e. the average global concentration of OH, which determines the lifetime of methane and hence its growth rate, should be considered as well. Other recent research has focused on a possible source of methane from vegetation, which has been identified both in laboratory experiments [Keppler *et al.*, 2006] as well as over the rain forest in South America [Sinha *et al.*, 2007]. In the decision diagram in Fig. 2.4, the effect of methane reductions is positive for both climate change as well as air quality goals.



Nitrous oxide is a very long-lived GHG with sources from the oceans and soils. The latter can be enhanced by fertilization. It has been suggested that the N_2O released from bio-fuel crops could negate the positive effects on the carbon cycle from a widespread use of bio-fuels [Crutzen *et al.*, 2007]. The spatial distribution of N_2O is very uniform, because of the long lifetime and the diffuse sources, making the quantification of source emissions quite challenging.

Several of the CFCs targeted by the Montreal protocol to protect the stratospheric ozone layer are also extremely potent GHGs. Recent research has indicated that the Montreal Protocol had significant effects on the radiative forcing from GHGs [Velders *et al.*, 2007]. After their phase-out, CFCs were replaced by HCFCs and HFCs, which have a shorter tropospheric lifetime and are a smaller source of chlorine in the stratosphere. All HCFCs are also GHGs, however.

Ozone in the troposphere has two important sources: it is formed from the photo-oxidation of hydrocarbons in the presence of nitrogen oxides (NO_x), and it is mixed down from the stratosphere [Lelieveld and Dentener, 2000]. Ozone is one of the main components of air pollution and its formation has been studied for several decades. Even though the basic chemistry of ozone formation is understood, accurate forecasts of ozone have remained an elusive goal [Pagowski *et al.*, 2005]. Atmospheric ozone is the GHG with the largest radiative forcing after CO_2 and methane (Fig. 2.3). Reductions in NO_x and/or VOCs have positive effects for both air quality and climate change (Fig. 2.5). However, depending on the location and meteorology, photochemical formation of ozone can be limited by the availability of NO_x and or VOCs, and this question



needs careful evaluation to design the most effective control strategies. Recent research has suggested that ozone may have an even stronger indirect effect on GHG distributions through the damage it causes to vegetation (Fig. 2.6): (1) increased levels of ozone may reduce the CO₂ uptake by vegetation, and may lead therefore to a net CO₂ increase, (2) the radiative forcing corresponding to this CO₂ increase could outweigh the direct radiative forcing by ozone [Sitch *et al.*, 2007].

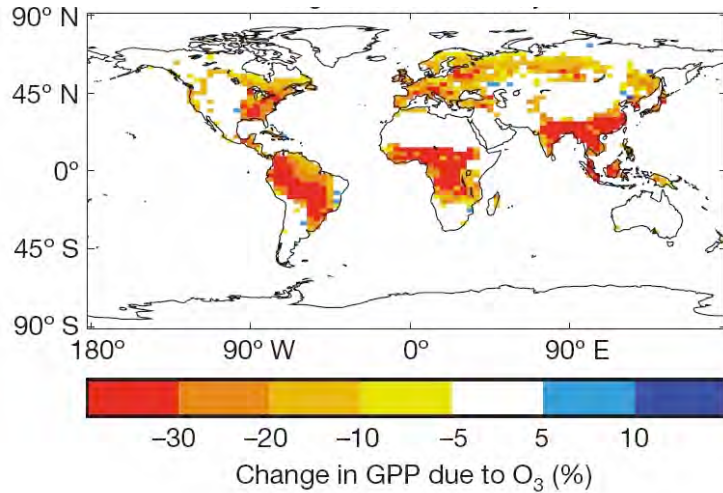


Figure 2.6: Change in gross primary productivity of ecosystems between 1901 and 2100 due to ozone-induced damage [Sitch *et al.*, 2007]

2.4 Introduction of Bio-Fuels

Intensive research efforts are currently focused on the development of alternative fuels from agricultural crops. These so-called bio-fuels can lead to a net reduction in the emissions of CO₂: bio-fuel crops take up CO₂ from the atmosphere during growth, and the bio-fuel use re-releases the CO₂ back to the atmosphere. However, energy is needed for growing the bio-fuel crops, their transport, and the bio-refining process. Most of this energy currently comes from fossil fuels, in particular coal, and this reduces the benefits for climate change [Farrell *et al.*, 2006]. For ethanol made from corn, the reduction in net CO₂ emissions is almost negligible (Fig. 2.7); for ethanol made from cellulose, the reduction in net CO₂ emissions is significant, but at present there are still important

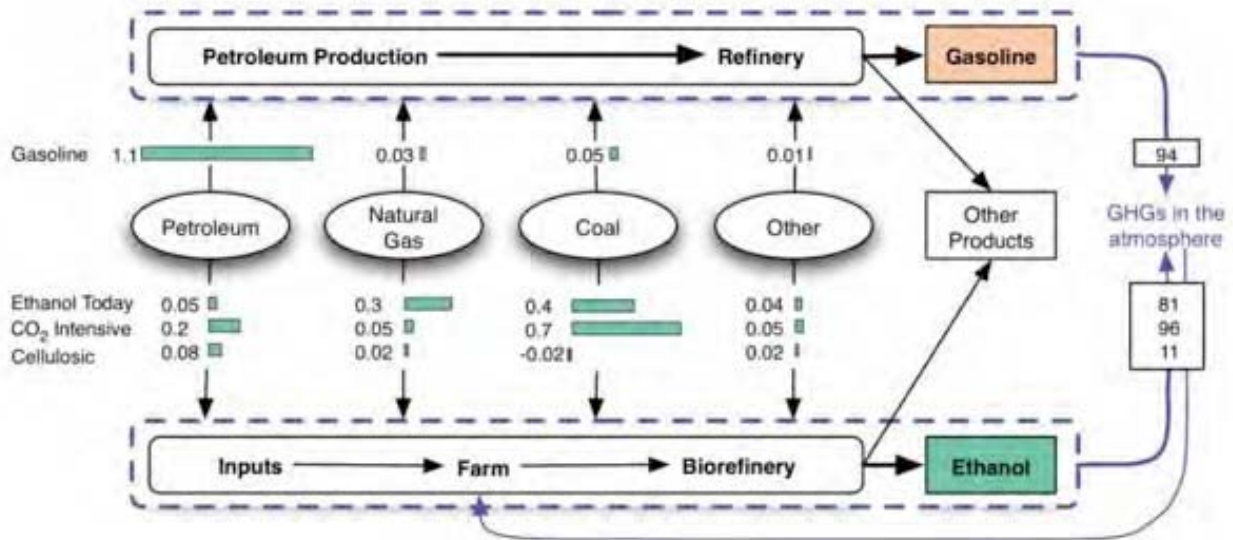
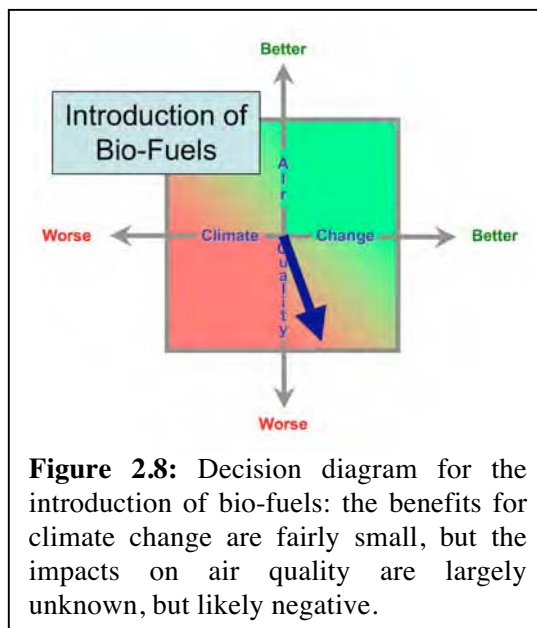


Figure 2.7: Fossil fuels required for the production of gasoline (top) and ethanol (bottom). The production and use of gasoline leads to similar GHG emissions as the use of corn ethanol; cellulosic ethanol could lead to significant reductions in GHG emissions [Farrell *et al.*, 2006].

technological hurdles in the large-scale production of cellulosic ethanol. In addition, as mentioned above, the nitrous oxide released from the fertilization of bio-fuel crops could negate the positive effects on the carbon cycle of resulting from a widespread use of bio-fuels [Crutzen *et al.*, 2007].

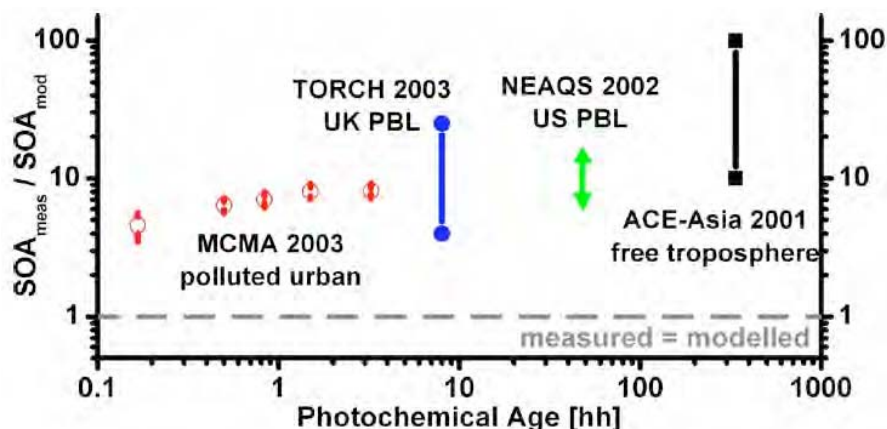
It will be critical to understand the impacts on air quality from a large-scale use of corn ethanol and other alternative bio-fuels. Currently, there are many gaps in our ability to reach that understanding: what are the emissions from (fertilized) bio-fuel crops, what are the emissions from the bio-refining process, and how does the use of bio-fuels alter the emissions from vehicles? A preliminary study on the air quality impacts of the use of E85 fuel indicated that enhanced evaporative emissions may lead to ozone increases in Los Angeles, and increased formation of acetaldehyde, which is an air toxic [Jacobson, 2007]. The decision diagram for the introduction of bio-fuels therefore reflects small positive effects for climate change but potentially negative effects on air quality (Fig. 2.8).



2.5 Particulate Matter: Important in Air Quality and Climate

Over the past 2 decades, emission reductions of SO₂ led to significant decreases in aerosol loadings over the U.S. (and decreased acidity of precipitation). As a result, the relative importance of organic aerosol (OA) has increased. The sources of organic aerosol (OA), however, are currently the subject of vigorous debate in the scientific community. The consensus is that most organic aerosol in rural areas is not directly emitted, but formed in the atmosphere from condensation of oxidized VOCs (secondary organic aerosol or SOA) [Zhang *et al.*, 2007]. Radiocarbon dating of OA typically shows a very high fraction of modern carbon, suggesting that most SOA is formed from biogenic VOCs [Bench *et al.*, 2007]. On the other hand, SOA typically correlates very well with the oxidation products of anthropogenic VOCs, suggesting that urban emissions plays an important role in its formation [de Gouw *et al.*, 2005]. Several studies indicated that there is much more SOA in urban air than models can account for [de Gouw *et al.*, 2005; Volkamer *et al.*, 2006]. Figure 2.9 summarizes some of the recent

Figure 2.9: The ratio between measured and modeled secondary organic aerosol (SOA) as a function of photochemical age, i.e. the degree of photochemical processing, of a polluted air mass [Volkamer *et al.*, 2006].



research aimed at explaining the observed levels of SOA using detailed chemical models, and the graph shows that models underestimate SOA by 1-2 orders of magnitude over a wide range of photochemical ages, i.e. the degree of photochemical processing of an air mass.

Given the relatively poor understanding of the sources of OA, it is very difficult to predict how a reduction in the emissions of precursors will affect the levels of OA in the atmosphere. Figure 2.10 gives a recent estimate of the sources of OA in the U.S. [de Gouw *et al.*, 2007]. The three main sources are (1) SOA from biogenic VOCs (isoprene, terpenes and other reactive VOCs), (2) SOA from anthropogenic VOCs, and (3) OA from biomass burning.

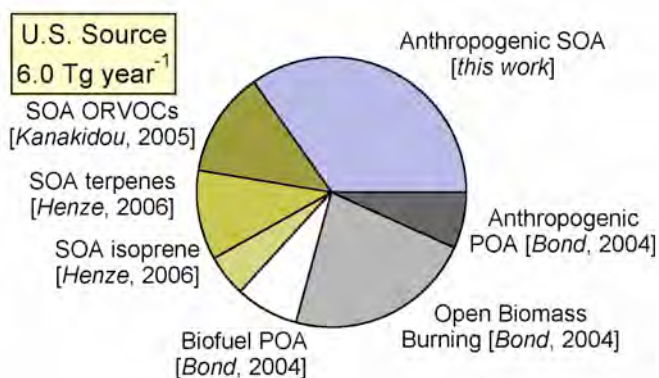


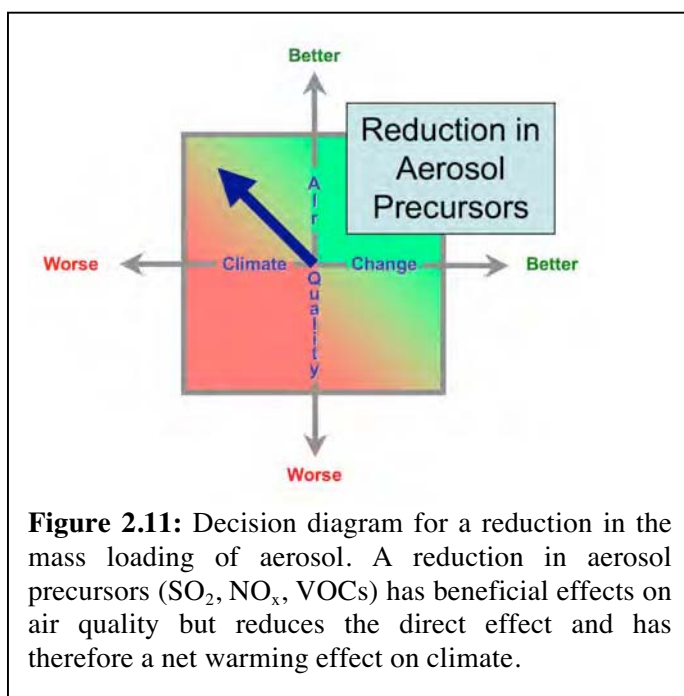
Figure 2.10: Source estimates of organic aerosol in the U.S. [de Gouw *et al.*, 2007].

It has been suggested that biogenic SOA will increase in the future as the emissions of biogenic VOCs increase with temperature [Tsigaridis and Kanakidou, 2007].

On the other hand, isoprene emissions could be negatively dependent on CO₂ [Rosenstiel *et al.*, 2003]. Anthropogenic SOA may decrease in the future, as the vehicle fleet continues to modernize and new technologies for emissions control are implemented. In contrast biomass burning OA may increase as a result of an increase in wildfires due to climate change, because of higher temperatures, less rainfall and a reduced ecosystem health, for example due to pine beetle attack.

In their turn, atmospheric aerosols influence climate change directly by scattering and absorption of radiation, and indirectly by their effects on clouds and precipitation (Fig. 1.1). The 4th assessment report of the IPCC concluded that a significant fraction of warming due to GHGs may have been negated by the cooling effects of aerosol through the scattering of sunlight. On the other hand, light-absorbing carbon in atmospheric aerosols may have contributed as much as greenhouse gases to regional warming trends in the lower atmosphere through the absorption of sunlight [Ramanathan *et al.*, 2007]. Globally, the overall direct effect of the interaction of aerosols with sunlight is believed to yield a net cooling (Fig. 1.1).

Air quality considerations have led to reductions in the emissions of aerosol precursors, notably SO₂, and will likely lead to further reductions in the future to comply with PM standards. Climate change policy will therefore be



complicated by the additional net increase in radiative forcing due to the reduction in aerosol loadings. Organic aerosol, however, is insufficiently understood at present to decide which emissions reductions are effective at decreasing the mass loading. In the decision diagram in Fig. 2.11, the effect of a reduction in aerosol precursors is positive for air quality but negative for climate change. Importantly though, a reduction in light-absorbing or black carbon, on the other hand, is positive for both air quality and climate change (Fig. 2.2).

2.6 Particulate Matter: Important for Clouds and Precipitation

Aerosol can act as cloud-condensation nuclei (CCN) and affect the microphysical and dynamical properties of clouds. An increase in CCN due to pollution leads to an increase in cloud droplet concentration, smaller cloud droplets, and increases in the reflectance of clouds, i.e. the so-called Twomey or cloud albedo effect [Twomey, 1977]. This albedo effect results in a significant radiative cooling for low clouds which radiate at temperatures similar to the surface but offer a strong contrast with the reflectance of the underlying surface, particularly over dark oceans. The albedo effect is still poorly quantified and represents one of the major uncertainties in predicting future climate states (Fig. 1.1). A dramatic illustration of the influence of pollution aerosol on cloud reflectance was observed in Eastern Europe (Fig. 2.12). The decrease in industrial activity resulting from the collapse of the former Soviet Union led to a decrease in emissions of aerosol precursors (SO_2), the effects of which could be observed in the variability of cloud reflectance [Krueger *et al.*, 2004]. Off the coast of California, the bright linear features in clouds associated with pollution particles emitted by ships are another vivid illustration of aerosol effects on cloud microphysics.

Multiple studies have indicated that the aerosol composition matters less than its size distribution for its cloud-nucleating characteristics [Dusek *et al.*, 2006; Ervens *et al.*, 2005].

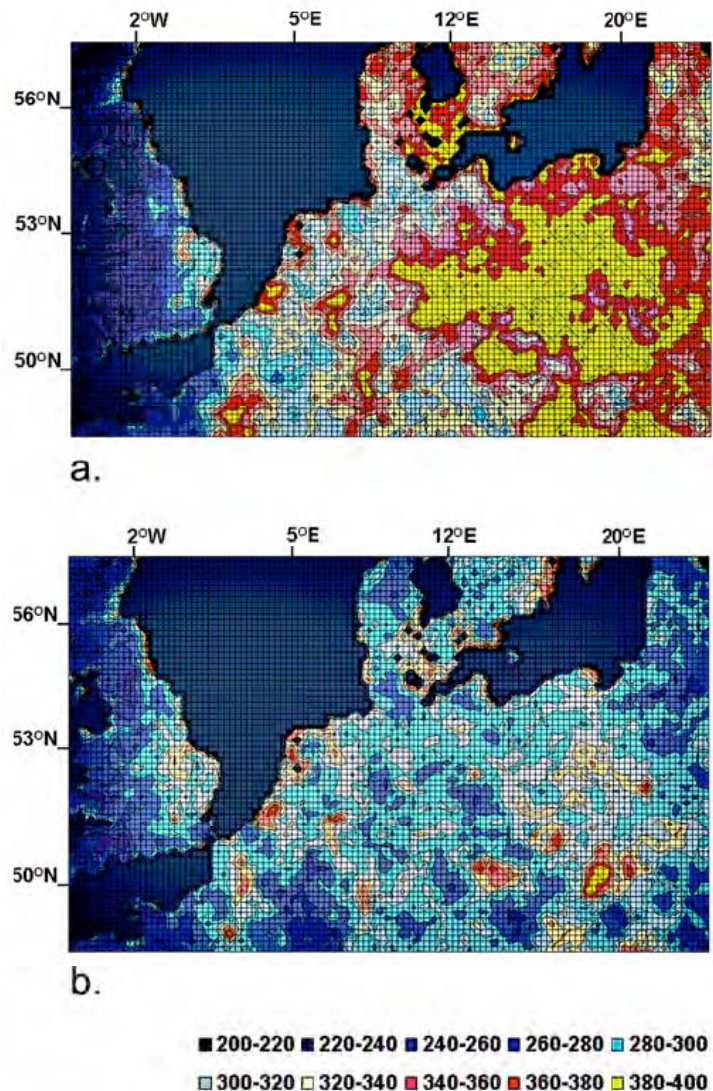


Figure 2.12: Variation of cloud reflectance over parts of Europe in January, February, November and December of (a) 1981-1984, and (b) 1996-1999, i.e. before and after the collapse of the former Soviet Union [Krueger *et al.*, 2004].

Nevertheless, there are still many uncertainties relating the concentrations of cloud droplets to that of CCN and aerosol concentration. Figure 2.13, for example, shows the concentration of cloud droplets versus the aerosol number concentration, and although a positive correlation is clearly visible from the data, the slope is different for different regions of the atmosphere. These slopes are influenced not only by aerosol size distribution and composition, but also by cloud dynamics. Since there is a direct relationship between these slopes and the associated cloud radiative forcing it is important to understand the underlying physical processes.

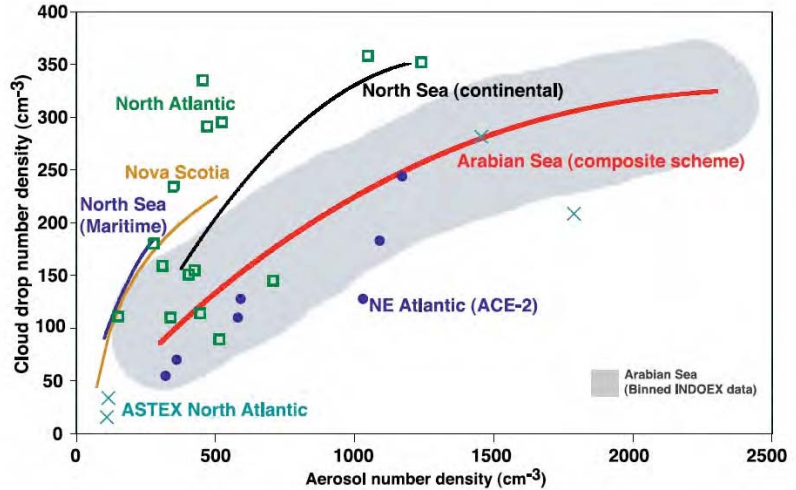


Figure 2.13: Increase in cloud drop with aerosol number concentration. The relationship is different for different regions of the atmosphere [Ramanathan *et al.*, 2001].

The effect of pollution aerosol on cloud albedo is widely assumed to be a cooling factor in the climate system, and thus a reduction in aerosol may have adverse effects for climate change, similar to what was said before about the direct radiative effects of aerosol (Fig. 2.11). Light absorbing aerosol like black carbon, on the other hand, should be considered in particular since it absorbs and radiates energy, and generally acts to reduce cloudiness [Ackerman *et al.*, 2000; Koren *et al.*, 2005] thereby further contributing to global warming. A reduction in emissions of absorbing aerosol would therefore be beneficial to both air quality and climate, similar to the implications for the direct radiative effect of black carbon discussed above (Fig. 2.2).

Changes in precipitation rates and rainfall patterns also must be considered, but those are highly uncertain [Ramanathan *et al.*, 2001]. An increase in CCN can affect precipitation rates and thus the lifecycle of clouds. On the other hand, the smaller droplets associated with high CCN concentrations tend to evaporate more rapidly, which may reduce cloud cover [Xue and Feingold, 2006]. Microphysical changes in clouds can induce dynamical feedbacks that modify boundary layer circulation and cloudiness. A distinct example is the transition from closed to open cellular convection associated with the transition from a non-precipitating to precipitating state: clouds tend to self-organize depending on the aerosol regime that they reside in, with dramatic effects on the radiative forcing of the system.

3. 2010 CalNexus Science Questions

The following preliminary list of science questions has been developed for guiding the field research of CalNex 2010. They are intended to be 1) feasible to address in the context of the proposed study 2) specific enough to provide a needed focus, but 3) general enough to cover the scientific issues of immediate policy interest. They will be revised as needed to form the basis of the Science Plans that will be developed by the participating agencies. These questions fall into three broad categories.

Emissions

A. How can we improve the emissions inventory for greenhouse gases, ozone and aerosol precursors including emissions from soil, ships, agriculture and other non-industrial or transportation related processes? What measurements can help validate the use of satellite data for biogenic VOC and NO_x emission inventories?

Critical uncertainties remain in our understanding of 1) the processes by which primary emissions are transformed within and removed from the atmosphere, and 2) how aerosols interact with the radiation flux in the atmosphere.

B. What emissions (natural and anthropogenic) and processes lead to sulfate formation over California coastal waters and in urbanized coastal areas? What is the contribution from ship emissions? How does Southern California compare and contrast with the San Francisco Bay Area?

C. What sources and processes contribute to atmospheric mercury concentrations in California?

Chemical Transformation and Climate Processes

D. How important are chemical processes occurring at night in determining transport and / or loss of nitrogen oxides, reactive VOC and ozone? Do regional models in California adequately represent these processes and their effect on air quality?

Both climate change and air quality problems originate from society's increased emissions of radiative forcing agents (CO₂, CH₄, N₂O, halocarbons, black carbon, aerosols) and air pollutants and their precursors (VOC, NO_x, SO₂, CO, air toxics). Our understanding of these emissions on both regional and global scales is critically limited.

E. What are the sources and physical mechanisms that contribute to high ozone concentrations aloft that have been observed in Central and Southern California?

F. Are there significant differences between Central Valley and South Coast Air Basin precursors or ozone formation chemistry? Will meteorological and/or precursor differences between the Central Valley and the South Coast Air Basin lead to different chemical transformation processes and different responses to emissions reductions? What is the importance of natural emissions to the ozone formation process? Are there regional differences in the formation rates and efficiency for particulate matter as well?

G. What are the impacts of aerosols in California on radiative forcing and cloud formation? What are the most important precursors and formation processes for secondary

organic aerosol? What is the role of aqueous phase processes in atmospheric transformations?

Transport and Meteorology

H. What are proper oceanic boundary conditions for coastal and regional atmospheric chemistry modeling? Are there variations in oceanic boundary conditions in northern and central California vs. the southern part of the state? What physical and chemical changes occur as a parcel of air moves from off-shore, through the shore zone, and inland?

Climate change and air quality problems have both global and regional scale aspects that interact through atmospheric transport. Critical uncertainties remain in our understanding of these interactions.

I. How best can we characterize and model air flow over coastal waters and the complex terrain of California? For example: what is the best representation of air flow in the southern San Joaquin Valley, particularly with respect to flow between the San Joaquin Valley and South Coast Air Basin versus recirculation north along the Sierra Nevada and Coastal ranges?

J. What are the major deficiencies in the representation of chemistry and meteorology in research and operational models and how can models be improved through the collection of additional measurements? What physical and chemical processes are not captured well by available models? Is there an optimum grid resolution to capture all of the relevant physical and chemical processes that occur?

K. What are the important transport corridors for key chemical species and under what conditions is that transport important?

L. What are the relative roles of regional (North American) sources and long range transport (from East Asia) on aerosol forcing over California?

It is expected that CalNex 2010 will be able to address each of the science questions listed above, although with differing degrees of emphasis. Prioritization of topics will occur during planning and execution of the study. The instruments that can be deployed on the various platforms and surface sites, and for how long they can be deployed, will be determined when there is clear understanding regarding the resources available for CalNex 2010. During the field study, the day-to-day deployment of the mobile platforms will determine the emphasis on particular questions.

4. Emission Inventory Assessment

Improving the quantitative understanding of the location, temporal variation, and speciation of gaseous and aerosol emissions into the atmosphere is critical to advancing the knowledge of tropospheric chemistry, transport, and transformation on a variety of spatial scales. Known or suspected inaccuracies in current emissions inventories of both anthropogenic and biogenic sources account for a substantial amount of the total uncertainty in model simulations of air quality [Jang and Fast, 2004] and climate change processes [IPCC, 2001]. Reports suggest that while some U.S. inventories are reasonably accurate (e.g., point source NO_x and SO₂: [Ryerson *et al.*, 1998]), others may have substantial errors (e.g., on-road emissions of CO: [Parrish *et al.*, 2002]; petrochemical alkenes: [Wert *et al.*, 2003]). A goal of the NOAA 2010 CalNex field study is to use ambient measurements to better constrain the emissions inventories of anthropogenic and biogenic compounds relevant to both regional air quality and climate change.

Quantitative information on the emissions from a variety of point and area sources is required to understand their relative impacts on the atmosphere, both in terms of air quality and of radiative effects from aerosol formation. In all of the diverse air basins of California a substantial fraction of the anthropogenic emissions are expected from on-road vehicles and other area sources. Many air basins also have large point source emissions, and these emissions are changing in response to changes in the energy infrastructure of the country (e.g. the expansion of biofuel production facilities). Other potentially significant anthropogenic emissions may come from off-road transport such as commercial shipping and agricultural operations. Substantial biogenic contributions to reactive VOC compounds involved in ozone and secondary organic aerosol formation are also expected. Finally, wildfires contribute sporadic, sometimes very large emissions.

Figure 4.0.1 provides an overview of the highly heterogeneous spatial distribution of anthropogenic NO_x emissions in California. The emissions are particularly concentrated in the large metropolitan Areas of Los Angeles and the San Francisco Bay area, which account for 43% and 19% of the population, respectively, but relatively smaller percentages of the NO_x emissions, 28% and 14%. Approximately 58% of the NO_x emissions come from smaller urban centers, distributed emissions along the transportation corridors connecting the cities, and from distributed sources, particularly within the California Central Valley. The potential for ozone and aerosol formation from these NO_x emissions will depend on the distribution of the emissions of other anthropogenic

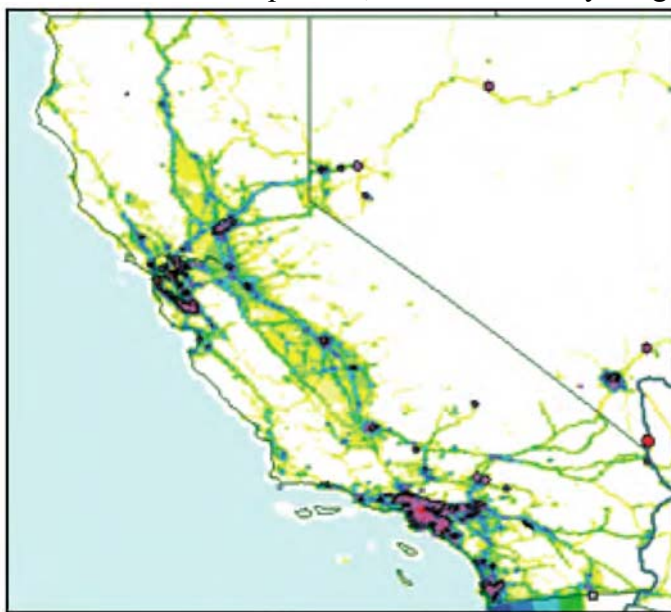


Figure 4.0.1. Spatial distribution of NO_x emissions within California. The colors reflect the relative amounts of gridded area emissions and the red circles indicate the location of large point sources. (c.f., Emissions Web Browser NOAA, National Geophysical Data Center [<http://map.ngdc.noaa.gov/website/al/emissions/>],).

and biogenic of species, particularly VOCs and ammonia.

California emissions differ from those in many other regions in that there are relatively small contributions from point source emissions. For example, in both the Los Angeles and San Francisco Bay metropolitan areas, point sources contribute about 10% to the total NO_x emissions.

The 2010 study will collect data that will help answer the following basic questions for a variety of source types. Direct emissions of a wide range of species will be studied, including aerosol (e.g., light absorbing carbon (LAC)) as well as gas-phase ozone and aerosol precursors (e.g., VOCs, NO_x, SO₂, CO, etc.) and greenhouse gases (CO₂, CH₄, etc.). The top-down approach that we use provides an independent assessment of existing inventories. This approach has six distinct features:

Measurement of ratios of co-emitted pollutants compared with predictions derived from existing emissions inventories: Most emission sources simultaneously emit more than one species. For example, all combustion processes emit CO₂ and usually CO, as well as a variety of trace species such as NO_x. Measurements of the ratios of species in the emission plume from a particular source provides a check on the inventory for that source, and may be used to identify a particular source among several possible emitters. Also, sources with differing emissions ratios, such as for (VOC/NO_x), can have substantially different impacts on the rates of photochemical transformations occurring downwind. Spatial patterns of transport and deposition of secondary photoproducts and aerosol particles may depend on ratios of direct emissions from a given source. Thus, more accurate estimates of emissions *ratios* will improve the ability to predict the various impacts of a given source on the atmosphere downwind.

Measurement of absolute amounts of emitted pollutants compared with estimates derived from inventories: Model-measurement differences can arise due to inaccuracies in the source emissions rates used as model input. Actual emissions rates can vary substantially on timescales of hours, days, seasons, or years, some of which may not be captured by a given inventory compilation. Improved estimates of the absolute amounts of emissions from a variety of different source types will minimize this potential source of model-measurement bias, and enhance the utility of models to usefully explore future “If ... then...” emissions control scenarios.

Measurements of spatial patterns of emissions compared with estimates derived from inventories: As an example, the geographic distribution of SO₂, NH₃, and VOC emissions will determine the relative contribution of anthropogenic sulfate to biogenic secondary organic aerosol for a given receptor region. The location and magnitude of aerosol light absorbing carbon (LAC) sources will influence the radiative impacts of transported emissions downwind. Regional surveys will provide data to evaluate and improve the spatial accuracy of current inventories for both air quality and climate-relevant species.

Measurement of temporal variations in emissions strength and composition compared with estimates derived from inventories: Biogenic emissions of isoprene and monoterpenes are highly dependent on sunlight, temperature, and drought conditions. Anthropogenic

emissions can also vary substantially across a range of timescales, including diurnal and day of week cycles. Variability in either can influence the chemical composition and radiative properties that result from their release to the atmosphere. *In-situ* measurements over the course of the 2010 summer field intensive will provide information on emissions variability on timescales of hours to weeks, covering the range of ambient conditions occurring during the study period.

Measurement of speciation in emissions compared with estimates derived from inventories: The impact of VOC emissions depends on the particular chemical species emitted as well as the total mass of the emissions. Some VOC species are particularly effective in photochemical ozone production and others in formation of secondary organic aerosol. The speciation of the VOC species will be determined in plumes from a diverse sample of emission sources.

Incorporation of satellite measurements in tests of inventories: Satellites are now capable of providing data useful for testing inventories, but these data have significant limitations that must be carefully evaluated for each situation in which these data are considered. For example, a satellite measurement usually represents a column average measurement, and the sensitivity of the measurement varies over the height of the column and depends significantly on ambient conditions such as aerosol loading. Where possible, satellite data will be incorporated into the emission inventory assessments.

Based upon these top-down measurement-inventory comparison approaches, we plan to address the following specific emission inventory issues and associated science questions during the 2010 intensive.

4.1. On-Road Vehicle Emissions

On-road vehicle emissions are perhaps the most important sector of the inventory, but they are difficult to quantify. These emissions are important because (1) they account for a major share of VOC, NO_x, and CO emissions; (2) they provide the majority of the most photochemically reactive anthropogenic VOCs; and (3) these emissions are localized in urban areas, which account for the majority of the nation's violations of the ozone and PM NAAQS. Accurate estimation of these emissions is difficult since it requires integration of the emission factors (e.g. grams emitted per km driven) for a diverse, constantly evolving vehicle fleet multiplied by highly variable activity factors (e.g. average km driven per unit time for each vehicle type under varying vehicle operating conditions such as the frequency of cold starts, high-load accelerations, etc.). During the 2010 field study California's on-road vehicle emission inventory will be assessed through ambient measurements.

How do current on-road vehicle emissions compare to those of the past two decades? At the present time, is the VOC to NO_x ratio in these emissions accurately represented in inventories, including diurnal and day of week cycles and spatial variations?

Traffic related sources have distinctive temporal patterns on diurnal, weekly and decadal time scales. Motor vehicles emit NO_x, VOCs, CO, CO₂ and aerosols. Compared to emissions from gasoline powered vehicles, emissions from diesel powered vehicles are relatively rich in NO_x and aerosols, particularly aerosols containing light absorbing carbon (LAC), and relatively poor in VOCs and CO. On weekdays, the emissions from gasoline powered vehicles peak during the morning and evening rush hours, whereas truck traffic tends to peak during midday. On weekends the truck traffic strongly decreases, as does the morning rush hour peak of the gasoline-powered vehicles. This weekly cycle results in lower NO_x concentrations on weekends, which have been observed at ground sites in urban areas (*Harley et al.*, 2005, and references therein) as well by satellite measurements of the NO₂ tropospheric column (*Beirle et al.*, 2003). The stronger reduction of the diesel engine emissions on weekends compared to the gasoline engine emissions leads to a maximum in the VOC to NO_x and CO to NO_x ratios on weekends. Since the first effect of NO_x emissions in an urban area is to titrate ambient ozone, average ozone levels are often higher on weekends compared to weekdays. Further, since photochemical ozone formation is hydrocarbon-limited in many urban areas, a reduction of the anthropogenic NO_x emissions can even result in higher maximum urban ozone concentrations on weekends compared to weekdays (*Harley et al.*, 2005, and references therein). Measurements in 2010 from various sites and platforms should provide further insight into diurnal and weekly patterns.

During the past two decades on-road vehicle emissions of NO_x, VOC and CO are believed to have dramatically decreased throughout the U.S., and particularly in California. Figure 4.1.1 shows this reduction for the South Coast Air Basin according to CARB's EMFAC on-road vehicle emission model. This model suggests that during the two decades of 1985-2005 the CO and VOC emissions have decreased more than a factor of two faster than the NO_x emissions. However, the modeled rate of decrease in NO_x emissions accelerated after 2000, and will approximately equal the rate of decrease of the CO and VOC emissions by about 2010.

The CO to NO_x emission ratio predicted by the EMFAC model has been tested through direct comparisons with ambient measurements of CO and NO_x (see e.g. *Fujita et al.*, 1992). Figure 4.1.2 shows such a comparison for the emissions in Fig. 4.1.1. The 1987 ambient average is from *Fujita et al.* (1992). The 1995, 2000 and 2003 averages (*Parrish*, 2006) and the 2006 average were derived from monitoring network data. The blue triangle, which is the average ratio measured in the one WP-3D flight conducted over the Los Angeles area in spring 2002 (see Fig. 4.1.3) during the ITCT-2K2 study, agrees well with the results from the routine monitoring data. The linear fit to the five ambient averages (solid red line) indicates that over the 1987 to 2006 period the emission ratio decreased by about 5.7 %/yr. The average decrease predicted by the EMFAC model is 4.1%/yr between 1985 and 2005, which is consistent with the difference in the CO and NO_x emission decreases given in Fig. 4.1.1.

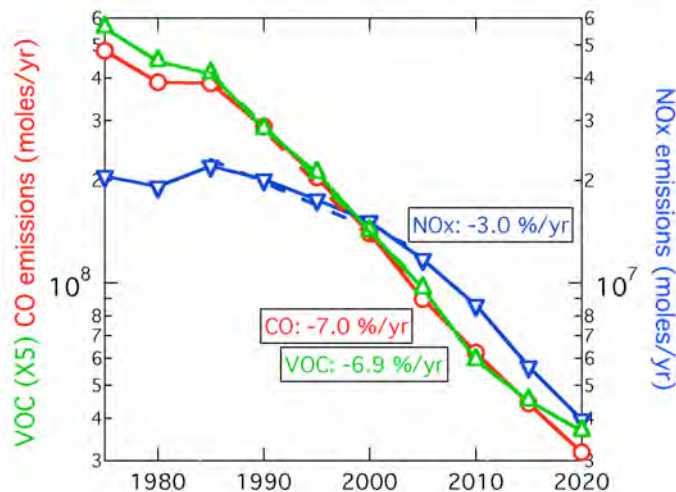


Figure 4.1.1. Logarithmic plot of VOC, CO and NO_x emissions in the South Coast Air Basin according to the EMFAC on-road vehicle emission model. The average rate of decrease for 1985-2005 is given by the slopes of the linear fits to the emissions. (The VOC emissions are given in moles C calculated from the mass of ROG emissions assuming an average ROG composition of CH₂)

Several points are notable regarding Fig. 4.1.2. The inventory suggests a smaller rate of decrease in the emission ratio than indicated by the ambient data, and suggests that the emission ratio will reach a minimum near 7.3 in 2010, followed by a slow increase through 2020. The 2006 ambient average from the monitoring data is already below this predicted minimum ratio (although the ambient CO levels have decreased to such an extent that the accuracy of the determination of that year's ambient ratio can be questioned). Judging from the experience in other urban areas (*Parrish*, 2006), the change in the ambient CO to NO_x ratio is primarily due to the decrease in CO emissions, and the slower decrease in the inventory ratio indicates that the NO_x emissions actually are not decreasing as rapidly as suggested by the inventory. The EMFAC inventory accurately approximates the observed CO to NO_x ratio up to about 2003. The data sets to be collected in 2010 will

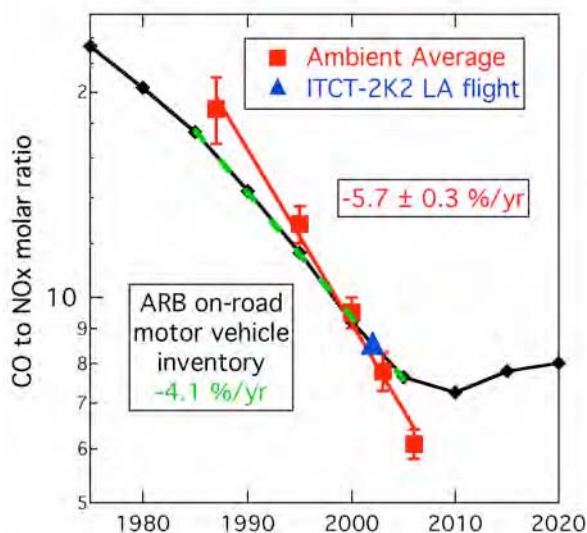


Figure 4.1.2. Comparison of CO to NO_x emission ratio for the South Coast Air Basin from the EMFAC emission model (black symbols) and ambient measurements.

determine if the EMFAC forecast minimum in the emission ratio has actually occurred by that date. Finally, it should be noted that Fig. 4.1.2 tests only the ratio of the emissions, and provides no information whether they are both accurate in absolute magnitude, or both under- or over- predicted.

Direct experimental measurements of the VOC to NO_x emission ratio would be of greater interest than the above tests of the CO to NO_x emission ratio, since the character of the ambient photochemistry is more directly related to the former. However, directly testing the VOC to NO_x emission ratio is much more difficult since a manifold of different, difficult-to-measure species constitute VOC. Fortunately, Fig. 4.1.1 indicates that the temporal dependence of the CO emissions is closely similar to that of VOC emissions, so tests of the inventory CO to NO_x ratio are expected to be simultaneous tests of the VOC to NO_x ratio. This similarity is expected since both CO and VOC are primarily emitted by gasoline fueled vehicles, and are controlled to very similar extents by catalytic converters, the primary control strategy for these emissions. During the 2010 study the relationship between these two emissions will be investigated in greater detail.

Aircraft transects of the South Coast Air Basin will provide information regarding spatial differences in the CO to NO_x emission ratio. Figure 4.1.3 presents an example flight conducted over the Los Angeles urban area in 2002. The color-coding of the flight track approximately marks regions of the urban area where different vehicle fleet compositions may be expected. In the major industrial area (red) a lower CO to NO_x emission ratio is observed (Fig. 4.1.4), which is consistent with a greater contribution of HD diesel vehicle emissions. Over the urban highway region (green and purple) a ratio close to the average flight ratio given in Fig. 4.1.2 is found. At the outskirts of the urban

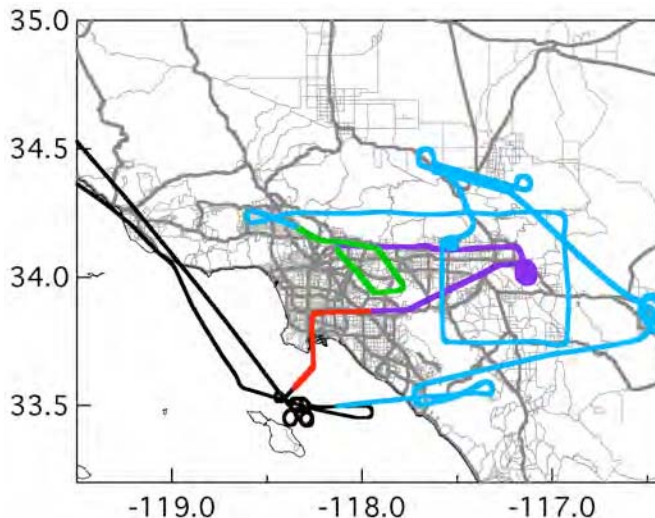


Figure 4.1.3. Map of Los Angeles urban area with 13 May 2002 WP-3D flight track. The color coding of the flight track indicates the different regions sampled: red -industrial Long Beach; purple and green –urban highway area; blue - outer urban area.

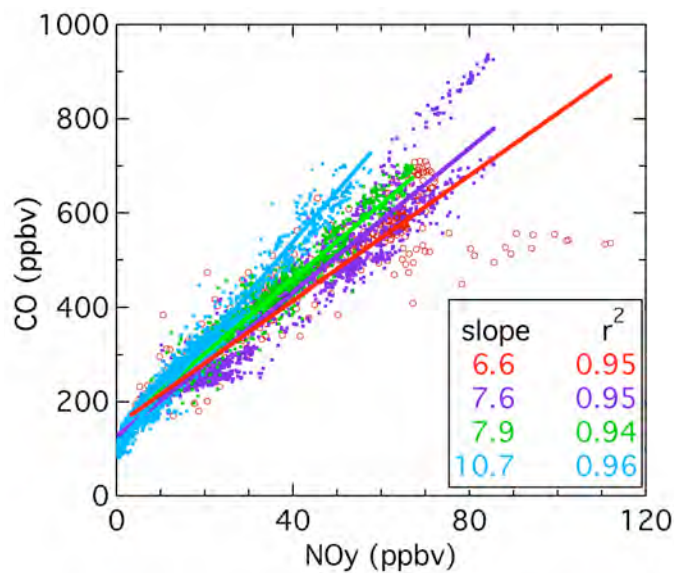


Figure 4.1.4. Correlation between measured CO and NO_y during the 13 May 2002 WP-3D flight. Colors show the data collected during the flight segments of the corresponding color.

area (blue) an even higher ratio is found, but in this region the ratio is potentially elevated above the emission ratio by removal of a fraction of the emitted NO_x before measurement.

Aircraft measurements can provide indications of variations in on-road vehicle emissions as a function of time of day. Figure 4.1.5 presents results from a top-down evaluation of mobile source emission inventories carried out in Houston and Dallas/Fort Worth. Ambient concentrations of CO, NO_y, and CO₂ were measured by NOAA research aircraft in urban emission plumes dominated by mobile sources during the 2000 and 2006 Texas Air Quality Studies. Mobile source emission ratios of CO/CO₂ derived from the aircraft data are compared with observations at a Houston highway tunnel in 2000 and with the 1999 and 2005 EPA National Emission Inventories. The observations and inventories both show approximately 50% decreases in mobile source CO emissions over this 6-year period. Observed estimates of mobile source CO emissions in either year are 2 to 3 times smaller than the corresponding EPA inventory values. Both the aircraft and tunnel measurements indicate a substantial increase in the CO/CO₂ emission ratio from the early afternoon to the evening measurement periods. This increase is attributed to the larger fraction of gasoline-fueled vehicles in the fleet during the evening commuter traffic maximum.

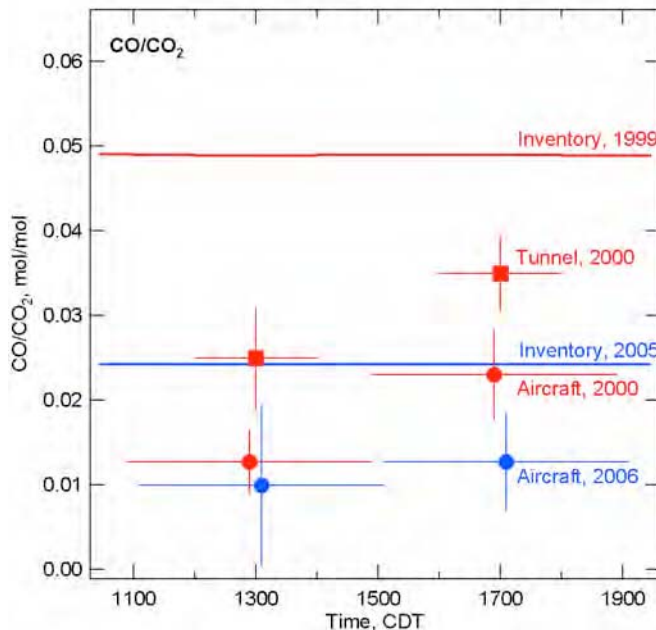


Figure 4.1.5. Observations of urban CO/CO₂ ratios over Houston and Dallas/Fort Worth derived from aircraft measurements (circles) and from a roadside monitor (squares) compared to the emission ratios of CO/CO₂ predicted by the MOBILE6 emissions model for motor vehicles (solid lines) in 1999/2000 (red) and 2005/2006 (blue).

Baumgardner et al. (2002) have analyzed the relationship between emissions of light absorbing carbon (LAC) and carbon monoxide in urban areas by comparing measurements from two sites in Mexico City and five urban areas in Germany. They found that the most important factors that affect the LAC to CO relationship are the ratio of diesel to gasoline usage and the combustion efficiency of vehicles in a particular urban area. Measurement of the LAC/CO ratio as well as the PM_{2.5} to CO ratio from the WP-3D aircraft and ground sites throughout California promises a further important evaluation of emission inventories.

Satellite-borne measurements have been used to map the spatial distribution of NO_x emissions on a global scale (*Martin et al.*, 2003). Studies have shown that satellites can document long-term emission trends, such as the strong increase in NO_x emissions due to the industrialization in China (*Richter et al.*, 2005), and can capture the weekly cycles of emissions over urban regions (*Beirle et al.*, 2003). Satellite column measurements and plume sampling by aircraft have demonstrated substantial reductions in atmospheric NO_x levels in response to emission controls

at eastern U.S. power plants (Frost *et al.*, 2006; Kim *et al.*, 2006). These previous studies examined satellite-retrieved NO₂ columns over large regions averaged over relatively long time periods (seasonal to annual). Our ongoing work has demonstrated that the footprints of current satellite-borne instruments like SCIAMACHY and OMI are small enough to examine the NO_x emission strength of isolated power plants and large metropolitan areas in the western United States (Fig. 4.1.6; Kim *et al.*, manuscript in preparation). Year-to-year

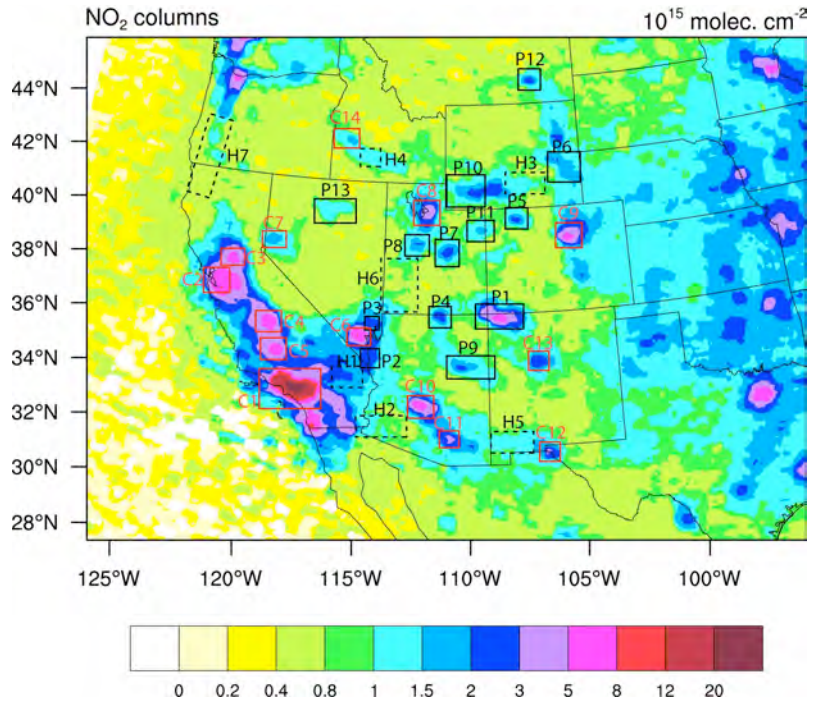


Figure 4.1.6. Boxes highlighting plumes from power plants (P), cities (C), and interstate highways (H) overlaid with summer 2005 average satellite NO₂ columns from the satellite-borne SCIAMACHY instrument.

trends in NO_x emissions from such sources can be evaluated with SCIAMACHY, which has operated since mid-2002. The daily frequency of OMI NO₂ column observations provides the possibility of detecting weekday vs. weekend emission variations for a particular year (e.g. Fig. 4.1.7).

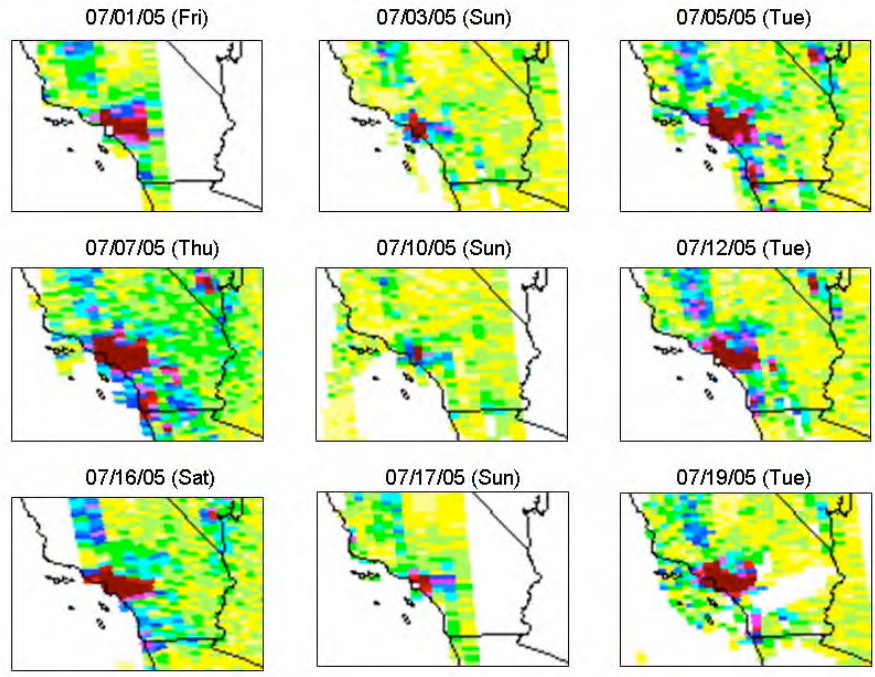


Figure 4.1.7. Snapshots of NO₂ columns in Los Angeles, CA observed by the satellite-borne OMI instrument during July of 2005.

As part of the 2010 field study we plan to compare satellite-derived and model-calculated NO₂ columns over California's urban areas. Satellite-based observations of the NO₂ columns over urban areas provide an opportunity to evaluate the integrated emission strength of the various urban source categories. Using the satellite

retrievals and model configurations that have given the best agreement for NO₂ columns over isolated power plants in the western U.S., we can use satellite-model comparisons of columns

over California's urban areas to assess the urban NO_x emission inventories.

The satellite data will also allow examination of the temporal variability of NO_x emissions over California on both long-term and weekly time scales. The long-term trend in the satellite NO₂ columns over California's urban areas will test emission trends predicted by emission inventories for those cities. The multiyear control program carried out in California and the rest of the U.S. has resulted in significant decreases in NO_x emissions from gasoline-powered vehicles (Ban-Weiss *et al.*, 2008; Bishop and Stedman, 2008). However, the NO_x emissions from diesel-powered vehicles have not decreased to the same extent as those from gasoline-powered vehicles. The satellite NO₂ column trends over California's urban areas should reflect emission reductions from individual mobile source categories and their relative contribution to the overall urban NO_x emissions. Clear differences between weekday and weekend urban NO_x emissions resulting primarily from motor vehicle use patterns have been documented by in-situ (Harley *et al.*, 2005) and satellite methods (Beirle *et al.*, 2003). We will evaluate whether weekly cycles in satellite NO₂ columns over California's urban areas exhibit the expected day-of-week changes in NO_x emissions. Because of differential control of gasoline and diesel vehicle emissions, the weekly cycle in urban NO_x emissions is predicted to have changed over the past decade (Harley *et al.*, 2005). We will look for evidence of annual changes to the weekly cycles in satellite NO₂ columns over California's urban areas.

References:

- Ban-Weiss, G. A., et al., 2008. Long-term changes in emissions of nitrogen oxides and particulate matter from on-road gasoline and diesel vehicles, *Atmos. Environ.*, **42**, 220-232.
- Baumgardner, D., G. Raga, O. Peralta, I. Rosas, T. Castro, T. Kuhlbusch, A. John, and A. Petzold, Diagnosing black carbon trends in large urban areas using carbon monoxide measurements, *J. Geophys. Res.*, 107, doi:10.1029/2001JD000626, 2002.
- Beirle, S., U. Platt, M. Wenig, and T. Wagner, 2003, Weekly cycle of NO₂ by GOME measurements: a signature of anthropogenic sources, *Atmos. Chem. Phys.*, 3, 2225-2232.
- Bishop, G. A., and D. H. Stedman, 2008. A decade of on-road emissions measurements, *Environ. Sci. Technol.*, **42**, 1651-1656.
- Fujita, E.M. et al., 1992. Comparison of emission inventory and ambient concentration ratios of CO, NMOG, and NO_x in California's South Coast air basin. *J. Air and Waste Manag. Assoc.*, 42, 264-276.
- Frost, G.J., et al., 2006. Effects of changing power plant NO_x emissions on ozone in the eastern United States: Proof of concept, *J. Geophys. Res.*, **111**, doi:10.1029/2005JD006354.
- Harley, R. A., L. C. Marr, J. K. Lehner, and S. N. Giddings, 2005. Changes in motor vehicle emissions on diurnal to decadal time scales and effects on atmospheric composition, *Environ. Sci. Technol.*, **39**, 5356-5362.
- Kim, S.-W., et al., 2006. Satellite-observed U.S. power plant NO_x emission reductions and their impact on air quality, *Geophys. Res. Lett.*, **33**, doi:10.1029/2006GL027749.
- Martin, R. V., et al., 2003. Global inventory of nitrogen oxide emissions constrained by space-based observations of NO₂ columns, *J. Geophys. Res.*, **108**, D17, 4537, doi:10.1029/2003JD003453.
- Parrish, D.D., 2006, Critical evaluation of US on-road vehicle emission inventories, *Atmos. Environ.* 40, 2288–2300.

Richter, A., et al., 2005. Increase in tropospheric nitrogen dioxide over China observed from space, *Nature*, **437**, 129-132.

4.2. Off-Road Mobile Emissions: Rail Transport

As on-road vehicle emission controls become increasingly effective, emissions from off-road vehicles constitute an increasingly large fraction of the total, so the proper inventorying of these emissions becomes increasingly important. Investigating rail transport is particularly important for two reasons. First, locomotive emissions are presently uncontrolled, and are believed to make significant contributions to total emissions of NO_x and PM in both urban and rural areas. Second, California is committed to reducing the emissions associated with goods movement to 2001 levels by 2010, and to reducing diesel PM risk to 85% below the 2000 level by 2020. Tracking progress toward these ambitious goals can only be accomplished through accurate off-road mobile emission inventories.

The spatial distribution of rail lines and highways in California provides an ideal opportunity for quantifying rail transport emissions and comparing those emissions to on-road vehicle emissions. Figure 4.2.1 shows the major highways and rail line to the northwest of Los Angeles. This is a very sparsely populated region, so the only significant emissions are those associated with the transportation corridors (see Fig. 4.0.1). WP-3D aircraft transects across the two interstate



Figure 4.2.1: Location of major interstate highways (yellow lines) and a section of the major Union Pacific rail line from Los Angeles to the Midwestern U.S. (black line). The black rectangle in the inset indicates the approximate area covered in the larger figure.

highways and the rail line under appropriate wind conditions will allow the quantification of emissions from both on-road and rail traffic under very similar meteorological conditions. Analysis of the measurements will provide direct determinations of the NO_x/CO₂ and PM/CO₂ emission ratios from these two major source categories, and allow a comparison with the ratios included in emission inventories. The instruments on the NOAA WP-3D aircraft will allow separate determinations of total PM and light absorbing carbon (LAC).

The detailed information derived from only a few aircraft transects will be combined with more systematic emission information to place the rail emissions in the context of overall emissions. First, the total NO₂ column measured by satellite can provide information regarding the total railroad NO_x emissions in the region identified in Figure 4.2.1, which can be directly compared with the absolute emissions included in the inventory. Second, combining the information on rail emissions, including the LAC/CO₂ emission ratio, with more general information on urban emissions as described in the preceding section, will allow the determination of the relative contribution of rail emissions to total urban emissions.

4.3. Point Source Emissions: Emerging Industries

As discussed in Section 2.4, there is a concerted effort underway to increase the production of biofuels (principally ethanol and biodiesel) to the point that they can make a significant contribution to the nation's total energy production. Such a production level will require the construction and operation of a new set of industrial facilities. These facilities include bio-refineries, which carry out the fermentation process that directly produces ethanol, and the plants that perform the transesterification process on the vegetable oil feedstock, that produces methyl esters (the chemical name for biodiesel) and glycerin, a byproduct that can potentially be used in soaps and other products. Very little is known concerning the emissions from these facilities. During the 2010 study we plan to sample the emission plumes from whatever facilities are in operation in California at that time. The goal is to provide an overview on these emissions, and to provide an early warning of any potential emerging air pollution impacts.

4.4. LLGHG Emissions: CH₄, Halocarbons

Are anthropogenic emissions of methane and halogenated species accurately inventoried?

As illustrated in Fig. 1.1, methane (CH₄) and halocarbons make substantial contributions to the atmospheric radiative forcing that drives global climate change. The atmospheric concentrations of these gases are much lower than that of CO₂, but they much more effective climate change agents on a per molecule basis. Table 4.4.1 gives the global warming potential (GWP) for several long-lived greenhouse gases. The GWP is a measure of the global warming effectiveness of each species compared to CO₂ and considers both the radiative properties and the atmospheric lifetime of the species.

Table 4.4.1. Properties of some long-lived greenhouse gases

Gas	GWP	Lifetime (years)
CO ₂	1	NR
CH ₄	25	12
N ₂ O	298	114
HFC-23	14,800	270
HFC-134a	1430	14
HFC-152a	124	1.4
CF ₄	7390	50,000
SF ₆	22,800	10,000

A great deal of experience in the quantification of criteria pollutants (CO, VOC, NO_x, SO₂) has been accumulated during the past few decades, but development of emission inventories for long-lived greenhouse gases (CO₂, CH₄, N₂O and a wide variety of halogenated species) is a relatively recent effort. Yet, establishing accurate emission inventories for these species is required to track progress toward achieving the ambitious goals that California has set: reduction of greenhouse gas emissions to 2000 levels by 2010, to 1990 levels by 2020, and to 80% below 1990 levels by 2050. This section discusses the guidance that ambient measurements can provide for quantifying urban emissions of methane as well as a large number of halogenated species.

Aircraft transects of California's urban areas can provide information regarding the magnitude and spatial variability in the emissions of a variety of greenhouse gases relative to the CO₂ or CO emissions. The emissions of CO₂ provide a useful reference, because they are relatively easy to estimate from total fuel use since nearly all of the carbon in the fuel is emitted as CO₂. The emissions of CO provide another useful reference since this gas is easily measured even from an airborne platform, but this reference has the disadvantage that CO emissions from the predominate urban source, on-road vehicles, is decreasing rapidly (e.g. Parrish, 2006). Figure 4.1.3 presents an example flight conducted over the Los Angeles urban area on 13 May 2002.

During that flight continuous measurements were made of CO₂ and CO concentrations, and a large number of whole-air samples were collected and analyzed to provide concentration measurements for the long-lived greenhouse gases listed in Table 4.4.2.

Table 4.4.2. Measured correlations of some long-lived greenhouse gases with CO₂ and CO.

GHG	Slope vs. CO ₂ (pptv/ppmv)	r	Slope vs. CO (pptv/ppbv)	r
CH ₄	8800 ± 900	0.92	460 ± 40	0.92
CFC-12	1.83 ± 0.34	0.80	0.090 ± 0.015	0.82
CFC-11	0.53 ± 0.13	0.69	0.028 ± 0.008	0.62
HCFC-22	19.8 ± 2.2	0.91	0.97 ± 0.12	0.89
HFC-134a	6.45 ± 0.44	0.96	0.327 ± 0.017	0.98
HCFC-141b	2.28 ± 0.31	0.87	0.126 ± 0.018	0.85
HCFC-142b	0.60 ± 0.07	0.90	0.030 ± 0.003	0.90
CFC-113	-0.15 ± 0.05	-0.54	-0.007 ± 0.003	-0.57
CH ₃ CCl ₃	0.57 ± 0.07	0.88	0.029 ± 0.004	0.85
Halon-1211	0.052 ± 0.008	0.83	0.0025 ± 0.004	0.82
Halon-1301	0.036 ± 0.013	0.55	0.0014 ± 0.007	0.46
HCFC-123	0.096 ± 0.028	0.63	0.0054 ± 0.0015	0.64

The correlations of two greenhouse gases with CO₂ (Fig. 4.4.1) measured over Los Angeles on the on 13 May 2002 flight provide examples of the determination of the Los Angeles urban area emissions of those gases relative to CO₂. Table 4.4.2 gives the slopes of the correlations for all of the long-lived greenhouse gases measured on that flight.

The slopes of the correlations with CO₂ given in Table 4.4.2 allow the calculation of the contribution of these two gases to the total greenhouse gas emissions for this urban area relative to the CO₂ contribution. The calculation is the product of the correlation slope, the GWP for the gas (given for some example species in Table 4.4.1), and the ratio of the molecular weight of the gas to that of CO₂. This last term is required because GWP is calculated on a mass, not a molar, basis. For the two example gases illustrated in Fig. 4.4.1, CH₄ and HCF-135a, the contributions are 8% and 1.9% of the CO₂ contribution, respectively.

The above results can be placed in the context of the total greenhouse gas emission inventory for California. Figure 2.1 summarizes that inventory. Imports of electricity represents about 10 of the 83% contribution from CO₂. Assuming that the Los Angeles CO₂ emissions are representative of the state, then urban emissions of CH₄ and HCF-135a contribute approximately 6% and 1.4% of the total inventory.

These numbers appear to be in reasonable accord with those in Fig. 2.1, but this agreement may be misleading, at least for CH₄. The emissions of CH₄ are believed to be dominated by agricultural activities and landfills, sources that are certainly under-represented in the Los Angeles area compared to the state as a whole. This may indicate that urban emissions of CH₄ make a larger contribution than currently included in the inventory. The 1.4% contribution of HCF-135a is 40% of the total from high GWP gases in Fig. 2, which is in exact agreement with the HCF-135a contribution in Table A-4 of *Bemis and Allen (2005)*.

During the 2010 study, we plan to conduct similar measurements throughout California. Particular emphasis will be placed on quantifying agricultural emissions of CH₄ and N₂O as well as the urban and industrial emissions illustrated here.

References:

Bemis, G., and J. Allen, 2005, Inventory of California Greenhouse Gas Emissions and Sinks: 1990 to 2002 Update, Energy Commission, Sacramento, CA, CEC-600-2005-025.

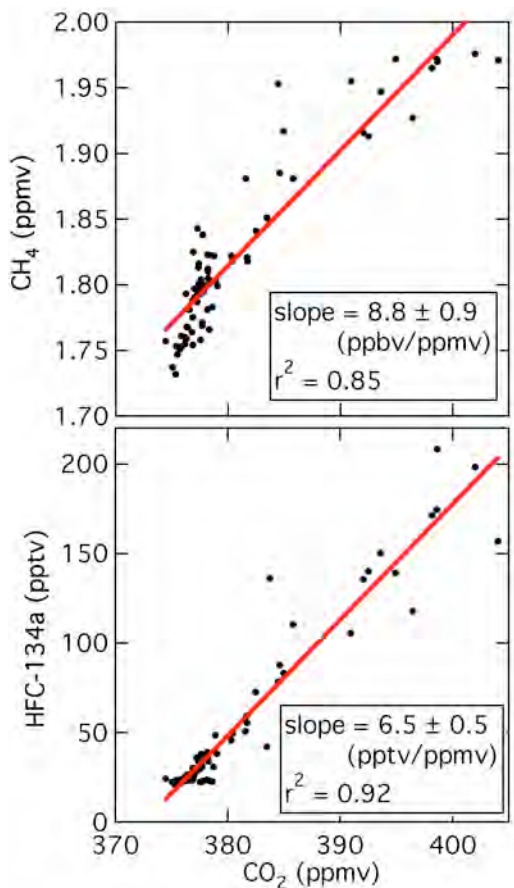


Figure 4.4.1. Correlation between two long-lived greenhouse gases and CO₂ measured on an aircraft flight over the Los Angeles metropolitan area.

4.5. Agricultural and Biogenic Emissions – CH₄, N₂O, Ammonia, VOC

In addition to the anthropogenic emissions discussed in several sections in this section, there are important biogenic emissions, both from natural ecosystems and from agricultural operations, of greenhouse gases (CH₄, N₂O) and aerosol (ammonia) and ozone (VOC) precursors. Some of these emissions will be tested through ambient measurements, specifically:

Methane and Nitrous Oxide: Methane (CH₄) and nitrous oxide (N₂O) are important greenhouse gases that have significant sources in California, both from agriculture and urban and industrial sources. We have had only limited experience in the measurement of these two species from the WP-3D aircraft – canister measurements of CH₄. During CalNex 2010 we are looking into the possibility of implementing fast-response, continuous measurements of both of these species aboard the NOAA WP-3D platform. If implemented, we will compare the observations to the emissions data available for these species.

Ammonia: In some regions of the United States, particularly California, secondary aerosol formation of ammonium nitrate can account for a significant fraction of the fine particle mass. Ammonium nitrate aerosol is formed from the reaction of gas-phase ammonia (NH₃) and nitric acid (HNO₃). Anthropogenic emissions of NH₃ and NO_x (NO + NO₂), which is oxidized to form HNO₃, can result in elevated ammonium nitrate levels. Fast-time response airborne measurements of ammonia (NH₃) will be made during CalNex 2010 aboard the NOAA WP-3D aircraft with a CIMS technique [Nowak *et al.*, 2007]. These fast-time response measurements contain information about NH₃ emissions from both area and point sources. Sources of NH₃ in California include agricultural activity, automobiles and likely industrial facilities. We will compare the NH₃ observations to the limited NH₃ emissions data available in most inventories, such as the Environmental Protection Agency (EPA) National Emission Inventory of 1999 (NEI99v3) [Frost *et al.*, 2006].

Biogenic VOC: Isoprene is a highly reactive, biogenic VOC emitted from deciduous trees. When biogenic emissions are mixed with pollution NO_x, they contribute to the photochemical formation of ozone. Isoprene emissions are significant in California, particularly over forested regions, but also over urban areas with significant tree cover. These emissions must be accounted for in air quality models. In this project we intend to evaluate the emission inventories through airborne data collected from the NOAA WP-3D aircraft.

Airborne measurements of isoprene will be made during CalNex 2010 by proton-transfer-reaction mass spectrometry (PTR-MS), and air samples collected in stainless-steel canisters analyzed post-flight using gas chromatography. The results from these two measurements have been compared for several missions and are generally found to agree within ±20% [de Gouw *et al.*, 2003; de Gouw and Warneke, 2007]. The fast-response measurements of isoprene contain information about isoprene emissions on spatial scales of 1-10 kilometers, and we will investigate how well they can be explained using existing emissions inventories.

Two methods will be used to evaluate the emission inventories. First, the inventories will be implemented into the FLEXPART transport model, which is then used to calculate isoprene mixing ratios at the aircraft location after varying transport times. The location- and time-specific emissions are calculated using the temperature and photoactive radiation (PAR) from the ECMWF meteorological fields that are used in FLEXPART to calculate the transport. Second,

the emissions of isoprene can be estimated directly from the measured mixing ratios, the boundary-layer height and the lifetime due to reactions with OH. This second method uses the temperature and PAR measured onboard of the aircraft to calculate the location- and time-specific emissions from the inventory. The analysis will be extended to other parts of the country using data from the southeastern U.S. obtained during SOS 1999, from eastern Texas during TexAQS 2000 and 2006, and from the northeastern U.S. during ICARTT 2004.

4.6. Sulfur Emissions in California – DMS, Industrial, On-road Vehicles

Are sulfur emissions from marine and land sources accurately inventoried in California?

The understanding of sulfur emissions and their atmospheric effects are poorly understood in California. Modeling for coastal southern California indicates that inventories lack a major source of sulfate aerosol precursors. Several hypotheses have been proposed to account for this missing source: 1) natural DMS emissions from the warm and shallow oceanic waters in southern California, 2) marine vessel emissions including maritime shipping and naval warships, and 3) transport from sources in Mexico or even trans-Pacific transport in Asia. Sulfur emissions, regardless of source or chemical form, are precursors to sulfate particles, which contribute to the aerosol burden. Sulfur emissions enter complex atmospheric chemistry cycles, and can substantially influence the cloud albedo and thus affect climate.

One goal of the 2010 field study is to improve our understanding of the sulfur budget in California, and particularly the emissions in the state and from the marine, near-coastal environment. In preparation for this work, data from the one aircraft flight conducted over the Los Angeles Basin during the ITCT 2K2 study is reviewed here in some detail. The flight track is shown in Fig. 4.1.3.

DMS Data: Generally the DMS concentrations observed in 2002 were moderate to low. Figure 4.6.1 shows all of the DMS measurements from whole air samples collected in canisters during all of the 2002 flights. DMS was also measured by PTR/MS continuously on the aircraft. Some of the highest measured concentrations are discussed in *de Gouw et al.* [2003]. Relatively higher concentrations were observed over cooler water to the north. Consistent with other work, DMS emissions are relatively high from cold, nutrient-rich, upwelling waters, which would suggest that the warm and shallow oceanic waters in Bight of Southern California (probably nutrient-poor?) would not be a strong DMS source. The limited data taken at low altitude off the coast from L.A., shown in more detail in Fig. 4.6.2, are consistent with this suggestion.

SO₂ Data: Figure 4.6.3 shows the SO₂ measurements made on the 13 May 2002 flight. Winds were generally northwesterly (onshore)

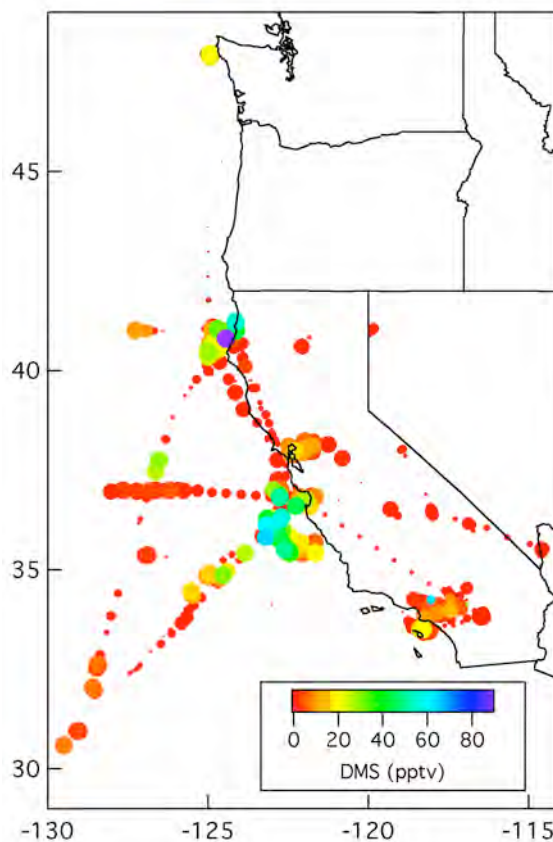


Figure 4.6.1. All 2002 measurements of DMS measured from the canisters collected on the NOAA WP-3D flights. The color indicates the DMS concentrations. The symbols are sized according to altitude, with the larger symbols at lower altitude. The data have been sorted so that the highest concentrations are plotted last (i.e. so the higher concentrations are more visible in the plot.)

during the early part of the flight and northeasterly (offshore) during the later part of the flight. Features of note:

- SO₂ concentrations in air over the ocean (both during onshore and offshore flow) were quite low.
- There were significant SO₂ sources throughout the LA urban area.

Sulfate Data: The NOAA WP-3D aircraft made sulfate measurements at 2.5-minute resolution (i.e. about 15 km spatial resolution.) Figure 4.6.4 shows those results. Features of note:

- In onshore flow during the early part of the flight, concentrations were low (only one measurement – 0.35 µg/m³).
- In contrast to SO₂, sulfate concentrations in offshore flow near the end of the flight were significant (five measurements – 0.92 µg/m³ average).
- Sulfate appears to be dominated by SO₂ sources throughout the LA urban area.

SO₂ Emission Inventory Tests: For testing emission inventories it is useful to compare ambient concentrations of co-emitted species. Continuous 1-second average measurements of CO, CO₂, SO₂ and NO_y provided 100m horizontal resolution. Figure 4.1.3 shows the WP-3D flight track for 13 May 2002 with four separate segments coded by different colors. The relationships between CO, CO₂, and SO₂ are shown color-coded for the separate flight segments in Fig. 4.6.5.

The first segment (red points) traversed the more industrialized area of Long Beach and Los Angeles. The emissions are relatively rich in CO₂ and SO₂ as expected from industrial point sources in that area. These point sources account for the SO₂ plumes observed with concentrations in the 10 to 40 ppbv range. These are clearly combustion sources because SO₂ and CO₂ are both elevated in these plumes.

The concentrations of many criteria pollutants over most of the LA regions are dominated by on-road vehicle emissions. The second (purple points) and fourth (blue points) flight segments

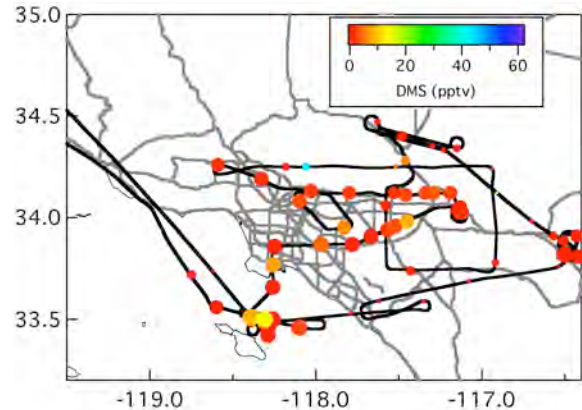


Figure 4.6.2. DMS data from Fig. 1 from the 13 May 2002 flight.

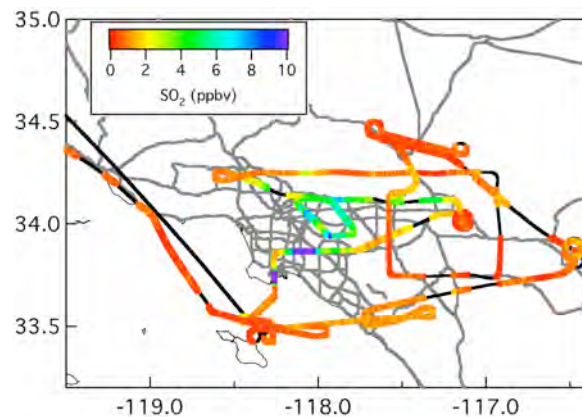


Figure 4.6.3. SO₂ data from 13 May 2002 flight.

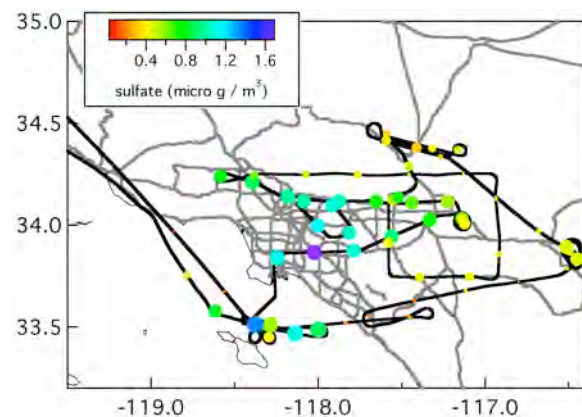


Figure 4.6.4. Sulfate data from 13 May 2002 flight with symbols sized as in Fig. 1.

traverse areas with a CO to CO₂ emission ratio of 1.5 to 2% (slopes of 15-20 in the upper panel of Fig. 4.6.5), which is characteristic of the 2002 vehicle fleet when dominated by light-duty vehicles. The lower overall slopes along the green and red flight segments indicate increasing importance of heavy-duty diesel vehicle emissions. It is important to note that vehicle emissions (at least in 2002) were a significant source of SO₂ as indicated by the relationships in lower two panels of Fig. 4.6.5. SO₂ concentrations in the 5 to 10 ppbv range are observed in regions of heavy vehicle traffic. It is clear that in LA, in 2002, on-road vehicle emissions were a significant source of SO₂ and thus sulfate. It should be noted that these data were collected before the most recent low-sulfur diesel fuel regulations were implemented.

A quick, zero order test of the SO₂ emission inventory can be carried out through several assumptions based on the correlations shown in Fig. 4.6.5:

- The median slope of SO₂ to CO = 0.008 represents the molar ratio of the SO₂ to CO emissions in the South Coast Air Basin.
- This median slope represents SO₂ emissions from vehicles and other area sources.
- The area sources of CO in the basin = 4074 tons/day in 2005, which implies the area sources of SO₂ in the basin are 74 tons/day.
- The inventory gives total SO_x emissions in the basin as 43 tons/day, but 88% of SO_x emissions statewide are from stationary sources and ships, which implies that in the inventory for the basin, only about 5 tons/day of SO_x are emitted by area sources.

This comparison suggests that the area sources of SO_x in the South Coast Air Basin are underestimated by a factor of about 15 in the inventory.

Preliminary Findings: Data from a single flight in the Los Angeles area suggests that:

- DMS is not likely an important contributor to sulfate in the LA area.
- Sulfate in the LA area is largely of local origin. The sulfate comes from local point sources with a significant contribution from the on-road vehicle fleet and other area sources, which is underestimated by a factor of 15 in the emission inventory.

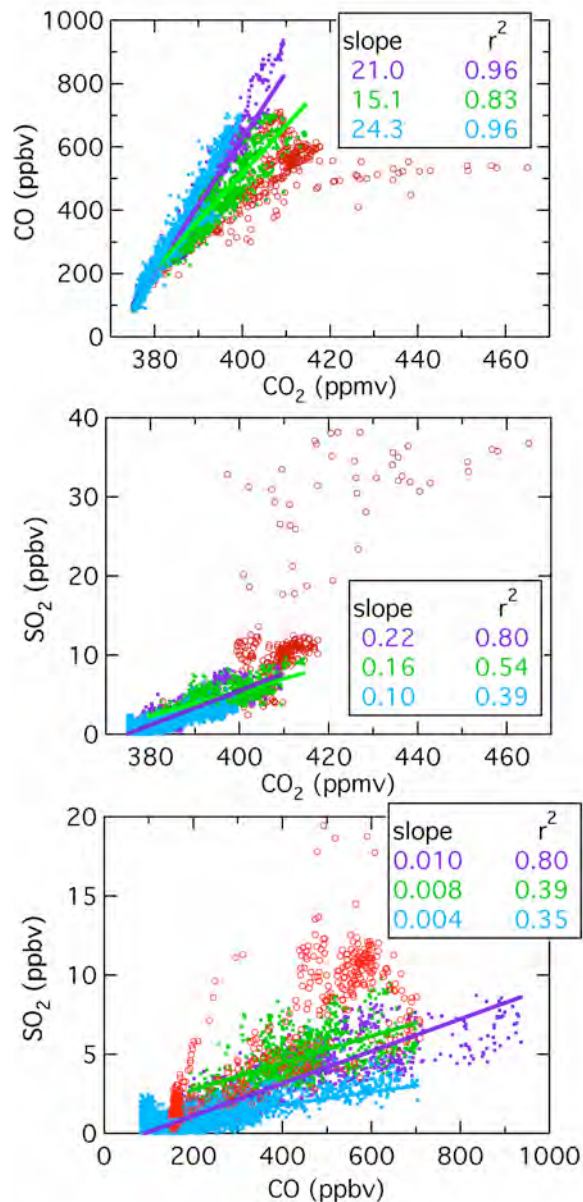


Figure 4.6.5. Relationships between measured concentrations of CO, CO₂ and SO₂ for the color-coded segments of the 13 May 2002 flight (Fig. 4.1.3). Slope and r² of linear least squares fits are given in

- No significant impact of marine vessel emissions on sulfate was obvious in this limited data set.

Work to be carried out in 2010:

- Conduct WP-3D flights to test if the point source inventory for LA can account for the SO₂ to CO₂ emission ratios observed in plumes from the industrial regions of Los Angeles.
- Examine the on-road vehicle inventory for 2002 and 2010 to test if they account for SO₂ emissions from this source. In 2002 SO₂ emissions were about 0.8% of CO emissions by molar ratio (i.e. about 1.8% by mass). Determine if the on-road vehicle emissions of SO₂ have decreased in response to controls of sulfur in diesel fuel.
- Test marine vessel emission inventories of sulfur through plume sampling in the shipping lanes in ports and coastal waters of California.
- Conduct flights to quantify the import of sulfur species into coastal southern California to determine if transport of Mexican or Asian emissions is important under some conditions.

Reference:

de Gouw, J. A., C. Warneke, D. D. Parrish, J. S. Holloway, M. Trainer, and F. C. Fehsenfeld, Emission sources and ocean uptake of acetonitrile (CH₃CN) in the atmosphere, *J. Geophys. Res.*, 108(D11), 4329, doi:10.1029/2002JD002897, 2003.

4.7. Ship emissions

Commercial marine vessel emissions in ports and coastal waters of California will be investigated aboard the NOAA vessel Ronald H Brown (RHB) during CalNex 2010. A previous study in the Houston Ship Channel (HSC) in 2006 demonstrated that exhaust emissions from commercial marine vessels (CMV: cargo ships; tankers; tugs; ferries; fishing boats) can be effectively sampled with the complement of aerosol and gas-phase instrumentation that is planned for deployment on the RHB in 2010. Those fast time response measurements combined with the logged Automated Information System (AIS) data that are constantly broadcast by all ships (greater than 300 gross tons) in 2006 provided the most extensive data set of real-time CMV emission factors currently available (Lack et al., 2008; Williams et al., 2008). Because of the intensity of CMV activity in California ports we expect to extend this data set and to sample a larger fraction of container ships and bulk freight carriers than we did in the HSC, where a large fraction of CMV were tanker ships. The use of RHB will provide a distinct advantage over other research vessels, since RHB is a flagged vessel of the U.S. government and does not require prior clearance to enter ports.

The measurements that will be made from RHB will provide mass-based emission factors for gaseous species, including NO, NO₂, SO₂, CO, CH₂O, VOCs (<C9), CO₂, and NH₃. We will also have the capability to determine mass-based emissions factors for a large number of aerosol parameters, including black carbon (BC), aerosol composition (sulfate, organic, nitrate, and ammonium), and aerosol size and mass. The measurements are typically taken very close to underway or stationary vessels (docked or anchored) so very little time (<10 minutes) for atmospheric processing has occurred. Thus the calculated emission factors are representative of emissions from the ship stacks, which is most representative of the data needed for emission inventory modeling. Further, with the anticipated more extensive data set we will explore these data for relationships useful for more accurately modeling inventories. Finally, if the state of California promulgated regulations requiring low-sulfur marine fuels are in force during the 2010 study, our measurements can provide an indication of the level of compliance since calculation of the fuel sulfur content from the mass-based SO₂ emission factor is straightforward (Lloyd's, 1995).

Under appropriate conditions of meteorology and CMV activity, measurements from RHB can be conducted downwind from target vessels to evaluate atmospheric processing of the emissions. This type of experiment was performed with excellent results during the TexAQS 2006 study. Figure 4.7.1 shows an encounter with an anchored vessel, the

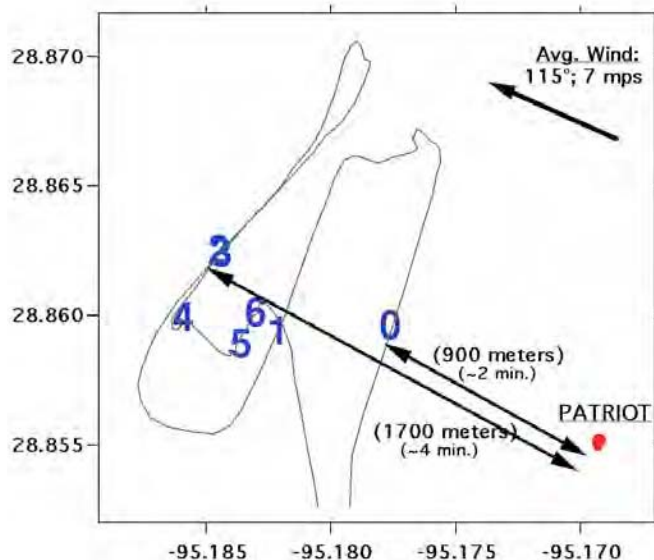


Figure 4.7.1. Cruise track of the RHB, the position of the tanker ship Patriot, wind conditions during the experiment, and the points of interception of the exhaust plume from Patriot.

tanker ship Patriot, during which RHB sampled the vessel's exhaust plume at successive downwind distances at night. This short duration experiment allowed the determination of the overall precision of the measured emission factors. Since photochemistry was absent, we expect the ratios of species in the exhaust plume to be conserved as the plume moves downwind. Figure 4.7.2 shows the emission factor determinations for the seven plume interceptions. The standard deviation of the determination of each emission factor indicates the precision that can be obtained in

a single transect. We intend to duplicate this effort, under both daytime and nighttime conditions, by taking advantage of ships at anchor offshore of the ports of Los Angeles

and Long Beach with appropriate meteorological conditions. If possible, collaboration with the P3 aircraft will allow us to extend this experiment to evaluate ship exhaust emissions processing further downwind. Under suitable conditions sampling of a selected target vessel emissions will be done in the near-field by RHB with further downwind sampling done by the P3.

Photochemical processing of ship emissions was evaluated in this manner during a previous study by the P3 aircraft (Gao et al., 2005).

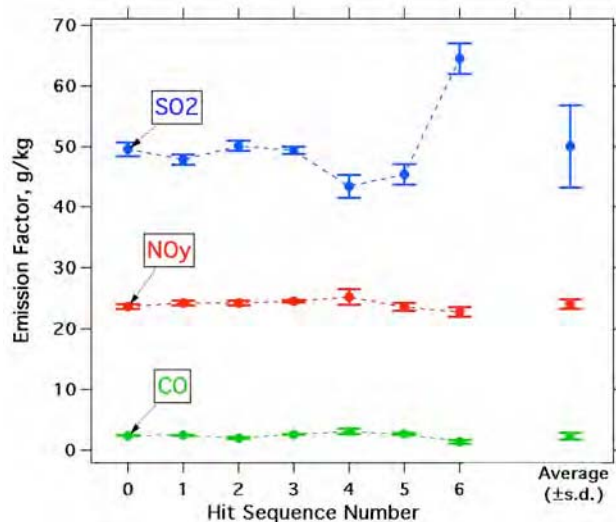
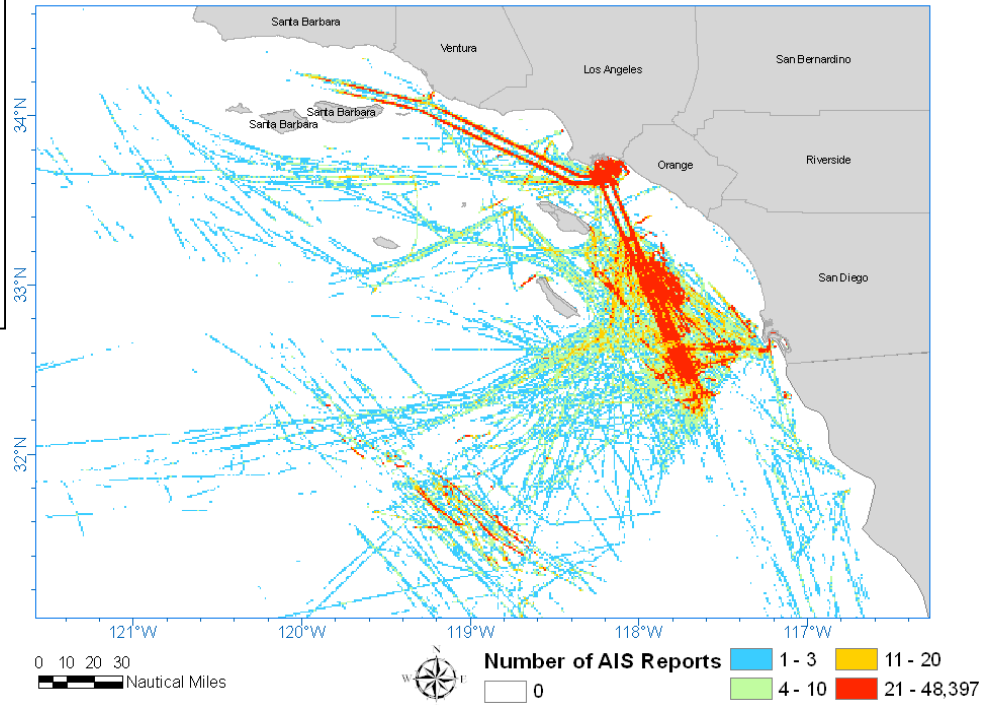


Figure 4.7.2. Emission factors for NO_y, SO₂, and CO determined from the seven interceptions of the exhaust plume from Patriot.

An extension of the above type of experiment that we plan for the CalNEX 2010 study will involve cooperation with target vessels. The logged AIS data that we acquire directly from target vessels provide a minimal set of information - name, IMO number, position, course, speed, vessel type. Some of this information must be further verified by reference to the many available ship databases, such as Lloyd's Directory. Ideally, we would like to have complete information about a target vessel when we are making the measurements. Indeed, some of this information, such as fuel type, engine load, fuel S-content, fuel consumption rate, can only be acquired at the time when the measurements are made. We intend to explore opportunities with shipping companies and ship owners to allow extensive studies of targeted vessels that will provide detailed emission data as functions of fuel type, ship speed and engine load, engine type (medium speed versus slow speed engines), and others. The need for these types of studies is clear from an examination of the literature on CMV emission factors. The hallmark of these data sets, and ours as well, is the large variability observed in emissions of virtually all measured species. This variability is difficult to capture in simple parameterizations for use in inventory modeling; thus average emission factors are used in inventory work. Unfortunately, this translates real variability in the measured data to large uncertainty in the emission inventory. It is expected that this situation can be improved with further research.

Figure 4.7.3.
 Number of AIS commercial marine vessel reports within 0.01° grid cell for August-October 2007 (plot created by C. Wang of CARB.)



Finally, we intend to evaluate the impact of pollution emissions from ships with at least three different approaches. One approach will be to make extensive measurements of ship traffic

offshore of Santa Barbara. Currently, the Santa Barbara Channel is a focal point for Asian-US CMV traffic (see Fig. 4.7.3), and has been projected to be the largest source of NO_x emissions in Santa Barbara County by 2030. For this experiment, with onshore flow we intend to make measurements both upwind and downwind of the Channel and to determine the extent of CMV traffic and the emissions from those ships. Under suitable conditions this approach will provide a direct determination of the impact of CMV emissions. A second approach will be to perform survey transits in the major ports of Los Angeles, Long Beach, and Oakland to evaluate loadings of aerosol and gaseous species in these areas. We intend to have prior discussions with the Captain of RHB, local pilots, Coast Guard VTS, and PIs on RHB to ensure the maximum benefit of this activity commensurate with the safe operation of the ship. A third approach will be to evaluate the offshore transport of pollution from coastal areas, the processing of that pollution over the water, and the return to land of those processed air masses. This type of land-sea breeze circulation pattern is common and has been shown to produce significant transformation of pollutants in Santa Monica Bay (c.f., Cass and Shair, 1984). This tracer study demonstrated that pollution emitted aloft (~300 m) in the land breeze at night was mixed to the surface of the marine boundary layer by convection over the relatively warmer water later in the night. Mass balance calculations showed that all of the tracer material emitted from the stack was brought back ashore at the surface the next morning. This circulation pattern not only provides recirculation of land-based pollutant emissions after nighttime processing over the water, but also will pick up fresh emissions from ship traffic in the region prior to transport onshore with the sea breeze. An extension of this activity will be to map the extent of pollutant transport westward over the ocean.

References.

Cass, G.R., and F.H. Shair, Sulfate accumulation in a sea breeze/land breeze circulation system, *J. Geophys. Res.*, 89, 1429-1438, 1984.

- Chen G., et al., An investigation of the chemistry of ship emission plumes during ITCT 2002, *J. Geophys. Res.*, 110, D10S90, doi:10.1029/2004JD005236, 2005.
- Lack, D. et al., Light absorbing carbon emissions from commercial shipping, *Geophys. Res. Lett.*, 35, L13815, doi:10.1029/2008GL033906, 2005.
- Lloyd's Register Engineering Services, Marine exhaust emissions research programme, Lloyd's Register of Shipping, 1995.
- Williams, E.J., B.M. Lerner, P.C. Murphy, S. Herndon, and M. Zahniser, Gas-phase species emission factors from commercial marine vessels during TexAQS 2006, manuscript in preparation, 2008.

4.8. VOC Speciation

During the CalNex 2010 field study anthropogenic VOCs and CO will be measured within and downwind from California's urban areas. The emission ratios of VOCs relative to CO and acetylene will be calculated using a method in which the ratio of a VOC to acetylene is plotted versus the photochemical age. The intercept at the photochemical age of zero gives the emission ratio. The so determined emission ratios will be compared to other measurement sets, including data from New York City and Boston, aircraft measurements from Los Angeles in 2002, and the average urban composition of 39 U.S. cities. A comparison will be made with California emission inventories. Such comparisons conducted in the past found substantial discrepancies, especially for the C₂-C₄ alkanes and most oxygenated species (*Warneke et al.*, 2007). For example, the emission inventory overestimated toluene by almost a factor of three.

4.9. Biomass Burning Emissions

Biomass burning is a major source of trace gases for the global atmosphere [Crutzen and Andreae, 1990]. In the western US these emissions are primarily associated with wild fires, which are extremely variable, occurring at largely unpredictable times. However, the warming climate in the western US is expected to lead to drier forests in the summertime, which implies an increasing importance of biomass burning emissions [Westerling et al., 2006]. Quantification of the emissions from wild fires, and investigation of the photochemical processing of the emissions can be studied in the same manner as outlined in the preceding sections for more predictable anthropogenic emission sources. During CalNex 2010 we will seek opportunities to investigate emissions from wild fires if the wild fire occurrence makes this practical. One particular focus will be the quantification of the LAC emissions, since these are particularly large in biomass burning emissions, and the new instrumentation on the WP-3D aircraft will present us with an opportunity for heretofore unavailable measurements.

References.

- Crutzen, P. J., and M. O. Andreae, Biomass burning in the tropics: Impact on atmospheric chemistry and biogeochemical cycles, *Science*, 250, 1669–1678, 1990.
- Westerling, A.L., H. G. Hidalgo, D.R. Cayan, T.W. Swetnam, Warming and earlier spring increase western U.S. forest wildfire activity, *Science*, 313, 940-943, 2006.

5. Transport and Meteorology

California presents a number of challenges to understanding and prediction of atmospheric transport pathways and mechanisms beyond those presented by previous NOAA study areas in the Southeast U.S. or Texas. The terrain and the coastline dominate the flow of air in California. The state consists of several basins divided by mountain ranges. Much of the coast is immediately mountainous, but the few areas of coastal plain are densely populated. Proper understanding of these processes is at or beyond the state of the art of regional numerical modeling. In addition, the impact of irrigation on the surface energy balance in the Central Valley is poorly represented in models. Four aspects of this transport have been selected for particular focus during CalNex 2010.

Measurements are critical to model evaluation, but an appropriate density of measurements to evaluate fine-scale models is expensive and difficult to achieve. A hierarchical observation strategy will be implemented. Wind profiling radars will provide continuous measurements of winds and daytime mixing height at several locations, setting a regional-scale context. Aircraft and ship measurements will target specific key locations for intensive and comprehensive measurements. The ship will include surface flux measurements as well as lidar winds and radiosoundings. At the larger scale, the national and global radiosonde network provide foundational measurements. The following sections provide more detailed descriptions of planned measurements.

5.1. Orographic Ventilation and Recirculation of Pollution in the Atmospheric Boundary Layer

Relevance

Orographic ventilation and recirculation of pollution in the Atmospheric Boundary Layer (ABL) have been recognized as important mesoscale transport processes in the formation of poor air quality in areas surrounded by complex topography (see, e.g., Henne et al. 2004). One such area is the Central Valley (CV) of California. Although state-of-the-art mesoscale models are capable of depicting the processes, it is not clear how accurate the simulated processes are, given the inevitable uncertainties in the physics and input parameters of the models. In addition, the conditions necessary for setting off and maintaining the processes are not well understood in terms of mesoscale and micrometeorological dynamics. We propose a combined field and modeling investigation to address these issues by taking observations within the ABL and the transition layer between the ABL and the free troposphere in the CV, and applying a numerical model to simulate and analyze the observed properties of the transport processes. In this proposed investigation, orographic ventilation and recirculation processes taking place along both the Coast Range and the Sierra Nevada slopes will be observed, simulated and analyzed. In particular, conditions for the initiation of deep dry/moist convective processes by boundary layer/slope flow transport of energy along the slopes will be analyzed and simulated.

Science Questions

Mesoscale circulation components are important in the orographic ventilation and recirculation of the ABL pollution in the CV. These components are dynamically complex because they interact with each other. Previous observational and modeling studies reveal the distinct features of these components (Bao et al. 2008). First, the low-level winds in the Sacramento Valley (SV) (Fig. 5.1.1) are characterized by the diurnal variation of the up-valley flow during the day, and

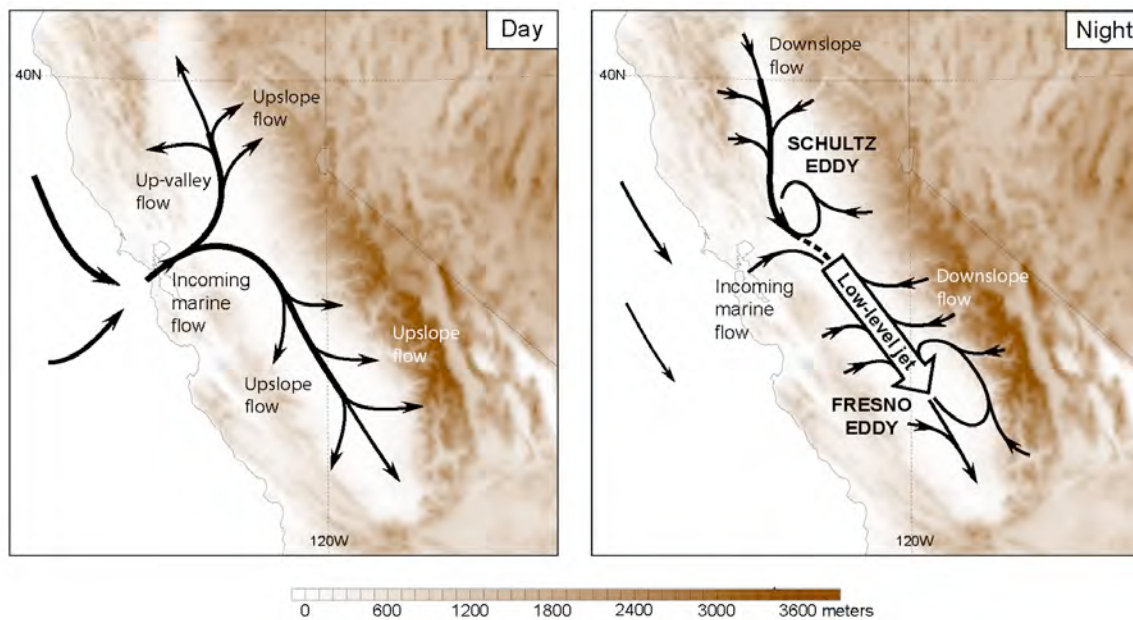


Figure 5.1.1: Conceptualization of low-level wind regimes in California associated with summertime poor air quality in the Central Valley.

the down-valley flow during the night. Second, the central CV is characterized by the splitting of the incoming flow from the San Francisco Bay area in daytime. Third, the flow in the San Francisco Bay area is characterized by the diurnal variation of the strength of the incoming flow from the Pacific Ocean that moves through the Carquinez Strait. Fourth, the flow in the San Joaquin Valley (SJV) is characterized by the incoming flow that moves towards the south, where a low-level jet typically develops at night, and interacts with the downslope flows along the foothills of the eastern side of the SJV to form the Fresno Eddy. In addition to the Fresno Eddy, interaction between the northward inflow and the nocturnal down-valley flow in the SV often leads to the formation of a counterclockwise local eddy to the north or northwest of Sacramento, known as the Shultz Eddy during the night. It remains a question whether or not these two eddies play a significant role in local pollution recirculation.

Despite the fact that significant knowledge has been accumulated on these mesoscale circulation components in the CV, questions still remain with respect to how they work together in the orographic ventilation and recirculation of the ABL pollution. The following are the important questions that we intend to address in the proposed investigation.

1. Can ABL development and transition from the valley floor to the slopes of the Coast Range and the Sierra Nevada be well-modeled using current parameterizations?

The current knowledge of the ABL development, on which the parameterizations of ABL processes in numerical weather prediction (NWP) and research models were formulated, has been mostly derived from observations obtained over flat, horizontally homogeneous surfaces. When the models are applied over complex topography (such as that surrounding the CV), the ABL parameterizations are assumed to be still valid. Some have argued that this is not a valid assumption. In our view, it remains a question as to whether the ABL mixing over steep slopes or mountain ridges can be well modeled by the parameterizations derived from the observations taken over flat land. Therefore, it is important to observe and understand the characteristics of ABL development and transition from the valley flatland to the slopes of the Coast Range and the Sierra Nevada. Atmospheric boundary layer wind profilers will be used to observe and analyze the structure of the ABL across the CV from the Coast Range to the Sierra Nevada, to determine the characteristics of turbulent mixing between the ABL and the free troposphere above the Coast Range and the Sierra Nevada mountain ridges, and to evaluate skills of the models in depicting the evolution and spatial transition of the ABL.

2. What is the role of up-/down-slope flows in the vertical ventilation and recirculation?

Up/down slope flows generated by the radiative warming/cooling of the mountain slopes of the Coast Range and the Sierra Nevada are important flow components in the CV. They enhance the pollution transport between the ABL and the free troposphere by driving ABL ventilation along slopes during daytime and re-circulating air from mountains to the valley during nighttime. During daytime the enhanced upslope transport is compensated by subsidence of air from above the ABL over the valley, while during nighttime the process is reversed. It is an objective of this investigation to assess the transport of pollution between the ABL and the free troposphere by the up-/down-slope flows. This will be achieved by the combination of observing and simulating these transport processes.

3. What is the role of up-/down-valley flows in the vertical ventilation and recirculation?

The up-/down-valley flows in the CV are unique in that they result from the exchange of “polluted” inland air and the “clean” marine air. This exchange is driven by the surface thermal contrast across the coast line and enhanced during nighttime by the nocturnal jet (particularly in the southern CV). The up-/down-valley flows supply air mass to the up-slope flows along the Coast Range and the Sierra Nevada, while during nighttime, they interact with the down-slope flows forming the Schultz Eddy in the northern CV and the Fresno Eddy in the southern CV. One objective of this investigation is to understand how the up-/down-valley flows interact with the up-/down-slope flows, and what role they play in the orographic ventilation and recirculation of the ABL pollution in the CV.

4. *What is the morphology of vertical ventilation and recirculation along the slopes of the Coast Range and the Sierra Nevada?*

In order to understand how poor air quality develops in the CV, it is important to know how pollution is ventilated and recirculated. To this end, we propose to simulate numerically the vertical transports in the CV associated with typical events of poor air quality. We will use the WRF model at high-resolution (~1 km) to enable us to assess the secondary circulation associated with the up-/down-valley and up-/down-slope flows at single mountain ranges in both the Coast Range and the Sierra Nevada. In particular, attention will be given to the roles of these flows in the overall orographic ventilation and recirculation.

5. *What are the characteristics of penetration of the ABL pollution into the free troposphere by vertical mixing and orographically enhanced pumping?*

Penetration of the ABL pollution into the free troposphere by vertical mixing and orographically enhanced pumping is a typical regional interactive process over the CV. In general, daytime radiative heating of high mountain slopes induces enhanced convection, which in turn strengthens air mass transport from the ABL to the free troposphere by the orographically enhanced pumping. This enhanced upward transport is compensated by air from the valley forming a near-surface air stream towards mountain tops. This closed circulation is reversed during nighttime as the surface radiative heating changes sign, rendering the air mass exchange between the ABL and the free troposphere in an opposite direction. The penetration of the ABL pollution into the free troposphere by vertical mixing and orographically enhanced pumping is not well documented and thus not well understood in the CV, despite the fact that a similar phenomenon has been investigated in the Alpine region. One objective of this investigation will be to assess and understand the role that the orographically enhanced pumping plays in the penetration of the ABL pollution into the free troposphere.

6. *How does entrainment of pollution from the free troposphere into the ABL affect the air quality in the CV*

As alluded to above, both the daytime compensating air mass above the CV and the down-slope flows entrain possibly polluted air from the free troposphere into the ABL of the CV. Such entrained pollution may later be recirculated both vertically and horizontally. How this process affects the development of poor air quality in the CV is not observationally documented and well understood meteorologically. Since this process involves the dynamics of entrainment at the ABL top and the nocturnal BL development over steep slopes and numerical models are known to lack skill in treating them properly, studying the process will benefit the improvement of the current ABL parameterizations in the models.

Research Approach

We propose to combine the piece-wise depiction of the real atmosphere by observations and the dynamically consistent, 4-dimensional approximation of the real atmosphere by numerical models to address the aforementioned science questions. In principle, meteorological models can provide answers for our questions regarding ventilation and pollution transport. However, it is not clear how much confidence we can put into those answers, due to uncertainties in the meteorological models. Therefore, in this section, we identify the observations and propose a field campaign that will provide the best constraints on the models and thereby can be used in their improvement. We will use an online coupled chemistry model to investigate the influence of orographic ventilation processes on the evolution of the near-surface ozone concentration. The observations taken during the proposed field campaign will be used to compare to the model simulation to identify required model. The overarching goal of this study is to better understand the orographic ventilation processes in the CV, and to evaluate and improve the skills of operational and research weather forecast models in air-quality prediction.

Planned Observations

A comprehensive suite of instruments and platforms will be deployed during CalNEX 2010. A brief description of the specific measurement capabilities and deployment strategies of these instruments follows.

Airborne ozone/aerosol lidar

A key instrument to address orographic ventilation and pollutant recirculation is the TOPAZ airborne ozone and aerosol lidar (Alvarez II et al., 2008), which will be flown on a NOAA Twin Otter aircraft. The airborne lidar will provide detailed, high-resolution 3-dimensional

measurements of the ozone and aerosol distribution over the CV, the Coastal Range, and the Sierra Nevada. Mapping out the 3-dimensional distribution of ozone and aerosol is crucial for elucidating how the up-down-slope, up-down-valley, vertical mixing, pumping, and entrainment

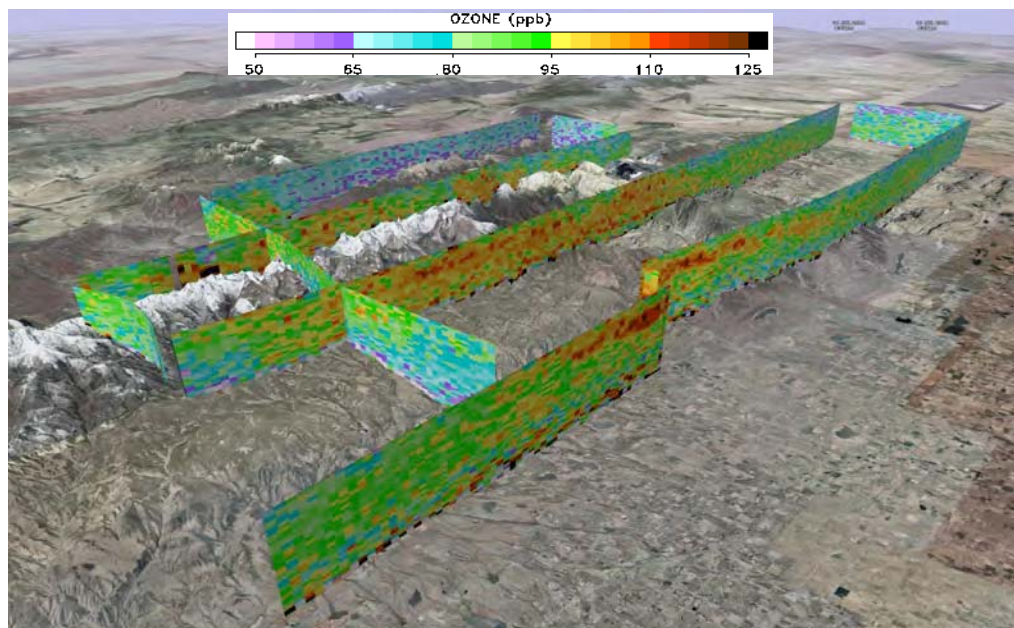


Figure 5.1.2: Ozone distribution measured with the TOPAZ lidar over the northern Colorado Front Range Mountains. Ozone profiles extend from about 5 km MSL to the surface.

processes interact with each other to transport and distribute pollutants within and beyond the CV. Figure 5.1.2 shows an example of TOPAZ ozone measurements taken during the summer of 2008 over the northern Colorado Front Range urban corridor and adjacent mountains. This particular case shows high ozone concentrations generated in the Denver area being transported up and over the Front Range Mountains by easterly upslope flow. The TOPAZ lidar also provides estimates of mixed layer height, which will be critical for studying the temporal evolution and spatial distribution of ABL height, especially in the transition zone from the valley floor to the slopes of the Coastal Range and the Sierra Nevada.

Airborne Doppler lidar

If funding is available the instrument package on the Twin Otter will be upgraded to include an airborne Doppler wind lidar. The Doppler lidar would provide profiles of horizontal wind speed and direction as well as vertical wind speed. Figure 5.1.3 depicts vertical wind speed measurements taken with the NOAA High Resolution Doppler Lidar (HRDL) (Tucker et al.,

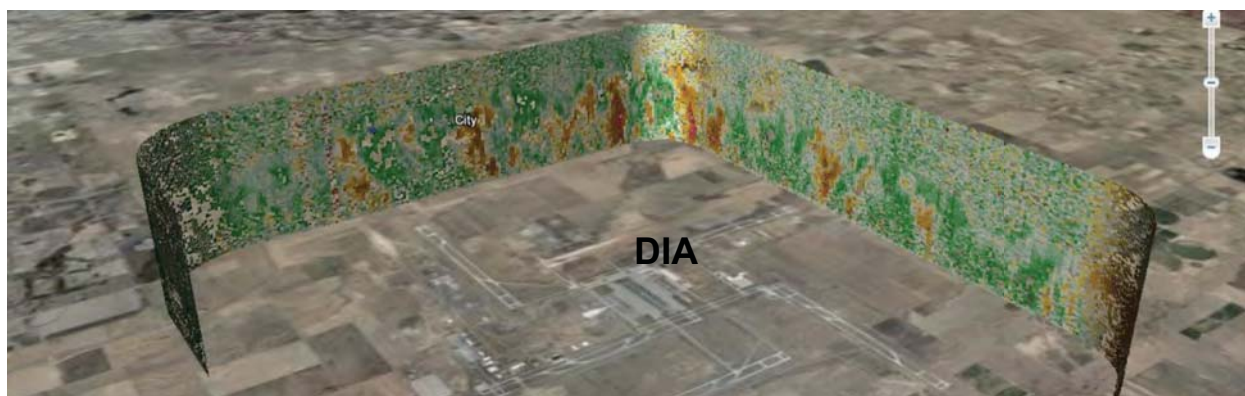


Figure 5.1.3: Vertical wind speed profiles measured with the HRDL lidar Denver International Airport (DIA). Profiles extend from approx. 3 km MSL to the surface. Warm colors represent updrafts and cool colors indicate downdrafts.

2008) from the Twin Otter during the summer of 2008 over the Denver metro area. Horizontal wind measurements will be obtained by incorporating a scanner, directed at nadir, to provide multiple components of the horizontal wind at spatial resolution similar to that of the TOPAZ instrument. A co-deployment of a Doppler lidar with TOPAZ would allow us to measure the flow characteristics in the CV directly and co-located in space and time with the ozone and aerosol measurements, thereby greatly enhancing the measurement capabilities on the Twin Otter. An airborne Doppler lidar will also enable mapping of mesoscale features such as the Sacramento and Fresno Eddies, which play an important part in transport and mixing of pollutants in the CV. The co-located ozone, aerosol and wind measurements would also enable measurement of horizontal and vertical fluxes of ozone and aerosols and thus provide a means to quantify pollutant transport processes. By directly observing vertical motion and turbulence, the Doppler lidar would provide an alternative way of measuring ABL height and characterizing the strength of mixing in the boundary layer.

Figure 5.1.4 shows a sample Twin Otter flight plan that could be used to examine ABL structure, horizontal and vertical flow patterns, and their impact on pollutant distributions over the CV and the adjacent mountain ranges. This sample flight pattern assumes that the Twin Otter is based in

Santa Barbara, CA and that the aircraft endurance is 5 hours. Flying back-to-back missions with about a 1-hour refueling break can extend mission duration and distance covered.

Airborne Multi-Axes Differential Optical Absorption Spectrometer (AMAX-DOAS)

Depending on available support, an AMAX-DOAS instrument is also being considered for the NOAA Twin Otter for deployment with the airborne ozone lidar. The AMAX-DOAS instrument will add novel trace gas remote sensing

capabilities to the aircraft to complement the lidar measurements. In particular, The AMAX-DOAS will enable 2-

dimensional characterization of NO₂, SO₂, and possibly BrO, IO, formaldehyde, glyoxal, ozone and other pollutants that absorb in the near UV and visible regions. These observations will provide information on distribution and transport of trace bases into and out of the Central Valley and their correlation with ozone concentrations.

Surface sensors

In addition to the airborne measurements, measurements from a number of ground-based sensors including the radar wind profiler network, micrometeorological stations, the HRDL Doppler lidar on the RV Ron Brown and a transportable Doppler wind lidar (deployed if funding becomes available) will be important for addressing the science questions outlined above. The wind profilers (at the sites to be determined) will measure hourly profiles of horizontal wind speed and direction from about 100m to several kilometers above ground at each network site, thus providing a continuous record of the structure of the wind field in the CV. These measurements will be key to characterize the diurnal patterns and day-to-day variations of the valley flows and the incoming flow from the Pacific Ocean. The wind profiler network data will also be used to produce sets of forward or backward trajectories (White et al., 2006). These trajectory calculations will be useful to characterize pollutant transport patterns and for aircraft and ship mission planning purposes. In addition, the wind profiler measurements of mixed layer height will be utilized to investigate ABL evolution.

When the RV Ron Brown is in the San Francisco Bay area the HRDL Doppler lidar will provide detailed measurements of the sea breeze entering the CV from the Pacific Ocean, the structure and height of the ABL both during day and night, and the formation and strength of the nighttime low-level jet. The mobile Doppler lidar will be deployed (if funding is available) for several days at a time at various strategic locations throughout the CV, such as where flow enters from San



Figure 5.1.4: Sample Twin Otter flight plan. Flight duration is 5 hours and distance covered is approx. 700 nautical miles.

Francisco Bay and the Los Angeles basin, and near the adjacent mountain ranges. The mobile Doppler lidar would be particularly well-suited to investigate the structure of the slope flows, as well as vertical ventilation and entrainment over the mountain slopes.

WP-3D aircraft chemical measurements

The WP-3D aircraft will be instrumented for making detailed, high-resolution (≈ 100 m), in situ measurements of the concentrations of a wide variety of chemical species, both within the ABL and in the lower free troposphere. The species measured include primary emissions and secondary pollutants. Hence it is an ideal platform for identifying pollutant plumes transported both within the ABL and lofted from the ABL to the free troposphere. The range of the WP-3D will allow it to investigate such plumes throughout California. The WP-3D observations will provide another data set for comparison with the model results. The WP-3D likely will not conduct flights dedicated solely to investigating pollutant transport mechanisms, but likely all flights will have portions that are useful for such model measurement comparisons.

Numerical modeling

We will apply the state-of-the-art Weather Research and Forecasting (WRF) model that is fully coupled with a chemistry model (WRF-Chem) in this investigation of orographic ventilation of pollution in the ABL driven by the secondary circulation at local mountain ranges. This model has been evaluated and used for mesoscale transport process studies in the CV (e.g., Bao et al. 2008; Michelson and Bao 2008). The WRF-Chem model is in principal suitable to simulate the transport processes with horizontal grid resolution of one kilometer or less and vertical resolution on the order of 10 meters. At this resolution, there is no need to utilize any parameterization schemes for deep convection and the conventional ABL mixing parameterization schemes will be replaced with the large-eddy simulation (LES) subgrid closure schemes. The WRF-Chem model simulations will be carried out using both the conventional ABL parameterization schemes and the LES subgrid closure schemes. The simulations will be compared with the observations at various resolutions for the purpose of evaluating the skills of the WRF-Chem in air quality modeling, and will be analyzed and diagnosed to address the science questions mentioned previously. These analyses will provide a better understanding of the conditions necessary for setting off and maintaining the orographic ventilation processes, and will help to develop conceptual models of the orographic ventilation processes under various meteorological conditions.

Finally, we also plan to perform very high resolution (a few hundred meters) to determine the relationship between the evolution of the ABL over complex topography and the surface forcing, and to compare this relationship with the observed one. The results from this investigation can be used to evaluate and improve the parameterization of the turbulent exchange between the ABL and the free troposphere over steep topography, and to understand the transition of such exchange from the valley to the mountains.

References

Alvarez II, R. J., W. A. Brewer, D. C. Law, J. L. Machol, R. D. Marchbanks, S. P. Sandberg, C. J. Senff, A. M. Weickmann, 2008: Development and Application of the TOPAZ Airborne Lidar System by the NOAA Earth System Research Laboratory, Proceedings of *24th International Laser Radar Conference*, Boulder, Colorado, USA, 23-27 June, 2008, 68-71.

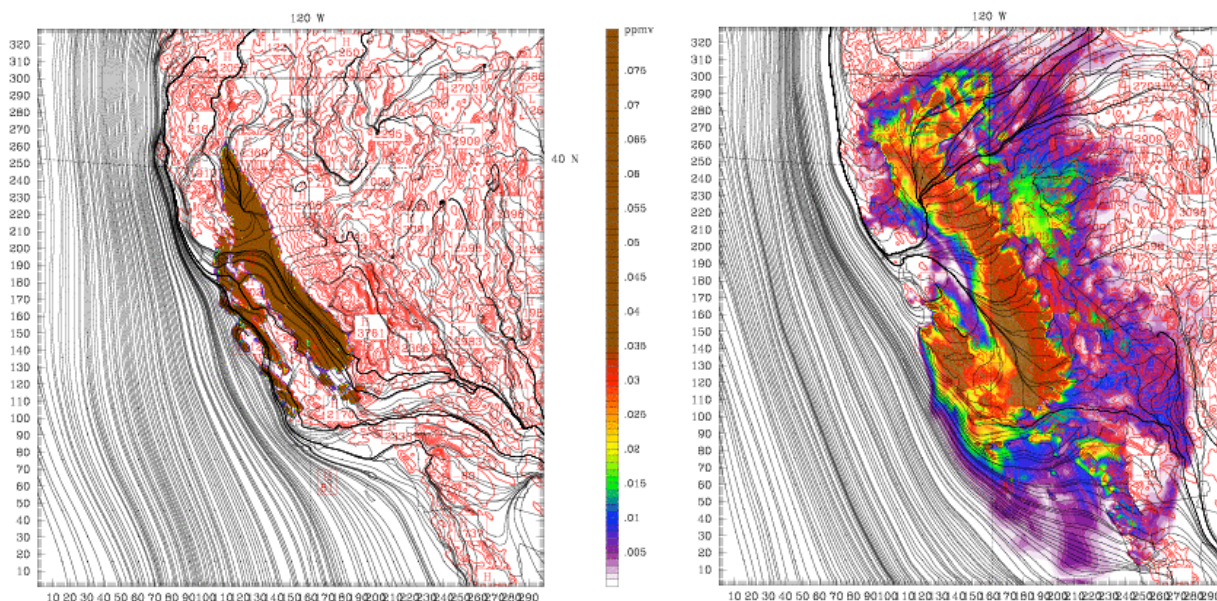
- Bao, J.-W., S. A. Michelson, P.O.G. Persson, I.V. Djalalova, and J. M. Wilczak, 2008: Observed and WRF-simulated low-level winds in a high-ozone episode during the Central California Ozone Study. *Journal of Applied Meteorology and Climatology*, to appear.
- Henne, S., M. Furger, S. Nyeki, M. Steinbacher, B. Neininger, S. F. J. deWecker, J. Dommen, N. Spichtinger, A. Stohl, and A. S. H. Prévôt, 2004: Quantification of topographic venting of boundary layer air to the free troposphere. *Atmos. Chem. Phys.*, **4**, 497-509.
- Michelson, S. A, and J.-W. Bao, 2008: Sensitivity of the WRF model simulated low-level winds in Central California to the atmospheric and soil conditions. *Journal of Applied Meteorology and Climatology*, to appear.
- Tucker, S. C., W. A. Brewer, R. M. Banta, C. J. Senff, S. P. Sandberg, D. C. Law, A. Weickmann, and R. M. Hardesty, 2008: Doppler lidar estimation of mixing height using turbulence, shear, and aerosol profiles, *J. Atmos. & Oceanic Tech.*, accepted for publication.
- White, A. B., C. J. Senff, A. N. Keane, L. S. Darby, I. V. Djalalova, D. C. Ruffieux, D. E. White, B. J. Williams, and A. H. Goldstein, 2006: A wind profiler trajectory tool for air quality transport applications, *J. Geophys. Res.*, 111, D23S23, doi:10.1029/2006JD007475.

5.2. Inter-regional transport

Previous major field campaigns in California [Southern California Air Quality Study (SCAQS-1987), San Joaquin Valley Air Quality Study (SJVAQS-1990), Southern California Ozone Study (SCOS-1997), Central California Ozone Study (CCOS-2000), California Regional Particulate Air Quality Study (CRPAQS-2000)] have investigated the meteorological transport of pollutants. However, each of these studies has largely focused on transport within a limited geographical region or even an individual air basin, making the implicit assumption that the most significant sources of pollutants are locally generated, and that inter-regional transport is generally of minor relevance. However, recent model studies (discussed below) have indicated that inter-regional transport can occur through several different pathways under the proper meteorological conditions. The goal of this component of the CalNex study will be to collect the observational data and perform the model simulations necessary to quantify the role of inter-regional transport on air quality throughout California. This study will be made possible because of the unique measurements provided by the NOAA P-3 aircraft and the Twin Otter airborne ozone lidar, in conjunction with ground-based wind profiling radars and possibly a Doppler lidar.

5.2.1 Inter-regional transport associated with the Central Valley. The two regions of California with the highest summertime ozone concentrations are the Los Angeles basin and the Central Valley. Model investigations of the potential role of transport to and from each of these regions were conducted using a passive tracer in the WRF-Chem air quality model (Bao et al., 2008). For the Central Valley simulation, the tracer was set to an initial concentration of 80 ppb at elevations below 200 m MSL within central California (Figure 5.2.1), which confined the tracer to the Central Valley, and some lower coastal elevations. The model meteorological fields were initialized at 12 UTC 29 July 2000, and were then allowed to run for the following 5 days using observed meteorological boundary conditions as forcing. At later times in the simulation transport was observed to occur 1) into the valley through the coastal mountain gaps near San

Fig. 5.2.1 Passive tracer surface concentration fields for the Central Valley study at the model initial time of 1200 UTC, 29 July 2000 (left panel) and 33 hours later (right panel).



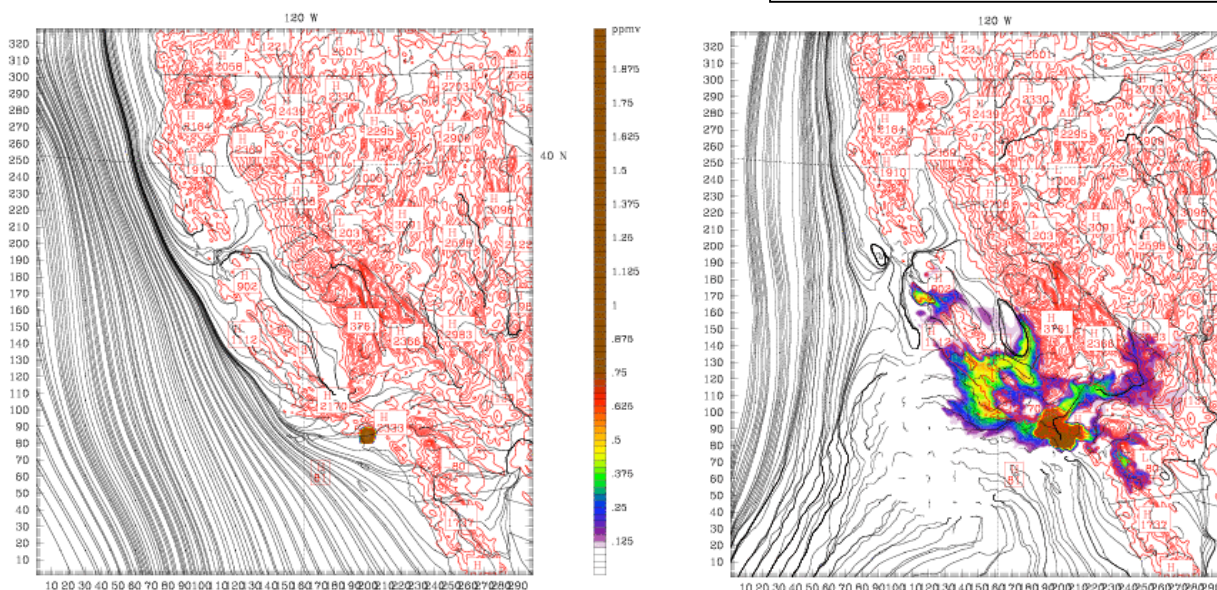
Francisco Bay and Monterey Bay; 2) into and out of the valley through the lower elevations of the coastal mountains in the Carizzo Plains area; flow out of the Valley through this gap later moved southward along the coast and into the LA basin; 3) out of the Central Valley and into the Mojave Desert; and 4) northward along the slopes of the Sierra mountains, recirculating flow to the Sacramento Valley from the San Joaquin Valley. Of these possible transport pathways, only transport through the Bay Area and Monterey Bay into the Central Valley have been investigated previously in detail as part of the CCOS (Persson et al. 2008) and MABLEX (Banta et al., 1993) studies.

The potential for transport from the Central Valley to the LA basin was also observed during the SCOS field program. A case study of a high ozone episode in the Los Angeles basin by Boucouvala and Bornstein (2003) indicated that flow in a deep layer up to 2 km agl in the basin was frequently from the north, suggesting that transport from the Central Valley to the LA basin was possible. However, adequate observations were not taken in the Central Valley to be able to confirm this pathway.

5.2.2 Inter-regional transport associated with the Los Angeles basin.

To understand potential transport pathways associated with emissions from the Los Angeles basin, a second WRF-Chem tracer simulation was run, using the same meteorological conditions as before, but this time using a constant rate of emission of a passive tracer from a 5x5 gridpoint (20x20 km) box located in central Los Angeles (Fig. 5.2.2). The initial advection of the tracer was to the south and east, towards San Diego and into Mexico, and into the Mojave Desert and Imperial Valley. However, on days 2 through 4 of the simulation a Catalina Eddy formed, advecting the tracer westward past Santa Barbara, and then northward along the coast in a “southerly surge” associated with a coastally trapped Kelvin wave. The tracer then penetrated into the Central Valley through the Carizzo Plain and even as far north as Monterey Bay/Pacheco Pass. Significant near surface concentrations then accumulated in the southern San Joaquin Valley, and some of these were

Fig. 5.2.2 Passive tracer surface concentration fields for the Los Angeles emission study at the model initial time of 1200 UTC, 29 July 2000 (left panel) and 99 hours later (right panel).



transported northwards towards Sacramento in southerly nocturnal flow along the slopes of the Sierra's.

A second, and more direct pathway for transport from the LA basin is in upper level winds (above 2 km agl) that are typically present over California during the summer months, associated with 700 and 500 mb high pressure that forms over the Great Basin. If Los Angeles basin emissions reached these altitudes, perhaps due to venting over the Santa Ynez and transverse inland mountain ranges north of Ventura, they could then be advected northward over the Central Valley producing high concentrations aloft which might then subside and be entrained into the boundary layer within the valley.

5.4.3 CalNex 2010 transport operational plan.

During CalNex 2010 we will rely heavily on the Twin Otter airborne ozone lidar, in conjunction with the WP-3D aircraft and wind profiling radars and Doppler lidar, to document the occurrence and strength of transport along each of these pathways. Flights perpendicular to the transport direction both within and outside of the Central Valley and along the transport path will be made to document the continuity of the ozone and wind fields. To the extent possible, wind profilers will be placed to be able to document transport winds along some of these pathways. Also, the mobile Doppler lidar will be positioned at several different locations that complement the fixed radar locations. The results of these observations will be combined with numerical modeling to determine quantitatively the frequency, magnitude and importance of transport along these inter-regional pathways.

Specific questions that will be addressed are:

- 1) What is the frequency of transport along the various inter-regional pathways? Are they a rare occurrence, or are they frequently occurring processes? To answer these and the following questions, model simulations spanning several months will be combined with more sporadic observations that document the ability of the model to adequately replicate the transport process.
- 2) What is the relative magnitude of transport along each of these pathways?
- 3) What large scale meteorological forcing is required for this transport to occur?
- 4) Is the transport associated with each pathway associated with extreme high ozone or PM episodes?
- 5) Is it essential to account for inter-regional transport in order to be able to adequately simulate ozone and PM within California?

References:

- Boucouvala, D. and R. Bornstein, 2003: Analysis of transport patterns during an SCOS97-NARSTO episode. *Atmos. Environ.*, 37, doi:10.1016/S1352-2310(03)00383-2.
- Banta R., L. Olivier, D. Levinson, 1993: Evolution of the Monterey Bay sea breeze layer as observed by pulsed Doppler lidar. *J. Atmos. Sci.*, 50, pp. 3959-3982.
- Persson, O., J.-W. Bao, S. Michelson, J. Wilczak, and S. Tanrikulu, 2008: The Central California Ozone Study (CCOS) Part I: Evaluation of MM5 Simulations. (In preparation).

5.3 Offshore Recirculation and Marine Boundary Layer Phenomena

Transport of pollution and aerosols in the California coastal region is a complex interplay of the atmosphere accommodating vastly different surface forcing from the land and ocean. The interaction of the topography and strong diurnal forcing of the land contrasts sharply with steadiness of the ocean surface. The predominant synoptic airflow in the coastal marine boundary layer (MBL) is parallel to land and the MBL develops a mean structure that varies strongly with distance from shore. This structure is highly baroclinic and tightly coupled to coastal upwelling of cold water, which is maximum in later summer. This background MBL structure dominates the dynamical characteristics of inflows to land, either through local passages in the coastal ranges or, in the case of sufficiently strong daytime convection, venting over the mountains.

The general MBL background structure is modulated on large scale by synoptic variations. Coastal eddies and southerly surges (described below) and different scales of land-atmospheric diurnal cycles often lead to mesoscale transport mechanisms that are at the limits of predictability in today's models. Field programs in the 1980's showed that the coastal influence of land extended out over the ocean much further than could be explained by conventional land-sea breeze MBL cycles. For example, satellite studies found the albedo of MBL clouds to be higher near the coast (because of indirect aerosol forcing) and this coastal influence can be detected 100's of km from shore. The basic dynamical processes that lead to the mean MBL structure are understood qualitatively, but the balances are poorly known and poorly resolved in models. The mesoscale responses to synoptic modulation are quite unexplored. The physical processes responsible for the spatial/temporal variability of pollutants and aerosols in the MBL have not been quantitatively investigated. It is also important to recognize that the LA Bight region is a clearly distinct MBL regime from the great length of California north of Pt. Conception. In the LA Bight the coast is oriented E-W, so mesoscale and synoptic forcing are at 90 degrees to each other. This results in much more small-scale horizontal mixing in the LA basin even in the absence of large eddies.

The following three sections discuss mesoscale flow features that are particularly important to understand from the perspective of pollutant transport in California, and the final section briefly discusses the investigations that are planned to advance this understanding.

5.3.1 MBL Structure: Coastal Jet and Coastal Oscillation

The predominant synoptic airflow in the MBL often takes the form of the California Coastal Jet (CJ) - a low level wind field, parallel to the coast, with a wind maximum of 25-30 m/s approximately at the top of the MBL. Studies using dropsondes have shown that the height and maximum speed of this jet peak both increase with distance from shore, corresponding to an increase in the height of the MBL (Burk and Thompson 1996, Parish 2000). Increased understanding of the mechanisms for MBL structure and formation are expected to lead to improved modeling and forecasting efforts for on-shore locations. The effect of synoptic and geostrophic conditions on the formation and strength of the CJ, the role of the CJ in modulating the diurnal coastal oscillation and the amplitude of that oscillation, and how these relationships differ between Northern vs. Southern CA have not been well studied. The potential presence of

a Southerly Surge (discussed below) during the experiment period would provide the opportunity to observe the interaction between the CJ and the leading edge of the surge.

Coastal oscillations, usually in the form of a land/sea-breeze near LA have been studied in the context of pollution buildup (e.g. Cass and Shair, 1984). Near Monterey Bay, studies were performed from a land-based site on days demonstrating different sea-breeze transitions (smooth to sudden) (Intrieri et al. 1990, Banta et al. 1993, Darby et al. 2002).

Ship-based in-situ and remote sensing instruments will enable the study the shape and development of the CJ, the relationship between the height of this jet and the depth of the MBL, as well as the roles of convective versus mechanical turbulence in the formation and structure of the MBL. Near any of the major CA coastal cities, a ship-based offshore location provides the opportunity to characterize the seaward side of the land/sea-breeze including horizontal extent, vertical structure, timing in development, and, if possible, presence or absence of return flow, as well as to further study the chemical transformations affected by the land/sea-breeze cycle in different locations along the California coast. Depending on ship location, measurement of gap flows (channeled through gaps in the terrain) may be possible along with observations of the types of pollutants transported through (into or out of) such gaps and potential recirculation of these pollutants away from or onto shore. Airborne ozone and aerosol lidar measurements will be useful for mapping out the extent of the flows and concentrations within, thus extending some of the ship-based chemistry measurements.

5.3.2 Southerly Surges.

A southerly surge (Fig. 5.3.1) is a form of coastally trapped disturbance (CTD) and is defined as the advection of a narrow band of stratus northward along the coast, with a rapid transition from northerly to southerly surface flow, as indicated for example, by coastal buoys. A surge typically covers 500-1000 km of coastline, propagates at an average speed of $7-9 \text{ m s}^{-1}$, and lasts 24-36 hours. Once or twice a month in summer, southerly winds develop along the coast that are not associated with fronts or troughs. The transition from northerly to southerly winds often corresponds to the end of a

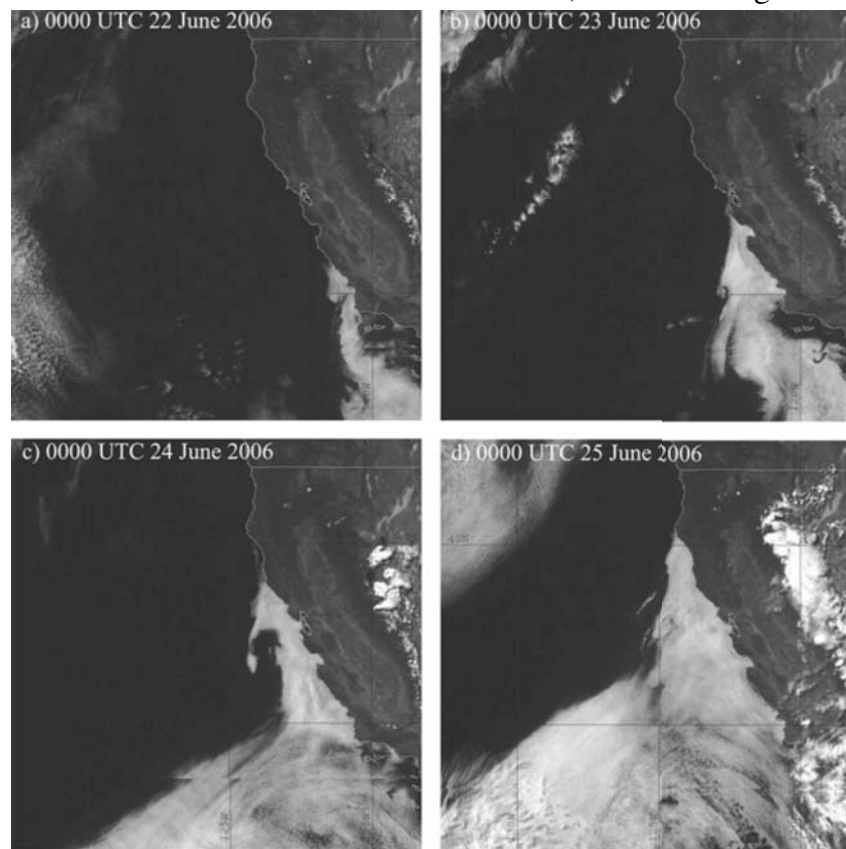


Figure 5.3.1. Goes-11 satellite imagery showing the northward progression of stratus clouds during a southerly surge event (from Parish et al.. 2008).

coastal heat wave and the abrupt onset of stratus. Mass and Albright (1987) found that southerly surges are deep (up to 5 km), and produce 2-3 C cooling between 500-1500 meters. In some cases the southerly surge is not entirely a mesoscale phenomenon; rather it is forced by a synoptic scale upper-level low off the southern California coast. The upper-level low deepens the cool marine air in the south, reversing the mesoscale pressure gradient, thus triggering the surge (Mass and Albright, 1987). Along the central California coast, at least four surges occurred over the period June to August 1995, during which a modeling study was conducted using the ETA model by the National Weather Forecast Office in Monterey (Archer and Reynolds, 1996).

The role of the southerly surge in pollution transport is important because it allows pollution originating in the L.A. basin to be transported northward along the coast, where it may enter the Central Valley through a low point in the coastal mountains (e.g., east of Estero Bay), or via transport southward along the Salinas Valley after entering to the north at Monterey Bay, or, depending on the surge's northward extent, through the Carquinez Strait.

The quick onset and, in some cases, lack of synoptic-scale forcing, make it difficult to forecast the southerly surge accurately, but once present, the cooperative agency coastal profiler network in southern and central California (Fig. 5.3.2) will be capable of detecting and monitoring this phenomenon. Once detected, the lidar aircraft will follow pollution transport by doing transects along and across the surge. The mobile Doppler lidar will be placed strategically along the western slope of the central valley to monitor transport into the valley through one or more of the mechanisms described above. When positioned properly, the R/V Ron Brown, with its vast array of chemical and meteorological measurements, will be able to help characterize pollutant transport, chemical transformation, and air-sea interaction.

5.3.3 Catalina Eddies

A Catalina Eddy (Fig. 5.3.3) forms when upper level large-scale northwesterly flow off Point Conception in the California Bight region interacts with the complex topography of the southern California coastline. As a result, a counter clockwise circulating low pressure area forms by the process of lee troughing, with its center in the vicinity of Catalina Island. This formation is accompanied by a southerly shift in coastal winds, a rapid increase in the depth of the marine layer, and a thickening of the coastal stratus.

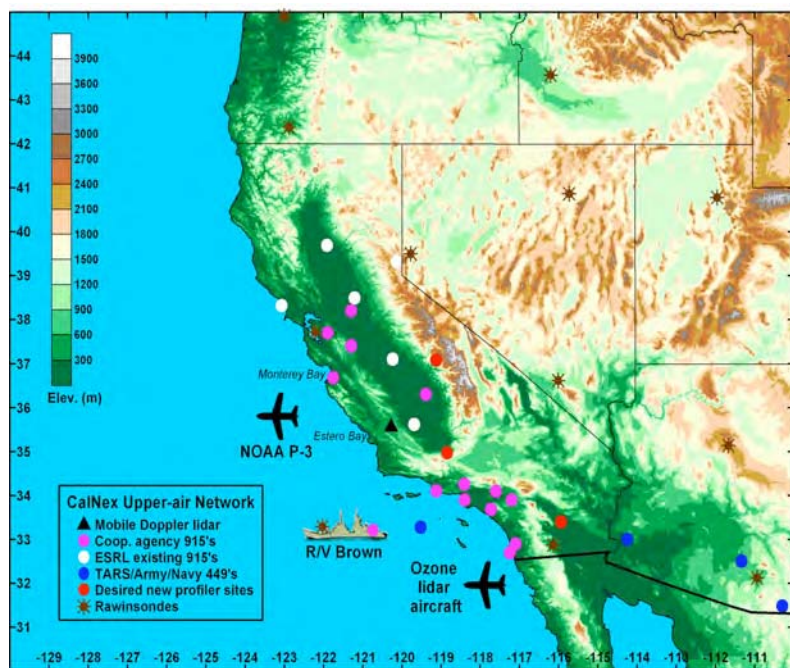


Figure 5.3.2. Existing upper-air networks deployed in California along with a strawman deployment plan for additional land-based upper-air instruments provided by ESRL.

Predominately these eddies occur between April and September with a peak in June. A typical Catalina Eddy will allow coastal low clouds and fog to persist into the afternoon. A strong Catalina Eddy may extend upwards to 1.8 km, allowing the clouds to move through the inland

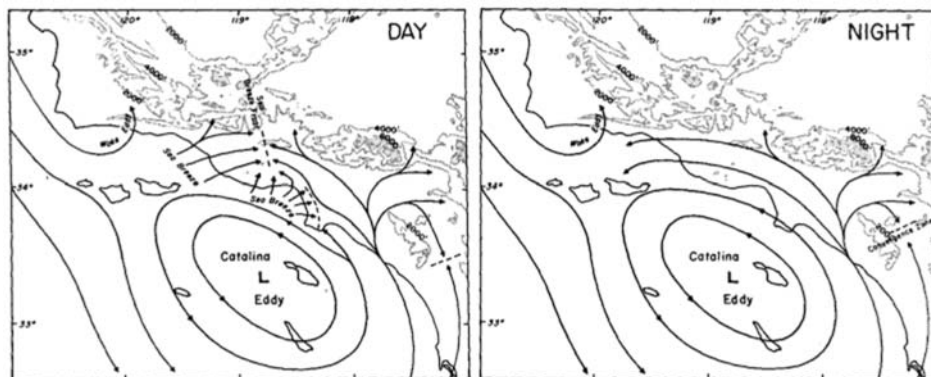


Figure 5.3.3. Schematic surface flow features in a Catalina Eddy (from Wakimoto, 1987).

valleys and even reach as far as the Mojave Desert. The Catalina Eddy is rarely prolonged; as daytime heating over the deserts causes air to rise, the resulting pressure gradient and increase in the normal onshore winds causes the vortex to dissipate. Whether the southerly flow on the east side of the eddy is able to propagate out of the bight region to create a southerly surge is largely dependent on the direction and strength of the synoptic-scale offshore flow (Skamarock et al., 2002).

Once the Catalina Eddy forms, air pollutants from the L.A. basin are rapidly transported northward toward Santa Barbara. However due to local effects of the sea breeze and a smaller-scale wake eddy that forms around Point Conception (Fig. 5.3.3), surface pollution concentrations may be quite variable (Wakimoto, 1987). While the overall dynamics of the Catalina Eddy cannot be measured with the ship, the R/V Ron Brown can help evaluate the offshore transport of pollution from the basin and the processing of that pollution over the water, while the aircraft can monitor the return to land of those processed air masses. Cass and Shair (1984) showed a significant transformation of pollutants with a land-sea breeze circulation uncomplicated by the other flow features associated with the Catalina Eddy and the complex terrain in the bight region.

As with southerly surges, the coastal profiler network in Southern California will help detect and monitor Catalina Eddies. Surface winds from the QuikSCAT satellite also will be useful. Since many Catalina Eddy events are shorter-lived than southerly surge events, it may be more difficult to get aircraft deployed to study these phenomena. Researchers in aircraft already in the air may be able to modify flight plans in order to observe eddy events. The lidar aircraft would be extremely useful to quantify how much ozone pollution is shed out of the eddy, versus how much is being recirculated around the eddy, by flying a series of transects across the eddy.

5.3.4 Planned investigations

A coordinated ship, coastal land, aircraft, satellite, and modeling study of MBL and free tropospheric properties is required to advance our understanding of these issues. For MBL dynamics, critical variables include SST, depth and slope of the BL, strength of the inversion, cloud thickness and LWP, surface fluxes, turbulence/TKE profiles, horizontal advection, and entrainment velocity. Using a combination of *in situ* and remote sensors, the ship (Ron Brown)

will be an excellent platform to address certain aspects of the problem. Studies of the marine boundary layer (MBL) with in-situ point measurements from a flux-package and large scale wind measurements from a radar wind profiler can be complemented by clear air Doppler wind lidar measurements.

The ship is best suited to temporal (diurnal) sampling at a fixed location or cross-coastal transects on time scales of a few days (a few 100 km). The ship is not ideal for studying spatial properties of rapidly evolving or rapidly moving mesoscale structures (such as the Catalina Eddy) where aliasing of spatial and temporal variations confuses the interpretation. Another weakness of the ship is the inability to get measurements of aerosol/chemical properties above the MBL. This is key information needed to assess the role of entrainment in MBL budgets. Thus, either occasional aircraft samples or innovative satellite observations are needed. Planned sampling strategies for the Ronald H. Brown include:

- Repeat transects from the coast out to sea (roughly normal to the mean flow) to characterize the mean structure and balance of the MBL dynamics, cloud properties, chemistry, and aerosols. These transects will be composited and used to provide a target for WRF and WRF-CEHM evaluation.
- Time series at several fixed locations to characterize the diurnal variations in these properties as a function of distance from shore.
- Two-dimensional surveys at one or two key inflow regions (e.g., SF) to characterize the distortion of MBL structure by the inflow process.

Strategies 1 and 2 will provide a natural forum for assessing both transport (synoptic, coastal oscillation, upslope), air-sea fluxes of pollutants and aerosols, and cloud-aerosol coupling.

References:

- Archer, S., and D. Reynolds, 1996: Mesoscale ETA forecasts of stratus surges along the California Coast. *Western Regional Technical Attachment*, No. 96-03, National Weather Service, Monterey, CA.
- Banta, R. M., 1995: Sea breezes shallow and deep on the California coast. *Mon. Wea. Rev.*, 123, 3614-3622.
- Banta, L. D., L. D. Olivier, and D. H. Levinson, 1993: Evolution of the Monterey Bay sea-breeze layer as observed by pulsed Doppler lidar. *J. Atmos. Sci.*, 50, 3959-3982.
- Burk, S. D., and W. T. Thompson, 1996: The summertime low-level jet and marine boundary layer structure along the California coast. *Mon. Wea. Rev.*, 124, 668-686.
- Cass, G. R., and F. H. Shair, 1984: Sulfate accumulation in a sea breeze/land breeze circulation system. *J. Geophys. Res.*, 89, 1429-1438.
- Darby, L. S., R. M. Banta, and R. A. Pielke, Sr., 2002: Comparisons between mesoscale model terrain sensitivity studies and Doppler lidar measurements of the sea breeze at Monterey Bay. *Mon. Wea. Rev.*, 130, 2813-2838.
- Intrieri, J. M., C. G. Little, W. J. Shaw, R. M. Banta, P. A. Durkee, and R. M. Hardesty, 1990: The Land/Sea Breeze Experiment (LASBEX). *Bull. Amer. Meteor. Soc.*, 71, 656-664.
- Mass, C. F., and M. D. Albright, 1987: Coastal southerlies and alongshore surges of the west coast of North America: Evidence of mesoscale topographically trapped response to synoptic forcing. *Mon. Wea. Rev.*, 115, 1707-1738.
- Parish, T. R., 2000: Forcing of the Summertime Low-Level Jet along the California Coast. *J. Appl. Meteor.*, 39, 2421-2433.

- Parish, T. R., D. A. Rahn, and D. Leon, 2008: Aircraft observations of a coastally trapped wind reversal off the California coast. *Mon. Wea. Rev.*, 126, 644-662.
- Skamarock, W. C., R. Rotunno, and J. B. Klemp, 2002: Catalina eddies and coastally trapped disturbances. *J. Atmos. Sci.*, 59, 2270-2278.
- Wakimoto, R. M., 1987: The Catalina Eddy and its effect on pollution over southern California. *Mon. Wea. Rev.*, 115, 837-855.

5.4. Longer-range Transport

The composition of the atmosphere over California is affected by transport of emissions from upwind sources into the state. Similarly, the atmospheric composition over downwind regions is affected by transport of California emissions out of the state. Discussed below are three aspects of these reciprocal transport issues that will be investigated during CalNex 2010.

5.4.1 U.S.-Mexico air quality issues.

Northern Mexico is generally sparsely populated, with the majority of the people living in the U.S.-Mexico border region, which comprises 14 pairs of inter-dependent “sister cities” containing 90% of the 14 million border area residents. The population and industrial development in this region are expected to increase dramatically in the coming decades. In 1983 the U.S. and Mexico signed the La Paz Agreement, which was intended to lead to binational cooperation for the protection and improvement of the environment in the border zone as defined in Figure 5.4.1.

From both the Mexico and California points of view, it is expected that air quality issues will be associated with air masses originating in the portion of the border region adjacent to California, which includes two of the sister city pairs (Tijuana-San Diego and Mexicali-Imperial Valley) that have the most significant air pollution problems. Figure 5.4.2 compares the ozone and aerosol concentrations observed in

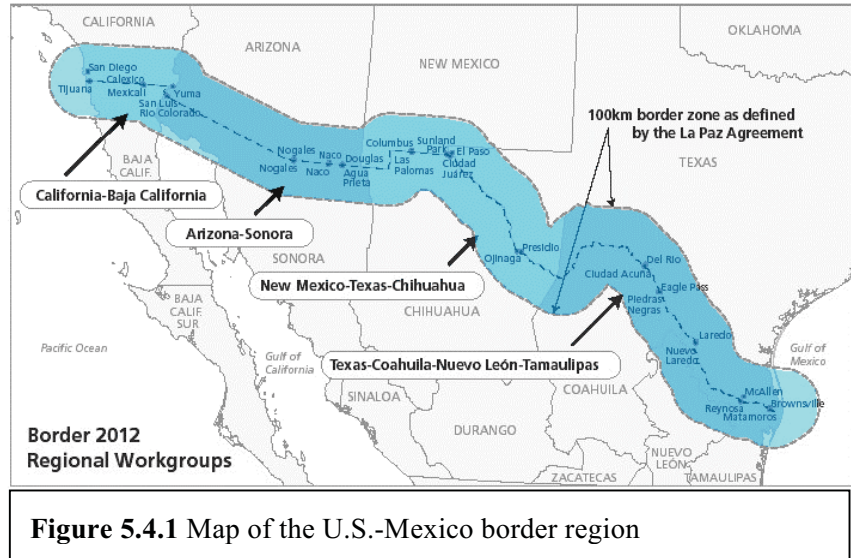


Figure 5.4.1 Map of the U.S.-Mexico border region

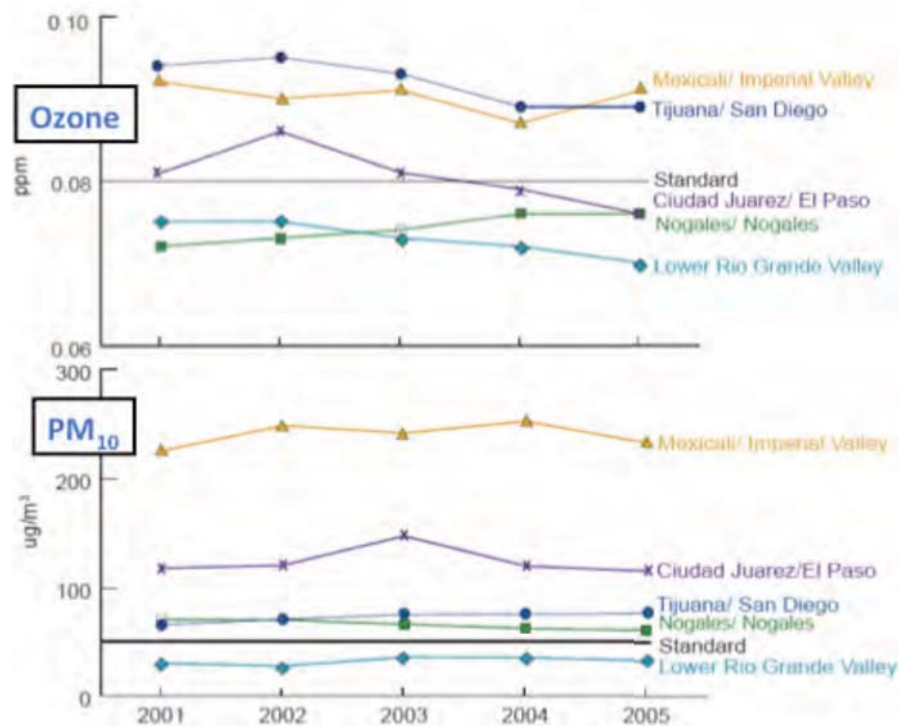


Figure 5.4.2 Average of 4th highest ozone concentration and highest three-year average of annual mean aerosol concentration for the more polluted border region areas (adapted from Border 2012, 2005).

different urban areas of the border region. The two California border regions account for the highest observed ozone and aerosol concentrations. Both of these pollutants are found at concentrations above the U.S. NAAQS in both areas.

It is also expected that the composition of the emissions in the border regions will be different from that observed in other areas of either country. Figure 5.4.3 presents an example (TCEQ, 2007). The on-road vehicle emissions in El Paso (one of a pair of border sister cities) differ significantly from other Texan urban areas. This difference is attributed to emission standards and vehicle fleets, which differ between El Paso and its Mexican sister city, Juarez. Differences are also expected in point source emissions, since US and Mexican emission standards for these sources also vary.

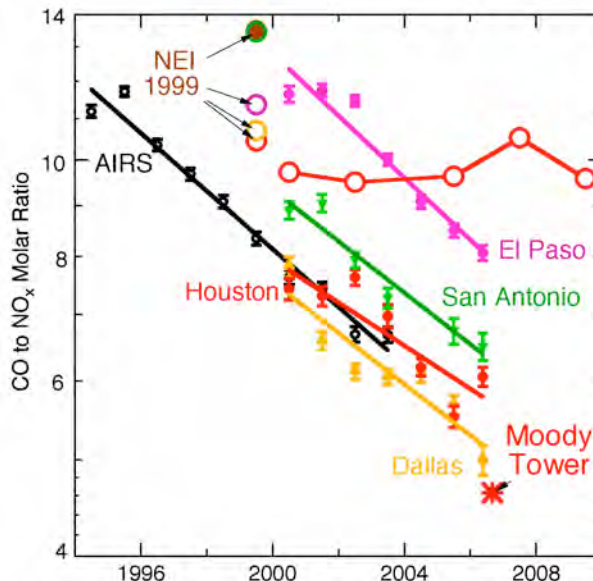


Figure 5.4.3. CO to NO_x ratio in on-road mobile emissions from monitoring data (solid symbols) compared to the emission inventories (open symbols), color-coded according to urban area. The black symbols are for all stations in the EPA AIRS network.

CalNex 2010 will conduct two investigations related to these US-Mexico air quality issues. First, cross border flights of the WP-3D aircraft will be conducted to determine if the differences in emissions (mobile sources, point sources) on the opposite sides of the border reflected in differences in atmospheric chemistry, such as ozone production efficiency, or aerosol composition or concentrations. Second, the results of these cross border aircraft flights will be combined with transport modeling to determine the balance and effects of cross-border transport of atmospheric pollutants between California and Northern Mexico.

5.4.2 Effect of intercontinental transport of Asian emissions into California.

East Asia is the heavily industrialized continental region most immediately upwind of California, but it lies approximately 9000km away on the western side of the North Pacific Ocean. Emissions of ozone and aerosol precursors from East Asia have increased rapidly over the past decade, and thus increasing impacts of transported Asian emissions on US air quality may be expected. However, quantification of these impacts is difficult.

Figure 5.4.4. Comparison of trends in MBL ozone concentration at the US Pacific Coast and Mace Head, Ireland.

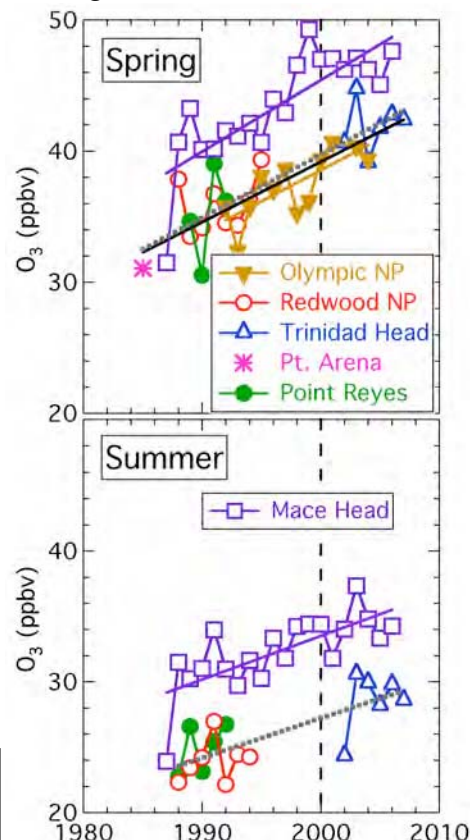


Figure 5.4.4 shows that spring and summer time ozone concentrations in air arriving at the US west coast from the Pacific marine boundary layer (MBL) have increased substantially over the past two decades (Parrish et al., 2008). Positive trends are also seen in fall and winter. It is tempting to attribute these increases to the increasing Asian emissions, but very similar trends are seen at Mace Head, Ireland, which is much more remote from the Asian emissions.

Figure 5.4.5 illustrates an analysis that provides a diagnosis of the photochemical environment to which air masses are subjected over the Pacific Ocean during their transport from Asia to California. Data are shown from three field studies conducted at the Pacific Coast of North America over a span of 21 years, all in springtime. In this plot the x-axis represents degree of photochemical aging of the sampled air masses. Since propane reacts more rapidly in the atmosphere than does ethane, the ratio of these two hydrocarbons decreases as fresh emissions are aged in the atmosphere. During the earliest study in 1985 at Pt. Arena it was found that ozone concentrations were lower in more aged air masses (to the left in Fig. 5.4.5). This relationship indicates that the environment over the Pacific Ocean lead to relatively rapid photochemical destruction of ozone during this early study. In contrast, during the later 2002 study and 2006 studies, the ozone concentrations decreased to a much smaller extent with hydrocarbon aging. This behavior indicates that the photochemical environment of the troposphere over the Pacific Ocean changed in the two decades covered by the studies. One possible cause of this change is that increasing emissions of ozone precursors from Asia are responsible for greater rates of ozone production over the downwind Pacific Ocean.

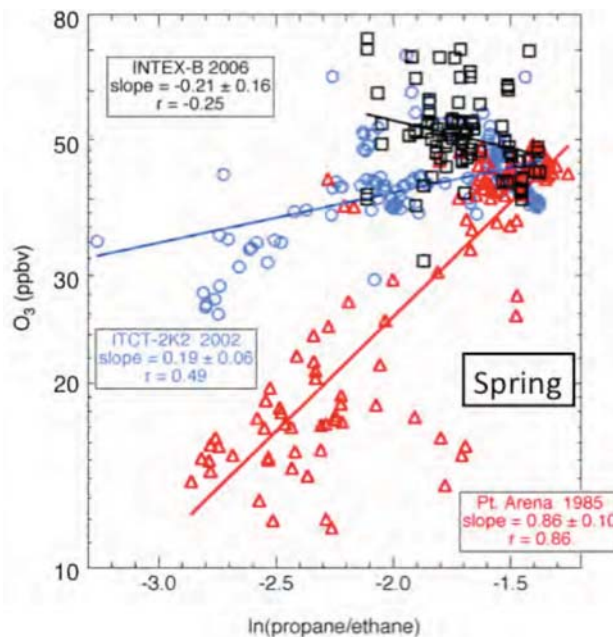


Figure 5.4.5. Relationships between O₃ concentration and the natural log of the propane to ethane ratio for MBL data sets (after figure from Parrish et al., 2004).

The Research Vessel Ronald Brown and the WP-3D aircraft will collect data sets during CalNex 2010 that can be analyzed in the manner of Fig. 5.4.5. These data sets will present seasonal contrasts to the three earlier studies, or, if conducted in the spring, will provide a further increase in the temporal span covered by the analysis.

5.4.3 Transport of California emissions to downwind states.

Transport of pollutants from California to the downwind continental US has received particular attention with respect to the Class I visibility areas of the national parks and wilderness areas in the western US. Increasingly it is also recognized that ozone levels in the western US are increasing, and are approaching the new NAAQS of 75 ppbv, even in the most rural areas. Figure 5.4.6 shows the pattern of observed rural ozone concentrations in the western US. Although there are too few monitors to clearly define detailed spatial gradients, there is a clear indication that the highest ozone levels are found downwind from the major urban areas of

California. This indication suggests a plume of ozone, transported from, and produced enroute from ozone precursors emitted in, California urban areas.

Currently we have very little understanding of the mechanisms responsible for the interstate transport of California emissions and their photochemical products including aerosols and ozone. Four first order questions arise that will be addressed during CalNex:

- Is this transport most effectively thought of as slow, relatively constant leakage, or intermittent, rapid surges?
- Do the Sierras and other mountain ranges represent a transport barrier, or a transport mechanism (c.f. Fig. 5.4.7)?
- Do California emissions leak around the mountains through lower elevations?

These first three questions will be addressed by comparing observations from WP-3D and lidar aircraft flights with transport modeling of such transport pathways.

- Can California emissions be directly observed at surface sites in downwind states?

Collaboration is being pursued with the Western Regional Air Partnership (<http://wrapair.org/>) and EPA funding to conduct such measurements.

References:

Border 2012: US Mexico Environmental Program, Indicators Report, 2005.

(Available from

<http://www.epa.gov/usmexicoborder/docs/BorderIndicatorsReportApril2006.pdf>)

Parrish, D.D., E.J. Dunlea, E.L. Atlas, S. Schauffler, S. Donnelly, V. Stroud, A.H. Goldstein, D.B. Millet, M. McKay, D.A. Jaffe, H.U. Price, P.G. Hess, F. Flocke, and J.M. Roberts, (2004), Changes in the photochemical environment of the temperate North Pacific troposphere in response to increased Asian emissions, *J. Geophys. Res.*, *109*, D23S18, doi:10.1029/2004JD004978.



Figure 5.4.6. Non-urban ozone concentrations in the western US. 2004-2006 3-year average of the 4th highest daily maximum 8-hour average. Orange indicates violation of new 75 ppbv standard. (from Tom Moore, 2008).

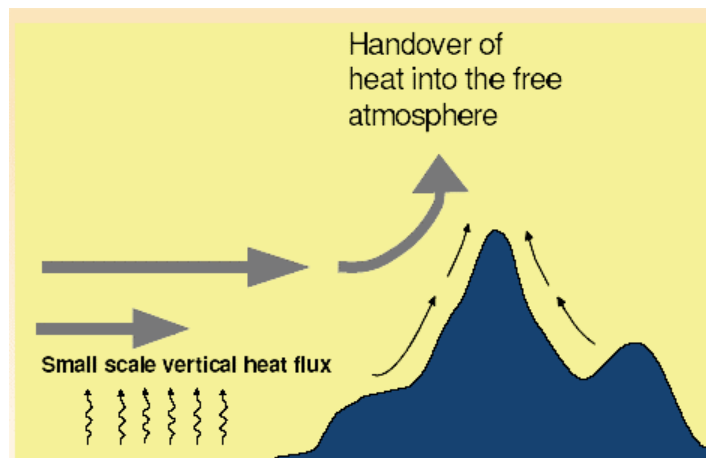


Figure 5.4.7. Schematic of different flow regimes contributing to the transfer of heat from the land surface to the free troposphere (from Summer School Trento, 17-23.08.2003, Lecture 4, Prof. Dr. F. Feder.)

Parrish, D.D., D.B. Millet, and A.H. Goldstein, Increasing ozone concentrations in marine boundary layer air inflow at the west coasts of North America and Europe, *Atmos. Chem. Phys. Discuss.*, 8, 13847-13901, 2008

TCEQ, 2007. Final Rapid Science Synthesis Report: Findings from the Second Texas Air Quality Study (TexAQS II). (Available from <http://www.epa.gov/usmexicoborder/docs/BorderIndicatorsReportApril2006.pdf>).

6. Chemical Transformation

6.1 Importance of Nighttime Transformations

Chemical transformations of primary air pollutants, such as VOC and NO_x , that lead to the formation of secondary pollutants, such as ozone and aerosol, are largely driven by photochemistry and therefore take place during daylight hours. A separate set of chemical reactions takes place in the dark, however, due to the oxidation of NO_x ($=\text{NO} + \text{NO}_2$) to the nocturnal nitrogen oxides, NNO_x ($=\text{NO}_3 + \text{N}_2\text{O}_5$), in the presence of ozone. These nocturnal nitrogen oxides are largely absent during daytime because of the instability of NO_3 with respect to photolysis and reaction with NO , which is generally a daytime species. At night, however, NNO_x is responsible for several chemical processes that consume (rather than produce) ozone, remove the NO_x and VOC precursors that are responsible for photochemical ozone production, lead to the formation of secondary organic and inorganic aerosol, and release gas-phase halogen compounds from chloride-containing aerosol (described in section 6.2). The degree to which these processes affect air quality and climate within California depends on several factors, including aerosol loading and composition within California, the emission of anthropogenic and biogenic hydrocarbons across different regions of the state, and the meteorology and transport within and across different California air basins. The key processes and their relevance within California are outlined below.

6.1.1. Efficiency of N_2O_5 hydrolysis.

Hydrolysis of dinitrogen pentoxide (N_2O_5) to nitric acid (HNO_3) is the key step in the non-photochemical conversion of NO_x to soluble nitrate. It is responsible for approximately half of NO_x removal on a global scale [Dentener and Crutzen, 1993] and is important to regional scale models of ozone and nitrate aerosol formation [Riemer, *et al.*, 2003]. The hydrolysis reaction does not readily occur in the gas-phase, but rather heterogeneously via uptake of N_2O_5 to particulate matter. Current parameterizations of the heterogeneous uptake efficiency are based on laboratory data on model aerosol substrates (e.g., [Davis, *et al.*, 2007]). Recent direct measurements of N_2O_5 from aircraft have shown that the actual uptake efficiency on real atmospheric aerosol can differ markedly from these parameterizations, and that this uptake efficiency is highly variable [Brown, *et al.*, 2006]. One key factor behind this variability appears to be the composition of the aerosol, with aerosol composed largely of acidic, inorganic sulfate giving uptake efficiencies similar to the laboratory determinations, and mixed organic and neutralized inorganic ammonium sulfate aerosol giving much smaller uptake.

This previous aircraft study took place in the Northeast U.S., which has a strong influence from coal-fired power plant sulfur emissions. In contrast to the Eastern U.S., the inorganic component

of particulate matter in California is generally poor in sulfate and richer in ammonium and nitrate, as figure 6.1.1 shows (e.g. [Mysliwiec and Kleeman, 2002]). Laboratory data indicates that the presence of nitrate in the aerosol phase should reduce the efficiency of N_2O_5 uptake [Mentel, et al., 1999]. However, no field data exist to test this hypothesis. California aerosol also has a significant contribution from organic matter, and our previous study indicated reduction in N_2O_5 uptake efficiency on mixed organic / inorganic aerosol, such as those found in California. Finally, the relative humidity range encountered in California, which is generally drier than in the Eastern U.S., may increase the lifetime of N_2O_5 , as some previous ground-based studies in the state have suggested [Platt, et al., 1984]. These aerosol and meteorological characteristics raise several important questions. The first is the influence in

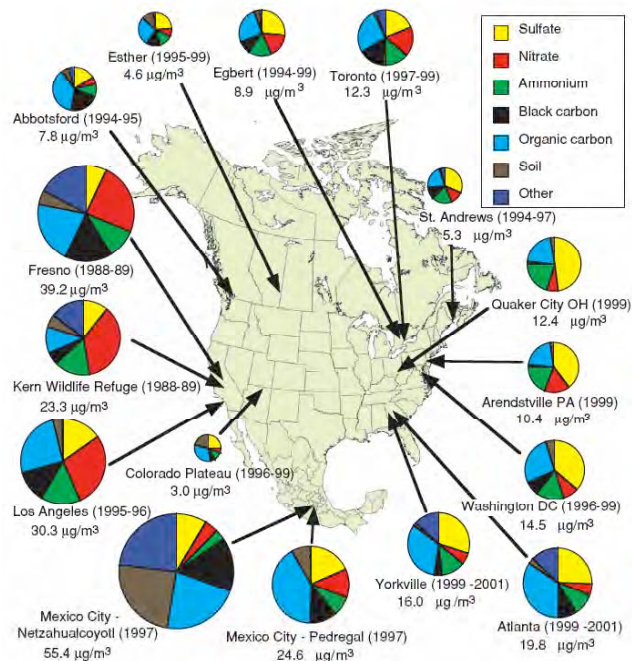


Figure 6.1.1 Aerosol loading and composition in representative regions of North America (from NARSTO PM Assessment)

regional variations in aerosol composition and relative humidity on the lifetime of N_2O_5 and the overnight transport or loss of NO_x emitted in late afternoon or at night. Depending on the nighttime transport patterns, the formation of a stable nighttime NO_x reservoir in the form of N_2O_5 could provide a mechanism for interbasin transport of NO_x . The second question is the role of nighttime processes that convert NO_x to soluble nitrate in the formation of secondary particulate matter in California, a significant air quality issue in the state. If N_2O_5 is a stable reservoir at night, nighttime oxidation of NO_2 by O_3 would provide only a small source of ammonium nitrate aerosol; if not, this mechanism would be comparable to daytime, photochemical NO_x oxidation to HNO_3 . This difference would affect the patterns of secondary PM formation within the state.

These questions could be addressed through nighttime aircraft sampling including measurements of NO_x , O_3 , NO_3 , N_2O_5 , HNO_3 and particulate matter. Research flights would sample plumes transported within and between different air basins (e.g., South Coast and San Joaquin Valley) at night to assess the rates of chemical transformations and the importance of reservoir species. Complementary to this effort would be surface sampling sites, either at ground sites within different air basins, or from ship based measurements off of the California coastline. These studies would provide input for regional air quality models of NO_x , O_3 and PM in California and extend the currently limited database of field determinations of the uptake efficiency of N_2O_5 .

6.1.2. Nocturnal VOC oxidation.

The nitrate radical, NO_3 , is a strong but selective oxidant. It is generally unreactive with alkanes and smaller aromatics, but more reactive towards some oxygenated VOC, such as aldehydes, and

toward alkenes. These trends make NO_3 a particularly important oxidant for biogenic VOC, which is generally unsaturated. Results from aircraft studies in the Northeast U.S., for example, show a clear evidence for overnight removal of isoprene in areas influence by NO_x emissions (and NO_3 production), as shown in Figure 6.1.2. The nitrate radical can also serve as an oxidant for urban and industrial VOC emissions depending on the reactivity of the VOC mixture.

Nocturnal VOC oxidation by NO_3 has several consequences. The first is that it removes the highest reactivity VOC, which are most efficient in formation ozone. In California, the reactive VOC mixtures are complex and vary greatly between different air basins. In the South Coast air basin, anthropogenic VOC constitutes by far the largest source of reactivity relevant to daytime photochemical ozone formation. However, many VOC's identified as the highest reactivity are those toward which NO_3 is reactive [Martien, *et al.*, 2003]. Biogenic VOC in the South Coast constitutes a much smaller fraction of the total, and they are less important for ozone formation because of the location of their emissions within the domain of the transport patterns [Benjamin, *et al.*, 1997; Martien, *et al.*, 2003]. In other regions, such as the mountain counties, biogenic VOC are thought to play a much greater role in ozone reactivity [Dreyfus, *et al.*, 2002]. Nighttime removal rates of reactive, biogenic VOC by NO_3 in these areas will depend on the transport of NO_x -containing air masses [Reissell, *et al.*, 2003].

Nocturnal VOC oxidation via NO_3 radical also leads to different sets of oxidation products than does photochemical oxidation or ozonolysis and, may potentially act as one source of secondary organic aerosol. Reaction of VOC with NO_3 gives organic nitrates in much larger yield than photochemical (i.e., OH) oxidation or ozonolysis. These organic nitrates can serve to transport reactive nitrogen, although their fates are generally rather uncertain. Recent laboratory studies have suggested that NO_3 oxidation of biogenic compounds can lead to more efficient production of secondary organic aerosol than does photooxidation (e.g., [Ng, *et al.*, 2008]).

The importance of NO_3 -driven VOC oxidation depends first on the efficiency of N_2O_5 hydrolysis described above. If N_2O_5 is stable, it provides a reservoir for NO_3 and makes it available as an

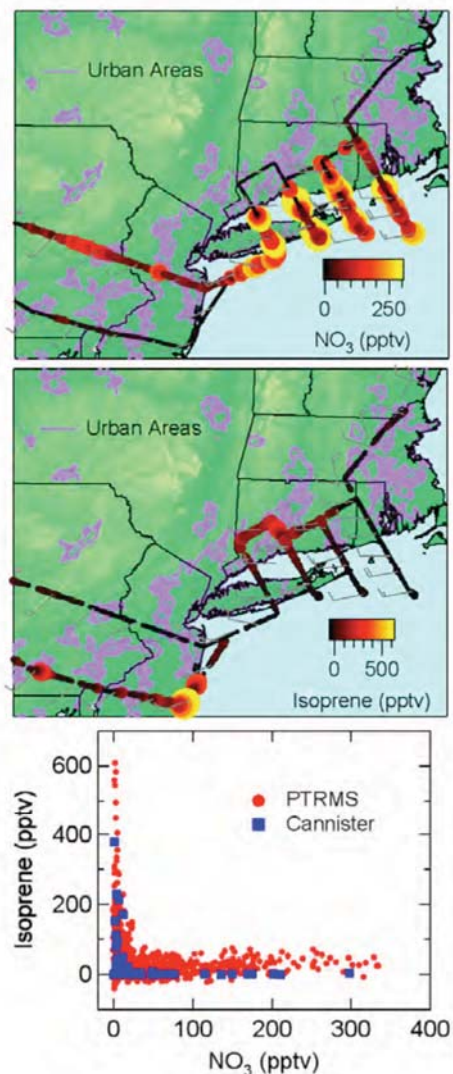


Figure 6.1.2 Distribution of NO_3 and isoprene and their anticorrelation measured during a P-3 flight over the Northeast U. S. in August 2004

oxidant. If not, it serves as a competitive NO_3 sink, limiting the oxidation potential of NO_3 . Nighttime oxidation via NO_3 also depends on the timing of VOC and NO_x emissions and their mixing and transport (both vertical and horizontal) within different air basins. Unlike OH or O_3 , whose sources and concentrations are diffusely distributed, NO_3 production depends on the presence of NO_x , which tends to occur in more discrete plumes downwind of large sources (see figure above). Therefore its mixing with VOCs, particularly of biogenic origin, is not uniform.

Aircraft measurements of NO_x -containing plumes downwind of urban and industrial areas, and point sources such as power plants, allow an investigation of the factors that control nocturnal VOC loss via NO_3 , and the formation of nitrogen containing oxidation products and secondary aerosol. Similar studies could be carried out from ship-based measurements under condition in which a nocturnal land breeze carried pollutants offshore.

6.1.3 Vertical stratification and mixing.

The diurnal variation in nitrogen oxide chemistry is linked to the dynamics of the planetary boundary layer. Daytime surface emission of NO_x are mixed within a relatively deep boundary layer, while surface-level nighttime emissions are mixed within a nocturnal boundary layer (NBL) that has a depth of order 0.1 km and is less efficiently mixed. Emissions from power plant stacks may occur above the NBL but remain poorly mixed in the vertical at night. Nocturnal NO_x emissions therefore tend to be more concentrated and vertically stratified than daytime emissions. Because both the sources and the sinks for NO_3 and N_2O_5 can be spatially stratified, their mixing ratios, and their influence on nitrogen oxide and ozone transport and loss at night can show large variability as a function of height above the surface.

Because of this nocturnal atmospheric chemical – dynamical coupling, the vertical distribution of nitrogen oxide species at night has been a topic of considerable recent interest. Modeling studies have consistently suggested strong vertical gradients of NO_3 and N_2O_5 within the nocturnal boundary layer (e.g., [Geyer and Stutz, 2004]).

Experimental studies with sufficient resolution to confirm these predictions have been sparse, however. Long path differential optical absorption measurements over multiple slant paths have achieved a resolution of several tens of meters within the boundary layer for continuous measurements of NO_3 , NO_2 , O_3 and other trace gases [Stutz, et al., 2004]. Recent nighttime vertical profiling

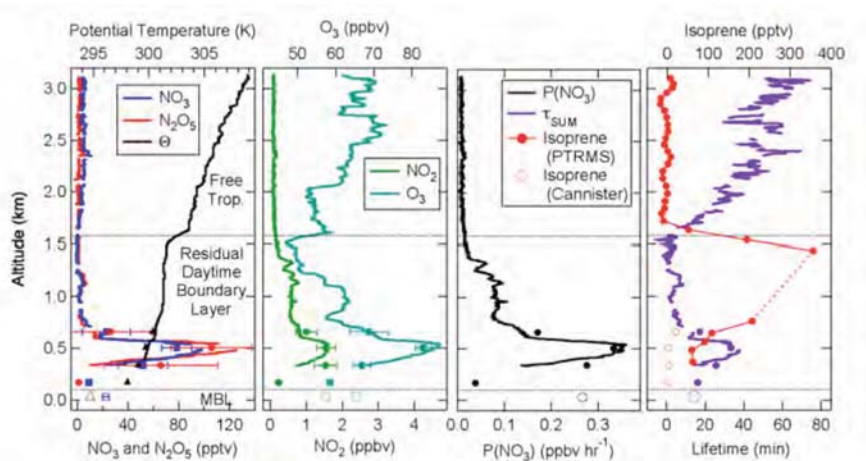


Figure 6.1.3. Nighttime P-3 vertical profile over a surface sampling site in the northeast U.S. in 2004

measurements from aircraft have provided higher resolution data [Brown, et al., 2007], although with the disadvantage that the altitude range of the aircraft permits sampling only of the top

portion of the NBL except for takeoff and landing. However, aircraft measurements have the distinct advantage of sampling a wide altitude range, from near-surface, through the residual daytime boundary layer and into the free troposphere. Figure 6.1.3 shows one example from a P-3 profile over a surface site in the Northeast U.S. This example shows stratified plumes in the daytime, residual boundary layer in which biogenic VOC oxidation takes place and free tropospheric air with long lifetimes for NO_3 and N_2O_5 . Within California, a similar combination of aircraft measurements and surface-level measurements at fixed sites (e.g., long-path DOAS at ground sites or *in-situ* measurements from a ship in the marine boundary layer) would provide a more complete picture of the mixing of surface level emissions through the NBL and the variation in nighttime chemical transformations over small altitude ranges in and above the NBL. Because of the vertical structures in pollutant mixing ratios introduced by the transport over complex terrain in California (e.g. [McElroy and Smith, 1991]), aircraft vertical profiling will be a critical component in understanding nighttime chemical transformation and transport of pollutants.

References

- Benjamin, M. T., et al. (1997), A spatially and temporally resolved biogenic hydrocarbon emissions inventory for the California South Coast Air Basin, *Atmos. Environ.*, 31, 3087-3100.
- Brown, S. S., et al. (2007), Vertical profiles in NO_3 and N_2O_5 measured from an aircraft: Results from the NOAA P-3 and surface platforms during NEAQS 2004, *J. Geophys. Res.*, 112, D22304, doi: 10.1029/2007JD008883.
- Brown, S. S., et al. (2006), Variability in nocturnal nitrogen oxide processing and its role in regional air quality, *Science*, 311, 67-70.
- Davis, J. M., et al. (2007), Parameterization of N_2O_5 reaction probabilities on the surface of particles containing ammonium, sulfate and nitrate, *Atmos. Chem. Phys. Discuss.*, 7, 16119-16153.
- Dentener, F. J., and P. J. Crutzen (1993), Reaction of N_2O_5 on Tropospheric Aerosols: Impact on the Global Distributions of NO_x , O_3 , and OH, *J. Geophys. Res.*, 98, 7149-7163.
- Dreyfus, G. B., et al. (2002), Observational constraints on the contribution of isoprene oxidation to ozone production on the western slope of the Sierra Nevada, California, *J. Geophys. Res.*, 107, 4365, doi:10.1029/2001JD001490.
- Geyer, A., and J. Stutz (2004), Vertical profiles of NO_3 , N_2O_5 , O_3 , and NO_x in the nocturnal boundary layer: 2. Model studies on the altitude dependence of composition and chemistry, *J. Geophys. Res.*, 109, D12307, doi: 10.1029/2003JD004211.
- Martien, P. T., et al. (2003), Evaluation of Incremental Reactivity and Its Uncertainty in Southern California, *Environ. Sci. Technol.*, 37, 1598-1608.
- McElroy, J. L., and T. B. Smith (1991), Lidar Descriptions of Mixing-Layer Thickness Characteristics in a Complex Terrain / Coastal Environment, *J. Appl. Meteor.*, 30, 585-597.
- Mentel, T. F., et al. (1999), Nitrate effect in the heterogeneous hydrolysis of dinitrogen pentoxide on aqueous aerosols, *Physical Chemistry Chemical Physics*, 1, 5451-5457.
- Mysliwiec, M. J., and M. J. Kleeman (2002), Source Apportionment of Secondary Airborne Particulate Matter in a Polluted Atmosphere, *Environ. Sci. Technol.*, 36, 5376-5384.
- Ng, N. L., et al. (2008), Secondary organic aerosol (SOA) formation from reaction of isoprene with nitrate radicals (NO_3), *Atmos. Chem. Phys.*, 8, 4117-4140.

- Platt, U. F., et al. (1984), Measurement of Nitrate Radical Concentrations in Continental Air, *Environ. Sci. Technol.*, 18, 365-369.
- Reissell, A., et al. (2003), Characterization of biogenic volatile organic compounds and meteorology at Azusa during SCOS97-NARSTO, *Atmos. Environ.*, 37, S181-S196.
- Riemer, N., et al. (2003), Impact of the heterogeneous hydrolysis of N_2O_5 on chemistry and nitrate aerosol formation in the lower troposphere under photosmog conditions, *J. Geophys. Res.*, 108, 4144, doi: 10.1029/2002JD002436.
- Stutz, J., et al. (2004), Vertical profiles of NO_3 , N_2O_2 , O_3 , and NO_x in the nocturnal boundary layer: 1. Observations during the Texas Air Quality Study 2000, *J. Geophys. Res.*, 109, D12306, DOI: 10.1029/2003JD004209.

6.2 The Importance of Halogens to the Atmospheric Environment of California

Halogen atoms and associated radicals (X, XO, where X= Cl, Br, and I) are potentially important reactants in the gas-phase photochemistry and aerosol particle formation and processing that occurs in California coastal-urban environments. Although there is observational evidence from various environments for activation of all of the halogens listed above, the current effort will focus mainly on understanding chlorine activation. This is due on part to the stronger reactivity of chlorine radicals toward VOCs, which may impact air quality in polluted coastal areas such as California's South Coast. For example, *Knipping and Dabdub* [2003] added active chlorine (mostly in the form of Cl₂) to their regional photochemical model of the Los Angeles Basin, and found that it can have a significant effect on O₃ production if sufficient Cl is present (tens to 100s of pptv Cl₂ equivalent). However, very little is definitively known about the sources of halogens, and their specific impacts on air quality in such environments. The CalNex field study will endeavor to further this knowledge through direct measurements of recently identified halogen activation mechanisms, as described in the following sections.

6.2.1 Chlorine Activation

Chlorine activation refers to the production of photochemically active gas phase forms of the halogen, such as Cl, ClO or Cl₂, from a chemically inert reservoir. Sources of these reactive species are uncertain, but may include oxidation of organic halogens such as methyl halides, and O₃ and HO_x radical reactions with halide-containing particles such as sea salt aerosol [*von Glasow and Crutzen, 2007; Finlayson-Pitts, 2003*]. These reactions are generally slow or inefficient, leading to only modest predicted levels of active chlorine [*Pechtl and von Glasow, 2007*]. Direct evidence for the occurrence of halogen chemistry has come from measurements of key source species, such as Cl₂ [*Finley and Saltzman, 2006*], and halogen radicals such as BrO, and IO. Observation-based analyses of halogen reaction partners and unique VOC reaction products have been used to provide estimates, or upper limits of the concentrations of halogens, chiefly Cl atoms, in certain environments.

Recent work by the NOAA/ESRL/CSD group has identified additional, potentially efficient reactive chlorine sources. Ambient measurements [*Osthoff et al. 2008*] have shown that substantial amounts of nitryl chloride (ClNO₂) can be produced at night through the reaction of N₂O₅ with chloride-containing aerosol particles. This chemistry is not limited to sea salt particles, as had been previously thought, but also occurs readily on sub-micron aerosol at modest chloride concentrations ([Cl⁻] ≥ 0.02M). The chloride content of the submicron aerosol derives from sea salt via heterogeneous acid displacement reactions that yield gas phase HCl, which in turn partitions to the submicron aerosol. Aerosol thermodynamic models predict that this partitioning will produce sufficient aerosol chloride to drive rapid conversion of N₂O₅ to ClNO₂ for gas-phase HCl levels of a few hundred pptv and for common aerosol substrates such as ammonium bisulfate (NH₄)HSO₄ [*Clegg et al., 1998*]. The role of submicron aerosol suggests that ClNO₂ production is a general process that is coupled to NO_x pollution sources and transport. Nitryl chloride has only slow loss processes at night but photolyzes readily in sunlight. Therefore, its nocturnal production and morning photolysis provides a source of atomic chlorine radicals and a mechanism for recycling of NO_x that would otherwise be lost during hydrolysis of N₂O₅. Further laboratory work has shown that a low-pH (<pH 2) pathway of the reaction of N₂O₅ on chloride-containing aerosol can lead to direct production of Cl₂ [*Roberts et*

al., 2008b], which may help to explain the reported measurements of Cl_2 . The limited observations available to date for quantification of either phenomenon have not yet established their spatial extent or their impact on morning oxidant photochemistry. However, conversion of N_2O_5 to ClNO_2 at low aerosol chloride concentration was recently confirmed in laboratory studies [Roberts *et al.*, 2008b], and the observed efficiencies were in the range (20 to 100%) required to explain the ambient measurements of Osthoff *et al.*, [2008].

6.2.2 Transport and Source Considerations in California Coastal Regions

The land-sea breeze circulation that is prevalent in many areas along the California coastline is conducive to the activation of halogens via nighttime NO_x reactions. Coastal urban areas represent large sources of NO_x , and the nighttime land-breeze phase of the diurnal circulation pattern may transport this NO_x into the marine boundary layer where sea salt and other chloride-containing aerosol are prevalent, thereby promoting formation of ClNO_2 and perhaps Cl_2 . On-shore transport of these air masses during the mid morning sea breeze may then deliver these photochemically active halogens or their photoproducts back into populated regions. This transport pattern is most common in the summer months when synoptic flow is weakest. This transport-chemical processing cycle is expected to be most important for the Southern California Air Basin for which a number of studies have highlighted the interaction of the land-sea breeze with coastal pollution sources and processing [Shair *et al.*, 1982; Cass and Shair, 1984; and McElroy and Smith, 1986]. Depending on the strength and geographic extent of the transport circulation, these active chlorine species and their photochemical products may be transported far into the air basin.

There are limited measurements of photochemical pollutants in the SCAB near-coastal ocean environment. A long-term (1997-2004) O_3 record is available for at Santa Rosa Island, one of the Channel Islands, and a short-term O_3 data set was reported for Catalina Island during the 1997 Southern California Ozone Study. Both data sets show episodes of high O_3 , > 90 ppbv, at night lasting for a number of hours. Other short-term measurement records have shown elevated particle and sulfate concentrations in this coastal environment [Cass and Shair, 1984]. Although these data sets do not include measurements of reactive nitrogen, the presence of high ozone levels in the Channel Islands is consistent with pollutant transport that could bring large NO_x levels over water, with significant production rates for N_2O_5 and presumably ClNO_2 . An example of such a transport episode is shown in Figure 6.2.1 [Osthoff *et al.*, 2008], with ClNO_2 in excess of 1 ppbv within NO_x and O_3 containing plumes on the Texas Gulf Coast.

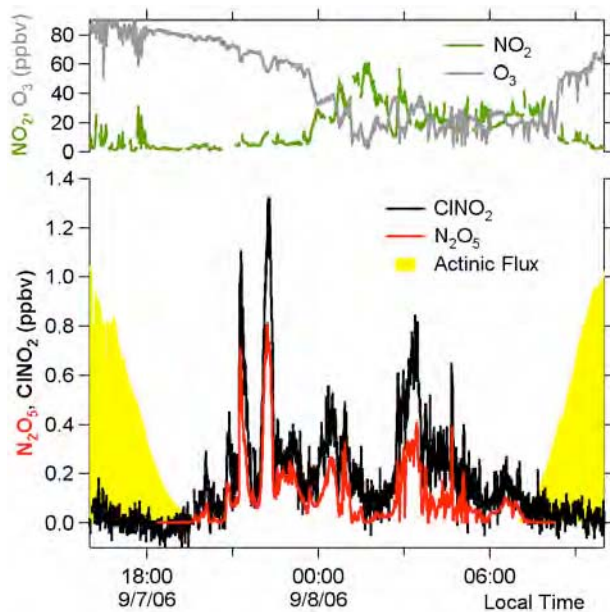


Figure 6.2.1. Concentrations measured from the Ronald H. Brown in the Houston/Galveston area during 2006.

There are also considerable NO_x sources from ship emissions in the California south coast region. These sources are a significant fraction of basin-wide NO_x emissions; they have been growing and are projected to continue to grow over the next decades [Vutukuru and Dabdub, 2008]. Shipping NO_x is known to efficiently produce ClNO_2 based on the observation in the Gulf of Mexico by Osthoff et al., [2008]. The importance of shipping NO_x as a halogen source relative to other urban NO_x will depend on the relative magnitude of the two sources and their mixing into air masses with chloride-containing aerosol.

6.2.3 Integrated Oxidant Chemistry as Reflected in Hydrocarbon Concentration Patterns

In situ measurements of chlorine containing species and the oxidants responsible for activating Cl atoms provide the detailed information necessary to understand the chemical transformations that drive halogen activation. As such, these data provide a snapshot of the instantaneous chemistry. The integrated contribution of various radical sources throughout the course of a diurnal cycle or a period of days can be estimated by comparison of the total radical source calculated from these measurements to those predicted from other sources, such as OH production from ozone photolysis. Such an integrated picture is important because it is the hydrocarbon oxidation processes that drive the photochemical production of ozone and secondary aerosol.

In situ measurements of the concentrations of specifically selected hydrocarbons provide a separate measure of the integrated impact of both the Cl atom and hydroxyl radical initiated chemistry. Figure 6.2.2 compares the rate constants for the oxidation of several hydrocarbons by OH and Cl, and associated atmospheric lifetimes. The relationships in this figure suggest two groups of three hydrocarbons (indicated by red and green symbols) that are well suited for the determination of the integrated impact. Each group provides one hydrocarbon concentration ratio that varies strongly as Cl oxidation progresses, but very little with OH oxidation (i-butane/ n-butane and n-hexane/toluene) and a second hydrocarbon concentration ratio that varies with OH oxidation but not Cl oxidation (i-butane/propane and toluene/ acetylene). Jobson et al. (1994) used the former ratios to demonstrate that the integrated contribution of Cl to hydrocarbon oxidation was much greater than the OH contribution during

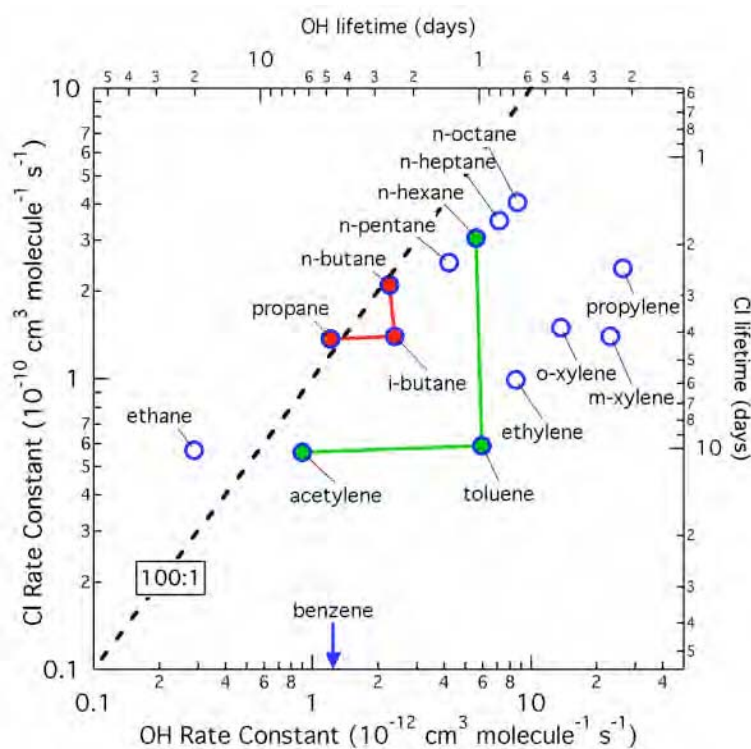


Figure 6.2.2. Comparison of reaction rate constants for oxidation of several hydrocarbons by OH and Cl radicals. The top and right-hand axes give the corresponding e-folding lifetimes for oxidation by OH and Cl at $1 \times 10^6 \text{ cm}^{-3}$ and $1 \times 10^4 \text{ cm}^{-3}$, respectively.

ozone depletion events in the polar sunrise period in the Arctic. Rudolph et al. (1997) used an analysis closely related to the latter ratios to estimate an upper limit of $2-7 \times 10^3 \text{ cm}^{-3}$ for the average Cl atom concentrations at marine boundary layer locations in the western Mediterranean, the eastern North Atlantic, and the North Sea in springtime.

Figure 6.2.3 illustrates the analysis of the more reactive hydrocarbons indicated by green symbols in Figure 6.2.2. The data were collected off the eastern coast of North America on the Ronald H. Brown during the 2004 ICARTT field study. The lifetimes of the two more reactive hydrocarbons in this group are about 0.5 day at the average OH concentrations expected in the summertime marine boundary layer. Thus, the analysis based on these ratios is expected to reflect the effects of the oxidation chemistry over a time scale of a day or two. The analysis in Figure 6.2.3 assumes that hydrocarbons are emitted at relatively constant ratios (given by the triangle in the figure) across the region under study. This assumption is justified by studies in the source region (e.g. Warneke et al., 2006, which provides the emission ratios utilized here). The solid lines in Figure 6.2.3 provide approximately orthogonal axes to gauge the integrated oxidation of the hydrocarbons in a sampled air mass, with the abscissa tracking OH oxidation and the ordinate Cl oxidation. The ICARTT data scatter about the OH oxidation line, with at most only modest displacement toward the Cl oxidation line, which indicates that the OH radical is predominately responsible for hydrocarbon oxidation. This is consistent with preliminary determinations from the Texas 2006 campaign showing an integrated contribution of Cl from ClNO_2 of less than 10% of total radical sources within one photochemical cycle. It is noteworthy, however, that the timing of Cl from ClNO_2 is such that it provides a radical source comparable to that of OH early (i.e., first three hours) in the day. Although its contribution may be small in an integrated sense, its timing may increase its importance for ozone formation at the start of a photochemical cycle.

Similar analyses will be conducted on hydrocarbon sets data collected during CalNex 2010. The analysis is expected to be particularly unambiguous in California, since in this region gasoline-powered vehicles are the primary source of the hydrocarbons of interest, and a very uniform hydrocarbon emission pattern is expected.

6.2.4 Implications for global atmospheric chemistry and climate

The 2006 NOAA study in the Gulf of Mexico provided the first in-field determination of both the presence of ClNO_2 and the efficiency of its production from heterogeneous reactions of NO_x species. Extrapolation of the efficiencies determined there to marine NO_x emissions worldwide indicates that production of ClNO_2 may

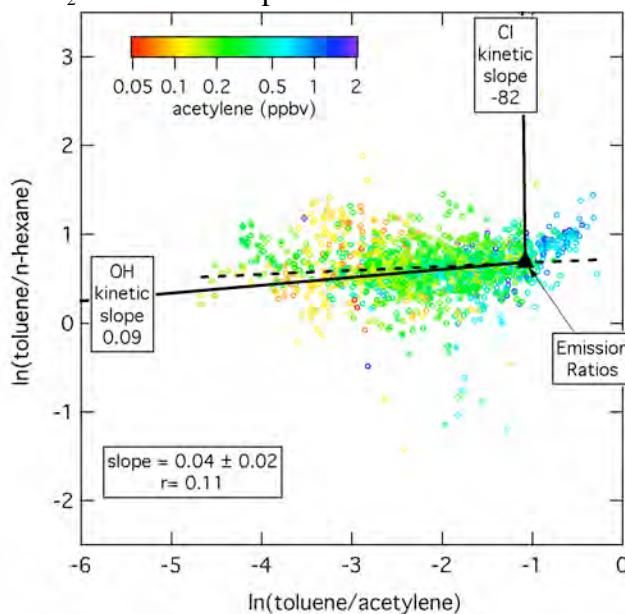


Figure 6.2.3. Log-log relationship between two hydrocarbon ratios. The triangle symbol indicates the estimated hydrocarbon ratios in the regional emissions. The solid lines indicate how the emission ratios are expected to evolve under purely Cl or purely OH oxidation. The dashed line gives the linear least squares fit to the measured concentration ratios.

amount to some 3 Tg of Cl per year, a significant fraction of global estimates for total Cl activation. Oxidant production on this scale would influence processes as varied as aerosol production from marine sulfur emissions, the lifetime of methane and the influence of halogens on tropospheric ozone loss. Data collected during the 2010 California study can serve to provide better estimates for the importance of NO_x emissions as a driver for these feedbacks to the global atmospheric chemical system.

6.2.5 Summary of CalNex Halogen Chemistry Research

Based on the preceding discussion, this work will focus on chlorine activation by reaction of N_2O_5 with chloride-containing aerosol particles and subsequent photochemistry with respect to the following questions:

1. How efficient is halogen activation by nitrogen oxides in coastal areas of California, and what are the factors that affect this efficiency?
2. How important are these mechanisms for halogen activation in comparison to others that have been proposed on the basis of laboratory studies?
3. What are the impacts of this halogen activation on ozone production in coastal California and elsewhere in the state?
4. What effect, if any, is there on aerosol production due to the presence of halogen atoms and associated oxidant chemistry?
5. What are the broader implications of these halogen activation mechanisms for global atmospheric chemistry?

6.2.6 Measurements Required for CalNex 2010

Table 6.2.1 lists the measurements required to address the above research questions. The NOAA/ESRL CSD group has reported the first measurements of ClNO_2 via iodide ion chemical ionization mass spectrometry (CIMS) [Osthoff *et al.*, 2008]. Inclusion of this measurement on the ship platform is essential to the proposed halogen activation research, and inclusion on the aircraft would represent the first-ever airborne measurements of this compound. The instrument is also used for measurement of PAN and can be used for di-halogens (e.g. Cl_2), although inlet considerations will require emphasis on only one class of compounds at particular times or on particular flights (e.g., PAN on daytime P-3 flights, ClNO_2 on nighttime P-3 flights). Roberts *et al.*, [2008a] have briefly described Di-halogen measurements by CIMS. Gas Phase HCl, HNO_3 (nitric acid) and HNO_2 (nitrous acid) are important for a complete description of the ClNO_2 (and Cl_2) production chemistry. Past measurements of these species on the NOAA R/V *Brown* have been carried out by a mist chamber sampling system with ion chromatography analysis. Identification of a measurement for these acid gases will be a priority for the 2010 study.

Aerosol-phase measurements of chloride (Cl^-), and, if possible, its distribution between super- and sub-micron aerosol, is important to understanding the mechanism for halogen activation. PILS and/or AMS instruments can provide sub-micron chloride at high time resolution, although their detection limits do not cover the entire range of Cl^- levels over which ClNO_2 production is rapid. Impactor collectors with IC analysis can provide sufficient sensitivity at lower time resolution for ship-based sampling. Particle pH measurements should be a factor in potential direct production of Cl_2 and can be obtained from a detailed cation / anion balance from, for example, PILS or AMS instruments.

Ship-based platforms have been used previously to quantify chlorine activation within the marine boundary layer and have the advantage of providing continuous measurements over a period of weeks to months in near coastal environments impacted by ship emissions and transport of urban emissions. Aircraft sampling from the NOAA WP-3 complements the continuous ship based measurements, in that it gives a broader picture of the geographic extent of chlorine activation due to inland transport of chloride aerosol and vertical mixing. The aircraft and ship will also aid in the exploration of the role of halogens in ship emissions processing through night-into-day measurements of the ship plumes similar to the experiments described by *Chen et al.*, [2005] which could, for example, yield a unique look at $\text{NO}_x/\text{N}_2\text{O}_5$ -induced Cl activation and subsequent plume oxidant chemistry that might be driven by Cl atoms.

6.2.7 Analysis and Interpretation

The results of the detailed gas and aerosol phase measurements proposed above will be analyzed on a number of different levels. The $\text{NO}_3/\text{N}_2\text{O}_5/\text{ClNO}_2/\text{Cl}_2/\text{Cl}^-$ and aerosol pH data can be interpreted on a process level in which the rates of formation and loss of the individual compounds yield fundamental information on aerosol uptake coefficients, ClNO_2 and Cl_2 production efficiencies, and photolysis of these compounds to produce halogen radicals. Radical budgets, and their influence on ozone and particle production can be inferred from these measurements given enough detail and sufficient observations. The data can also provide inputs to or comparison data for chemical transport models, such as that described by [*Knipping and Dabdub*, 2003] for the greater Los Angeles Basin, to assess the impact of Cl activation on the a regional basis for coastal and inland environments of Southern California and other regions of the state.

Table 6.2.1. Measurements Needed to Address the goals of Halogen Activation Research.

Compound/Parameter	Platform(s)	Method/Technique	Priority [†]
$\text{NO}_3, \text{N}_2\text{O}_5$	Ship	CRDS	1
	Aircraft	CRDS	1
ClNO_2	Ship	CIMS	1
	Aircraft	CIMS	2
Cl_2/BrCl	Ship	CIMS	1
	Aircraft	CIMS	2, 3
HCl	Ship	Mist/IC or other	1
DMS	Ship	GC/MS	1
DMS in seawater	Ship	GC/S det.	1
$\text{HNO}_3, \text{HNO}_2$	Ship	Mist/IC or other	2
HNO_3	Aircraft	CIMS	1
Solar Flux, spectrally resolved	Ship	Spectral Radiometry	1
	Aircraft	Spectral Radiometry	1
Aerosol Chloride	Ship	PILS/AMS/Imp	1
	Aircraft	PILS/AMS	2
Aerosol Nitrate	Ship	PILS	1
Aerosol pH*	Ship	PILS/AMS/Imp	1
Aerosol Nucleation	Ship	SMPS	1

[†](1) essential, (2) important, (3) useful

*Modeled from detailed aerosol composition measurements

References:

- Cass, G. R., and F. H. and Shair (1984), Sulfate accumulation in a sea breeze/land breeze circulation system, *J. Geophys. Res.*, *89*, 1429-1438.
- Chen, G., et al. (2005), An investigation of the chemistry of ship emission plumes during ITCT 2002, *J. Geophys. Res.*, *110*, doi:10.1029/2004JD005236.
- Clegg, S. L., et al. (1998), A thermodynamic model of the system H-NH₄-Na-SO₄-NO₃-Cl-H₂O at 298.15K, *J. Phys. Chem. A.*, *102*, 2155-2171.
- Finlayson-Pitts, B.J., (2003) The tropospheric chemistry of sea salt: A molecular-level view of the chemistry of NaCl and NaBr, *Chem Rev.*, *103*, 4801-4822.
- Finley, B. D., and E. S. Saltzman (2006), Measurement of Cl₂ in coastal urban air, *Geophys Res Lett*, *33*, L11809, doi:11810.11029/12006GL025799.
- Jobson, B. T., H. Niki, Y. Yokouchi, J. Bottenheim, F. Hopper, and R. Leitch (1994), Measurements of C₂-C₆ hydrocarbons during the Polar Sunrise 1992 Experiment: Evidence for Cl atom and Br atom chemistry, *J. Geophys. Res.*, *99*(D12), 25,355–25,368.
- Knipping, E. M., and D. Dabdub (2003), Impact of Chlorine Emissions from Sea-Salt Aerosol on Coastal Urban Ozone, *Environ. Sci. Technol.*, *37*, 275-284.
- McElroy, J. L., and T. B. and Smith (1986), Vertical pollutant distributions and boundary layer structure observed by airborne LIDAR near the complex Southern California coastline., *Atmos. Environ.*, *20*, 1555-1566.
- Osthoff, H. D., et al. (2008), High levels of nitryl chloride in the polluted subtropical marine boundary layer, *Nature Geosciences*, *1*, 324-328.
- Pechtl, S., and R. von Glasow, Reactive chlorine in the marine boundary layer in the outflow of polluted continental air: A model study, *Geophys. Res. Lett.*, *34*, L11813, doi:10.1029/2007GL029761.
- Roberts, J. M., et al. (2008a), N₂O₅ Oxidizes Chloride to Cl₂ in Acidic Atmospheric Aerosol, *Science*, *10.1126/science.1158777*.
- Roberts, J. M., et al. (2008b), Production of ClNO₂ and Cl₂ from N₂O₅ uptake on model aerosol substrates, *Geophys. Res. Lett.*, *submitted*.
- Rudolph, J. et al., The indirect determination of chlorine atom concentration in the troposphere from changes in the patterns of non-methane hydrocarbons, *Tellus B*, *49*, 592-601, 1997.
- Shair, F. H., et al. (1982), Transport and dispersion of airborne pollutants associated with the land breeze-sea breeze system., *Atmos. Environ.*, *16*, 2043-2053.
- von Glasow, R., and P. J. Crutzen (2007), Tropospheric Halogen Chemistry, in *The Atmosphere*, edited by R. F. Keeling.
- Vutukuru, S., and D. Dabdub, (2008) Modeling the effects of ship emissions on coastal air quality: A case study of southern California, *Atmos. Environ.*, *42*, 3751-3764.

6.3 Secondary Organic Aerosol Formation

Particulate matter (PM) in the atmosphere contains a significant -and in many cases dominant- fraction of organic material, and California is no exception [Zhang *et al.*, 2007]. This particulate organic matter (POM) can be directly emitted from primary sources or formed in the atmosphere from oxidation and condensation of volatile organic compounds (VOCs). The latter process is often referred to as secondary organic aerosol (SOA) formation.

Results from the Los Angeles area serve to illustrate how our understanding of the sources of POM has changed over the years. Measurements of molecular tracers in the aerosol suggested that primary emissions from motor vehicles were a large source of POM [Schauer *et al.*, 1996], whereas measured ratios between organic carbon (OC) and elemental carbon (EC) in filter samples showed the occasional importance of secondary formation [Turpin and Huntzicker, 1995]. Recent research using aerosol mass spectrometry (AMS), on the other hand, showed a dominance of oxygenated organic aerosol over hydrocarbon-like organic aerosol, suggesting that secondary formation was much more important than previously recognized, and in fact the dominant source of aerosol in the LA Basin [Zhang *et al.*, 2007].

Efforts to explain the formation of SOA from the removal of measured hydrocarbons have generally failed to explain the data: studies both in the northeastern U.S. [de Gouw *et al.*, 2005], and Mexico City [Volkamer *et al.*, 2007; Kleinman *et al.*, 2008] suggested that the observed SOA formation is an order of magnitude higher than model predictions. The reasons for this discrepancy are unknown at present, but may include (i) SOA yields from hydrocarbons may be higher than previously recognized [Ng *et al.*, 2007], (ii) SOA is formed from semi-volatile precursors that are not measured by existing instruments [Robinson *et al.*, 2007], and (iii) the formation of SOA from biogenic precursors is more efficient in polluted atmospheres [Weber *et al.*, 2007]. The latter reason could also explain why many radiocarbon studies have indicated that the carbon in POM is mostly modern [Schichtel *et al.*, 2008].

The need to understand SOA formation is all the more urgent given the challenges associated with global warming. If biogenic VOCs are indeed a major precursor for SOA in polluted atmospheres, then SOA formation is expected to increase in a warmer world [Tsigaridis and Kanakidou, 2007]. However, if other factors in polluted air are determining SOA formation [Weber *et al.*, 2007], then SOA may actually decrease in the U.S. as a result of emissions controls on vehicles.

Improving our understanding of SOA formation in California is one of the major objectives of CalNex, and we propose a two-pronged approach involving (i) a ground site in the LA basin for the most detailed characterization of urban emissions and the early stages of SOA formation, and (ii) aircraft measurements inside and downwind from the LA basin to follow the air masses over longer processing times, and in the Central Valley and Sierra Nevada to study the influence of agricultural and biogenic emissions on SOA formation.

A ground site in the LA Basin will be equipped with state-of-the art measurements of organic carbon species both in the gas and aerosol phases. Measurements during the night, when

chemical processing of most hydrocarbons is at a minimum, will be useful to determine the direct emissions of hydrocarbons and primary organic aerosol. Measurements during the day are expected to show the onset of SOA formation in the morning with the maximum degree of processing in the afternoon. Instruments planned for this site include a two-channel in-situ gas chromatography-mass spectrometry instrument for very detailed measurements of gas-phase hydrocarbons and oxygenated species [Goldan *et al.*, 2004], and we propose to collaborate with Prof. Jimenez from the University of Colorado on his measurements with aerosol mass spectrometry (AMS) [Canagaratna *et al.*, 2007]. Two new instruments that are currently being developed for use at this site include (i) a chemical ionization mass spectrometer (CIMS) for measurements of the organic acids in the gas phase [Veres *et al.*, 2008] that constitute a large fraction of organic carbon in both the gas and aerosol phases [de Gouw *et al.*, 2005; Sorooshian *et al.*, 2007], and (ii) an incoherent broadband cavity-enhanced absorption spectrometer for measurements of glyoxal [Washenfelder *et al.*, 2008], an important intermediate in the formation of SOA [Volkamer *et al.*, 2007].

The formation of SOA will be followed over longer time scales using flights of the NOAA WP-3D aircraft inside and downwind from the LA Basin, and in the Central Valley and Sierra Nevada. To that aim the NOAA WP-3D is equipped with several instruments that measure organic species in the gas and aerosol phases, including (i) a whole air sampler to collect canisters for off-line hydrocarbon analysis, (ii) a proton-transfer-reaction mass spectrometry instrument (PTR-MS) for fast-response measurements of aromatic and biogenic SOA precursors and other products of VOC oxidation [de Gouw and Warneke, 2007], and (iii) an AMS for fast-response measurements of aerosol chemical composition.

References

- Canagaratna, M.R., et al. (2007), Chemical and microphysical characterization of ambient aerosols with the aerodyne aerosol mass spectrometer, *Mass Spec. Rev.*, *26*, 185-222.
- de Gouw, J.A., et al. (2005), Budget of organic carbon in a polluted atmosphere: Results from the New England Air Quality Study in 2002, *J. Geophys. Res.-Atmos.*, *110*, D16305, doi:10.1029/2004JD005623.
- de Gouw, J.A., and C. Warneke (2007), Measurements of volatile organic compounds in the Earth's atmosphere using proton-transfer-reaction mass spectrometry, *Mass Spec. Rev.*, *26*, 223-257.
- Goldan, P.D., W.C. Kuster, E. Williams, P.C. Murphy, F.C. Fehsenfeld, and J. Meagher (2004), Nonmethane hydrocarbon and oxy hydrocarbon measurements during the 2002 New England Air Quality Study, *J. Geophys. Res.-Atmos.*, *109*, D21309, doi:10.1029/2003JD004455.
- Kleinman, L.I., et al. (2008), The time evolution of aerosol composition over the Mexico City plateau, *Atmos. Chem. Phys.*, *8*, 1559-1575.
- Ng, N.L., J.H. Kroll, A.W.H. Chan, P.S. Chhabra, R.C. Flagan, and J.H. Seinfeld (2007), Secondary organic aerosol formation from m-xylene, toluene, and benzene, *Atmos. Chem. Phys.*, *7*, 3909-3922.
- Robinson, A.L., et al. (2007), Rethinking organic aerosols: semivolatile emissions and photochemical aging, *Science*, *315*, 1259-1262.
- Schauer, J.J., W.F. Rogge, L.M. Hildemann, M.A. Mazurek, and G.R. Cass (1996), Source apportionment of airborne particulate matter using organic compounds as tracers, *Atmos. Environ.*, *30*, 3837-3855.

- Schichtel, B.A., et al. (2008), Fossil and contemporary fine particulate carbon fractions at 12 rural and urban sites in the United States, *J. Geophys. Res.-Atmos.*, *113*, D02311, doi:10.1029/2007JD008605.
- Sorooshian, A., N.L. Ng, A.W.H. Chan, G. Feingold, R.C. Flagan, and J.H. Seinfeld (2007), Particulate organic acids and overall water-soluble aerosol composition measurements from the 2006 Gulf of Mexico Atmospheric Composition and Climate Study (GoMACCS), *J. Geophys. Res.-Atmos.*, *112*, D13201, doi:10.1029/2007JD008537.
- Tsigaridis, K., and M. Kanakidou (2007), Secondary organic aerosol importance in the future atmosphere, *Atmos. Environ.*, *41*, 4682-4692.
- Turpin, B.J., and J.J. Huntzicker (1995), Identification of Secondary Organic Aerosol Episodes and Quantitation of Primary and Secondary Organic Aerosol Concentrations During SCAQS, *Atmos. Environ.*, *29*, 3527-3544.
- Veres, P., et al. (2008), Development of negative-ion proton-transfer chemical-ionization mass spectrometry (NI-PT-CIMS) for the measurement of gas-phase organic acids in the atmosphere, *Int. J. Mass Spectrom.*, *274*, 48-55.
- Volkamer, R., et al. (2006), Secondary organic aerosol formation from anthropogenic air pollution: Rapid and higher than expected, *Geophys. Res. Lett.*, *33*, L17811, doi:10.1029/2006GL026899.
- Volkamer, R., F.S. Martini, L.T. Molina, D. Salcedo, J.L. Jimenez, and M.J. Molina (2007), A missing sink for gas-phase glyoxal in Mexico City: Formation of secondary organic aerosol, *Geophys. Res. Lett.*, *34*, L19807, doi:10.1029/2007GL030752.
- Washenfelder, R.A., A.O. Langford, H. Fuchs, and S.S. Brown (2008), Measurement of glyoxal using an incoherent broadband cavity enhanced absorption spectrometer, *Atmos. Chem. Phys. Discuss.*, *8*, 16517-16553.
- Weber, R.J., et al. (2007), A study of secondary organic aerosol formation in the anthropogenic-influenced southeastern United States, *J. Geophys. Res.-Atmos.*, *112*, D13302, doi:10.1029/2007JD008408.
- Zhang, Q., et al. (2007), Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes, *Geophys. Res. Lett.*, *34*, L13801, doi:10.1029/2007GL029979.

6.4 Ammonium Nitrate Processing

In California, particulate matter in the troposphere is often dominated by ammonium nitrate aerosol. This is in contrast to other regions of the United States, where sulfate aerosol is usually much more abundant than ammonium nitrate [Malm *et al.*, 2004]. Consequently, understanding the formation, transport, and fate of ammonium nitrate aerosol in California is critical to developing strategies to improve air quality in this region. Fine particulate ammonium nitrate is formed in the accumulation mode from the association of gas phase ammonia (NH_3) and nitric acid (HNO_3) precursors. Anthropogenic emissions of both NH_3 and NO_x (which oxidizes to form HNO_3) control the abundance of ammonium nitrate in the atmosphere. Since ammonium nitrate is a secondary pollutant that forms over time, its abundance is often greater at downwind locations than in source regions. Ammonium nitrate levels can exceed federal air quality standards for particulate matter, and the sources and processes responsible for these exceedances have been studied extensively [Russell *et al.*, 1986; Chow *et al.*, 1994; Solomon *et al.*, 2002]. Despite decades of study, uncertainties related to ammonium nitrate formation remain. For example, ammonium nitrate can cause large visibility reductions that are not reproduced in models as a result of large uncertainties in precursor emissions [Park *et al.*, 2006].

A complete understanding of the processes involved in ammonium nitrate formation requires a description of the vertical distribution of ammonium nitrate and its precursors. Aerosols may be present in layers aloft that are not captured by measurements from ground-based instruments. These elevated layers are important to visibility reduction and transport of reactive nitrogen. Measurements of aerosol size distributions from an aircraft showed multiple elevated aerosol layers with a complex vertical structure over the Los Angeles Basin [Collins *et al.*, 2000]. Layers of particles were also observed during flights from the NOAA WP-3 aircraft over the San Joaquin Valley, Los Angeles Basin, and Mojave Desert in April and May, 2002. Gas-phase NH_3 and HNO_3 were converted into particulate ammonium nitrate downwind of regions with high NH_3 emissions (Figure 6.4.1), as evidenced by depletion of gas phase HNO_3 and enhancements in particulate nitrate and particle volume. This gas to particle conversion was also observed far from NH_3 emission regions at higher altitudes within the boundary layer [Neuman *et al.*, 2003]. These particle layers, which were observed in well-mixed boundary layers where other directly emitted gases and secondary pollutants

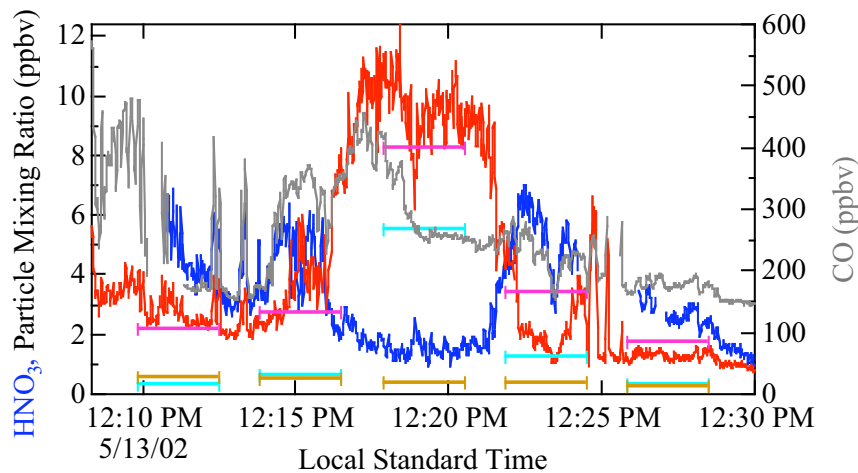


Figure 6.4.1. One second measurements of HNO_3 (blue) and fine particle mixing ratio (red) obtained near Rubidoux in the eastern Los Angeles Basin on 13 May 2002. Fine particulate NO_3^- (light blue), NH_4^+ (pink), and sulfate (orange) concentrations are shown as bars, where the length indicates the averaging time for each sample. CO mixing ratios (right axis) are shown in gray. The aircraft was flying at 0.7 km.

exhibited no vertical gradients, were caused by lower ambient temperatures at higher altitudes that reduced the dissociation constant for ammonium nitrate aerosol (Figure 6.4.2).

New instruments aboard the NOAA WP-3 aircraft will provide further information about ammonium nitrate formation and transport. Fast response measurements of NH_3 [Nowak *et al.*, 2007], nitrate, ammonium [DeCarlo *et al.*, 2006] and CCN have been added to the aircraft payload since the 2002 study. These measurements, in combination with the measured HNO_3 concentrations and particle size distributions, can be used to study the thermodynamic equilibrium for ammonium nitrate aerosol [Nowak *et al.*, 2006] and whether its abundance is limited by NH_3 or HNO_3 precursors. By following plumes of ammonium nitrate downwind, the time evolution of the conversion of gas phase compounds to particulate matter can be examined. This will be valuable for understanding the atmospheric effects of NH_3 and NO_x emissions on downwind locations. For example, the partitioning of nitrate between the gas and aerosol phases affects nitrogen deposition patterns, which can degrade water and agricultural resources. Also, the concentration of CCN in the atmosphere determines the effect of aerosols on precipitation amount and patterns. One goal of CalNex 2010 is to determine the effect of ammonium nitrate formation on measured CCN concentrations including the ammonium nitrate formed in the upper part of the boundary layer.

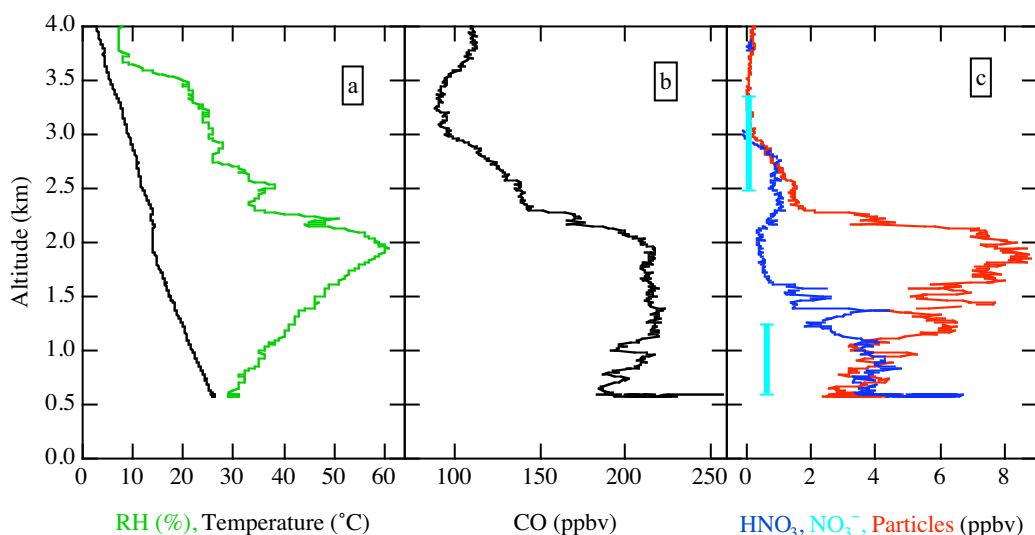


Figure 6.4.2 One second measurements recorded during a descent of the NOAA WP3-D over the San Joaquin Valley on 17 May 2002. Ambient temperature (black) and RH (green) are shown versus aircraft altitude (a). Panel b shows CO versus aircraft altitude, and panel c shows HNO_3 (blue), NO_3^- (light blue) and fine particle mixing ratios (red). Fine particle mixing ratios are calculated from fine particle volume, assuming the particle composition to be ammonium nitrate.

References:

- Chow, J. C., J. G. Watson, E. M. Fujita, Z. Lu, and D. R. Lawson (1994), Temporal and spatial variations of $\text{PM}_{2.5}$ and PM_{10} aerosol in the Southern California Air Quality Study, *Atmos. Environ.*, 28, 2061-2080.
- Collins, D. R., H. H. Jonsson, H. Liao, R. C. Flagan, J. H. Seinfeld, K. J. Noone, and S. V. Hering (2000), Airborne analysis of the Los Angeles aerosol, *Atmos. Environ.*, 34, 4155-

4173.

- DeCarlo, P. F., J. R. Kimmel, A. Trimborn, J. Jayne, A. C. Aiken, M. Gonin, K. Fuhrer, T. Horvath, K. S. Docherty, D. R. Bates and J. L. Jimenez (2006). A Field-Deployable High-Resolution Time-of-Flight Aerosol Mass Spectrometer. *Analytical Chemistry*, 78 (24), 8281-8289.
- Malm, W. C., B. A. Schichtel, M. L. Pitchford, L. L. Ashbaugh, and R. A. Eldred (2004), Spatial and monthly trends in speciated fine particle concentration in the United States, *J. Geophys. Res.*, 109, D03306, doi:10.1029/2003JD003739.
- Neuman, J. A., *et al.* (2003), Variability in ammonium nitrate formation and nitric acid depletion with altitude and location over California, *J. Geophys. Res.*, 108(D17), 4557, doi:10.1029/2003JD003616.
- Nowak, J. B., *et al.* (2006), Analysis of urban gas phase ammonia measurements from the 2002 Atlanta Aerosol Nucleation and Real-Time Characterization Experiment (ANARChE), *J. Geophys. Res.*, 111, D17308, doi:10.1029/2006JD007113.
- Nowak, J. B., J. A. Neuman, K. Kozai, L. G. Huey, D. J. Tanner, J. S. Holloway, T. B. Ryerson, G. J. Frost, S. A. McKeen, and F. C. Fehsenfeld (2007), A chemical ionization mass spectrometry technique for airborne measurements of ammonia, *J. Geophys. Res.*, 112, D10S02, doi:10.1029/2006JD007589.
- Park, R. J., D. J. Jacob, N. K., R. M. Yantosca (2006), Regional visibility statistics in the United States: Natural and transboundary pollution influences, and implications for the Regional Haze Rule, *Atmos. Environ* 40, 5405–5423.
- Russell, A. G., and G. R. Cass, Verification of a mathematical model for aerosol nitrate and nitric acid formation and its use for control measure evaluation (1986), *Atmos. Environ.*, 20, 2011-2025.
- Solomon, P. A., L. G. Salmon, T. Fall, and G. R. Cass (2002), Spatial and temporal distribution of atmospheric nitric acid and particulate nitrate concentrations in the Los Angeles area, *Environ. Sci. Technol.*, 26, 1594-1601.

7. Aerosol Properties and Radiative Effects

7.1 Relevance:

Aerosol particles scatter and absorb solar radiation affecting visibility (Malm et al., 1994) and the Earth's radiative balance (e.g., Rasool and Schneider, 1971; Charlson et al., 1992; Ramanathan and Vogelmann, 1997). These particles can also act as cloud condensation nuclei (CCN) and ice nuclei (IN), thereby influencing the albedo (first indirect effect, Twomey, 1974), lifetime (Albrecht, 1989), precipitation (Warner, 1968; Rosenfeld, 2000) and extent (Ramanathan et al., 2001) of clouds. Aerosol concentrations and their optical and radiative impacts are particularly high in regions downwind of sources, where diurnally averaged clear-sky, surface radiative forcings reach up to 30 Wm^{-2} (Russell et al., 1999; Ramanathan et al., 2001; Conant et al., 2003). International field campaigns over the past 12 years have studied aerosol properties and their direct radiative effects downwind of Eastern North America (1996 – TARFOX; 2004 – ICARTT), Southwestern Europe (1997 – ACE-2), Southeast Asia (1999 – INDOEX), Eastern Asia (2001 – ACE-Asia), West Coast of the United States (ITCT 2002); East Coast of the United States (ICARTT 2004), Gulf of Mexico (TexAQS/GoMACCS 2006), and International Polar Year experiments (ARCPAC/ICEALOT, 2008). During these years, our scientific tools for measuring aerosol and their radiative properties and our understanding of aerosol chemistry and transport and transformation processes have evolved tremendously (IPCC, 2007). Nevertheless, the current understanding of aerosol effects on climate, both with respect to their direct radiative impact and the multiple (and mutual) effects of aerosol on clouds, leaves us with many unanswered questions. This situation is exacerbated by the complexity and regional/temporal variability of aerosol chemistry that is the source of large uncertainties in the optical, radiative, and cloud nucleating properties of the aerosol. At this time aerosols pose the largest uncertainty in calculations of radiative forcing of the climate system (Figure 1.1 above from IPCC, 2007).

As part of CalNex 2010, we propose to study the processes controlling the formation, transport and transformation of aerosol particles (see section on Chemical Transformation above) and the effect of chemical composition and mass size distribution on the optical, radiative, and cloud nucleating properties of the aerosol, as well as their effect on cloud optical depth. One of the strengths of the CalNex study will be the synergy of the aerosol measurements with the extensive gas-phase measurements, especially on the P-3 and Ron Brown. This information about particle sources facilitates interpretation of processes. An example of the tight correlation of gas-phase and aerosol species is shown in Figure 7.1, which shows data taken over the western United States in 2002. It compares gas-phase and particle measures of biomass burning influence.

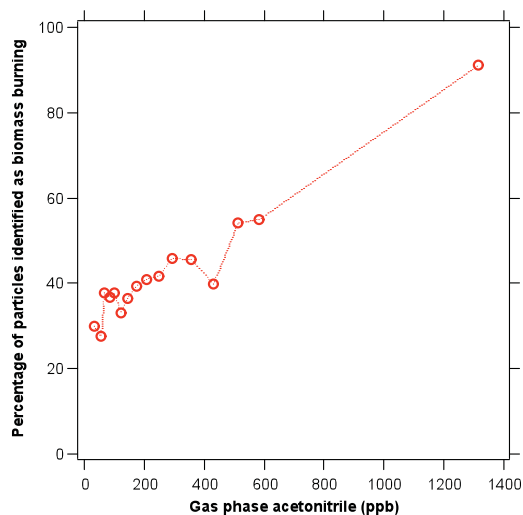


Figure 7.1: Correlation between acetonitrile, a gas phase compound formed in fires, and the percentage of particles identified as biomass burning by their carbon and potassium content. Data are from the NOAA P-3 over the western United States in 2002. The slope and intercept provide information on the relative strengths of sources and sinks of these species.

Besides aerosol sources, aerosol loss processes are also important. Again, simultaneous measurements of gas-phase and aerosol species are crucial. An example is the sulfur budget where by measuring both gas-phase and aerosol species the conversion of SO₂ to sulfate can be distinguished from loss of sulfur from the atmosphere.

Below we separate our science questions into aerosol “direct” radiative effects in cloud-free conditions and aerosol “indirect effects” where the focus is on aerosol-cloud interactions.

7.2 Direct Radiative Effects

Whether aerosols have a net warming or cooling effect on the atmosphere depends on the relative amounts of light scattering and absorption. This is quantified by measuring the amount of aerosol, its size distribution and its single scattering albedo (SSA), which is the ratio of scattering to extinction (scattering + absorption). The warming or cooling effect depends primarily on the SSA and whether the aerosols are above bright or dark land or ocean. Fairly small changes in the SSA (about 10%) can change the net effect from warming to cooling or vice versa.

Much but not all, of the aerosol light absorption comes from primary emissions such as diesel soot. This absorption is heavily modified by changes in the atmosphere as organics, sulfate, nitrates, and other species condense upon or react with the soot-containing particles. Aerosol light scattering is also dependent on these species. Emissions of diesel exhaust drop significantly on weekends in California (Blanchard and Tanenbaum, 2003), providing the opportunity to separate their effects from other sources. Light scattering by aerosols comes from reflective components including organics, sulfates, and nitrate. As organics can make up a significant fraction of the aerosol mass, understanding the sources and burden of secondary organic aerosol (Figure 2.9) is important not only for determining the aerosol mass budget but also aerosol climate and health effects.

The magnitude of aerosol direct climate forcing is influenced by the degree to which particles reversibly take up water. As particles grow due to the uptake of water they scatter and absorb more light. Many particles emitted from primary sources take up little water when fresh but take up more water as they are processed in the atmosphere. CalNex will provide excellent opportunities to measure the transformations that result in increased water uptake, light scattering, and absorption.

Aerosol Direct Effect Scientific Questions: The aerosol-radiation research plan is focused on several scientific questions described below.

<p>1. What are the regional scale aerosol optical properties in California under different meteorological conditions and how do these properties change with altitude, location, distance from source, and time of day?</p>
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Strategy: Measure/calculate aerosol properties under a variety of conditions e.g. downwind of different point and regional sources; at various altitudes and distances from sources; at different times of day; under different meteorological conditions; and from different platforms. Compare

directly measured aerosol scattering, backscattering, extinction and absorption coefficients with those calculated from the measured size distributions and chemical composition (local closure).

Many field experiments have focused on the characterization of tropospheric aerosol properties to improve estimates of aerosol direct radiative forcing of climate. Both aircraft and *in situ* shipboard measurements have played an important role in these experiments as they provide information about aerosol chemical composition, size distributions, optical properties, and mass loadings in the boundary layer (Quinn and Bates, 2005) and aloft (REF). This information is required to fully understand the impact of regional aerosol plumes on climate and air quality. CalNex builds on previous field experiments with improved instrumentation, especially for absorbing aerosols, and an emphasis on interpretation of aerosol properties using measured gas-phase species.

2. How well can chemical transport models and coupled models define the regional aerosol distribution?

Strategy: Compare measured aerosol chemical and optical properties with those determined from models. Develop new or confirm previously reported parameterizations relating aerosol chemical properties to optical properties for use in combined chemical transport – radiative transfer models.

Radiative transfer models are used to calculate regional aerosol radiative forcing. They require as input regional aerosol optical properties (single scattering albedo, backscatter fraction, mass scattering efficiencies, the functional dependence of scattering on RH) and aerosol mass distributions calculated from chemical transport or coupled models. Aerosol sampling during CalNex 2010 will be used to validate and refine the ability of these models to define the three dimensional aerosol distribution in this region (see section on Validation of Forecasting Models). The complex coastal terrain of California will present the models with challenges.

Previous work has shown that constraining radiative transfer calculations by observed optical properties increases estimates of direct climate forcing of aerosols relative to values obtained with model-prescribed optical properties (Bates et al., 2006). Such calculations indicate the value of using empirically derived data in guiding model estimates of climate forcing by aerosols. Data from past field experiments have also been used to empirically determine relationships between the mass fraction of particulate organic matter (POM) in the aerosol and the dependence of light scattering and extinction on relative humidity (Quinn et al., 2005). These empirically-based parameterizations have then been made available for implementation in models. Such parameterizations will be developed for the CalNex study region and compared to those developed for other regions.

3. What is the direct (clear-sky) radiative impact of the aerosols in the California study region?

Strategy: Measure/calculate clear sky radiative forcing under a variety of conditions (e.g. downwind of different point and regional sources; at various altitudes and distances inland; at different times of day; under different meteorological conditions). Compare aerosol radiative effects measured by sun photometers, flux radiometers, and satellite retrievals. Integrate the

results of these measurements/comparisons to assess the regional clear-sky direct radiative forcing (c.f., Figure 7.2).

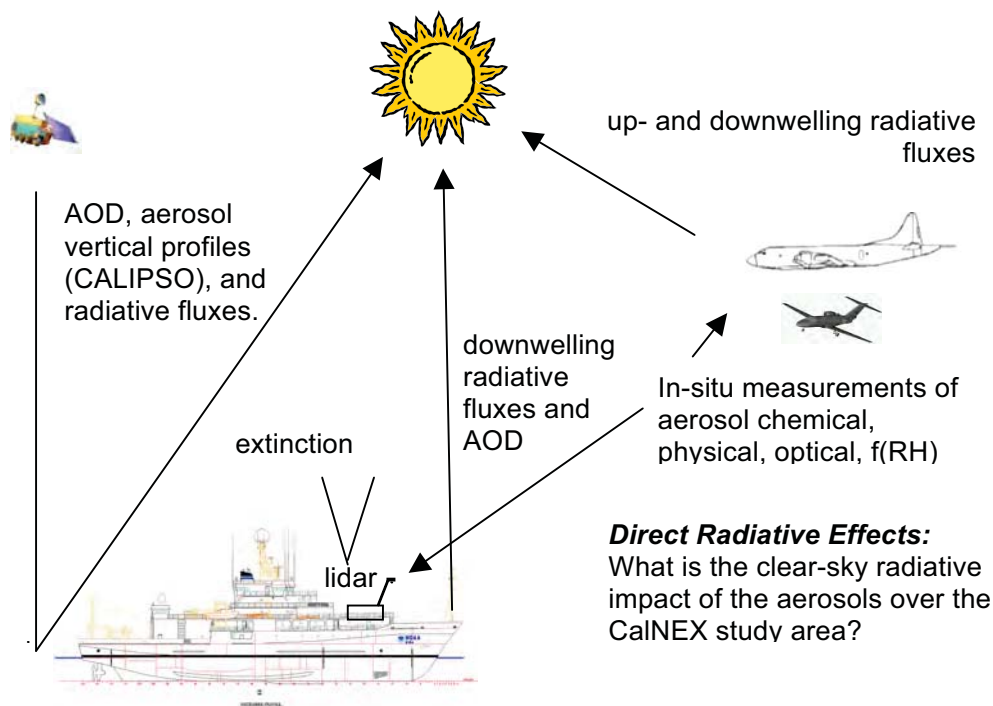


Figure 7.2. Schematic of platform deployment for measurements of the clear-sky radiative effect

The radiative impacts of aerosol are particularly high downwind of major source regions, where diurnally averaged clear sky surface forcings range up to 30 Wm^{-2} (Russell et al., 1999; Ramanathan et al., 2001; Conant et al., 2003). CalNex 2010 will provide an opportunity to combine radiative flux and aerosol optical depth measurements at the surface, within the atmospheric column and from satellite. In 2010 a number of satellite sensors, including the CALIPSO lidar will be able to provide aerosol data from space. To reap the maximum benefit from these satellite measurements it is critical that we test and validate these measurements with in-situ and lower atmosphere/surface based column measurements (Diner et al., 2004). These measurements during CalNex 2010 will be made under a variety of aerosol/meteorological conditions.

4. What are the dominant aerosol chemical components affecting aerosol light scattering (haze)?

Strategy: Calculate aerosol mass fractions and mass scattering efficiencies using multiple linear regression and Mie modeling approaches.

Aerosol chemical composition varies greatly depending on regional sources and the atmospheric processing that occurs downwind of those sources. As a result, the dominant chemical components that determine aerosol light extinction and haze vary regionally. Organic aerosol

dominated the total sub-micron aerosol mass and light scattering in the marine boundary layer off the New England coast during the summer of 2002 (Bates et al., 2005). This situation is not characteristic of aerosols downwind of Asia or Europe (Quinn and Bates, 2005) or other regions of the U.S. Aerosol measured during GoMACCS in the Houston-Galveston area was dominated by ammonium sulfate (Bates et al., 2008). The aerosol chemical and optical measurements made during CalNex will improve our understanding of the dominant aerosol mass and scattering fractions and their health and radiative (e.g. water uptake, cloud nucleating properties) impacts. This information will be available to develop possible mitigation strategies for the CalNex region.

5. How does the aerosol chemical composition affect the humidity dependence of aerosol light scattering?

Strategy: Compare directly measured $f(RH)$ (extinction and scattering) with values calculated from aerosol size distributions and chemical composition. Compare $f(RH)$ values during periods of different organic mass fraction. Compare aerosol extinction at the surface measured by several techniques. Compare $f(RH)$ to measures of photochemical processing.

A major finding during previous experiments was that $f(RH)$ (extinction and scattering) was a function of the POM mass fraction (Quinn et al., 2006; Massoli et al., 2008). As POM mass fraction increases, water uptake by the aerosol decreases so that light extinction and scattering by the aerosol also decreases. This behavior was observed during ACE-Asia, ICARTT, INDOEX, and GoMACCS. Relationships between POM mass fraction and $f(RH)$ will be developed for CalNex and compared to these other regions. Quantifying the relationship between POM mass fraction and $f(RH)$ on a regional basis will improve parameterizations in coupled chemical transport-radiative transfer models. During CalNex, the nature of the organics (oxygenated vs. hydrocarbon-like and speciation) will be considered in the investigation of the POM- $f(RH)$ relationship.

6. What is the amount of light absorbing aerosol over California and how does it vary from offshore to inland locations?

Strategy: Measure the absorbing component of the aerosol at surface stations and with airborne in-situ instruments. Compare to gas-phase tracers in order to determine the sources of the light absorbing aerosol.

The deployment of numerous instruments that will measure aerosol chemical composition and optical properties (light scattering, absorption, and extinction) will enable assessment of the prevalence of light absorbing aerosol in the region and its spatial and temporal variability. These data will allow calculation of the aerosol single scattering albedo, which determines whether the aerosol has a net cooling or warming effect. Measurements of the vertical distribution of light absorption will provide important information on heating rates and potential modifications to boundary layer stability.

Having three different and complementary techniques to measure light absorption by aerosol particles will provide one of the best airborne measurements ever accomplished. One of the

science benefits will be new information on how particles change their light absorption properties as the aerosol is chemically processed downwind of sources. A new instrument to measure single particle albedo may also be deployed at a ground site

Participants and Platforms

NOAA and their extramural partners will instrument and deploy the WP-3, *RV Ronald H. Brown* and a small aircraft devoted to aerosol radiation studies. The *in situ* and suborbital remote sensing measurements will be guided in the field with a hierarchy of model products and satellite observations.

Deployment Strategy (regional characterization and direct radiative forcing)

Chemical forecast models and satellite data will be used to determine the location and vertical distribution of aerosol plumes for targeted characterization of regional radiative forcing.

- Measure/calculate aerosol properties and clear sky radiative forcing under a variety of conditions (e.g. downwind of different point and regional sources; at various altitudes and distances inland; at different times of day; under different meteorological conditions).
- Compare directly measured aerosol scattering, backscattering, and absorption coefficients with those calculated from the measured size distributions and chemical composition (local closure).
- Compare directly measured $f(RH)$ (extinction and scattering) with values calculated from aerosol size distributions and chemical composition.
- Compare measured aerosol properties with those determined from chemical transport models and coupled regional models such as the Weather Research and Forecasting-Chemistry (WRF-CHEM) model.
- Comparison of aerosol optical depth spectra measured by sunphotometers and retrieved from satellite radiances
- Compare clear sky forcings derived from models using measured aerosol properties and flux radiometers.
- Integrate the results of these measurements/comparisons to assess the regional clear-sky direct radiative forcing.

Table 2.1. Proposed measurements and platforms for aerosol characterization and direct radiative forcing studies.

CATEGORY	Parameters to Measure	Platform			
		RHB	WP-3	Plane*	Satellite
Aerosol Chemistry	Anions and cations	X	X	O	
	Elemental carbon (EC)	X	X	O	
	Organic carbon (OC)	X	X	O	
	Particulate organic matter (POM)	X	X		
	Organic carbon (speciated)	O			
	Organic functional groups	O			
	Trace elements	X	X		
Aerosol Physical and Optical Measurements	Number concentration	X	X	O	
	Number size distribution	X	X		
	Absorption (spectral)	X	X	O	
	Scattering and backscattering (spectral)	X		O	
	Extinction	X	X	O	
	Aerosol light scattering hygroscopic growth	X			
	Aerosol light extinction hygroscopic growth	X	X		
	Aerosol hygroscopic growth	O			
Lidar backscatter profiles	O				
Radiation Measurements	Aerosol Optical Depth (spectral)	X		O	
	Radiative fluxes, solar and longwave, upwelling and downwelling (spectral)	O	O	O	
	Direct, diffuse, and total irradiances (spectral where possible)	O	O	O	
	UV flux	O	X	O	
Satellite-retrieved Fields of:	Aerosol Optical Depth (spectral)				Terra (MODIS, MISR)
	Radiative fluxes, solar and longwave				Aqua (MODIS)
	Surface albedo (spectral where possible)				
	Aerosol vertical profiles				CALIPSO
Meteorological Measurements	Wind speed, direction, RH, T, pressure,	X	X	O	
	cloud type and amount, visibility	X			

RHB – NOAA R/V *Ronald H. Brown*

PLANE – small plane devoted to aerosol radiation studies

X – indicates NOAA in-house capability

O – indicates needed measurement

* Note: the NOAA WP-3 will include complementary aerosol instrumentation (Table X, page XX) that may be used in this study.

7.3 Aerosol –Cloud Interactions (Indirect Effects)

The effects of aerosol on clouds and precipitation cover a range of physical processes and scales. The impacts of aerosol on cloud radiative properties are termed “indirect effects”. The most important variables for aerosol-cloud interactions are the number of aerosol particles sufficiently large to act as cloud nuclei, the amount of water available to the cloud, and the updraft velocity of air entering the base of a cloud. The number of cloud nuclei can change the brightness, depth, cloud fraction, and other aspects of a cloud. Changing cloud brightness or fraction also changes the energy balance of the atmosphere, leading to important dynamic responses that in some cases may partly compensate for the immediate impact of the aerosol, and in other cases might enhance it.

Various aerosol effects on clouds have different temporal and spatial scales. For example, ship tracks have been a useful means to investigate the immediate response of marine clouds to an aerosol perturbation. As the marine boundary layer readjusts, however, the broader spatial scales may need to be investigated with different tools.

The overarching science question to be addressed is:

How do the maritime and continental aerosol over the California study area affect cloud microphysical and macrophysical properties, and how do clouds affect aerosol size distribution and chemical properties?

The study area is characterized by a range of aerosol types, as discussed in the previous section on “Chemical Transformations”. The size distribution and composition of these particles are expected to vary greatly based on emissions, chemical processes (e.g., gas-to-particle conversion and heterogeneous processes), and transport (advection, recirculation, venting, and fumigation). This range of aerosol conditions will provide a means of investigating the extent to which aerosol amount and composition affect cloud microphysics, and in particular cloud optical depth. By addressing the following specific science questions our goal is to provide important information for evaluating the Twomey (1974) indirect effect, i.e., the effect of aerosol on cloud reflectance, and to reduce the uncertainty in cloud radiative forcing depicted in the IPCC chart (Figure 1). We will also explore the effect of aerosol on precipitation.

Focused Science Questions:

1. What is the indirect effect of aerosols on marine stratus clouds?

- *Strategy: Compare cloud optical depth (measured) and drop number concentrations (inferred) from remote sensing with those predicted by models of cloud activation given observed aerosol characteristics and updraft velocity. After sorting by liquid water path, such observations give an estimate of the first (Twomey) indirect effect on clouds.*

The optical depth of a cloud is controlled by the water content of a cloud and the number concentration of cloud droplets. The number of droplets in turn is controlled by the updraft velocity and the number and size distribution of aerosol particles. Surface observations of the liquid water content and cloud droplet number have been used to measure the aerosol indirect effect on continental stratus clouds (Feingold et al., 2003). Similar measurements should work especially well for marine stratus because they are often tightly coupled to the surface, where

detailed measurements of the number, size, and cloud-nucleating properties can be made. Shipborne surface aerosol, Doppler lidar updraft velocity, liquid water, and optical depth measurements will provide the essential measurements for drop closure. Drop concentration will be inferred from adiabatic assumptions (reasonable for this environment), or from other methods (McComiskey et al., 2008). Polar-orbiting satellites will provide retrievals of cloud optical depth and drop size, which will provide valuable supporting data. Models will ingest aerosol size distribution/composition and vertical velocity measurements from ship or aircraft, and will compare measured and model-derived drop concentrations.

Depending on the schedule overlap between the various platforms, occasional overflights of either the P3 or light aircraft would provide information on free tropospheric aerosols being entrained into the tops of the clouds.

2. How well do dynamical boundary layer models represent real clouds?

- *Strategy: Assess the ability of large eddy models to represent observed cloud microphysical processes, cloud dynamical and microphysical evolution, cloud fraction and precipitation development.*

The measurements to be acquired during CalNex 2010 represent an opportunity to test various models of aerosol-cloud interactions within a dynamical framework. Observations will provide constraints on boundary layer thermodynamic profiles, wind velocity components, microphysical properties, cloud depth, and precipitation formation. Visible satellite imagery will provide a geostationary view of cloud fields at 1-km resolution. Polar-orbiting satellites will provide high-resolution imagery and retrievals of cloud optical depth and drop size. Large eddy simulation models that integrate coupled dynamics, aerosol and cloud microphysics, and radiation (e.g., Jiang et al. 2008) will be applied to a number of case studies. Model simulations will be used to test hypotheses pertaining to aerosol indirect effects, including aerosol effects on cloud fraction and precipitation initiation.

3. How important is composition in determining the cloud condensation nucleating properties of an aerosol?

The literature contains a wealth of studies regarding the importance of aerosol composition for cloud drop activation, particularly with respect to inorganic, and more recently, water-soluble organic compounds. In addition, chemical effects on droplet activation such as nitric acid, surfactants, and organic films have been shown to be of potential importance (e.g., Nenes et al. 2002). The complexity of aerosol sources in the study area will afford an excellent opportunity to study the importance of composition vis-à-vis droplet formation.

- *Strategy: Compare measured CCN spectra with those calculated by thermodynamic models of aerosol activation, given measured aerosol size distribution and (size-resolved) chemical composition (CCN closure)*

The cloud condensation nucleus spectrum is an important property of the aerosol population and represents the number of particles that will grow to droplet sizes at a prescribed water vapor supersaturation. It is important to establish whether aerosol-CCN closure experiments can be

achieved under a range of aerosol conditions, including those containing high organic aerosol fractions or fresh emissions. Organic species may represent a large source of uncertainty in closure studies (Charlson et al., 2001). Many aerosol-CCN comparisons implement Köhler theory and assume a mixture of a pure soluble salt, such as ammonium sulfate and insoluble material, neglecting detailed treatment of organic materials. Theoretical and laboratory studies indicate that organics may alter the activation characteristics of aerosol by reducing the mass accommodation coefficient of water (Bigg et al., 1986; Saxena et al., 1995; Feingold and Chuang, 2002; Nenes et al.) or by decreasing droplet surface tension (Facchini et al., 1999). Partially soluble aerosols (Shulman et al., 1996) and soluble gases (Laaksonen et al., 1998) may also contribute to uncertainties in the predictions of Köhler theory when the concentrations or properties of such species are unknown. A recent study in Riverside, California (Cubison et al., 2008) points to the importance of identifying the mixing state of aerosol if successful closure is to be achieved.

Advances in the measurement of aerosol chemical composition and, in particular, characterization of POM make it more possible now than in past experiments to relate variability in composition to cloud droplet activation. Data collected during GoMACCS were used to parameterize the relationship between hydrocarbon-like organic aerosol (HOA) and critical diameter for activation (Quinn et al., 2008). It was found that increasing HOA content of the aerosol led to an increase in the required critical diameter for activation at a fixed supersaturation. The range of aerosol and gas-phase conditions in the California study area, along with further advances in instrumentation prior to CalNex 2010, will provide more information for parameterizing the effect of composition on cloud drop activation.

4. What are the concentrations and sources of ice nucleating aerosols? Are their properties changed by anthropogenic emissions of sulfate, nitrate, and organic compounds?

Ice nuclei are important to the initiation of precipitation from mixed phase clouds. One approach is to study ice nuclei outside of clouds where aerosol size distributions and chemistry can be measured simultaneously. Laboratory data have shown that ice nuclei can be partially deactivated by sulfate or organic coatings. Nitrate may have similar effects. California should provide an environment with varied sources of ice nuclei (dust, soot, etc.) and various amounts of atmospheric processing of those particles.

- *Strategy: Fly an ice nucleus counter on the P-3 in the free troposphere to measure the concentrations and properties of ice nuclei. Compare these data to PALMS mass spectrometer measurements of aerosol mixing state as well as AMS and liquid sampler data on chemical composition. Gas-phase compounds will provide measures of aging and photochemical processing.*

5. What are the primary controlling factors for precipitation formation in marine stratus?

- *Strategy: Measure liquid water path, surface or cloud-base rain rate, and drop concentration to test hypotheses on drizzle formation.*

Prior field studies have suggested a power-law dependence of cloud-base precipitation on cloud liquid water path and drop concentration at the scale of a GCM grid box. We will combine direct and inferred measurements of these properties, together with a cloud radar, which is very sensitive to precipitation-sized drops, to study precipitation in marine stratocumulus, and to assess these functional dependences. We will compare these results to those from cloud modeling. We will test the extent to which aerosol factors (e.g., low concentrations, or giant CCN) or other dynamical mechanisms (such as mesoscale modulation of cloud water path) are controlling the initiation of precipitation.

**Deployment Strategy (indirect radiative forcing):
Experimental approach to indirect effects and precipitation**

The *R/V Ronald H. Brown* will be an important focal point for the CalNex 2010 aerosol-cloud precipitation experiments. Clouds at the top of the marine boundary layer are often coupled to the surface so that aerosol measurements on the ship represent the particles forming nuclei for the cloud. *Brown* will have an extensive suite of instrumentation to characterize the aerosol properties at ship level. A Doppler lidar will measure updraft velocities just below cloud base to an accuracy better than most aircraft measurements. Remote sensing of cloud liquid water path and cloud optical depth along with the aerosol and updraft measurements will constitute a package that will enable measurement of the essential components of the albedo response of a stratiform cloud to aerosol perturbations. This same package will shed light on precipitation development, particularly with the addition of cloud radar (see schematic in Fig. 7.3.) An example of data analysis from the same cloud regime, although at a fixed site on the California coast, is shown in Figure 7.4. The slopes of these responses of cloud optical and microphysical responses to changes in aerosol can be quantified and compared to theory.

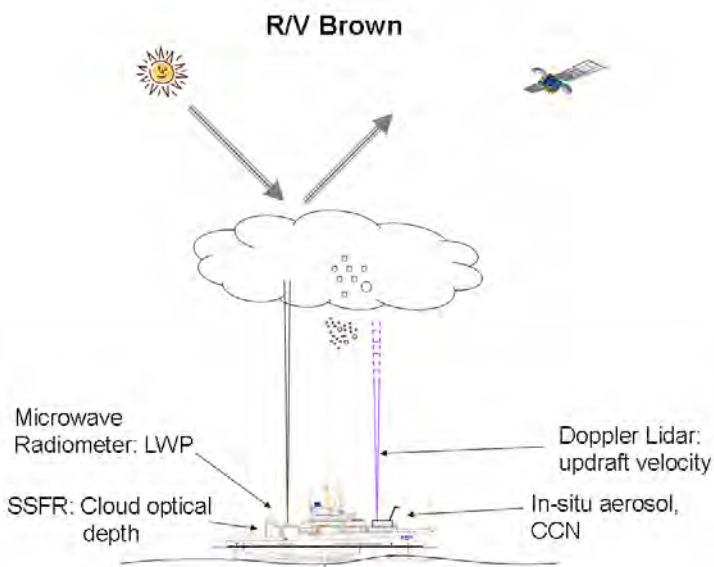


Figure 7.3. Schematic of R/V Brown cruising under clouds while measuring surface aerosol (also representative of sub-cloud aerosol), cloud optical depth and liquid water path. This set of measures allows one to assess aerosol effects on cloud optical depth for clouds of known LWP.

While the primary focus of the R/V Brown will be on the albedo experiment, as described in Figures 7.3 and 7.4, we will also be undertaking a number of other experiments associated with drop activation and the onset of precipitation. First, we will be

comparing a number of different methods that derive cloud drop concentration from remote sensors, from in-situ aerosol and remote updraft measurements, and from a combination of cloud models and observations. Some of these are extant methods, and others are under development.

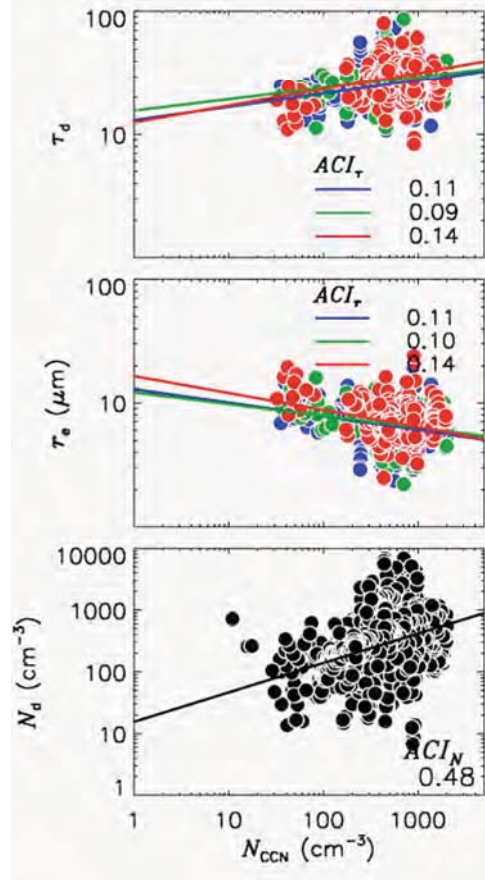


Figure 7.4. An example from McComiskey et al. (2008) of how surface data can be used to infer the albedo effect. Here scatter plots show cloud optical depth t_d , drop effective radius, r_e , and drop concentration N_d vs. the number concentration of CCN for various LWP bands during the 2005 deployment of the DOE Atmospheric Radiation Measurement Mobile Facility at Pt Reyes California. The slopes (ACI) reflect the magnitude of the effect of aerosol on the cloud optical and microphysical properties.

The addition of an aerosol lidar with high spatial resolution will be of great advantage for this experiment. It will also be of great use for measurement of aerosol hygroscopicity under ambient conditions and compared with other more traditional methods (e.g. Feingold and Morley, 2003). Second, we will be examining the relationship between aerosol, cloud microphysics, and precipitation formation. This study will benefit greatly from the deployment of a cloud radar.

The main role of the WP-3 will be to examine the physics of aerosol particles relevant to cloud droplet and ice activation. The formation of liquid cloud droplets depends on cloud condensation nuclei (CCN), which will be measured on the P-3. These data will be compared to

aerosol size distributions, chemistry, and gas-phase species to understand the sources, transformations, and sinks of cloud nuclei. We propose to deploy an analogous instrument for measuring ice nuclei (IN) during upper tropospheric flight legs that would examine the number and properties of particles that can cause ice to form in clouds.

Based upon climatology, it is expected that stratus and stratocumulus clouds will persist over the ocean for the deployment period. Ship maneuvering will proceed based on the variability (in amount and composition) of local aerosol pollution sources such as ship tracks, and recirculation events.

Table 2.2. Proposed measurements and platforms for aerosol indirect radiative forcing studies.

CATEGORY	Parameters to Measure	Platform			
		RHB	WP-3	Plane*	Satellite
Aerosol Chemistry	Anions and cations	X	X	O	
	Elemental carbon (EC)	X	X		
	Organic carbon (OC)	X	X		
	Particulate organic matter (POM)	X	X	O	
	Organic carbon (speciated)	O			
	Organic functional groups	O			
	Trace elements	X	X		
Aerosol/Cloud microphysical and optical measurements	Aerosol number concentration	X	X	O	
	Aerosol number size distribution	X	X	O	
	Aerosol absorption (spectral)	X	X	O	
	Scattering and backscattering (spectral)	X		O	
	Aerosol extinction	X	X	O	
	Aerosol light scattering hygroscopic growth	X			
	Aerosol light extinction hygroscopic growth	X	X		
	Aerosol hygroscopic growth	O			
	Lidar backscatter profiles	X or O			
	CCN	X	O	O	
	Cloud drop size distribution		X	O	
	Cloud water content		X	O	
	Droplet residual properties				
Ice nuclei		O			
Radiation Measurements	Aerosol Optical Depth (spectral)	X		?	
	Radiative fluxes, solar and longwave, upwelling and downwelling (spectral)	O	O	O	
	Direct, diffuse, and total irradiances (spectral where possible)	O	O	O	
	UV flux	O	X	O	
	Cloud optical depth	O			
	Cloud reflectance				
	Cloud liquid water path	X, O?			
	Cloud radar	X			
Satellite-retrieved Fields of:	Aerosol Optical Depth (spectral)				Terra (MODIS, MISR)
	Radiative fluxes, solar and longwave				Aqua (MODIS)
	Surface albedo (spectral where possible)				Aqua (MODIS)
	Aerosol vertical profiles				CALIPSO
	Cloud optical depth				Terra
	Cloud reflectance				Terra
Meteorological Measurements	Wind speed, direction, RH, T, pressure, cloud type and amount, visibility	X	X	O	
		X			
	Updraft velocity	X(lidar)	X	O	

RHB – NOAA R/V *Ronald H. Brown*

PLANE – small plane devoted to aerosol-cloud-radiation studies;

* Note: the NOAA WP-3 will include complementary aerosol instrumentation (Table 4, page 49) that may be used in this study.

X – indicates NOAA in-house capability

O – indicates needed measurement

References

- Albrecht, B.A., 1989. Aerosols, Cloud Microphysics, and Fractional Cloudiness, *Science*, **245**, 1227-1230.
- Bates et al. 2008
- Bates, T.S., P.K. Quinn, D.J. Coffman, J.E. Johnson, and A.M. Middlebrook, 2005. The dominance of organic aerosols over the Gulf of Maine during NEAQS 2002. *J. Geophys. Res.*, submitted.
- Bates, T.S., T. L. Anderson, T. Baynard, T. Bond, O. Boucher, G. Carmichael, A. Clarke, C. Erlick, H. Guo, L. Horowitz, S. Howell, S. Kulkarni, H. Maring, A. McComiskey, A. Middlebrook, K. Noone, C. D. O'Dowd, J. Ogren, J. Penner, P. K. Quinn, A. R. Ravishankara, D. L. Savoie, S. E. Schwartz, Y. Shinozuka, Y. Tang, R. J. Weber, and Y. Wu, 2006. Aerosol direct radiative effects over the northwest Atlantic, northwest Pacific, and North Indian Oceans: estimates based on in-situ chemical and optical measurements and chemical transport modeling, *Journal??*, **6**, 1657 – 1732..
- Bigg, E.K., 1986. Discrepancy between observation and prediction of concentrations of cloud condensation nuclei, *Atmos. Res.*, **20**, 81-86.
- Blanchard & Tanenbaum 2003
- Charlson, R.J., S.E. Schwartz, J.M. Hales, R.D. Cess, J.A. Coakley, Jr., J.E. Hansen, and D.J. Hofmann, 1992. Climate forcing by anthropogenic aerosols, *Science*, **255**, 423-430.
- Charlson, R.J., J.H. Seinfeld, A. Nenes, M. Kulmala, A. Laaksonen, M.C. Facchini, 2001. Reshaping the theory of cloud formation, *Science*, **292**, 2025-2026.
- Conant, W.,C., J.H. Seinfeld, J. Wang, G.R. Carmichael, Y. Tang, I. Uno; P.J. Flatau, K.M. Markowicz, and P.K. Quinn, 2001. A model for the radiative forcing during ACE-Asia derived from CIRPAS Twin Otter and R/V Ronald H. Brown data and comparison with observations, *J. Geophys. Res.*, **108(D23)**, 8661 doi:10.1029/2002JD003260.
- Conant, W.C., J.H. Seinfeld, J. Wang, G.R. Carmichael, Y. Tang, I. Uno; P.J. Flatau, K.M. Markowicz, and P.K. Quinn, 2003. A model for the radiative forcing during ACE-Asia derived from CIRPAS Twin Otter and R/V Ronald H. Brown data and comparison with observations, *J. Geophys. Res.*, **108(D23)**, 8661 doi:10.1029/2002JD003260.
- Cubison et al. 2008
- Diner et al., 2004. PARAGON – an integrated approach for characterizing aerosol climate impacts and environmental interactions, *Bull. Am. Meteor. Soc.*, **85**, 1491-1501.
- Feingold et al. 2003
- Feingold, G. and P.Y. Chuang, 2002. Analysis of the influence of film-forming compounds on droplet growth: Implications for cloud microphysical processes and climate, *J. Atmos. Sci.*, **59**, 2006-2018.
- Feingold, G., and B. Morley, 2003. Aerosol hygroscopic properties as measured by lidar and comparison with in-situ measurements. *J. Geophys. Res.*, **108**, No. D11, 4327, doi:10.1029/2002JD002842.
- Fountoukis, C., Nenes, A., Meskhidze, N., Bahreini, R., Brechtel, F., Conant, W. C., Jonsson, H., Murphy, S., Sorooshian, A., Varutbangkul, V., R. C. Flagan, and J. H. Seinfeld, 2007. Aerosol–cloud drop concentration closure for clouds sampled during ICARTT, *J. Geoph. Res.*, **112**, D10S30, doi:10.1029/2006JD007272.
- Jiang et al. 2008

- Laaksonen, A., P. Korhonen, M. Kulmala, and R.J. Charlson, 1998. Modification of the Köhler equation to include soluble trace gases and slightly soluble substances, *J. Atmos. Sci.*, **55**, 853-862.
- Massoli et al. 2008
- Malm, W.C., J.F. Sisler, D. Huffman, R.A. Eldred, and T.A. Cahill, 1994. Spatial and seasonal trends in particle concentration and optical extinction in the United States, *J. Geophys. Res.*, **99**, 1347-1370.
- McComiskey, A. M., G. Feingold, A. S. Frisch, D. D. Turner, M. A. Miller, J. C. Chiu, Q. Min, and J. A. Ogren, 2008. An assessment of aerosol-cloud interactions in marine stratus clouds based on surface remote sensing. *J. Geophys. Res.*, in review.
- Nenes et al. 2002
- Nenes et al.
- Quinn 2006
- Quinn, P.K. and T.S. Bates, 2005. Regional aerosol properties: Comparisons from ACE 1, ACE 2, Aerosols99, INDOEX, ACE Asia, TARFOX, and NEAQS, *J. Geophys. Res.*, in press.
- Quinn, P.K., T.S. Bates, D.J. Coffman, and D.S. Covert, 2008. Influence of particle size and chemistry on the cloud nucleating properties of aerosols, *Atmos. Chem. Physics*, **8**, 1029-1042.
- Quinn, P. K., et al., 2005. Impact of particulate organic matter on the relative humidity dependence of light scattering: A simplified parameterization, *Geophys. Res. Lett.*, **32**, L22809, doi:10.1029/2005GL024322, 2005.
- Ramanathan, V., and A.M. Vogelmann, 1997. Greenhouse Effect, Atmospheric Solar Absorption, and the Earth's Radiation Budget: From the Arrhenius-Langely Era to the 1990's, *Ambio*, **26** (1), 38-46.
- Ramanathan, V., P.J. Crutzen, J.T. Kiehl, and D. Rosenfeld, 2001. Aerosols, climate, and the hydrological cycle, *Science*, **294**, 2119-2124.
- Rasool, S. I., and S. H. Schneider, (1971??). Atmospheric carbon dioxide and aerosols: Effects of large increases on global climate, *Science*, **173**, 138-141.
- Rosenfeld, D., 2000. Suppression of rain and snow by urban and industrial air pollution, *Science*, **287**, 1793-1796, 2000.
- Russell, P.B., J. M. Livingston, P. Hignett, S. Kinne, J. Wong, A. Chien, R. Bergstrom, P. Durkee and P. V. Hobbs, 1999. Aerosol-induced radiative flux changes off the United States mid-Atlantic coast: Comparison of values calculated from sunphotometer and in situ data with those measured by airborne pyranometer, *J. Geophys. Res.*, **104**, 2289-2307.
- Saxena, P., L. M. Hildemann, P. H. McMurry, J.H. Seinfeld, 1995. Organics alter hygroscopic behavior of atmospheric particles, *J. Geophys. Res.*, **0**, **100** 18755-18770.
- Shulman, M.L., M.C. Jacobson, R.J. Charlson, R.E. Synovec, and T.E. Young, 1996. Dissolution behaviour and surface tension effects of organic compounds in nucleating cloud droplets, *Geophys. Res. Lett.*, **23**, 277-280, 1996.
- Twomey, S., Aerosols, Clouds and Radiation, 1991. *Atmos. Environ.*, **25A** (11), 2435-2442.
- Twomey 1974
- Warner, J., 1968. A Reduction in Rainfall Associated with Smoke from Sugar-Cane Fires--An Inadvertent Weather Modification?. *J. Appl. Meteo.* **7**, 247-251.

8. Forecast Models

Through initiatives and mandates NOAA's National Weather Service (NWS) is committed to improving current air quality forecasts of ozone and providing operational forecasts of particulate matter for the entire United States. The forecasting system requires an adequate understanding of the basic chemical and dynamical processes that determine atmospheric composition, reliable emission inventories, dependable forecast models and observing networks and platforms that provide information needed for model verification. Similar to the ICARTT/NEAQS-2004 and TexAQS-2006 studies, NOAA will deploy several air quality forecast models during the CalNEX-2010 field campaign. In addition to NOAA's forecasts, several other air quality models from other countries, universities, and private corporations will also be forecasting in real-time during the 2010 study. The evaluation of these models with data collected in the 2010 field study will allow valuable insight concerning the applicability of the various components that compose regional and larger-scale air quality forecast models. By systematically comparing results from several forecast models with the detailed data collected during CalNEX-2010, conclusions can be drawn concerning the reliability of different modeling approaches for conditions relevant to California during the study period.

8.1 Science Questions

An air quality forecast model is essentially a computational synthesis of our collective understanding of how anthropogenic pollutants are emitted, transformed, and transported. The various measurements and platforms that constitute the CalNEX-2010 field study will provide diverse, and rigorous tests to this basic understanding. A model-measurement comparison should not only characterize the accuracy of the forecast model, but also identify elements of the model that limit its accuracy, and point the way to better forecasts. On the other hand utilizing the predicted meteorological and chemical fields from forecast models is also an important component of a well-integrated field campaign. There is also an important time interval, during the first examination of a day's measurements, when it is extremely valuable to principal investigators and experiment planners to know what the forecast models predicted. These inherent synergisms between the field experiment and the forecast models are the impetus and framework for the forecast component of the CalNEX-2010 study.

1. *How well can air quality models forecast air quality in California?* One of the important goals of the CalNEX-2010 air quality study will be to determine how well current state-of-the-art air quality models can forecast air quality in the various basins and air sheds within California. There is a twenty-year precedence for the statistical evaluation of ozone predicted by air quality models based primarily on comparisons with the EPA AIRS air quality monitoring network. Model evaluation studies for aerosols and the precursors for aerosol and ozone are severely limited by a lack of data both aloft and at the surface. The 2010 study is unique in that it will provide a glimpse of both the gas-phase oxidant component of air quality (i.e. ozone) and the particulate-phase components (i.e. PM_{2.5} and PM₁₀ aerosol) over a large region and altitude extent of California.

Model evaluations are most meaningful when results from two or more independent models are available for coincident comparisons. The cross-evaluation of several air quality forecasts is an important aspect of the CALNEX-2010 evaluation study. There are fundamental differences in the basic formulation and meteorological foundations of the current operational and research air quality forecast models. Most models use off-line meteorology to drive pollutant transport, while other models such as the WRF-CHEM use

online, or lock-step calculation of meteorology and pollution transport. The effect that these different model formulations have on California air quality predictions justifies a detailed statistical evaluation between the various models. Other important elements to air quality forecasts, such as the treatment of vertical transport and turbulent mixing, the photochemical mechanism, and the sensitivity to horizontal resolution can only be compared and evaluated within the context of multiple model forecasts.

2. How accurately do the forecast models represent the individual processes controlling air pollution formation and transport? While the first science question addresses the end result of pollution formation, and the raw output of the model forecasts, it is important from a scientific perspective to determine how accurately the forecast models represent the individual processes controlling air pollution formation and transport. Three broad subsets of processes are the focus the CalNex-2010 field program.

Emissions estimates: Air quality forecast models are fundamentally limited by the accuracy of the emissions estimates of ozone and aerosol precursors imposed on the model. A key focus of the aircraft and ship-based platforms during CALNex-2010 is the evaluation of emissions inventories on a relative as well as an absolute basis. Air quality forecast models are an important, computational intermediate that relate the emissions inventories to atmospheric concentrations. The model evaluation study will provide the developers of the forecast models a clear picture on the ability of the models to capture both relative and absolute precursor abundances, allowing indirect evaluations of the magnitude and relative location of the sources in the emissions inventories.

Photochemical and physical transformations: Since ozone and particulates are, to a large degree, secondary products formed during the oxidation and transport of primary emitted species, the accuracy of air quality forecasts is highly dependent on the veracity of the model's treatment of various transformation processes. The aircraft and ship-based studies of individual sources and urban regions planned for CalNex-2010 lend themselves directly to the evaluation of the photochemical and/or aerosol mechanisms within each forecast model. The forecast models predict key oxidants (OH, O₃ in the daytime, NO₃ and N₂O₅ at night), as well as the various secondary products produced from primary nitrogen, sulfur, anthropogenic and biogenic hydrocarbon emissions that will be measured during the field study. Comparisons between observed and modeled relationships among the various secondary and primary emitted species in combination with oxidant abundances will allow both quantitative and relative evaluations of the individual forecast models.

Meteorology and transport: Experience from previous research has unequivocally shown that the key to understanding pollution at the surface is to understand the processes controlling pollution aloft. The various upper-air platforms within the CalNex-2010 field program (aircraft, wind profilers, ozone and aerosol lidars, and doppler lidar) provide broad coverage in terms of area, physical, and photochemical parameters with which to evaluate the forecast models. Since forecasting inter-basin and off-shore transport, convection, and vertical transport correctly are prerequisite to accurate air quality forecasts, it is particularly important to evaluate the model's ability to adequately characterize the various scales of transport, from near surface to synoptic and regional scales.

8.2 Previous Evaluation Studies: A Blueprint for CalNex-2010

Eight forecast models with significant differences in terms of basic structure, physical parameterizations, photochemical mechanisms, and emissions processing were evaluated in both the ICARTT/NEAQS-2004 and TexAQS-2006 studies. In near real-time model forecasts were compared with O₃ and PM_{2.5}

measurements at several AIRNow surface sites, and with O₃, its precursors and PM_{2.5} taken at ground sites with enhanced measurement capabilities. Results were also compared in near real-time with many of the gas-phase and aerosol measurements taken aboard the *Ronald H. Brown* research vessel during the 2004 study. Time series of preliminary observations and model forecasts of O₃, CO, reactive nitrogen, and a number of surface and upper-air meteorological parameters were posted on a web site in near real-time that was accessible to the planners, participants and forecasters involved with the field programs, allowing a qualitative glimpse of forecast reliability relative to the observations. The reader is referred to the web-link: <http://www.etl.noaa.gov/programs/2006/texaqs/verification/> for the day-by-day real-time forecast comparisons of 13 surface and upper-air variables at 14 surface sites from the air quality models operating during TexAQS-2006.

The O₃ forecasts from the eight models available during the two studies were additionally used to generate ensemble O₃ and PM_{2.5} forecasts, and bias-corrected ensemble forecasts that were also made available in near real time. Post-deployment analysis revealed that the ensemble forecasts of O₃, as well as the ensemble forecasts of PM_{2.5}, are statistically more accurate than those from any individual forecast model. The CalNex-2010 study would likewise realize this added benefit of having the best available air quality forecasts afforded by centralizing the results of the forecast models.

Close collaboration between the individual air quality forecast groups and the evaluation team is essential to the success of a formal evaluation study. Planning and coordination with study participants well in advance of the experiment are necessary to ensure:

- 1) A pre-deployment consensus on evaluation protocol, model domains, the most useful data sets and model products.
- 2) Availability of the most up-to-date emissions inventories from agencies willing to supply information to the forecast community.
- 3) Availability of the optimum set of forecast information, and how it is provided or displayed, during the field experiment.

8.3 Regional Air Quality Forecast Models

Hourly air quality forecasts, typically 36 to 72 hour forecasts, will be available at several model resolutions. Nested domains of 3 and 9 km centered over California within a 27 km grid covering the entire U.S. for the WRF-CHEM model are currently available. Forecasts from the NCEP/NWS model (WRF/CMAQ) at 12 km resolution over the U.S. will also be available. These two forecast models are top priorities in terms of model evaluation studies due to their spatial detail, the effort and expense put into the basic physics and dynamics, and the importance they serve as operational or community based forecast models. At least two other regional scale air quality forecast models operational during ICARTT/NEAQS-2004 and TexAQS-2006 are planning to be available during CalNex-2010. The BARON AMS, Inc. MAQSIP-RT model has provided air quality forecasts at 5, 15 and 45 km resolution during the previous field studies. Forecasts from the Canadian National AURAMS forecast model will also be available, which currently covers all of North America at 21 km horizontal resolution. The University of Iowa STEM-2K3 model has also participated in the previous model inter-comparisons with 20 km resolution, and availability during 2010 is not guaranteed but likely as well.

Any and all real-time regional air quality forecast models operational for California during the field campaign are encouraged and welcome to participate. The only requirements are the availability of daily forecasts in a timely manner, sufficient meteorological and constituent information to contribute

meaningfully to the inter-comparison, and a willingness to openly collaborate and share results with the other air quality forecast groups.

8.4 Model Evaluation

Similar to the 2 previous studies, the CALNex-2010 study will involve:

- 1) A real-time comparison phase based on the surface networks and preliminary field measurements. This phase focuses on summary information and statistics from real-time data collected from the AIRNow surface network and any additional enhanced surface monitoring sites collected in real-time. It is intended as a first look into relative model performance related specifically to predictions of surface air-quality.
- 2) A post-field study phase where evaluations of mobile-platform data are performed for the study period based on preliminary measurements. This phase is mostly computational and software development necessary for the final statistical analysis. Preliminary data from the available mobile (aircraft and ship) and remotely sensed (satellite and lidars) are collected and processed for model inter-comparisons. Likewise, the software infrastructure for processing the model results for the times and locations of the various mobile and remote platforms is developed and tested in this phase.
- 3) A final evaluation phase based on finalized, quality assured data. The post-analysis of model forecasts is scientifically the most important aspect of the evaluation study. Only through a quantitative, statistical framework with sufficient sampling throughout the entire study period can relative model performance be judged fairly. Examples of bias statistics for the eight models based on NOAA WP-3 aircraft observations from the 2 previously mentioned field studies are publicly available at the following web site: <http://www.esrl.noaa.gov/csd/2006/modelevel/>. More than two dozen variables, relating mostly to ozone chemistry and PM_{2.5} composition, are available for model-to-model intercomparison in the TexAQS-2006 study. This same type of summary evaluation will be available for the forecast models participating in CalNex-2010.

The software, hardware, and personnel are already in place within the CSD and PSD labs at NOAA/ESRL to accommodate the forecast model evaluation project.

9. Science Synthesis and Assessment: Providing Timely and Relevant Information for Policy Makers

Scientific research often proceeds at a measured pace with findings reported in due course in scholarly journals. However, the rapid pace of climate change and air quality policy development often requires a more demanding schedule. As a result, intensive field studies, such as the one planned in this document, have been criticized for not providing results on a time scale to most effectively guide policy decisions. NOAA has employed three mechanisms for meeting this challenge: formulation of Fact Sheets and Synthesis Reports that provide the most relevant results of a field study, and the organization of informal presentations and conferences tailored to transfer scientific results to scientific, decision-maker, and lay audiences. These are executed on an accelerated schedule that meets the requirements of policy makers while still providing sufficient time for accurate scientific analysis of the data.

The International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) study provides a successful example of fact sheets rapidly disseminating findings to policy makers. In the months following the field work, nine two page “Fact Sheets” were developed to present the most relevant study findings as rapidly as possible. Each Fact Sheet addresses a single issue and provides the essential background, findings and conclusions as clearly and concisely as possible – hence the two page format. All nine ICARTT Fact Sheets are available from the ICARTT web site (<http://esrl.noaa.gov/csd/ICARTT/>).

A different approach was used in the Second Texas Air Quality Study (TexAQS II). Early in the study planning process, a Rapid Science Synthesis team was formed, which developed a well-defined approach for obtaining the required experimental data or model calculations, evaluated this information as it became available during the execution of the study, formulated significant “Preliminary Findings” for each question immediately upon completion of the study, and produced a “Final Report” within ten months of the study conclusion. These reports can be found at <http://esrl.noaa.gov/csd/2006/>.

Fact Sheets, Synthesis Reports, and tailored presentations could play important roles in the CalNex 2010 Study. Such opportunities will become clear as the study progresses. It may well be that the climate research aspects will be more heavily represented in the Fact Sheets, since this research area has not been the focus of as much study in California as has air quality.

10. Mobile Platform Descriptions

NOAA WP-3D Lockheed Orion

During intensive field campaigns, one of NOAA's four-engine Lockheed WP-3D Orions (Figure 10.1) is instrumented to provide a highly sophisticated airborne air chemistry and aerosol research platform. This aircraft makes in situ measurements of a wide suite of atmospheric species, most on a one-second scale, which gives approximately 100m spatial resolution. The operating range of the WP-3D is ample to permit sampling of the primary pollution source regions, and to follow the transport and transformation of their emissions throughout California and surrounding regions. Figure 10.2 shows the range of the WP-3D operating out of the Los Angeles area with a range of 700 nautical miles, assuming a return to the base of operations. This operational range is based upon a maximum instrument load in the fuselage and in external pods under the wings.

The WP-3D aircraft is operated by a crew of seven (aircraft commander, pilot, flight engineer, navigator, flight director/meteorologist, and two technicians) and can carry in addition several science personnel. The planned payload relies on having the full aircraft space and payload weight capacity available. The aircraft and crew are from NOAA's Aircraft Operations Center (AOC).

Instrumentation

Species measured by the WP-3D can include primary pollutants, secondary species and a wide range of other parameters. Table 4 lists the proposed instrumentation package for the WP-3D during CalNex 2010. Figure 10.3 illustrates the proposed payload configuration.



Figure 10.1: NOAA WP-3D Orion.

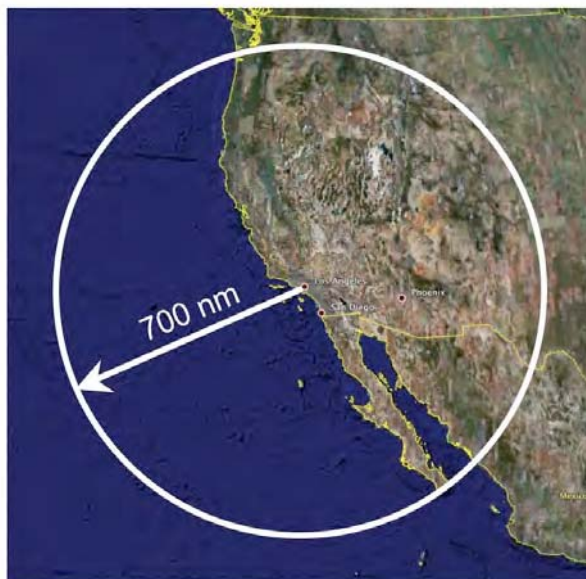


Figure 10.2. Operating range of the NOAA WP-3D aircraft.

Table 4: Proposed 2010 scientific payload for the NOAA WP-3D Orion aircraft.

Species	Instrument
Ozone (O ₃)	NO/O ₃ chemiluminescence
Nitric oxide (NO)	NO/O ₃ chemiluminescence
Nitrogen dioxide (NO ₂)	UV photolysis & NO/O ₃ chemiluminescence
Total reactive nitrogen oxides (NO _y)	Au conversion & NO/O ₃ chemiluminescence
Carbon dioxide (CO ₂) and methane (CH ₄)	Cavity ring-down spectroscopy (CRDS) or ICOS
PANs (PAN, PPN, etc.)	Chemical ionization mass spectrometer (CIMS)
NO ₃ , N ₂ O ₅ and NO ₂	CRDS
Aerosol bulk composition	Aerosol mass spectrometer (AMS) and PILS
Single particle aerosol mass spectrometry	PALMS
Aerosol low turbulence inlet	LTI
Aerosol number and size distribution (0.003 - 8 μm)	Nucleation mode aerosol size spectrometer (NMASS), UHSAS, WLOPC
Single particle aerosol soot mass	SP2
Cloud aerosol and drop size distributions	DMT probes
Water vapor (H ₂ O)	TDL absorption, dewpoint/frostpoint hygrometer
Air temperature	Rosemount total temperature
<i>In-situ</i> volatile organic compounds (VOC), oxygenated VOC, acetonitrile (CH ₃ CN)	Proton transfer reaction mass spectrometer (PTRMS)
VOC, alkyl nitrates, halocarbons	Whole air samples, GC-FID/MS
Formaldehyde (CH ₂ O)	DFG TDL absorption
Sulfur dioxide (SO ₂)	UV pulsed fluorescence
Carbon monoxide (CO)	Vacuum UV resonance fluorescence
HNO ₃	SiF ₅ ⁻ CIMS
NH ₃	acetone CIMS
Total (dry), sub-μm (as f(RH)) aerosol extinction	CRD-AES
Dry sub-μm aerosol absorption	Particle soot absorp. photometer (PSAP) or PAS
Cloud condensation nucleus (CCN) counter	CCN spectrometer
Actinic flux	Spectroradiometry
Spectral irradiance	SSFR and CG4
¹⁴ CO ₂ from whole-air canister samples	Accelerator MS
CO ₂ , CO, N ₂ O, and CH ₄ (1 sec)	QCL TDL absorption
Hydrogen peroxide	CIMS

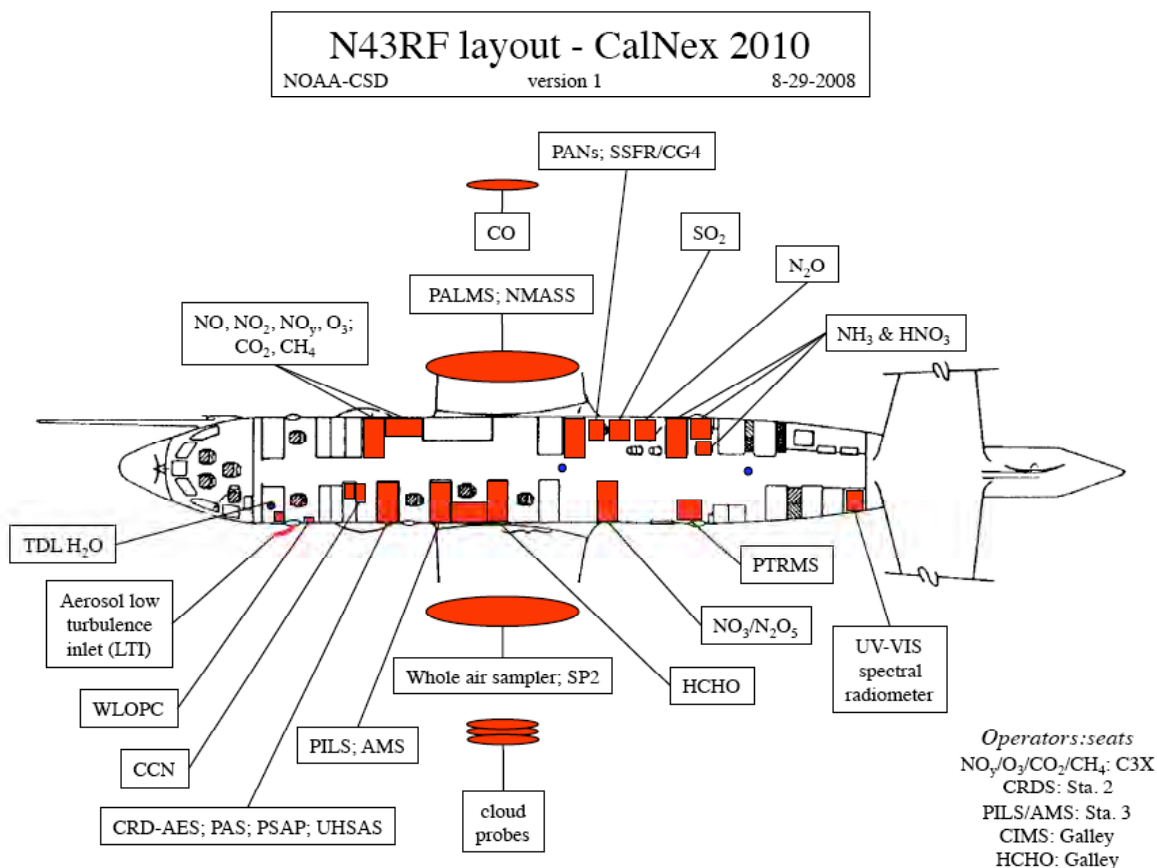


Figure 10.3. Proposed 2010 payload for the NOAA WP-3D Orion aircraft.

Operations

AOC operates the WP-3D aircraft under visual flight rules (VFR) and Instrument Flight Ranging (IFR) conditions, with some restrictions. As the external wing stores lack icing protection, flight into known icing conditions is not permitted. Minimum operating altitudes are determined by local flight conditions, but cannot override FAA regulations. Typical minimum daytime horizontal flight levels are 500 feet over land and 300 feet over water, depending on local air traffic and obstructions. We have in the past sampled over water for short periods at 150 feet. Over land, flying missed-approach patterns over local airfields permitted a temporary decrease in minimum operating height.

Typical Flight Planning Schedule

For the past fourteen years NOAA has used a WP-3D aircraft extensively for air chemistry and aerosol research. From this experience an operational schedule for flight planning has evolved.

On the day before a planned flight:

1300 hrs local:

- After discussions with the modelers and obtaining any needed input from others, the flight planner submits the requested flight plan to AOC for review and for AOC coordination with the appropriate FAA and military authorities.
- After submission this flight plan still can be fine-tuned to react to changes in weather and/or model forecasts.

Late in the afternoon:

- Pre-flight flight readiness and flight goals briefing for all instrument PIs and the project science team.
- The flight planner reviews the latest available weather and model forecast and adjusts the flight plan if necessary.

On the day of the flight:

3-4 hrs before take-off:

- The flight planner reviews the latest weather and model forecast and adjusts flight plan if necessary.

About 2 hrs before take-off:

- Flight crew (pilots, navigator, and flight director) are briefed on the final flight plan, and last-minute adjustments are discussed.
- After the meeting the flight crew files the flight plan with the FAA and confirms with military contacts if necessary.

Flight plans

Preliminary flight plans have been developed. In any given flight, the focus will be on more than just one objective or science question. The flight plans will use the allotted resources (i.e. flight hours) in the most prudent way by addressing as many questions and/or objectives as possible on each flight.

The flights will reach into the suspected source regions to study the primary emissions by gathering information on the signatures of the primary emission mix. This allows, by comparison with existing emissions inventories, an assessment of their accuracy to be made. In the downwind regime the flights will follow the advected plumes to study dispersion and chemical and physical conversions within the plumes at progressing transport times.

Actual flight plans can only be finalized in the field according to the encountered meteorology and transport regimes. Nevertheless, very effective flight strategies and patterns have been developed over the years and they will be used in the CalNex 2010 study. Since several objectives and science questions will be addressed in each flight, several strategies and patterns might be combined.

Coordination with Lidar aircraft

The capabilities on the *in-situ* (WP-3D) and the remote sensing NOAA Twin Otter (Lidar) aircraft strongly complement each other for many kinds of studies. Therefore, flights on any given day will be coordinated between the flight planners of the WP-3D and the Lidar aircraft during the flight planning process in the field to take advantage of having these two valuable resources available simultaneously.

NOAA Twin Otter Remote Sensing Aircraft

An important component of the 2010 experiment will be a differential absorption lidar (DIAL) deployed on a NOAA Twin Otter aircraft for remote sensing of local and regional ozone and aerosol distribution. Previous field studies have benefited greatly from airborne measurements of ozone and aerosol profiles to characterize the three-dimensional structure of pollution plumes and measure variability in mixing layer height (*Alvarez et al.*, 1998, *Senff et al.*, 1998, *Banta et al.*, 1998, *Banta et al.*, 2005). Airborne remote sensing enables tracking of plumes from urban areas and point sources, identification of isolated regions and layers of high ozone concentration, observations of atmospheric layering as characterized by aerosol structure, and investigation of local meteorological effects such as sea breezes and urban heat islands on pollution transport and mixing.

Inclusion of a remote sensing aircraft will also provide information on the three-dimensional representativeness of *in situ* observations made on the WP-3D and other aircraft during those periods when the flight tracks of the two aircraft sample the same region.

Aircraft Platform

The new ozone/aerosol instrumentation will be mounted on the NOAA DeHavilland Twin Otter. The NOAA remote sensing aircraft will tentatively be based at ??? and will fly unpressurized at approximately 3-4 km above ground level for missions extending over approximately four to five hours. Relevant operating specifications for the aircraft during the experiment are expected to be as follows:

- Ground speed: 65 m s⁻¹
- Endurance: 4-5 hours
- Range: 550 nm
- Over-water capability
- Capability for multiple flights/day

On-board sensors

Flight plans for the Twin Otter will specifically address scientific objectives associated with the transport and evolution of pollution plumes, boundary layer structure, air quality forecasting, and intercomparison of observations. The primary instrument to be deployed on the aircraft will be a down-looking ozone/aerosol DIAL system, which produces profiles of ozone and aerosol structure in the boundary layer and lower troposphere. The lidar system employs three tunable wavelengths in the ultraviolet spectral region between 280 and 300 nm. Each wavelength is characterized by a different ozone absorption cross-section, enabling measurements to be made over a wide range of ozone values. The multi-wavelength capability of the system also provides flexibility for the correction of potential errors in ozone calculations caused by aerosol backscatter gradients. Ozone measurements will be made at a horizontal resolution of approximately 600 m and vertical resolution of 90 m. Precision of the ozone measurement is expected to vary from about 3 to 10 ppbV, depending on range and amount of intervening ozone. The longest of the three wavelengths at approximately 300 nm, which is least absorbed by ozone, is used to measure aerosol backscatter profiles, after correction for ozone extinction. Resolution for the aerosol measurements will be 600 m horizontally and 15 m vertically. Onboard the aircraft, a global positioning system provides a precise location for each lidar measurement, as

for the plume tracking measurements in Figure 5 in the Transport and Mixing section. Data are analyzed and displayed on board the aircraft in real time, enabling adjustment or changes in the science mission if unexpected features or events are observed.

A key measurement objective for the CalNex 2010 study will be the characterization of the structure of the boundary layer, including mixing layer height. Mixing layer height is estimated from the gradient of the lidar aerosol signal, as indicated in Figure 16. Investigation of mixed layer properties over different surfaces and the relationship with ozone concentrations will be important for understanding layering, transport, and vertical mixing. To provide additional information on surface properties, we also radiometer on the aircraft alongside the ozone lidar to measure surface skin temperature.

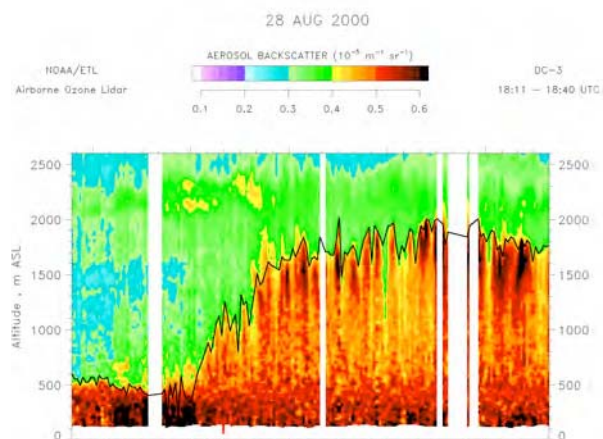


Figure 16: Vertical profile of lidar-observed aerosol backscatter showing a sharp change in mixing layer height at the Gulf of Mexico coast.

At this time, we are investigating the feasibility of incorporating a dropsonde capability on the NOAA Twin Otter. Dropsondes, particularly over the ocean, can provide information on wind structure associated with pollution layers, providing important information on the potential source of plumes observed distant from known sources. This decision will be based on the availability of funding and on assurances that reliable dropsondes can be procured.

NOAA R/V Ronald H. Brown

Circulation of polluted air over the coastal Pacific waters plays an important role in shaping the air quality in California's coastal cities. These same pollutants can also affect the regional radiation budget, as well as precipitation and the lifetime and extent of clouds. The polluted air is a result of both re-circulation of pollution from urban areas within California and long-range transport.

An instrumented ship is an ideal platform to study the meteorological and chemical processes occurring off the coast of California and within the port areas of the state. A ship can be used to



Figure 17. The NOAA Research Vessel *Ronald H. Brown*

sample polluted air masses as they move offshore or onshore and study the chemical transformations in the polluted marine boundary layer. Indeed, deployment of *R.V. Ronald H. Brown* (see Figure 17) during ICARTT in 2004 and TexAQS in 2006 demonstrated the value of this platform for characterizing both transport and chemical processing within the marine boundary layer. Measurements from on-shore sites alone yield data that are frequently difficult to interpret due to contamination by local land-based sources, while aircraft measurements have only short duration within the marine boundary layer and result in limited data.

Ship Capabilities and Facilities

The operational capabilities and shipboard facilities of *Ronald H. Brown* are shown in Table 5 (see also <http://www.moc.noaa.gov/rb/index.html>). The instrumentation (payload) capacity of *R.V. Ronald H. Brown* is not limited by weight or power constraints. Typically, atmospheric sampling instruments are placed in seagoing laboratories ('sea-tainers') on the forward upper

(02) deck (see Figure 17). Air samples are collected using towers or masts that extend 6-8 m above the deck (approximately 16 - 18 m above the water line). Sampling is conducted around the clock, unless contamination from the ship exhaust is expected to be prolonged. Remote sensing meteorological measurements are also included in the instrument package, to define the structure and extent of the MBL and thus place the chemical measurements in context. Augmentation of the on-board radar wind profiler with additional lidar instruments is critical for this activity.

Table 5. Performance specifications and facilities for *Ronald H. Brown*.

Parameter	Specification
Length (ft/m)	274 / 83.5
Range (nm/km)	11,300 / 20,900
Endurance (days)	35
Cruising speed (kts / mps)	12 / 6.2
Maximum speed (kts / mps)	15 / 7.7
Officers / Engineers / Crew	5 / 4 / 16
Scientific staff	34 (maximum)
Laboratory/office space (sq. ft.)	4100
Telecommunications, data	INMARSAT-A
Telecommunications, voice	Cell & satellite phones, VHF radios

The ship is capable of staying out to sea for long periods, which allows for repeated sampling of air masses in a particular region, such as coastal California. However, with an average cruising speed of 12 knots the ship is not a rapidly moving platform. Within certain constraints *Ronald H. Brown* is capable of extended near-shore running, which is especially valuable for examination of pollution plumes advected off the shore and for examination of meteorological phenomena such as land-sea breeze effects. The ship is fully capable of nighttime operations, though with some restrictions when near shore.

The instrumentation proposed for deployment on RHB (see Table 6) will provide characterization of the atmospheric dynamics, gas-phase chemistry, aerosol chemical, physical, and optical properties, and radiation fields in this complex environment. Central to this field deployment will be techniques that yield information on the interactions between gas-phase and aerosol chemistry and how the evolving aerosol properties affect the radiation fields. A critical requirement is understanding how these chemical effects are influenced by transport to, from, and within the MBL. Thus particular emphasis has been placed on the need to understand the dynamical structure of the MBL at large scales via remote sensing instruments. Smaller scales will also be studied with the addition of instrumentation to investigate the turbulence structure from the surface layer to the top of the MBL. Coincident with this activity will be measurements of chemical fluxes of CO₂, and possibly O₃.

Table 6. Proposed instrumentation for deployment on *Ronald H. Brown*.

Parameter	Method
Photolysis rates (j-values)	Spectral radiometer
Ozone (O ₃)	UV absorbance
Ozone	NO chemiluminescence
Carbon monoxide (CO)	Nondispersive IR
Carbon dioxide (CO ₂)	Nondispersive IR
Sulfur dioxide (SO ₂)	Pulsed UV fluorescence
Nitric oxide (NO)	Chemiluminescence
Nitrogen dioxide (NO ₂)	Photolysis/chemiluminescence
Total reactive nitrogen oxides (NO _y)	Au tube/chemiluminescence
Peroxyacyl nitric anhydrides (PANs)	GC/ECD
Alkyl nitrates (RONO ₂)	GC/MS
Nitrate radical (NO ₃); Dinitrogen pentoxide (N ₂ O ₅)	Cavity ring-down spectrometry
Nitric acid (HNO ₃)	Mist chamber/IC
Water vapor (H ₂ O)	Nondispersive IR
Continuous Speciation of VOCs	PTR-MS/CIMS
VOC Speciation	GC/MS
Formaldehyde (HCHO)	CHD fluorimetry
Radon (Rn)	Radon gas decay
Seawater/atmospheric CO ₂	Nondispersive IR
Enhanced measurement of radiative fluxes	Spectral radiometers
Aerosol optical depth	MicroTOPS
Irradiance	Portable Radiation Package (PRP)
Size-resolved aerosol composition and gravimetric mass	Impactors (IC, XRF, and thermal-optical OC/EC)
OC/EC	On-line thermal optical
Ionic Aerosol Composition	Particle In Liquid Sampler (PILS)-IC
Aerosol Size and Composition	Aerosol Mass Spectrometer
Organic function groups	FTIR
Aerosol scattering (400, 550, 700 nm)	TSI Model 3563 Nephelometer
Aerosol absorption (400, 550, 700 nm)	Radianc Research PSAP
Aerosol number	CNC
Aerosol size distribution	Twin DMAs and an APS
Aerosol light scattering hygroscopic growth f(RH)	Twin TSI 3563 nephelometers
Aerosol size hygroscopic growth g(RH)	Tandem DMAs
Aerosol light extinction hygroscopic growth f(RH)	Cavity ring-down spectrometer
Total and sub-micron aerosol extinction	Cavity ring-down spectrometer
Ozone/aerosol vertical profiles	O ₃ /Aerosol Lidar (OPAL)
Wind/temperature vertical profiles	915 MHz wind Radar
High-resolution BL winds/aerosol	Doppler Lidar (HRDL)
Wind profiles/microscale turbulence	C-band radar
Temperature/relative humidity profiles	Radiosondes
Surface energy balance (fluxes)	Eddy covariance (bow mounted)
High resolution BL turbulence structure	Doppler mini-Sodar

Ship Operations

Because the ship cannot rapidly deploy to different areas to take advantage of sampling opportunities, meteorological forecasting is essential for planning ship operations. Coordination of these forecasts (meteorological and air quality) with ship track planning in 2004 and 2006 was very successful. This activity will be augmented in 2010 by more frequent communication between the ship and forecast personnel on shore. In addition extensive coordination between the ship and the various aircraft will be required. Efforts will be made to maximize opportunities for measurement comparisons between the ship and the various aircraft.

A significant restriction on ship operations, and therefore ship track planning, is the need for the relative wind to be forward of the beam of the ship in order to avoid sample contamination from the ship exhaust. Accurate forecasting of surface winds is essential for this; just as essential is having several sampling options available (see below). Since this strategy worked very well during ICARTT 2004 and TexAQS 2006, it will be expanded upon for 2010.

Ship Sampling Objectives

There are four major scientific objectives, each associated with unique, but necessarily overlapping, sampling strategies.

Characterization of sources: Near-shore and within port (e.g. Long Beach, San Francisco Bay) survey tracks are planned under conditions when polluted continental air is expected to be transported into the surface marine layer (i.e. nighttime, early morning, or late day). Also, special effort will be made to characterize marine vessel emissions (MVE).

Study of transport and transformation processes: A focus of the proposed research is the study of the chemical and physical evolution of polluted air masses within the marine boundary layer. When possible, plumes advected offshore will be sampled at successively longer distances downwind to examine chemical transformations related to plume aging in the MBL. Opportunities to sample well-aged plumes that have remained in the MBL for several days may be possible. Also, since significant chemical transformations occur at night, these studies of polluted air masses will occur during the entire diurnal cycle. Of particular interest is how the chemical and physical evolution of aerosols affects their optical properties.

Study of coastal impacts: Along-shore cruise tracks and transits into ports are planned to characterize the effects of the recirculation of air masses by the sea-breeze/land-breeze circuit.

Study of radiative effects of aerosols: Cruise tracks are planned to examine aerosol properties in both polluted and clean conditions. In-situ MBL measurements will be coordinated with aircraft measurements and satellite overpasses to assess the direct and indirect radiative effects of the aerosol. A particular focus will be on the stratus deck that lies off shore of southern California and the effects of the transport of the Los Angeles urban plume into that stratus deck.

11. Other Measurements

Ground-based Measurements

Upper-air observations

California experiences a heterogeneous and complex diurnal cycle of meteorology caused by its proximity to the Pacific Coast, large urban areas and a variety of heterogeneous land-surface types that produce local circulations, and varying synoptic regimes experienced during different seasons. A characterization of the meteorological processes controlling the stagnation and transport of atmospheric pollutants within, and into and out of California is therefore required in order to gain a better understanding of the region's air quality.

NOAA and partners in CalNex 2010 will enhance the upper-air observing system in selected regions of California by deploying a network of integrated boundary layer observing systems similar to that deployed in the 2000 CCOS study (Figure 6). These ir

wind speed and wind direction in the boundary layer and lower free troposphere and derived mixing heights. Each profiler will also include a radio acoustic sounding system (RASS) for temperature profiling. The vertical coverage of the wind profilers is typically 120 m to 4000 m, depending on atmospheric conditions, and the profiles are sampled with either 60-m or 100-m vertical resolution. The vertical coverage of the temperature profilers is typically 120 m to 1500 m, but degraded performance can be expected in high wind conditions. In addition, four of the profiler sites deployed by the NOAA/ESRL Physical Sciences Division will include a global positioning system (GPS) receiver for integrated water vapor measurements and a 10-m tower for characterizing surface meteorology (pressure, temperature, relative humidity, wind, precipitation, solar and net radiation). The long-term meteorological measurements collected both during CalNex 2010 and in previous California field studies will also elucidate how the mixing and transport mechanisms outlined in Section 2b respond to diurnal, seasonal, and annual cycles.

Additional profiler deployments may be added for the intensive observing period in 2006. During this period, serial rawinsondes will be launched (by non-NOAA participants) in the California area at a site to be determined.

Hourly data from the existing and enhanced wind profiler networks will be available in real-time via web sites hosted by NOAA. An interactive web-based profiler trajectory tool developed by the NOAA Environmental Technology Laboratory will also be available to help scientists document transport in the region and to help in the planning and execution of missions for the mobile platforms during the 2010 intensive.

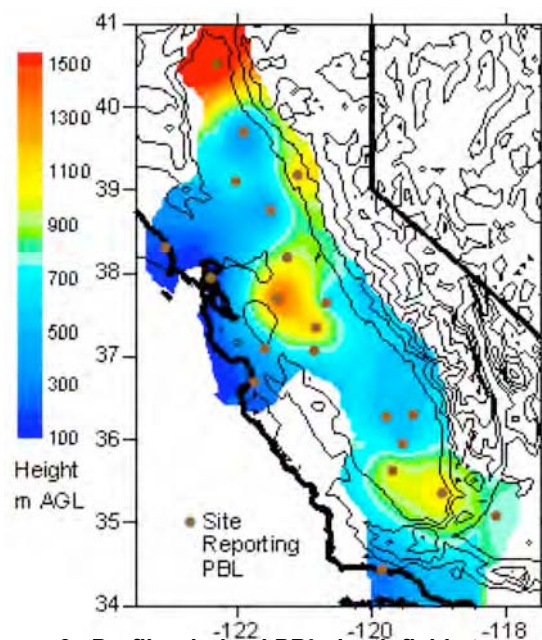


Figure 6. Profiler derived PBL depth field at 1500 PST on 31 July 2000. The dots indicate radar wind profilers deployed for CCOS .

Ground-based chemical measurements Surface “super-sites” have been found to be very useful for complementing and extending the measurements available from aircraft. These sites include both in situ and remote instrumentation comparable to the WP-3D and *Ronald H. Brown* instrument packages plus instrumentation that cannot be deployed on either platform. It will be highly desirable that CalNex 2010 deploy one or more such sites. Development of more definite ideas will be a goal of the ongoing planning process. Suggestions include a series of three sites at progressively further downwind distances from a particular urban area, or within the Central Valley.

Satellite Observations

Background

Retrievals of aerosol and trace gas information from current research and operational satellites have great potential to assist in several of the CalNex science objectives. Instruments on NASA and NOAA satellites are currently able to observe several of EPA’s criteria pollutants (Table 7). While polar-orbiting satellites (e.g., MODIS) provide coverage once a day globally, geostationary satellites (e.g., GOES) provide coverage over the continental United States once every fifteen minutes. A multiple platform and sensor approach, integrating *in situ* and satellite data with modeling, might be essential to address CalNex science objectives.

Table 7. A list of NOAA and NASA satellites and their measurement capabilities.

Satellite Platform: Web site	Instruments	Some key data products	Vertical Resolution
NASA Aura: http://eos-aura.gsfc.nasa.gov	TES OMI	CO, CH ₄ , O ₃ , HNO ₃ , NO ₂ O ₃ , NO ₂ , SO ₂ , H ₂ CO, aerosol optical depth, aerosol type	Trop. column/4 km Trop. column
NASA Aqua: http://eos-pm.gsfc.nasa.gov	MODIS* AIRS* AIRS* AIRS*	Aerosol optical depth O ₃ CO Aerosol optical depth	Trop. column UTLS Trop. column Trop. column
NASA Terra: http://eos-am.gsfc.nasa.gov	MOPITT MISR MODIS*	CO Aerosol optical depth Aerosol optical depth	Trop. column Trop. column Trop. column
NASA CALIPSO http://www.calipso.larc.nasa.gov	CALIOP	Aerosol backscatter ratio	Trop. vertical profile
NOAA GOES http://www.ssd.noaa.gov/PS/FIRE/GASP/gasp.html	Imager	Aerosol optical depth (30 minute interval)	Trop. column (land and water)
NOAA N16, N17, N18 http://www.osdpd.noaa.gov/PSB/EPS/Aerosol/Aerosol.html	AVHRR	Aerosol optical depth	Trop. column, (water only)
NOAA GOES http://www.orbit.nesdis.noaa.gov/smcd/emb/gsip/index	Imager	Shortwave flux (hourly)	Surface

html			
NOAA GOES	Imager	UV (erythemal) flux (hourly)	Surface
NASA http://asd-www.larc.nasa.gov/ceres/ASDeceres.html	CERES	Shortwave and longwave flux	Top of the atmosphere; surface

* Available through NOAA in near real time

Although satellite data have some disadvantages compared with other means of observing ozone and aerosols, the advantages of including satellite information currently outweigh the disadvantages. Accuracies of satellite retrieved aerosol optical depths and trace gases are not as good as measurements made from ground because satellite retrievals tend to have higher uncertainties. These uncertainties are associated with converting slant column retrievals to column amounts and isolating the tropospheric column from the total column in the case of trace gases. For aerosol retrievals, difficulties in modeling aerosol type and variability in surface reflectance lead to large uncertainties. Nevertheless, while the ability to measure trace gases and aerosols at the desired spatial resolution, temporal resolution, and accuracy might not be realized for several years, the benefits of exploiting these measurements for air quality studies are so substantial that the validation required to exploit them should be pursued immediately. .

Satellite data of aerosols and trace gases have three potential applications for the CalNex field campaign:

Using the satellite data in near real time:

- Image loops (especially from GOES) for aircraft/ship flight deployment
- Comparisons with *in situ* measurements
- Assimilation into forward trajectory models to forecast plume location

Retrospective looks at the data collected during CalNex:

- Comparisons of satellite and ground/aircraft/ship based measurements of various parameters
- Validation of satellite retrievals using *in situ* measurements. Assessment of uncertainties in the retrieval algorithms due to various assumptions. Reprocessing of satellite data with assimilated field measurements
- Extending the spatial (horizontal) dimension for studying problems such as contributions of long range transport to local air quality

Using the satellite data in modeling studies:

- Verifying chemistry and transport model forecasts with satellite data
- Diagnosing sources of uncertainties in chemistry and transport models
- Assimilating satellite data to improve initial and boundary conditions in the models
- Radiative effects of aerosol

These applications will cover various CalNex research topics as described below.

Emissions Verification

Satellite retrievals of CO, NO₂, SO₂, and H₂CO will be a good data resource for quantifying emissions from various sources in California. Studies have determined isoprene emissions from OMI H₂CO data (Millet et al., 2008). AIRS and MOPITT CO retrievals have thus far been primarily used to track plumes from biomass burning; plumes from biomass burning stay aloft

and can be detected from satellites. It is unclear how useful satellite measurements of CO can be to study urban/industrial emissions if CO remains close to the ground. However, studies can be carried out to determine their usefulness, especially in combination with OMI's light absorbing aerosol index to characterize the source as diesel or gasoline. Satellite data have not been used to study processes at small spatial scales, and CalNex will provide that opportunity. For the satellite community, these studies can be very beneficial, as they will expose limitations in satellite retrievals and offer insights into needed improvements in sensor technologies and algorithms, so that these kinds of routine applications can be realized.

Long Range Transport

Satellite data have been very useful in diagnosing long-range transport within the free troposphere where it is detectable by satellites. We plan to address the issue of entrainment of pollutants transported from remote sources into the boundary layer, and the impact on local air quality. The NASA lidar satellite instrument CALIPSO can measure tropospheric vertical profiles of aerosol backscatter ratio. These measurements, combined with GOES, MODIS, OMI, and MISR aerosol optical depth retrievals, are valuable for providing a three-dimensional look at pollution plumes. Additionally, integrating data from multiple sensors optimizes the information on aerosol type, and location in space (horizontal and vertical scale) and time (GOES aerosol observations have a refresh rate of 30 minutes).

Numerical Modeling

NOAA's National Weather Service has a mandate to issue nationwide hourly ozone (by 2009) and PM_{2.5} forecasts (by 2014). The NWS has already begun issuing ozone forecasts for the northeast and conducting experimental PM_{2.5} forecasts. It is currently using the Eta-CMAQ modeling system and will soon migrate to the WRF model with integrated meteorology and chemistry. Primary sources of uncertainty in model forecasts are uncertainties in initial/boundary conditions and emissions. Satellite data have the potential to improve forecasts by providing more precise initial/boundary conditions. *In situ* data collected during CalNex will also be useful in verifying forecasts and diagnosing various sources of uncertainties. In addition, a retrospective analysis of the CalNex data from an integrated satellite-*in situ*-model approach will help to determine biases and errors in the air quality modeling system.

Aerosols and Radiative Forcing

Estimating the radiative impact of aerosols requires concurrent aerosol and radiation measurements. The spatial (and temporal) variability of both quantities is readily observed by satellites. Aerosol optical depth (the primary factor affecting radiative forcing) over the ocean has been retrieved operationally at NOAA/NESDIS for over two decades. For example, AVHRR observations have been used to estimate the aerosol indirect effect for summertime stratiform clouds in the Northeastern Atlantic (Matheson, Coakley and Tahnk, 2004). Instruments flown on NASA satellites have also been providing aerosol data: TOMS has the ability to estimate absorbing aerosols, and the MODIS instrument is capable of estimating aerosol optical depth both over land and ocean in two different particle size regimes (fine and coarse modes). These measurements, coupled with top of atmosphere (TOA) and surface fluxes derived from the Clouds and the Earth's Radiant Energy System (CERES) instrument on NASA's EOS satellites, have been used to estimate the direct radiative forcing of aerosols in the shortwave and longwave part of the electromagnetic spectrum. In addition, satellite derived

radiative fluxes can be used to constrain models at the upper and lower boundaries of the atmosphere for estimating the radiative impact of aerosols. However, before satellite measured fluxes can be used in assessing the radiative effects of aerosols they need to be thoroughly tested and evaluated with surface measurements; their consistency must also be characterized.

Validation of Satellite Retrievals using CalNex

NOAA/NESDIS will use data collected during CalNex in evaluating various assumptions made in our GOES and AIRS aerosol optical depth retrieval algorithms. The aerosol algorithms use look-up tables created using a continental aerosol model, for which the single scattering albedo is ~0.9. This includes assumptions about aerosol type, size distribution, and refractive index. However, studies have shown that there are significant variations in aerosol type and size distributions over the CONUS. These variations are largely dictated by sources of pollution (e.g., forest fires, urban/industrial, or dust). Ground-based and aircraft-based observations of aerosol parameters (size distribution, vertical profiles, etc.) will be used to build new aerosol models and create new look-up tables. Sensitivity studies will be performed to test the impact of measured aerosol information on GOES aerosol optical depth retrievals.

Infusing satellite Data into Environmental Applications (IDEA)

IDEA is a two-dimensional, near real-time system that integrates MODIS aerosol optical depth, PM_{2.5} measurements, meteorological data, and models for use by EPA and state and local forecasters in monitoring and predicting PM_{2.5} concentrations for public notification (Al Saadi *et al.*, 2005). IDEA was developed in a cooperative project between NOAA, EPA and NASA to provide real-time views of AOD from MODIS, compare these with the EPA AIRNow ground monitors, include trajectory information for forecast guidance, and provide a brief analysis for the public. Planning is underway at NESDIS to transition IDEA to NOAA to run in an operational (24-hour, seven-day) environment. This product will be a very useful forecast tool to coordinate ship/aircraft deployment.

References

- Ackerman, A.S., O.B. Toon, D.E. Stevens, A.J. Heymsfield, V. Ramanathan, and E.J. Welton (2000), Reduction of tropical cloudiness by soot, *Science*, 288, 1042-1047.
- Bench, G., S. Fallon, B. Schichtel, W. Malm, and C. McDade (2007), Relative contributions of fossil and contemporary carbon sources to PM 2.5 aerosols at nine Interagency Monitoring for Protection of Visual Environments (IMPROVE) network sites, *J. Geophys. Res.-Atmos.*, 112, D10205, doi:10.1029/2006JD007708.
- CARB (2007), The California Almanac of Emissions & Air Quality - 2007 Edition, California Air Resources Board, Planning and Technical Support Division, Sacramento, CA.
- Crutzen, P.J., A.R. Mosier, K.A. Smith, and W. Winiwarter (2007), N₂O release from agro-biofuel production negates global warming reduction by replacing fossil fuels, *Atmos. Chem. Phys. Discuss.*, 7, 11191-11205.
- de Gouw, J.A., et al. (2007), Sources of particulate matter in the northeastern United States: 1. Direct emissions and secondary formation of organic matter in urban plumes, *J. Geophys. Res.-Atmos.*, submitted.
- de Gouw, J.A., et al. (2005), Budget of organic carbon in a polluted atmosphere: Results from the New England Air Quality Study in 2002, *J. Geophys. Res.-Atmos.*, 110, D16305, doi:10.1029/2004JD005623.

- Dlugokencky, E.J., et al. (2003), Atmospheric methane levels off: Temporary pause or a new steady-state?, *Geophys. Res. Lett.*, *30*, 1992, doi:10.1029/2003GL018126.
- Dusek, U., et al. (2006), Size matters more than chemistry for cloud-nucleating ability of aerosol particles, *Science*, *312*, 1375-1378.
- EPA (2007), Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990 – 2005, EPA-430-R-07-002, U.S. Environmental Protection Agency, Washington D.C.
- Ervens, B., G. Feingold, and S.M. Kreidenweis (2005), Influence of water-soluble organic carbon on cloud drop number concentration, *J. Geophys. Res.-Atmos.*, *110*, D18211, doi:10.1029/2004JD005634.
- Farrell, A.E., R.J. Plevin, B.T. Turner, A.D. Jones, M. O'Hare, and D.M. Kammen (2006), Ethanol can contribute to energy and environmental goals, *Science*, *311*, 506-508.
- Jacobson, M.Z. (2007), Effects of ethanol (E85) versus gasoline vehicles on cancer and mortality in the United States, *Environ. Sci. Technol.*, *41*, 4150-4157.
- Kepler, F., J.T.G. Hamilton, M. Brass, and T. Rockmann (2006), Methane emissions from terrestrial plants under aerobic conditions, *Nature*, *439*, 187-191.
- Koren, I., Y.J. Kaufman, D. Rosenfeld, L.A. Remer, and Y. Rudich (2005), Aerosol invigoration and restructuring of Atlantic convective clouds, *Geophys. Res. Lett.*, *32*, L14828, doi:10.1029/2005GL023187.
- Krueger, O., R. Marks, and H. Grassl (2004), Influence of pollution on cloud reflectance, *J. Geophys. Res.-Atmos.*, *109*, D24210, doi:10.1029/2004JD004625.
- Lelieveld, J., and F.J. Dentener (2000), What controls tropospheric ozone?, *J. Geophys. Res.-Atmos.*, *105*, 3531-3551.
- NARSTO (2005), Improving emission inventories for effective air quality management across North America: A NARSTO assessment, NARSTO-05-001.
- Pagowski, M., et al. (2005), A simple method to improve ensemble-based ozone forecasts, *Geophys. Res. Lett.*, *32*, L07814, doi:10.1029/2004GL022305.
- Parrish, D.D. (2006), Critical evaluation of US on-road vehicle emission inventories, *Atmos. Environ.*, *40*, 2288-2300.
- Ramanathan, V., P.J. Crutzen, J.T. Kiehl, and D. Rosenfeld (2001), Aerosols, climate, and the hydrological cycle, *Science*, *294*, 2119-2124.
- Ramanathan, V., F. Li, M.V. Ramana, P.S. Praveen, D. Kim, C.E. Corrigan, H. Nguyen (2007), Atmospheric Brown Clouds: Hemispherical and regional variations in long range transport, absorption, and radiative forcing, *J. Geophys. Res.*, *112*, D22S21, doi:10.1029/2006JD008124.
- Ramanathan, V., et al. (2007), Warming trends in Asia amplified by brown cloud solar absorption, *Nature*, *448*, 575-578.
- Rosenstiel, T.N., M.J. Potosnak, K.L. Griffin, R. Fall, and R.K. Monson (2003), Increased CO₂ uncouples growth from isoprene emission in an agriforest ecosystem, *Nature*, *421*, 256-259.
- Sinha, V., J. Williams, P.J. Crutzen, and J. Lelieveld (2007), Methane emissions from boreal and tropical forest ecosystems derived from in-situ measurements, *Atmos. Chem. Phys. Discuss.*, *7*, 14011-14039.
- Sitch, S., P.M. Cox, W.J. Collins, and C. Huntingford (2007), Indirect radiative forcing of climate change through ozone effects on the land-carbon sink, *Nature*, *448*, 791-794.
- Tsigaridis, K., and M. Kanakidou (2007), Secondary organic aerosol importance in the future atmosphere, *Atmos. Environ.*, *41*, 4682-4692.

- Twomey, S. (1977), The influence of pollution on the shortwave albedo of clouds, *J. Atmos. Sci.*, *34*, 1149-1152.
- Velders, G.J.M., S.O. Andersen, J.S. Daniel, D.W. Fahey, and M. McFarland (2007), The importance of the Montreal Protocol in protecting climate, *Proc. Nat. Acad. Sci.*, *104*, 4814-4819.
- Volkamer, R., et al. (2006), Secondary organic aerosol formation from anthropogenic air pollution: Rapid and higher than expected, *Geophys. Res. Lett.*, *33*, L17811, doi:10.1029/2006GL026899.
- West, J.J., A.M. Fiore, V. Naik, L.W. Horowitz, M.D. Schwarzkopf, and D.L. Mauzerall (2007), Ozone air quality and radiative forcing consequences of changes in ozone precursor emissions, *Geophys. Res. Lett.*, *34*, L06806, doi:10.1029/2006GL029173.
- Xue, H.W., and G. Feingold (2006), Large-eddy simulations of trade wind cumuli: Investigation of aerosol indirect effects, *J. Atmos. Sci.*, *63*, 1605-1622.
- Zhang, Q., et al. (2007), Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes, *Geophys. Res. Lett.*, *34*, L13801, doi:10.1029/2007GL029979.