instruments and photoelectric aerosol sensors in source-sampling of black carbon aerosol and particle bound

A series of measurements have been performed at Hill Air Force Base to evaluate real-time instruments for
measurements of black carbon aerosol and particle-bound PAHs emitted from spark and ignition compression
vehicles. Vehicles were operated at idle or fast idle in one set of measurements and were placed under load on a
dynamometer during the second series. Photoacoustic instruments were developed that operated at a wavelength of
1047 nm where gaseous interference is negligible, although sensitivity to black carbon is good. Compact, efficient,
solid-state lasers with direct electronic modulation capabilities are used in these instruments. Black carbon
measurements are compared with samples collected on quartz fiber filters that were evaluated using the thermal
optical reflectance method. A measure of total particle-bound PAH was provided by photoelectric aerosol sensors
(PAS) and is evaluated against a sum of PAH mass concentrations obtained with a filter-denuder combination. The
PAS had to be operated with a dilution system held at approximately 150 degrees C for most of the source sampling
to prevent spurious behavior, thus perhaps compromising detection of lighter PAHs. PA and PAS measurements
were found to have a high degree of correlation, perhaps suggesting that the PAS can respond to the polycyclic
nature of the black carbon aerosol. The PAS to PA ratio for ambient air in Fresno, CA is 3.7 times as large in winter
than in summer months, suggesting that the PAS clearly does respond to compounds other than BC when the
instrument is used without the heated inlet


The negative health effects of repeated dust exposure have been well documented. In California's San Joaquin
Valley, agricultural operations may contribute substantially to airborne particulates. We evaluated four management
systems to assess impacts on dust production and soil properties for a cotton (Gossypium hirsutum L.)-tomato
(Lycopersicon esculentum Mill.) rotation: standard tillage with (STCC) and without (STNO) cover crop, and
conservation tillage with (CTCC) and without (CTNO) cover crop. Gravimetric analysis of total dust (TD, < 100-μm
aerodynamic diameter) and respirable dust (RD, 4-μm aerodynamic diameter) samples collected in the plume
generated by field implements showed that dust concentrations for CTNO treatments were about one-third of their
STNO counterparts for both cumulative TD and RD measured throughout the two-year rotation, primarily due to
fewer in-field operations. The TD and RD production for STNO and STCC was comparable, whereas the CTCC
system produced about twice as much TD and RD as CTNO. Energy dispersive spectroscopy (EDS) analyses
showed absolute increases of 8 and 39% organic fragments in STCC and CTCC over STNO and CTNO,
respectively, while organic fragments in the TD increased by 6% in both cover crop treatments. Soil C content was
positively correlated with clay content and increased by an average of 0.12 and 0.07% in the cover crop and non-
cover crop treatments, respectively, although soil C for each treatment showed a distinct response to a field texture
gradient. While dust emissions show an immediate decrease due to fewer field operations for the conservation tillage
treatments, long-term sampling is necessary to determine the effects that increased aggregation through organic
matter additions may have on dust production

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When long records of climate (precipitation, temperature, stream runoff, etc.) are available, either from instrumental
observations or from proxy records, the objective evaluation and comparison of climatic episodes becomes
necessary. Such episodes can be quantified in terms of duration (the number of time intervals, e.g. years, the process
remains continuously above or below a reference level) and magnitude (the sum of all series values for a given
duration). The joint distribution of duration and magnitude is represented here by a stochastic model called BEG, for
'bivariate distribution with exponential and geometric marginals'. The model is based on the theory of random sums,
and its mathematical derivation confirms and extends previous empirical findings. Probability statements that can be
obtained from the model are illustrated by applying it to a 2300-year dendroclimatic reconstruction of water-year
precipitation for the eastern Sierra Nevada-western Great Basin. Using the Dust Bowl drought period as an example, the chance of a longer or greater drought is 8%. Conditional probabilities are much higher, i.e. a drought of that magnitude has a 62% chance of lasting for 11 years or longer, and a drought that lasts 11 years has a 46% chance of having an equal or greater magnitude. In addition, because of the bivariate model, we can estimate a 6% chance of witnessing a drought that is both longer and greater. Additional examples of model application are also provided. This type of information provides a way to place any climatic episode in a temporal perspective, and such numerical statements help with reaching science-based management and policy decisions. Copyright (C) 2005 Royal Meteorological Society


The US Environmental Protection Agency requires that only oxygenated gasoline may be sold in regions that are not in compliance with national air quality standards. Several non-attainment regions are located in California, and most of the gasoline sold there is oxygenated with methyl tertiary butyl ether (MTBE). California is planning to discontinue the use of MTBE in gasoline by January 2004. This policy will generate greater demand for ethanol, which is the leading substitute for MTBE. Most of the ethanol required in California will be imported from other states, unless California develops an ethanol production industry. The costs of producing ethanol in California may exceed the benefits, unless substantial value is attributed to non-market, public goods, such as maintaining agriculture and reducing unemployment in rural areas. We examine the firm-level economics of using corn and other agricultural products to produce ethanol in California, and the potential regional economic impacts of building and operating an ethanol plant. The cost of production is greater than the current price of ethanol for all of the feedstocks we consider. Production generates economic activity, but at current prices for inputs and outputs, substantial subsidies will be required to encourage firms to produce ethanol in California. (c) 2004 Elsevier Ltd. All rights reserved


The influence of particulate organic material (POM) and the contribution of biomass smoke on air quality and visibility remain a paramount issue in addressing regional haze concerns in US national parks. Measurements during the Yosemite Aerosol Characterization Study (July-September 2002) indicated an aerosol dominated by POM (similar to 70% of identified species) and strongly influenced by biomass smoke. Here we report aerosol size hygroscopic growth measurements for dry (RH < 5%) aerosol diameters of 100 and 200 nm as measured with a controlled relative humidity tandem differential mobility analyzer. Hygroscopic growth was found to be negligible for relative humidity (RH) < similar to 40% within the sensitivity of the method. For RH > 40%, particle size typically increased smoothly with RH, and overall hygroscopic growth at high RH was low to moderate in comparison to the range of values reported in the literature. For RH > 80%, both monomodal and bimodal growth profiles were observed during the study, with 200 nm particles more often splitting into bimodal profiles (68% of cases), indicating some degree of external mixing. Trimodal growth profiles were observed on two occasions during periods of changing meteorology and aerosol composition. For bimodal profiles for 200 run dry particles, particle diameter growth factors at RH = 80% (D(RH = 80%)/D-o where D-o is measured at RH < 5%) were 1.11 +/- 0.04 and 1.29 +/- 0.08 for the more and less hygroscopic modes, respectively. Ensemble D/D-o was calculated using a cubic-weighted sum of D/D-o of individual modes. For 200 nm particles, average ensemble D(RH = 80%)/D-o was 1.15 +/- 0.05 and D(RH = 90%)/D-o was 1.31 +/- 0.06, and were slightly large for 100nm particles. These growth factors are dramatically lower than those for typical ambient aerosol ionic components such as sulfate, nitrate and sodium salts and sulfuric acid. An inverse relationship between the POM fraction of PM2.5 and hygroscopicity was particularly evident for 200nm particles with D(RH = 80%)/D-o approaching similar to 1.1 as the POM/ ionic mass ratio exceeded 10. Linear correlations with several measurements of POM and select biomass smoke markers were - 0.74 < R < -0.59 for 200 nm and - 0.43 < R < -0.25 for 100 nm particles. The limited hygroscopic growth of the carbon dominated, biomass smoke influenced aerosol at Yosemite has important implications to assessing the role of POM in visibility degradation in national parks. (c) 2004 Elsevier Ltd. All rights reserved

Ammonia emissions contribute to the formation of secondary particulate matter (PM) and violations of the National Ambient Air Quality Standard. Ammonia mass concentration measurements were made in February 1999 upwind and downwind of an open-lot dairy in California, using a combination of active bubbler and passive filter samplers. Ammonia fluxes were calculated from concentrations measured at 2, 4, and 10 m above ground at three locations on the downwind edge of the dairy, using micrometeorological techniques. A new method was developed to interpolate fluxes at six additional locations from ammonia concentrations measured at a single height, providing measurements at sufficient spatial resolution along the downwind border of the dairy to account for the heterogeneity of the source. PM measured up- and downwind of the dairy demonstrated insignificant ammonium particle formation in the immediate vicinity of the dairy and negligible contribution of dissociated ammonium nitrate to measured ammonia concentrations. Ammonium nitrate concentrations measured downwind of the dairy ranged from 26 to 0.26 μg m(-3) and from 2 to 43% of total PM2.5 mass concentrations. Measured ammonia fluxes showed that liquid manure retention ponds represented relatively minor sources of ammonia in winter on the dairy studied. Ammonia emission factors derived from the measurements ranged from 19 to 143 g head(-1) day(-1), showing an increase with warmer, drier weather and a decrease with increased relative humidity and lower temperatures.


Ammonia (NH3) emissions contribute to the formation of secondary particulate matter (PM) 10 μm and under (PM10). Dairies are significant sources of NH3 in the San Joaquin Valley (SJV) of California, where the National Ambient Air Quality Standard for PM10 is frequently exceeded. Detailed descriptions of diets, animal demographics, and production levels were obtained for two commercial open-lot dairies in the SJV and used to compute nitrogen intake for each feeding group (g N day(-1)). Models derived from nutrition trials with cows, heifers, and calves were used to estimate urea-N excretion from N intake. Air NH3 concentrations were also measured at the same dairies over 1-week periods in February 1999. NH3 fluxes calculated from vertical profiles of concentrations at two or three locations downwind of the dairies were augmented with estimates of flux based on single-height concentrations measured at five or six additional downwind locations to compute NH3 emission rates. NH3 emission potentials, estimated from urea-N excretion, exceeded NH3 emission rates measured by the micrometeorological methods by 1.5- and 3-fold on the two dairies. A diurnal pattern in NH3 emission factors based on measurements showed peak emission occurring between 1:00 p.m. and 6:00 p.m. at both dairies. NH3 emission potentials and measured NH3 emission rates were higher for Dairy 2, which reported feeding heifers dietary crude protein in excess of National Research Council recommendations.


Evaporative loss of particulate matter (with aerodynamic diameter < 2.5 μm, [PM2.5]) ammonium nitrate from quartz-fiber filters during aerosol sampling was evaluated from December 3, 1999, through February 3, 2001, at two urban (Fresno and Bakersfield) and three nonurban (Bethel Island; Sierra Nevada Foothills, and Angiola) sites in central California. Compared with total particulate nitrate, evaporative nitrate losses ranged from < 10% during cold months to > 80% during warm months. In agreement with theory, evaporative loss from quartz-fiber filters in nitric...
acid denuded samplers is controlled by the ambient nitric acid-to-particulate nitrate ratio, which is determined mainly by ambient temperature. Accurate estimation of nitrate volatilization requires a detailed thermodynamic model and comprehensive chemical measurements. For the 14-month average of PM2.5 acquired on Teflon-membrane filters, measured PM2.5 mass was 8-16% lower than actual PM2.5 mass owing to nitrate volatilization. For 24-hr samples, measured PM2.5 was as much as 32-44% lower than actual PM2.5 at three California Central Valley locations.


Tillage-induced erosion of herbicides bound to airborne soil particles has not been quantified as a mechanism for off-site herbicide transport. This study quantifies the release of two preemergent herbicides, metolachlor and pendimethalin, to the atmosphere as gas- and particle-phase species during soil incorporation operations. Fine particulate matter (PM2.5) and gas-phase samples were collected at three sampling heights during herbicide disking into the soil in Davis, CA, in May 2000 and May 2001 using filter/PUF sampling. Quartz fiber filters (QFFs) were used in May 2000, and Teflon membrane filters (TMFs) were used in May 2001. The field data were combined with laboratory filter/PUF partitioning experiments to account for adsorption to the filter surfaces and quantify the mass Of PM2.5-bound herbicides in the field samples. Laboratory results indicate a significant adsorption of metolachlor, but not pendimethalin, to the quartz filter surfaces. Metolachlor partitioning to PM2.5 collected on TMF filters resulted in corrected PM2.5 field partition coefficient values, K-p,K-corr = C-p/ C-g of similar to10(-3.5) m(3)/mug, indicating its preference for the gas phase. Pendimethalin exhibited more semivolatile behavior, with K-p,K-corr values that ranged from 10(-3) to 10(-1) m(3)/mug and increased with sampling height and distance downwind of the operation. An increase in pendimethalin enrichment at a height of 5 m suggests winnowing of finer, more sorptive soil components with corresponding higher transport potential. Pendimethalin was enriched in the PM2.5 samples by up to a factor of 250 compared to the field soil, indicating that further research on the processes controlling the generation of PM-bound herbicides during agricultural operations is warranted to enable prediction of off-site mass fluxes by this mechanism.


Gasoline samples (n = 20) collected from San Francisco Bay area refineries and service stations had mercury concentrations ranging from 0.08 to 1.4 ng g(-1); diesel samples (it = 19) had concentrations of 0.05-0.34 ng g(-1). These relatively low levels show little evidence for mercury enrichment or contamination into these fuels from the refining process. Combustion of these fuels in the San Francisco Bay area contributes 0.7-13 kg Hg yr(-1) to the environment, with an average of 5 kg Hg yr(-1). Assuming the fate of this emission is to the atmosphere, the total flux from the combustion of these fuels represents less than 3% of the total atmospheric emissions in the San Francisco Bay area. (C) 2004 Elsevier Ltd. All rights reserved.

Fine (PM2.5) and coarse (PM2.5-10) particulates were collected simultaneously by using a versatile air pollutant system at a traffic sampling site during daytime and nighttime sampling periods during August 2003 to March 2004. A flame atomic absorption spectrophotometer coupled with hollow cathode lamps were used for chemical analysis. Enrichment factor and principal component analysis were used to compare chemical components and to find the possible emission sources at this traffic sampling site. The variation of metallic element concentrations on fine and coarse particulates during daytime and nighttime was also discussed in this study. Soil dust, traffic exhaust, marine salt and anthropogenic activities were the major pollutant sources at the traffic sampling site in central Taiwan. (c) 2004 Elsevier B.V. All rights reserved


Evapotranspiration, a major component in terrestrial water balance and net primary productivity models, is difficult to measure and predict. This study compared five models of potential evapotranspiration (PET) applied to a ponderosa pine forest ecosystem at an AmeriFlux site in Northern California. The AmeriFlux sites are research forests across the United States, Canada, Brazil, and Costa Rica with instruments on towers that measure carbon, water, and energy fluxes into and out of the ecosystems. The evapotranspiration models ranged from simple temperature and solar radiation-driven equations to physically-based combination approaches and included reference surface and surface cover-dependent algorithms. For each evapotranspiration model, results were compared against mean daily latent heat from half-hourly measurements recorded on a tower above the forest canopy. All models calculate potential evapotranspiration (assuming well-watered soils at field capacity), rather than actual evapotranspiration (based on soil moisture limitations), and thus overpredicted values from the dry summer seasons of 1997 and 1998. A soil moisture function was integrated to estimate actual evapotranspiration, resulting in improved accuracy in model simulations. A modified Priestley-Taylor model performed well given its relative simplicity. (c) 2004 Elsevier Ltd. All rights reserved


To determine the size and chemical composition of particles derived from on-road vehicle emissions, individual particles were sampled continuously with an aerosol time-of-flight mass spectrometer (ATOFMS) at the Caldecott Tunnel in Northern California. In this tunnel, traffic is segregated, such that in theory only light duty vehicle emissions or a mix of heavy- (HDV) and light-duty vehicle (LDV) emissions can be sampled separately. Two studies were carried out, one in November 1997 and another in July 2000, time periods with average ambient temperatures of 10-15 and 26-32 °C, respectively, with the instrument operating at ambient outdoor temperatures. Analysis of the chemical composition of the particles sampled in these studies shows that sampling conditions can strongly impact the determination of suitable markers for identifying particles emitted from different vehicle types during ambient studies. Differences in the results of these two studies are shown to be related to the different ambient temperatures at which the measurements were carried out. Particles sampled from HDV-influenced traffic in the 1997 study were 16 times more likely to have mass spectra containing peaks at both m/z 128 (naphthalene) and 156 (dimethylnaphthalene/ naphthaldehydes) and 51 times more likely to have mass spectra containing peaks at both m/z 156 and 170 (trimethylnaphthalene/methylnaphthaldehyde) than were particles sampled from the LDV-only traffic tunnel. The peaks corresponding to m/z 156 and 170 are on average 2 and 4 times more intense in the mass spectra of the HDV-influenced data set than in the LDV-only data set. In contrast, in the 2000 experiment, the peaks at m/z 128 and 156 were present in 1% and 2% of the particles, respectively, with no preference for traffic type. These results show the usefulness of naphthalene and its derivatives for identification of the vehicle source of particulate emissions, under appropriate conditions, and highlight the fact that ambient conditions can strongly affect potential marker ions for source apportionment studies, necessitating a combination of controlled laboratory and field measurements for identification of stable marker ions.

Source contributions to primary airborne particulate matter calculated using the source-oriented UCD/CIT air quality model and the receptor-oriented chemical mass balance (CMB) model are compared for two air quality episodes in different parts of California. The first episode occurred in the San Joaquin Valley on 4-6 January 1996, with peak 24 h average PM2.5 concentrations exceeding 100 μg m⁻³. This episode was characterized by low photochemical activity and high particulate nitrate concentrations, with localized regions of high particulate carbon concentrations around urban centers. The second episode occurred in the South Coast Air Basin on 7-9 September 1993, with peak 48 h average PM2.5 concentrations reaching 86 μg m⁻³. This episode was characterized by high photochemical activity and high secondary organic aerosol concentrations. The results from the two independent source apportionment calculations show strong agreement for source contributions to primary PN12.5 total organic mass at 7 receptor sites across the two studies, with a correlation slope of 0.84 and a correlation coefficient (R) of 0.70. Agreement for source contributions to primary PN12.5 total mass was similarly strong, with a correlation slope of 0.83 and a correlation coefficient (R²) of 0.55. Wood smoke was identified as the dominant source of primary PM2.5 at urban locations in the SJV by both source apportionment techniques. Transportation sources including paved road dust, gasoline engines, and diesel engines, were identified as the dominant source of primary PM2.5 at all locations in the SoCAB by both models. The amount of secondary particulate matter (organic and inorganic) was in good agreement with the measured values minus the primary material identified by the CMB calculation. The UCD/CIT air quality model is able to predict source contributions to airborne particulate matter at all locations and times throughout the study domain. The regional plots of source contributions to primary PM2.5 mass concentrations generated by the UCD/CIT air quality model suggest that high concentrations (25 μg m⁻³) of primary PM2.5 mass released from the combustion of fuel with high sulfur content exist in areas adjacent to the Los Angeles International Airport and the port of Los Angeles. Emissions profiles for these sources should be developed so that they can be included in future CMB calculations.

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The San Joaquin Valley (SJV), in California has one of the most severe particulate air quality problems in the United States during the winter season. In the current study, measurements of particulate matter (PM) smaller than 10 μm in aerodynamic diameter (PM10), fine particles (PM1.8), and ultrafine particles (PM0.1) made during the period December 16, 2000-February 3, 2001, at six locations near or within the SJV are discussed: Bodega Bay, Davis, Sacramento, Modesto, Bakersfield, and Sequoia National Park. Airborne PM1.8 concentrations at the most heavily polluted site (Bakersfield) increased from 20 to 172 μg/m³ during the period December 16, 2000-January 7, 2001. The majority of the fine particle mass was ammonium nitrate driven by an excess of gas-phase ammonia. Peak PM0.1 concentrations (8-12 hr average) were similar to 2.4 μg/m³ measured at night in Sacramento and Bakersfield. Ultrafine particle concentrations were distinctly diurnal, with daytime concentrations similar to 50% lower than nighttime concentrations. PM0.1 concentrations did not accumulate during the multiweek stagnation period; rather, PM0.1 mass decreased at Bakersfield as PM1.8 mass was increasing. The majority of the ultrafine particle mass was associated with carbonaceous material. The high concentrations of ultrafine particles in the SJV pose a potential serious public health threat that should be addressed.


To reduce public exposure to diesel particulate matter (DPM), the California Air Resources Board has begun adoption of a series of rules to reduce these emissions from in-use heavy-duty vehicles. Passive diesel particulate filter (DPF) after-treatment technologies are a cost-effective method to reduce DPM emissions and have been used
on a variety of vehicles worldwide. Two passive DPFs were interim-verified in California and approved federally for use in most 1994-2002 engine families for vehicles meeting min engine exhaust temperature requirements for successful filter regeneration. Some vehicles, however, may not be suited to passive DPFs because of lower engine exhaust temperatures. The purpose of this study was to determine the applicability of two types of passive DPFs to solid waste collection vehicles, the group of vehicles for which California recently mandated in-use DPM reductions. We selected 60 collection vehicles to represent the four main types of collection vehicle duty cycles-roll-offs, and front-end, rear, and side loaders-and collected second-by-second engine exhaust temperature readings for one week from each vehicle. As a group, the collection vehicles exhibited low engine exhaust temperatures, making the application of passive DPFs to these vehicles difficult. Only 35% of tested vehicles met the temperature requirements for one passive DPF, whereas 60% met the temperature requirements for the other. Engine exhaust temperatures varied by vehicle type. Side and front-end loaders met the engine exhaust temperature requirements in the greatest number of cases with similar to50-90% achieving the required regeneration temperatures. Only 8-25% of the rear loader and roll-off collection vehicles met the engine exhaust temperature requirements. Solid waste collection vehicles represent a diverse fleet with a variety of duty cycles. Low engine exhaust temperatures will need to be addressed for successful use of passive DPFs in this application.


Tomato (Lycopersicon esculentum L.) production in the San Joaquin Valley (SJV) of California is challenged by air pollution and weeds. Differential ozone (O-3) tolerance of tomato cultivars and weed species may alter crop-weed competition. A study was conducted in open top chambers (OTCs) at the Kearney Research and Extension Center, Parlier, CA, to assess O-3 impacts on competition between tomato and a C-4 weed, yellow nutsedge (Cyperus esculentus L.). Processing tomato (cv. HD 8892 and EMP 113) and nutsedge (locally collected biotypes) were grown in pots for 4 to 8 wk. Population ratios ranged from a tomato plant alone (0:1) to a nutsedge plant alone (1:0), and included 1:1, 2:1, and 3:1. Ozone exposures were to 12 h means of 19.8, 78.0, and 142.3 nL/L. Chlorophyll content of leaves of tomato and nutsedge was reduced with increasing O-3. Carbon assimilation was reduced in nutsedge but not in tomato. Root respiration was not affected in either species. Tomato main stem length, shoot, and root biomass declined at the highest O-3 concentration under all levels of nutsedge competition. Nutsedge was much less affected. In the absence of O-3 exposure, interspecific competition (all population ratios combined) reduced tomato and nutsedge shoot and root biomass. Tomato was more sensitive to O-3 than nutsedge, but nutsedge was more sensitive to competition than was tomato. Nutsedge allocated greater resources to reproductive structures (tubers) at the highest O-3 exposure. As nutsedge reduced tomato productivity under low and moderate O-3 concentrations, it may become even more difficult to control, exert greater competitiveness, and colonize fields more rapidly because of greater tuber production, in projected near-future environments. Under conditions of greatly increasing ambient O-3 concentrations, nutsedge may become less competitive because of its sensitivity to O-3.


A total of 62 winter-storm events in the period 1964-99 over the Folsom Lake watershed located at the windward slope of the Sierra Nevada were simulated with a 9-km resolution using the fifth-generation Pennsylvania State University-NCAR Mesoscale Model (MM5). Mean areal precipitation (MAP) over the entire watershed and each of four Subbasins was estimated based on gridded simulated precipitation. The simulated MAP was verified with MAP estimated (a) by the California Nevada River Forecast Center (CNRFC) for the four subbasins based on eight operational precipitation stations, and (b) for the period from 1980 to 1986, on the basis of a denser precipitation observing network deployed by the Sierra Cooperative Pilot Project (SCPP). A number of sensitivity runs were performed to understand the dependence of model precipitation on boundary and initial fields, cold versus warm start, and microphysical parameterization. The principal findings of the validation analysis are that (a) MM5 achieves a good percentage bias score of 103% in simulating Folsom basin MAP when compared to MAP derived from dense precipitation gauge networks; (b) spatial grid resolution higher than 9 km is necessary to reproduce the spatial MAP pattern among subbasins of the Folsom basin; and (c) the model performs better for heavy than for light and moderate precipitation. The analysis also showed significant simulation dependence on the spatial resolution of the boundary and initial fields and on the microphysical scheme used.
We simulated forest dynamics of the regional ponderosa pine-white fir conifer forest of the San Bernardino and Sierra Nevada mountains of California to determine the effects of high ozone concentrations over the next century and to compare the responses to our similar study for loblolly pine forests of the southeast. As in the earlier study, we linked two models, TREGRO and ZELIG, to consider both physiological effects within individual trees and competitive interactions within forest communities. We represented regional effects by simulating at three sites in California, Lassen National Park, Yosemite National Park, and Crestline in the San Bernardino Mountains. At each of these locations, we simulated the response to altered pollutant conditions of 0.5, 1.5, 1.75, and 2 times ambient ozone. Of the two major dominant species in this forest, white fir showed little response, but ponderosa pine was predicted to show large effects. Ambient ozone at Crestline (approximately 110 ppm h. and larger than twice the ambient concentration at either of the other sites) was predicted to decrease individual tree carbon budgets by 10%. This effect was predicted to lead to a decrease in ponderosa pine abundance under average climatic conditions by 16%, were these concentrations to continue over the next century. A doubling of ozone at Crestline over the next 100 years was predicted to decrease this budget by an additional 11%, leading to a decline in abundance of 4%. Effects at the other sites were predicted to be smaller (effects of current ambient ozone on abundance of 10% at Yosemite and 0% at Lassen) in proportion to the smaller exposures at those sites. Decreases in chronic moisture availability at all three sites were predicted to reduce these effects, particularly if ozone exposures rise. (C) 2004 Elsevier B.V. All rights reserved


Contra Costa County, California during January 2004. Mixing ratios of N2O5, an intermediate compound in the atmosphere's nocturnal cleansing process, ranged up to 200 pmol/mol at night. The highest N2O5 concentrations were correlated with low O-3 and high NO2 concentrations. The calculated steady state lifetime for N2O5 ranged from 5 to 30 min. The total HNO3 produced by N2O5 hydrolysis over a 14 h night was comparable to ambient NO2 concentrations, and is estimated to be a factor of nine bigger than the HNO3 produced during the day


[1] Two Aerodyne aerosol mass spectrometers (AMSs) were deployed at Trinidad Head on the north Californian coast during the National Oceanographic and Atmospheric Administration Intercontinental Transport and Chemical Transformation 2002 (ITCT 2K2) experiment, to study the physiochemical properties of submicron aerosol particles within the Pacific marine boundary layer. One AMS was modified to allow the study of sea salt-based particles, while the other used a temperature cycling system on its inlet. The reported loadings increased by a factor of 2 when the temperature approached the dew point, which is due to the inlet performance and has implications for other AMS experiments and applications. The processed data were compared with those of a particle into liquid sampler-ion chromatograph and showed that the ammonium, sulfate and organic fractions of the particles were consistently found within a single, normally acidic, accumulation mode at around 300 - 400 nm. However, when influenced by land-based sources, vehicle emissions and increased ammonium loadings were seen. The concentrations of nitrate in the accumulation mode were low, but it was also found within sea salt particles in the coarse mode and can be linked to the displacement of chloride. The organic fraction showed a high degree of chemical ageing and evidence of nitrogen-bearing organics was also observed. The particulate organic data were compared to the volatile organic carbon data derived from an in-situ gas chromatograph-mass spectrometer-flame ionization detector and
relationships were found between the gas and particle phase chemicals in both the overall concentrations and the levels of oxidation.


The extent of mass loss on Teflon filters caused by ammonium nitrate volatilization can be a substantial fraction of the measured particulate matter with an aerodynamic diameter less than 2.5 mum (PM2.5) or 10 mum (PM10) mass and depends on where and when it was collected. There is no, straightforward method to correct for the mass loss using routine monitoring data. In southern California during the California Acid Deposition Monitoring Program, 30-40% of the gravimetric PM2.5 mass was lost during summer daytime. Lower mass losses occurred at more remote locations. The estimated potential mass loss in the Interagency Monitoring of Protected Visual Environments network was consistent with the measured loss observed in California. The. biased mass measurement implies that use of Federal Reference Method data for fine particles may lead to control strategies that are biased toward sources of fugitive dust, other primary particle emission, sources, and stable secondary particles (e.g., sulfates). This analysis clearly supports the need for speciated analysis of samples collected in a manner that preserves volatile species. Finally, although there is loss of volatile nitrate (NO3-) from Teflon filters during sampling, the NO3- remaining after collection is quite stable. We found little loss of NO3- from Teflon filters after 2 hr under vacuum and 1 min of heating by a cyclotron proton beam.


The impact of aerosol particulate matter of mean mass aerodynamic diameter less than or equal to 2.5 mum (PM2.5 aerosols) on health, visibility, and compliance with the U.S. EPA’s regional haze regulations is a growing concern. Techniques that can help better characterize particulate matter are required to better understand the constituents, causes, and sources of PM2.5 aerosols. Measurement of the C-14/C ratio of the PM2.5 aerosols, the absence of C-14 in fossil carbon materials, and the known C-14/C levels in contemporary carbon materials allow the use of a two-component model to derive contemporary and fossil carbon contents of the particulate matter. Such data can be used to estimate the relative contributions of fossil fuels and biogenic aerosols to the total aerosol loading. Here, the methodology for performing such an assessment using total suspended particulate hi-vol aerosol samplers to collect PM2.5 aerosols on quartz fiber filters and the technique of accelerator mass spectrometry to measure C-14/C ratios is presented and illustrated using PM2.5 aerosols collected at Yosemite National Park.


Analysis is monitored by the change in a laser signal either reflected from or transmitted through a filter punch. Elemental carbon (EC) in suspended particulate matter collected on quartz-fiber filters is defined as the carbon that evolves after the detected optical signal attains the value it had prior to commencement of heating, with the rest of the carbon classified as organic carbon (OC). Heretofore, operational definitions of EC were believed to be caused by different temperature protocols rather than by the method of monitoring charring. This work demonstrates that thermal/optical reflectance (TOR) corrections yield equivalent OC/EC splits for widely divergent temperature protocols. EC results determined by simultaneous thermal/optical transmittance (TOT) corrections are 30% lower than TOR for the same temperature protocol and 70-80% lower than TOR for a protocol with higher heating temperatures and shorter residence times. This is true for 58 urban samples from Fresno, CA, as well as for 30 samples from the nonurban IMPROVE network that are individually dominated by wildfire, vehicle exhaust, secondary organic aerosol, and calcium carbonate contributions. Visual examination of filter darkening at different temperature stages shows that substantial charring takes place within the filter, possibly due to adsorbed organic gases or diffusion of vaporized particles. The filter transmittance is more influenced by the within-filter char, whereas the filter reflectance is dominated by charring of the near-surface deposit that appears to evolve first when oxygen is added to helium in the analysis atmosphere for these samples. The amounts of charred OC (POC) and EC are also estimated from incremental absorbance. Small amounts of POC are found to dominate the incremental
absorbance. EC estimated from absorbance are found to agree better with EC from the reflectance charring correction than with EC from the transmittance charring correction.


The chemical mass balance (CMB) equations have been used to apportion observed pollutant concentrations to their various pollution sources. Typical analyses incorporate estimated pollution source profiles, estimated source profile error variances, and error variances associated with the ambient measurement process. Often the CMB model is fit to the data using an iteratively re-weighted least-squares algorithm to obtain the effective variance solution. We consider the chemical mass balance model within the framework of the statistical measurement error model (e.g., Fuller, W.A., Measurement Error Models, Wiley, New York, 1987), and we illustrate that the models assumed by each of the approaches to the CMB equations are in fact special cases of a general measurement error model. We compare alternative source contribution estimators with the commonly used effective variance estimator when standard assumptions are valid and when such assumptions are violated. Four approaches for source contribution estimation and inference are compared using computer simulation: weighted least squares (with standard errors adjusted for source profile error), the effective variance approach of Watson et al. (Atmos, Environ., 18, 1984, 1347), the Britt and Luecke (Technometrics, 15, 1973, 233) approach, and a method of moments approach given in Fuller (1987, p. 193). For the scenarios we consider, the simplistic weighted least-squares approach performs as well as the more widely used effective variance solution in most cases, and is slightly superior to the effective variance solution when source profile variability is large. The four estimation approaches are illustrated using real PM2.5 data from Fresno and the conclusions drawn from the computer simulation are validated. (C) 2003 Elsevier Ltd. All rights reserved


Chemical mass balance (CMB) analysis is a standard approach for apportioning observed pollutant concentrations to their various pollution sources. To use CMB analysis, the researcher must assume that all sources affecting the airshed are identifiable, and that the pollution source profile associated with each source can be speciated. We consider the performance of several solutions to the CMB equations for cases in which one or more solutions affecting the airshed are unknown. We demonstrate that the presence of unknown sources in the airshed can lead to substantial (and sometimes surprising) errors when estimating the known Source contributions. A simple illustration of the effect of unknown sources on the problem is given and the vulnerability of iterative estimators (such as the effective variance estimator) in the presence of unknown sources is explained. Methods for detecting unknown sources are proposed and evaluated. We propose a test for detecting unknown sources that is based on an intercept term included in the CMB equations. The approaches considered are compared via computer simulation, and with an example using real PM2.5 data from the San Joaquin Valley Air Quality Study. We find that when unknown sources affect the airshed, a modified weighted least squares approach is superior to all other methods (including the effective variance approach). (C) 2004 Elsevier Ltd. All rights reserved


Urban speciated fine particulate data from the Speciation Trends Network from January 2001 to February 2002 were studied in both eastern and western locations of the United States. The seasonal variability of PM2.5 mass, organic carbon, elemental carbon, sulfate ion, nitrate ion, and ammonium cation concentrations were analyzed. Their relationships with ozone and meteorology were also examined. The results reveal that differences in meteorology and emissions have a significant impact on the observed seasonality in species concentrations in Fresno and Atlanta. Based on a parallel analysis of regional PM2.5 episodic events, this influence appears to be general and may typify the difference between eastern and western cities in the United States. In Atlanta, ozone, sulfate, and ammonium were high in the summer when temperatures and humidities were high, whereas organic carbon concentrations were relatively flat year-round. In Fresno, however, ozone concentrations were high but sulfate concentrations were very low even in the summer, whereas PM2.5 concentrations were much higher in the winter and dominated by organics. Meteorologically, in Fresno, it was hot and dry in the summer but cool and humid in the winter. Organic carbon, nitrate, and ammonium ion concentrations were observed to be the highest in late fall and winter when the average
relative humidity was the highest (above similar to 60%). Much lower mixing heights and frequent stagnations in the winter in Fresno were the major factors influencing the observed high concentrations of various species. The wintertime organic aerosols in Fresno were predominately primary in origin. However, on some very high organic concentration days, up to 30% of the observed organic aerosols could be attributed to secondary organic aerosols (SOAs). These very high organic aerosol concentration days in the winter typically had mild temperatures, high humidities, low dilution rates, and an abundance of nitrate particles. These conditions were favorable for additional SOA formation through the acid catalyzed heterogeneous reactions at night on top of the already high primary organic emissions. (C) 2004 Elsevier Ltd. All rights reserved


This paper investigates the microphysical pathways and sensitivities within the Reisner2 bulk microphysical parameterization (BMP) of the fifth-generation Pennsylvania State University-National Center for Atmospheric Research (PSU-NCAR) Mesoscale Model (MM5) for a precipitation event over the central Sierra Nevada on 12 February 1986. Using a single sounding initialization, the MM5 was run two-dimensionally at 2-km horizontal grid spacing, which was needed to realistically simulate the embedded convective cells within the orographic cloud. Unlike previous modeling studies of this event, a microphysical budget over the windward slope was calculated for each experiment, in which the importance of each microphysical process was quantified relative to the water vapor loss (WVL) rate. For the control MM5, the largest microphysical processes that contribute to surface precipitation over the Sierra windward slope are condensation (63% of WVL), snow deposition (33%), riming to form graupel (35%), and melting of graupel (28%). The amount of supercooled water aloft is larger than observed and in previous modeling studies of this event using the Regional Atmospheric Modeling System (RAMS). The surface precipitation and microphysical processes over the Sierra Nevada are most sensitive to those parameters associated with the snow distribution, cloud condensation nuclei (CCN) concentrations, and snow/graupel fall speeds, while there is less sensitivity to ice initiation and autoconversions; however, all experiments overpredict the surface precipitation over the windward slope. If ice production is turned off in the cloud-ice region (above 7 km or < 250 K), deposition acting on the small amount of cloud ice nucleated at warmer temperatures can still generate a similar snow cloud below 4 km and surface precipitation. The precipitation differences between the BMPs in the MM5 are greater than any single process experiment within Reisner2. The process experiments do help reveal some of the fundamental differences between BMP schemes.


This paper investigates the impact of barrier width and freezing level on the microphysical processes and pathways within the Reisner2 bulk microphysical parameterization (BMP) using a two-dimensional version of the fifth-generation Pennsylvania State University-National Center for Atmospheric Research (PSU-NCAR) Mesoscale Model (MM5). As the barrier half-width is decreased incrementally from 50 km (relatively wide mountain) to 10 km (narrow mountain) for a deep orographic cloud and a 750-mb freezing level, the percentage of water vapor loss (WVL) rate over the windward slope leading to snow deposition decreases from 23% to 7%, while condensation increases from 74% to 93% of WVL rate. A narrow (10 km) barrier has less snow aloft, twice as much cloud water over the windward slope, and a shallow region of intense riming over the crest that results in twice as much graupel as the wide (50 km) barrier. It is found that a relatively wide barrier (greater than or equal to 30 km half-width) allows more time for snow growth aloft; therefore, it is more sensitive to snow parameters over the windward slope such as the slope intercept for number concentration and fall speeds. In contrast, a narrower barrier is more sensitive to rain and graupel processes, such as the cloud water autoconversion and graupel fall speeds. The wide barrier has a larger sensitivity to cloud water processes when the freezing level is elevated to 500 mb, while the narrow barrier is more sensitive to snow processes when the freezing level is lowered to 1000 mb. For a 1000-mb freezing level, the lack of riming and accretion reduces the rapid increase in maximum precipitation that is shown to occur when the barrier half-width is reduced from 20 and 10 km for a higher freezing level.

Crouch, J., Houck, J.E., 2004. Comment on "PCDD/F, PCB, HxCBz, PAH, and PM emission factors for fireplace and woodstove combustion in the San Francisco Bay region". Environmental Science & Technology 38 (6), 1910-1911

This research assessed in-vehicle exposures to black carbon (BC) as an indicator of diesel particulate matter (DPM) exposures. Approximately 50 h of real-time Aethalometer BC measurements were made inside vehicles driven on freeway and arterial loops in Los Angeles and Sacramento. Video tapes of the driver's view were transcribed to record the traffic conditions, vehicles followed, and vehicle occupant observations, and these results were tested for their associations with BC concentration. In-vehicle BC concentrations were highest when directly following diesel-powered vehicles, particularly those with low exhaust pipe locations. The lowest BC concentrations were observed while following gasoline-powered passenger cars, on average no different than not following any vehicle. Because diesel vehicles were over-sampled in the field study, results were not representative of real-world driving. To calculate representative exposures, in-vehicle BC concentrations were grouped by the type of vehicle followed, for each road type and congestion level. These groupings were then re-sampled stochastically, in proportion to the fraction of statewide vehicle miles traveled (VMT) under each of those conditions. The approximately 6% of time spent following diesel vehicles led to 23% of the in-vehicle BC exposure, while the remaining exposure was due to elevated roadway BC concentrations. In-vehicle BC exposures averaged 6 mg m\(^{-3}\) in Los Angeles and the Bay Area, the regions with the highest congestion and the majority of the state's VMT. The statewide average in-vehicle BC exposure was 4 mg m\(^{-3}\), corresponding to DPM concentrations of 7-23 mg m\(^{-3}\), depending on the Aethalometer response to elemental carbon (EC) and the EC fraction of the DPM. In-vehicle contributions to overall DPM exposures ranged from approximately 30% to 55% of total DPM exposure on a statewide population basis. Thus, although time spent in vehicles was only 1.5 h day\(^{-1}\) on average, vehicles may be the most important microenvironment for overall DPM exposure. (C) 2004 Elsevier Ltd. All rights reserved


[1] Field measurements of a wide suite of trace gases and aerosols were carried out during April and May 2002, along with extensive chemical transport modeling, as part of the NOAA Intercontinental Transport and Chemical Transformation study. Here, we use a combination of in-situ ground-based measurements from Trinidad Head, CA, chemical transport modeling, and backward trajectory analysis to examine the impact of long-range transport from Asia on the composition of air masses arriving at the California coast at the surface. The impact of Asian emissions is explored in terms of both episodic enhancements and contribution to background concentrations. We find that variability in CO concentrations at the ground site was largely driven by North American emissions, and that individual Asian plumes did not cause any observable pollution enhancement episodes at Trinidad Head. Despite this, model simulations suggest that Asian emissions were responsible for 33% of the CO observed at Trinidad Head, providing a larger mean contribution than direct emissions from any other region of the globe. Surface ozone levels were found to depend primarily on local atmospheric mixing, with surface deposition leading to low concentrations under stagnant conditions. Model simulations suggested that on average 4 +/- 1 ppb of ozone (10% of observed) at Trinidad Head was transported from Asia.


Though an important predecessor of modern field experiments, the findings of this 1950s investigation have remained largely out of scientific limelight.

Gullette, B.K., Touati, A., Hays, M.D., 2004. PCDD/F, PCB, HxCBz, PAH, and PM emission factors for fireplace and woodstove combustion in the San Francisco Bay region (vol 37, pg 1758, 2003). Environmental Science & Technology 38 (13), 3792

A direct sensitivity analysis technique was used for three-dimensional atmospheric ozone formation potential (also termed reactivity) assessment in central California. Spatially and temporally resolved absolute and relative reactivities of 31 organic compounds and CO were calculated. In order to compare different species, the emissions of all the targeted organic compounds were perturbed equally. This perturbation followed the same spatial distribution as the total anthropogenic VOC emissions. Despite the variability (both spatial and temporal) in the absolute values, relative reactivities were fairly constant. Different types of domain-wide reactivity metrics were considered. All the three-dimensional metrics showed a high level of inter-species consistency among them and had a low day-to-day variability. Domain-wide metrics were comparable with box model scales, but showed a less dynamic inter-species behavior. Ranking of the three-dimensional metrics was very similar to the box model scales. It was also found that including the biogenic VOC emissions in the perturbation pattern has little effect on the results. Finally, local relative reactivities for six sites were fairly consistent in ranking but more variable than the domain-wide metrics. (C) 2003 Elsevier Ltd. All rights reserved


Direct sensitivity analysis is applied for 3-D assessment of ozone reactivity (or ozone formation potential) in the Eastern United States. A detailed chemical mechanism (SAPRC-99) is implemented in a multiscale air quality model to calculate the reactivity of 32 explicit and 9 lumped compounds. Simulations are carried out for two different episodes and two different emission scenarios. While absolute reactivities of VOCs show a great deal of spatial variability, relative reactivities (normalized to the reactivity of a base mixture) produce a significantly more homogeneous field. Three types of domain-wide relative reactivity metrics are formed for 1-h and 8-h averaging intervals. In general, ozone reactivity metrics (with the exception of those based on daily peak ozone) are fairly robust and consistent between different episodes or emission scenarios. The 3-D metrics also show fairly similar rankings for VOC reactivity when compared to the box model scales. However, the 3-D metrics have a noticeably narrower range for species reactivities, as they result in lower reactivity for some of the more reactive, radical-producing VOCs (especially aldehydes). As expected, episodes and emission scenarios with less radical availability have higher absolute reactivities for all species and higher relative reactivities for the more radical-producing species. Finally, comparing the results with those from a different domain (central California) shows that relative reactivity metrics are comparable over these two significantly different domains


Air pollution in California's San Joaquin Valley (SJV) rivals that of the Los Angeles area and ranks among the worst in the United States for particulate matter (PM) and ozone. The application and validation of an atmospheric chemical transport model to the SJV will aid in the design of emissions control programs to improve air quality. The extensive data required for meaningful Eulerian modeling of airborne PM in the SJV region were collected as a part of the 1995 Integrated Monitoring Study (IMS95). In the current study, the CIT-UCD source-oriented air quality model is applied to the IMS95 data set to verify model performance in the SJV. This article represents the first published application of a full-scale photochemical grid model with diagnostic meteorological data to simulate PM concentrations in the SJV and is the first study outside of the Los Angeles area to include complete PM model performance statistics. The CIT-UCD model results show excellent agreement with most measurements collected during the IMS95 4-6 January 1996 modeling episode. The fractional bias (FBIAS) for SJV ozone and PM10 are approximately 0.16 and -0.19, respectively, for all SJV stations excluding Bakersfield. Most modeled criteria gases, PM precursor gases, and chemically speciated PM concentrations show strong agreement with their corresponding measurements at the Chowchilla, Fresno, Kern Wildlife Refuge, and Bakersfield sampling stations. Furthermore, the modeled PM size distribution of nitrate, ammonium ion, and sulfate agree well with cascade impactor measurements made at Bakersfield on 5 January 1996. Given the robust model agreement with both gas and condensed phase measurements, it appears that the CIT-UCD model adequately captures the fundamental transport and chemical reactivity of air pollutants in the IMS95 domain during a typical severe pollution episode. These results suggest that the CIT-UCD model can be used to explore control scenarios designed to improve air quality in the SJV. (C) 2004 Elsevier Ltd. All rights reserved

We examine the ozone production efficiency in transpacific Asian pollution plumes, and the implications for ozone air quality in California, by using aircraft and surface observations in April-May 2002 from the Intercontinental Transport and Chemical Transformation 2002 (ITCT 2K2) campaign off the California coast and the Pacific Exploration of Asian Continental Emission-B (PEACE-B) campaign over the northwest Pacific. The observations are interpreted with a global three-dimensional chemical transport model (GEOS-CHEM). The model reproduces the mean features observed for CO, reactive nitrogen oxides (NOy), and ozone but underestimates the strong (similar to 20 ppbv) stratospheric contribution to ozone in the middle troposphere. The ITCT 2K2 aircraft sampled two major transpacific Asian pollution plumes, one on 5 May at 5-8 km altitude with CO up to 275 ppbv but no elevated ozone and one on 17 May at 2.5-4 km altitude with CO up to 225 ppbv and ozone up to 90 ppbv. We show that the elevated ozone in the latter plume is consistent with production from peroxyacetylnitrate (PAN) decomposition during subsidence of the plume over the northeast Pacific. This production is particularly efficient because of the strong radiation and low humidity of the subsiding environment. We argue that such PAN decomposition represents a major and possibly dominant component of the ozone enhancement in transpacific Asian pollution plumes. Strong dilution of Asian pollution plumes takes place during entrainment in the U.S. boundary layer, greatly reducing their impact at U.S. surface sites. California mountain sites are more sensitive to Asian pollution because of their exposure to the free troposphere. Model results indicate a mean Asian pollution enhancement of 7 ppbv ozone at Sequoia National Park in May 2002 on those days when the 8-hour average ozone concentration exceeded 80 ppbv.


Recent studies, primarily in Europe, have reported associations between respiratory symptoms and residential proximity to traffic; however, few have measured traffic pollutants or provided information about local air quality. We conducted a school-based, cross-sectional study in the San Francisco Bay Area in 2001. Information on current bronchitis symptoms and asthma, home environment, and demographics was obtained by parental questionnaire (n = 1,109). Concentrations of traffic pollutants (particulate matter, black carbon, total nitrogen oxides [NOX], and nitrogen dioxide [NO2]) were measured at 10 school sites during several seasons. Although pollutant concentrations were relatively low, we observed differences in concentrations between schools nearby versus those more distant (or upwind) from major roads. Using a two-stage multiple-logistic regression model, we found associations between respiratory symptoms and traffic-related pollutants. Among those living at their current residence for at least 1 year, the adjusted odds ratio for asthma in relationship to an interquartile difference in NOX was 1.07 (95% confidence interval, 1.00-1.14). Thus, we found spatial variability in traffic pollutants and associated differences in respiratory symptoms in a region with good air quality. Our findings support the hypothesis that traffic-related pollution is associated with respiratory symptoms in children.


Present air quality standards to protect vegetation from ozone are based on measured concentrations (i.e., exposure) rather than on plant uptake rates (or dose). Some familiar cumulative exposure-based indices include SUM06, AOT40, and W126. However, plant injury is more closely related to dose, or more appropriately to effective dose, than to exposure. This study develops and applies a simple model for estimating effective ozone dose that combines the plant canopy's rate of stomatal ozone uptake with the plant's defense to ozone uptake. Here the plant defense is explicitly parameterized as a function of gross photosynthesis and the model is applied using eddy covariance (ozone and CO2) flux data obtained at a vineyard site in the San Joaquin Valley during the California Ozone Deposition Experiment (CODE91). With the ultimate intention of applying these concepts using prognostic models and remotely sensed data, the pathways for ozone deposition are parameterized (as much as possible) in terms of canopy LAI and the surface friction velocity. Results indicate that (1) the daily maximum potential for plant injury (based on effective dose) tends to coincide with the daily peak in ozone mixing ratio (ppbV), (2) potentially there
are some significant differences between ozone metrics based on dose (no plant defense) and effective dose, and (3) nocturnal conductance can contribute significantly to the potential for plant ozone injury. Published by Elsevier Ltd


[1] We report hourly in-situ observations of C-1-C-8 speciated volatile organic compounds (VOCs) obtained at Trinidad Head CA in April and May 2002 as part of the NOAA Intercontinental Transport and Chemical Transformation study. Factor analysis of the VOC data set was used to define the dominant processes driving atmospheric chemical composition at the site, and to characterize the sources for measured species. Strong decreases in background concentration were observed for several of the VOCs during the experiment due to seasonal changes in OH concentration. CO was the most important contributor to the total measured OH reactivity at the site at all times. Oxygenated VOCs were the primary component of both the total VOC burden and of the VOC OH reactivity, and their relative importance was enhanced under conditions when local source contributions were minimal. VOC variability exhibited a strong dependence on residence time (s(\text{ln}X) = 1.55(\text{tau})^{-0.44}, r(2) = 0.98; where s(\text{ln}X) is the standard deviation of the natural logarithm of the mixing ratio), and this relationship was used, in conjunction with measurements of Rn-222, to estimate the average OH concentration during the study period (6.1 x 10(5) molec/cm(3)). We also employed the variability-lifetime relationship defined by the VOC data set to estimate submicron aerosol residence times as a function of chemical composition. Two independent measures of aerosol chemical composition yielded consistent residence time estimates. Lifetimes calculated in this manner were between 3 - 7 days for aerosol nitrate, organics, sulfate, and ammonium. The lifetime estimate for methane sulfonic acid (similar to 12 days) was slightly outside of this range. The lifetime of the total aerosol number density was estimated at 9.8 days


The first observations of size-dependent cloud and fog drop inorganic ion and trace metal concentrations obtained using the Colorado State University 5-Stage cloud water collector (CSU 5-Stage) during field studies of orographic clouds (Whiteface Mountain, NY, July 1998) and radiation fogs (Davis, CA, January 1999) are reported. Although some mixing between drop sizes occurs, the CSU 5-Stage effectively separates the largest drops (> approximate to30 mum in diameter) from the smallest ones (< &AP;10 &mu;m in diameter) permitting the discernment of size-dependent drop composition not possible with previous two- or three-stage collectors. At Whiteface, pH and the concentrations of the "major" ions -NH4divided by, NO3-, and SO42--appeared largely independent of drop size as measured by a two-stage collector. The same major ion concentrations differed in Davis fogs by up to a factor of approximately 10 in the two-stage collector with consistently higher small drop concentrations. In both locations, CSU 5-Stage data generally indicate a greater range of concentrations is present across the drop size spectrum. CSU 5-Stage data show "U"-shaped profiles of major ion concentration vs. drop size at Whiteface and "L"-shaped profiles at Davis and the maximum/minimum concentration differences between fractions increased up to a factor of 2 (Whiteface) and 30 (Davis). Lower concentration species at both locations showed multiple concentration vs. drop size profiles with CSU 5-Stage data again exhibiting more variability than observed with the two-stage collector. While rarely reported, significant nitrite concentrations relatively higher in the larger drops were observed, and copper concentrations merit further investigation in the Davis fogs. The findings presented here are consistent with other studies. The implications and benefits of the increased resolution of size-dependent drop composition provided by the CSU 5-Stage are explored for the Davis fogs in a companion paper (Moore et al., Atmos. Environ. (2004), this issue). (C) 2003 Elsevier Ltd. All rights reserved


Size-resolved fog drop chemical composition measurements were obtained during a radiation fog campaign near Davis, California in December 1998/January 1999 (reported in Reilly et al., Atmos. Environ. 35(33) (2001) 5717; Moore et al., Atmos. Environ. this issue). Here we explore how knowledge of this size-dependent drop composition-
particularly from the newly developed Colorado State University 5-Stage cloud water collector-helps to explain additional observations in the fog environment. Size-resolved aerosol measurements before and after fog events indicate relative depletion of large (> 2 μm in diameter) particles during fog accompanied by a relative increase in smaller aerosol particle concentrations. Fog equivalent air concentrations suggest that entrainment of additional particles and in-fog sedimentation contributed to observed changes in the aerosol size distribution. Calculated deposition velocities indicate that sedimentation was an important atmospheric removal mechanism for some species. For example, nitrite typically has a larger net deposition velocity than water and its mass is found preferentially in the largest drops most likely to sediment rapidly. Gas-liquid equilibria in fog for NO3-/HNO3, NH4+/NH3, and NO2-/HONO were examined. While these systems appear to be close to equilibrium or relative equilibrium during many time periods, divergences are observed, particularly for low liquid water content (<0.1 g m⁻³) fogs and in different drop sizes. Knowledge of the drop size-dependent composition provided additional data useful to the interpretation of these deviations. The results suggest that data from multi-stage cloud water collectors are useful to understanding fog processes as many depend upon drop size. (C) 2003 Elsevier Ltd. All rights reserved


One pathway for release of mercury (Hg) from naturally enriched sites is emission to the atmosphere. Elemental Hg, when emitted, will enter the global atmospheric pool. In contrast, if reactive gaseous Hg or Hg²⁺ (as HgCl₂, HgBr₂, or Hg(OH)₂) is formed, it will most likely be deposited locally. This study focused on the measurement of elemental Hg flux and reactive gaseous Hg concentrations at the Sulphur Bank Superfund Site, an area of natural Hg enrichment with anthropogenic disturbance and ongoing geothermal activity. Mean Hg emissions ranged from 14 to 11000 ng m⁻² h⁻¹, with the highest emissions from anthropogenically disturbed materials. Reactive gaseous Hg concentrations were the highest ever reported for a natural setting (0.3-76 ng m⁻³). Measured Hg fluxes were used within a Geographic Information System to estimate mercury releases to the atmosphere from the site. Results indicated similar to17 kg of Hg y⁻¹ of is emitted to the atmosphere from the 3.8 km² area, with half from mine waste, ore, and tailing piles and half from relatively undisturbed naturally enriched substrate.


Particle number distributions were measured simultaneously upwind and downwind of a suburban-agricultural freeway to determine relationships with traffic and meteorological parameters. Average traffic volumes were 6330 vehicles/hr with 10% heavy-duty vehicles, and volumes were higher in July than November. Most downwind particle number distributions were bimodal, with a primary mode at similar to10-25 nm, indicating that newly formed particles were sampled. Total downwind 6-237 nm particle number concentrations (N-tot) ranged from 9.3 x 10³ to 2.5 x 10⁵ cm⁻³, with higher daily average concentrations in November compared with July. N-tot correlated with wind speed, temperature, and relative humidity. Upwind photochemically initiated nucleation likely led to elevated background nanoparticle concentrations in July, as evidenced by increasing upwind distribution modal diameter with increasing temperature and a strong correlation between upwind N-tot and solar radiation. Also in summer, N-tot showed stronger correlation with heavy-duty vehicle volumes than wind speed, temperature, and relative humidity. These results indicate the importance of measuring background particle size distributions simultaneously with roadside distributions. There may be a minimum vehicle volume from which useful real-world vehicle particle number distributions can be measured at roadside, even when collecting samples within 10 m of the traveled lanes.


Two collocated, eight-stage rotating drum impactors were deployed at Trinidad Head (California) during the spring of 2002 as part of the Intercontinental Transport and Chemical Transformation 2002 (ITCT 2K2) experiment. One of the samplers operated at ambient relative humidity while the other was operated at a relative humidity of 55%. The impaction substrates from these samplers were analyzed using synchrotron X-ray fluorescence (SXRF) to
provide continuous measurements of the size-resolved aerosol elemental composition with 3-hour time resolution. The aerosol elemental composition data identified three significant mineral dust episodes near the beginning of the time series. The backward air mass trajectory calculations from the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model and the PM10 to PM2.5 elemental mass ratios are consistent with the long-range transport of mineral dust from Asian sources. The data from the paired ambient relative humidity and low-relative-humidity samplers show that the aluminum, silicon, and iron elemental mass distributions are a function of relative humidity. In each case, the elemental mass distributions shifted toward smaller sizes as the relative humidity was reduced. This behavior indicates that the mineral dust transported from Asia to the west coast of the United States is somewhat hygroscopic upon its arrival. The hygroscopic nature of the aged mineral dust should increase its ability to nucleate cloud droplets (i.e., act as cloud condensation nuclei). Measurements of transported Asian mineral dust made at a high-elevation mountain site in Oregon (i.e., Crater Lake National Park) during the spring of 2002 show a strong correlation between the silicon and sulfur elemental mass concentrations. The ratio of calcium to sulfur makes it unlikely that this coarse sulfur is derived from gypsum (i.e., CaSO4). Instead, it indicates that the coarse mineral dust most likely accumulates sulfate coatings either near the source region or during transport across the Pacific Ocean.


This research has developed an integrated model of a dairy farm that predicts monthly ammonia emission factors based on farming practices and climate conditions, including temperature, wind speed, and precipitation. The model can be used to predict the seasonal and geographic variations in ammonia emission factors, which are important for accurately predicting aerosol nitrate concentrations. The model tracks the volume of manure and mass of ammoniacal nitrogen as the manure moves through the housing, storage, application, and grazing stages of a dairy farm. Most of the processes of ammonia volatilization are modeled explicitly, but poorly understood processes are parameterized and tuned to match empirical data. The tuned model has been compared to independent experimental data and is shown to be robust over the range of experimental conditions. We have characterized the differences in emissions resulting from changes in climate conditions and farming practices and found that both of these factors are significant and should be included when developing a national inventory. (C) 2003 Elsevier Ltd. All rights reserved.


The US National Assessment of the Potential Consequences of Climate Variability and Change provides compelling arguments for action and adaptive measures to help mitigate water resource, agricultural production and environmental quality impacts of future climate change. National resource planning at this scale can benefit by the development of integrated impact analysis toolboxes that allow linkage and integration of hydroclimate models, surface and groundwater hydrologic models, economic and environmental impact models and techniques for social impact assessment. Simulation models used in an assessment of climate change impacts on water resources, agriculture and environmental quality in the San Joaquin Basin of California are described in this paper as well as the challenges faced in linking the component models within an impacts assessment toolbox. Results from simulations performed with several of the tools in the impacts assessment toolbox are presented and discussed. After initially attempting model integration with the public domain, GIS-based modeling framework Modular Modeling System/Object User Interface (MMS/OUI), frustration with the framework's lack of flexibility to handle monthly timestep models prompted development of a common geodatabase to allow linkage of model input and output for the linked simulation models. A GIS-based data browser was also developed that works with both network flow models and makes calls to a model post-processor that shows model output for each selected node in each model network. This data and output browser system is flexible and can readily accommodate future changes in the model network configuration and in the model database. (C) 2003 Elsevier Ltd. All rights reserved.


A generalized approach for estimating season-specific diurnal profiles of anthropogenic heating for cities is presented. Each profile consists of heat released from three components: building sector, transportation sector, and
metabolism. In turn, the building sector is divided into heat released from electricity consumption and heat released from heating fuels such as natural gas and fuel oil. Each component is developed separately based on a population density formulation. The profiles are based on commonly available data resources that are mapped onto the diurnal cycle using seasonal profile functions. Representative winter and summer weekday profiles are developed and presented for six large US cities. The diurnal profiles have morning and evening peaks, with summertime maxima up to 60 W m\(^{-2}\). Anthropogenic heating in winter is generally larger, with maxima up to 75 W m\(^{-2}\). While these analyses were carried out at the city-scale the paper discusses how the same data sources could be applied at scales down to the individual census tract (or traffic analysis zone), resulting in high spatial resolution profiles and larger maxima corresponding to higher population densities in the urban core. Based on our analysis of San Francisco we find that the urban core region may have a daytime population density that is 5-10 times that of the city-scale value. Hence, the corresponding anthropogenic heating values in the urban core will be 5-10 times the magnitudes of the city-scale values presented in this paper. (C) 2004 Elsevier Ltd. All rights reserved


The East Bay Children's Respiratory Health Study is examining associations between traffic-related pollutant exposures and respiratory health among children who reside and attend schools at varied proximity to northern California freeways. Chronic exposures are being inferred from outdoor pollutant concentrations at neighborhood schools. This paper reports primarily weeklong integrated NO2 and NOx concentrations measured with passive samplers placed outside at 10 elementary schools during 14 weeks in spring and 8 weeks in fall 2001. Measurements were also made outside selected student residences to examine spatial variability within three school neighborhoods. Regional concentrations of NO2 and NOx varied widely from week to week. School site data were normalized to measurements at a nearby regional monitoring station to facilitate analysis of relative pollutant exposures at the neighborhood schools. Normalized concentrations were consistent at each school throughout the study. Schools located upwind or far downwind of freeways were generally indistinguishable from one another and regional pollution levels. For school and neighborhood sites within 350 m downwind of a freeway, concentrations increased with decreasing downwind distance. The highest normalized concentrations occurred at a school located directly adjacent to a major freeway and a shopping center. In this case, normalized NO2 and NOx were similar to 60% and similar to 100% higher than regional background levels. At three schools within 130-230 m downwind of a freeway, normalized NO2 and NOx were similar to 20-30% and similar to 50-80% higher than regional levels. Validation testing of the passive samplers indicated precision of better than 5% for both NO2 and NOx when samplers were deployed outside for 1-week periods. Passive sampler results agreed with co-located chemiluminescence measurements to within 8% for NO2 and 3% for NOx. (C) 2003 Elsevier Ltd. All rights reserved


The field measurement program of the Central California Ozone Study (CCOS) was conducted during the summer of 2000 with an overall goal of improving the understanding of ozone formation over central and northern California. Measurements of actinic flux were made as part of the study using spectroradiometers located at University of California, Davis; Sunol, California, and the Desert Research Institute in Reno, Nevada. The measured actinic flux was compared with the standard Peterson flux for a high ozone episode that occurred at the end of July. The standard Peterson flux was found to be greater than the measured flux across the spectral range. The measured actinic flux was used, along with standard quantum yields and absorption cross-section data to calculate the photolysis rate parameters for nitrogen dioxide, ozone and formaldehyde, and a radiative transfer model was used to simulate these same photolysis rate parameters. The simulated photolysis rate parameters for nitrogen dioxide could be up to 56% greater than the photolysis rate parameters derived from the measured actinic flux; for ozone the difference was as great as 160%; for the molecular reaction of formaldehyde the difference was as great as 89%; and for the radical producing channel the difference was as great as 126%. A simple atmospheric chemistry box-model was used to estimate the significance of these differences for air quality assessment. For a typical high ozone episode day 31 July, differences between modeled ozone concentrations based on photolysis rate parameters versus those derived from measured actinic flux were less than 7% change in concentration, while differences in HO concentrations were as high as 15%. (C) 2004 Elsevier Ltd. All rights reserved

This paper presents a preliminary research result of spatially quantifying and allocating the potential activity of residential wood burning (RWB) by using demographic, hypsographic, climatic and topographic information as independent variables. We also introduce the method for calculating PM2.5 emission from residential wood combustion with the potential activity as primary variable. A linear regression model was generated to describe spatial and temporal distribution of the potential activity of wood burning as primary heating source. In order to improve the estimation, the classifications of urban, suburban and rural were redefined to meet the specifications of this application. Also, a unique way of defining forest accessibility is found useful in estimating the activity potential of RWB. The results suggest that the potential activity of wood burning is mostly determined by elevation of a location, forest accessibility, urban/nonurban position, climatic conditions and several demographic variables. The analysis results were validated using survey data collected through face-to-face and telephone interviews over the study area in central California. The linear regression model can explain approximately 86% of the variation of surveyed wood burning activity potential. The total PM2.5 emitted from woodstoves and fireplaces is analyzed for the study region at county level. (C) 2003 Elsevier Ltd. All rights reserved


The diurnal evolution of the three-dimensional summer-season mean wind and temperature structure in California's Sacramento and San Joaquin Valleys (collectively called the Central Valley) is investigated using data from 22 radar wind profiler/radio acoustic sounding systems (RASS) operated as part of the Central California Ozone Study in 2000. The profiler network revealed, for the first time, that the persistent summer-season flow pattern documented by surface observations extends 800 - 1000 m above the surface. At most locations, upvalley winds persist during both day and night except at the upper ends of the valleys and close to the valley sidewalls where diurnal wind reversals occur. Wind speeds exhibit pronounced diurnal oscillations, with amplitudes decreasing with height. A low-level wind maximum occurs in the lowest 300 m, with a sharp decrease in speed above the maximum. Especially well defined nocturnal low-level jets occur at sites in the southern San Joaquin Valley, where maximum speeds of 10 m s(-1) or more occur 1 - 2 h before midnight at heights near 300 m. The afternoon mixed layer, generally deeper than 1000 m, increases in depth with up-valley distance in both valleys. At night, temperature inversions develop in the lowest several hundred meters with near-isothermal layers above. Mean temperatures in the lowest 500 m of the valleys are always warmer than at the same altitude over the coast, and temperature increases from the lower to upper valleys. The diurnal oscillations of the coast valley and along-valley temperature and pressure difference reach a maximum in late afternoon and a minimum in early morning. These oscillations are in phase with the diurnal variation of westerly onshore flows. The along-valley wind maxima, however, occur 1 - 2 h before midnight, whereas the along-valley pressure gradient maxima are usually found just before sunset.


A unique set of soil samples was collected as part of the Fugitive Dust Characterization Study. The study was carried out to establish whether or not source profiles could be constructed using novel analytical methods that could distinguish soil dust sources from each other. The soil sources sampled included fields planted in cotton, almond, tomato, grape, and safflower, dairy and feedlot facilities, paved and unpaved roads (both urban and rural), an agricultural staging area, disturbed land with salt buildup, and construction areas where the topsoil had been removed. The samples were collected using a systematic procedure designed to reduce sampling bias, and were stored frozen to preserve possible organic signatures. For this paper the samples were characterized by particle size (percent sand, silt, and clay), dry silt content (used in EPA-recommended fugitive dust emission factors), carbon and nitrogen content, and potential to emit both PM10 and PM2.5. These are not the "novel analytical methods" referred to above; rather, it was the basic characterization of the samples to use in comparing analytical methods by other
scientists contracted to the California Air Resources Board. The purpose of this paper is to document the methods used to collect the samples, the collection locations, the analysis of soil type and potential to emit PM10, and the sample variability, both within field and between fields of the same crop type.


Two case studies are performed to improve ammonia emissions inputs used to model fine particulate matter (PM2.5 is the portion of particulate matter smaller than 2.5 gm aerodynamic diameter) formation of ammonium sulfate and ammonium nitrate. Ammonia emissions are analyzed in detail for North Carolina and the San Joaquin Valley (SJV) of California, with a focus on the Charlotte, NC, and Fresno, California metropolitan areas. A new gridded ammonia emissions inventories suitable for atmospheric modeling for the two case study cities was also developed. Agricultural sources accounted for the bulk of ammonia emissions in both case studies. Livestock waste contributed about 80% in North Carolina and 64% in the SJV, while fertilizer application contributed about 6-7% in both domains. Forests and non-agricultural vegetation contributed 5% in North Carolina and 12% in the SJV. Motor vehicles accounted for about 6% of ammonia emissions in North Carolina and 14% in the SJV. In the Charlotte and Fresno urban areas, the distribution of emissions is less heavily weighted toward agricultural sources and more heavily weighted toward highway vehicles (highway vehicles account for an estimated 64% of emissions in Charlotte and 51% of emissions in Fresno). The emissions estimates for agricultural sources (livestock and fertilizer application) decline to approximately 14% in the winter for both the Charlotte and Fresno urban areas. Emissions estimates for soils and vegetation also decline to approximately 0 during the winter for both the Fresno and Charlotte area. As a result, motor vehicles account for a larger fraction (approximately 73% and 76% for Charlotte and Fresno, respectively) of winter ammonia emissions, particularly in the Charlotte urban area. (C) 2003 Elsevier Ltd. All rights reserved


The fifth-generation Pennsylvania State University-National Center for Atmospheric Research Mesoscale Model (MM5) has been used to simulate high-wind events in the complex terrain of western Nevada. The objective was to determine the resolution necessary to produce accurate forecasts of high surface wind and to explore utilizing numerical model output as warning decision guidance in data-sparse areas. Two high-wind cases were simulated by the MM5 to demonstrate the feasibility of high-resolution models in the West. These events produced sustained surface winds of greater than 39 kt (20 m s(-1)), and wind gusts in excess of 78 kt (40 m s(-1)), which resulted in extensive damage. In both cases, the MM5 simulation was able to capture the mountain waves responsible for the high winds. The operational Eta Model, in comparison, did not indicate the existence of high-wind events. Results suggested that a model horizontal grid spacing of 5 km or less is necessary to predict accurately high-wind events in the complex terrain of Nevada


A systematic sampling and analysis approach was followed to acquire chemical source profiles for six types of geological dust in California's San Joaquin Valley. Forty-seven samples from 37 locations included: (1) urban and rural paved roads, (2) residential and agricultural unpaved roads and parking areas, (3) almond, cotton, grape, safflower, and tomato fields, (4) dairy and feedlot surfaces, (5) salt-laden lake and irrigation canal drainage deposits, and (6) building and roadway construction/earthmoving soil. These samples were dried, sieved, resuspended, sampled through a PM10 inlet onto filters, and chemically analyzed to construct PM10 source profiles (fractional mass abundances and uncertainties) for 40 elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Mo, Pd, Ag, Cd, In, Sn, Sb, Ba, La, Au, Hg, Tl, Pb, and U), 7 ions (Cl-, NO3-, PO43-, Na+, K+, and NH4+), organic and elemental carbon (OC and EC), 8 carbon fractions (OC1, OC2, OC3, OP, EC1, EC2, and EC3), and carbonate carbon. Individual source profiles with analytical precisions were averaged and compared to quantify differences in chemical abundances for: (1) duplicate laboratory resuspension sampling, (2) multiple sampling within the same agricultural field, (3) sampling at different locations for the same land-use activity, (4) sampling of different activities regardless of location, and (5) grouping of
different activities into generalized emission inventory source categories. Distinguishing features were found among composite source profiles of six source types. Elemental carbon and Pb marked paved road dust; Na+, Na, S, and SO42- marked salt deposits; OC, PO42-, P, K+, K, and Ca characterized animal husbandry; and several metals (Ti, V, Mn) marked construction soil, with abundances 2-10 times higher than those of other profiles. High-sensitivity X-ray fluorescence analysis resulted in detectable alkali and rare earth elements. Ga, Zr, Sn, and Ba were found in some of the paved road dust profiles; toxic species such as As, Mo, Cd, Sb, and U were found in salt deposits from canal drainage; and Pd, Rh, Sr, and Tl were found in construction dust. The profile-compositing methodology can be used for evaluating similarities and differences for other source characterization studies.


Crop yield inconsistently correlates with apparent soil electrical conductivity (ECa) because of the influence of soil properties (e.g., salinity, water content, texture, etc.) that may or may not influence yield within a particular field and because of a temporal component of yield variability that is poorly captured by a state variable such as ECa. Nevertheless, in instances where yield correlates with ECa, maps of ECa are useful for devising soil sampling schemes to identify soil properties influencing yield within a field. A west side San Joaquin Valley field (32.4 ha) was used to demonstrate how spatial distributions of ECa can guide a soil sample design to determine the soil properties influencing seed cotton (Gossypium hirsutum L.; 'MAXXA' variety) yield. Soil sample sites were selected with a statistical sample design utilizing spatial ECa measurements. Statistical results are presented from correlation and regression analyses between cotton yield and the properties of pH, B, NO3-N, Cl-, salinity, leaching fraction (LF), gravimetric water content, bulk density, percentage clay, and saturation percentage. Correlation coefficients of -0.01, 0.50, -0.03, 0.25, 053, -0.49, 0.42, -0.29, 0.36, and 0.38, respectively, were determined. A site-specific response model of cotton yield was developed based on ordinary least squares regression analysis and adjusted for spatial autocorrelation using maximum likelihood. The response model indicated that salinity, plant-available water, LF, and pH were the most significant soil properties influencing cotton yield at the study site. The correlations and response model provide valuable information for site-specific management.


[1] An inversion technique has been developed to determine volume fractions of an atmospheric aerosol composed primarily of ammonium sulfate and ammonium nitrate and water combined with fixed concentration of elemental and organic carbon. It is based on measured aerosol backscatter obtained with 9.11- and 10.59-μm wavelength continuous wave CO2 lidars and modeled backscatter from aerosol size distribution data. The technique is demonstrated during a flight of the NASA DC-8 aircraft over the Sierra Nevada Mountain Range, California, on 19 September 1995. Volume fraction of each component and effective complex refractive index of the composite particle were determined assuming an internally mixed composite aerosol model. The volume fractions were also used to recompute aerosol backscatter, providing good agreement with the lidar-measured data. The robustness of the technique for determining volume fractions was extended with a comparison of calculated 2.1-μm backscatter from size distribution data with the measured lidar data converted to 2.1-μm backscatter using an earlier derived algorithm, verifying the algorithm as well as the backscatter calculations.


Fertilizer application represents a significant fraction of ammonia emissions from all sources in the United States. Previously published ammonia inventories have generally suffered from poor spatial and temporal resolution, erroneous activity levels, and highly uncertain emission factors. Here we present an ammonia emission inventory for fertilizer application that for the first time incorporates county-level data at monthly resolution, and includes more accurate activity levels and emission factors. The inventory shows that considerable variations in emissions can occur within a state. The emissions generally peak at two times of the year, in spring and in fall. The timing of these peaks depends on crop schedules. Overall, the new inventory shows the importance of determining emissions at
sub-annual time resolution, and at spatial resolution better than statewide average values as reported in previous inventories.


Recent and anticipated growth in passenger ferry service has been complicated by concerns about air pollution from marine engines that are only starting to be regulated. While marine engines are known to be a significant and growing source category in some locations, sparse data and analytical difficulties have prevented rigorous comparisons of marine and on-land passenger travel. Using data gathered in the San Francisco Bay Area, we model emissions from three passenger ferries and the matching on-land travel that would be used by commuters if ferry service were not available. The results are analyzed parametrically for levels of ridership and induced travel demand, and for new technologies, including selective catalytic reduction and natural gas fuel. Results indicate that under some conditions, passenger ferries reduce some emissions (including particulate matter emissions) relative to the matching on-land service but increase others. Emissions of NOx are particularly problematic—all the technologies examined lead to increased NOx emissions due to ferry commuting. Some of the emissions comparisons are sensitive to mode split, ridership, or induced travel demand. However, NOx emissions are not-ferry commuting always raises NOx emissions, even with the most advanced technologies. Implications for local air quality regulators and for technology development are discussed. (C) 2003 Elsevier Ltd. All rights reserved


Passive samplers have been shown to be an inexpensive alternative to direct sampling. Diffusion denuders have been developed to measure the concentration of species such as ammonia (NH3), which is in equilibrium with particulate ammonium nitrate. Conventional denuder sampling has required active sampling that inherently requires air pumps and, therefore, electrical power. To estimate emissions of NH3 from a fugitive source would require an array of active samplers and meteorological measurements to estimate the flux. A recently developed fabric denuder was configured in an open tube to passively sample NH3 flux. Passive and active samplers were collocated at a dairy farm at the California State University, Fresno, Agricultural Research Facility. During this comparison study, NH3 flux measurements were made at the dairy farm lagoon before and after the lagoon underwent acidification. Comparisons were made of the flux measurements obtained directly from the passive flux denuder and those calculated from an active filter pack sampler and wind velocity. The results show significant correlation between the two methods, although a correction factor needed to be applied to directly compare the two techniques. This passive sampling approach significantly reduces the cost and complexity of sampling and has the potential to economically develop a larger inventory base for ambient NH3 emissions


The US Clean Air Act Amendments require PM10 transportation conformity and attainment demonstrations. This study examines the policy implications and validity of a proposed PM10 transportation conformity method called equivalent emissions (EE) that uses a linear, non-chemical model to incorporate emissions trading into PM10 transportation conformity determinations. We evaluate the new method by comparing predictions from EE to predictions from a mechanistic air quality model that uses non-linear chemical mechanisms to calculate the formation of secondary PM10. Results indicate that the EE method over estimates reductions of secondary PM10 formation allowing the primary fraction to rise while secondary PM10 is not actually declining in the atmosphere. Thus, conformity could be established between air quality and transportation plans using EE, resulting in projects being funded that might prolong public exposure to unhealthy levels of PM10 depending on the specifics of the non-attainment area. (C) 2003 Published by Elsevier Science Ltd

Vegetation removes tropospheric ozone (O-3) mainly through uptake by stomata. O-3 reduces growth, photosynthesis, and carbohydrate allocation. Effects on mesophyll photosynthesis, may reducing carbohydrate source strength and, indirectly, carbohydrate translocation. Alternatively direct translocation, itself, could explain all of these observations. O-3-reduced root proliferation inhibits exploitation of soil resources and interferes with underground carbon sequestration. Simulations with cotton suggest O-3-disrupted root development could indirectly reduce shoot photosynthesis. Strong evidence for O-3 impacts on both carbon assimilation and carbon translocation exists, but data determining the primacy of direct or indirect O-3 effects on either or both processes remain inconclusive. Phloem loading may be particularly sensitive to O-3. Further research on metabolic feedback control of carbon assimilation and phloem loading activity as affected by O-3 exposure is required. (C) 2003 Elsevier Ltd.


Atmospheric particulate matter (PM) is a heterogeneous material. Though regulated as un-speciated mass, it exerts most effects on vegetation and ecosystems by virtue of the mass loading of its chemical constituents. As this varies temporally and spatially, prediction of regional impacts remains difficult. Deposition of PM to vegetated surfaces depends on the size distribution of the particles and, to a lesser extent, on the chemistry. However, chemical loading of an ecosystem may be determined by the size distribution as different constituents dominate different size fractions. Coating with dust may cause abrasion and radiative heating, and may reduce the photosynthetically active photon flux reaching the photosynthetic tissues. Acidic and alkaline materials may cause leaf surface injury while other materials may be taken up across the cuticle. A more likely route for metabolic uptake and impact on vegetation and ecosystems is through the rhizosphere. PM deposited directly to the soil can influence nutrient cycling, especially that of nitrogen, through its effects on the rhizosphere bacteria and fungi. Alkaline cation and aluminum availability are dependent upon the pH of the soil that may be altered dramatically by deposition of various classes of PM. A regional effect of PM on ecosystems is linked to climate change. Increased PM may reduce radiation interception by plant canopies and may reduce precipitation through a variety of physical effects. At the present time, evidence does not support large regional threats due to un-speciated PM, though site-specific and constituent-specific effects can be readily identified. Interactions of PM with other pollutants and with components of climate change remain important areas of research in assessment of challenges to ecosystem stability. Published by Elsevier Science Ltd


Rapid methods for characterizing soil microbial communities are essential to assess responses to perturbations and to improved management practices. This study compared the composition of microbial communities in 47 agricultural soil and adjacent land use samples collected in the San Joaquin Valley, CA. Microbial communities were characterized by DNA fingerprinting of the Intergenic Transcribed Spacer (ITS) region, using primers universal for bacteria or eucarya. Bacterial DNA fingerprints were more complex (containing 25-30 bands) than were eucaryotic fingerprints (8-15 bands). Field replicates from within an agricultural field were more similar to one another than samples collected in different fields under the same crop type or in close proximity to one another. Microbial communities in almond, grape, and tomato soils across different locations were more similar to one another than samples collected in different fields under the same crop type or in close proximity to one another. Microbial communities in almond, grape, and tomato soils across different locations were more similar to one another than communities in cotton and safflower soils. Bacterial DNA fingerprints were significantly correlated with soil electrical conductivity, soil texture, inorganic carbon, and nitrogen content but not with pH and organic carbon content. The grouping of soil samples based on their soil reflectance properties was similar to the grouping based on the bacterial ITS analysis. Despite similarities among communities under some crops and at some locations, there is tremendous unexplained diversity within agricultural soil microbial communities. More extensive sampling is needed to better understand the driving forces underlying microbial community composition. (C) 2003 Published by Elsevier Science B.V


Laboratory studies have provided a foundation of knowledge regarding vehicle emissions, but questions remain regarding the relationship between on-road vehicle emissions and changes in vehicle speed and engine load that
occur as driving conditions change. Light-duty vehicle emissions of CO, NOx, and NMHC were quantified as functions of vehicle speed and engine load in a California highway tunnel for downhill and uphill traffic on a similar to 4% grade. Emissions were measured throughout the day; average speed decreased inside the tunnel as traffic volume increased. Emissions of CO were typically 16-34 g L⁻¹ (i.e., grams of CO emitted per liter of gasoline consumed) during downhill driving and ranged from 27 to 75 g L⁻¹ during uphill driving. Downhill driving and moderate-speed uphill driving resulted in similar CO emission factors. The factor of 2 increase in CO emissions observed during higher-speed uphill driving is likely evidence of enriched engine fuel/air ratios; this was unexpected because uphill driving observed in this study occurred at moderate engine loads within the range experienced during the city driving cycle of the U.S. emissions certification test. Emissions of NOx (as NO₂) were typically 1.1-3.3 g L⁻¹ for downhill driving and varied between 3.8 and 5.3 g L⁻¹ for uphill driving. Unlike observations for CO, all uphill driving conditions resulted in higher NOx emission factors as compared to downhill driving. NOx emissions increased with vehicle speed for uphill driving but not as strongly as CO emissions. Emissions of CO and NOx are functions of both vehicle speed and specific power; neither parameter alone captures all the relevant effects on emissions. In contrast to results for CO and NOx reported here and results for NMHC reported previously by Pierson et al. (Atmos. Environ. 1996, 30, 2233-2256), emissions of NMHC per unit of fuel burned for downhill driving were over 3 times greater than NMHC emissions for uphill driving. Emission rates of CO and NOx varied more with driving conditions when expressed per unit distance traveled rather than per unit fuel burned while NMHC emission rates normalized to distance traveled were approximately constant for uphill versus downhill driving during peak traffic periods.


A new procedure to measure the total volume of emissions from heavy crude oil storage tanks is described. Tank flashing losses, which are difficult to measure, can be determined by correcting this value for working and breathing losses. The procedure uses a fan or blower to vent the headspace of the storage tank, with subsequent monitoring of the change in concentrations of oxygen or other gases. Combined with a separate determination of the reactive organic carbon (ROC) fraction in the gas, this method allows the evaluation of the total amount of ROC emitted. The operation of the system is described, and results from measurement of several storage tanks in California oil fields are presented. Our measurements are compared with those obtained using the California Air Resources Board (CARB) 150 method.


Recent studies associate particulate air pollution with adverse health effects. The indoor exposure to particles of outdoor origin is not well-characterized, particularly for individual chemical species. In response to this, a field study in an unoccupied, single-story residence in Clovis, CA, was conducted. Real-time particle monitors were used both outdoors and indoors to quantify PM2.5 nitrate, sulfate, and carbon. The aggregate of the highly time-resolved sulfate data, as well as averages, of these data, was fit using a time-averaged form of the infiltration equation, resulting in reasonable values for the penetration coefficient and deposition loss rate. In contrast, individual values of the indoor/outdoor ratio can vary significantly from that predicted by the model for time scales ranging from a few minutes to several hours. Measured indoor ammonium nitrate levels were typically significantly lower than expected solely on the basis of penetration and deposition losses. The additional reduction is due to the transformation of ammonium nitrate into ammonia and nitric acid gases indoors, which are subsequently lost by deposition and sorption to indoor surfaces. This result illustrates that exposure assessments based on total outdoor particle mass can obscure the actual causal relationships for indoor exposures to particles of outdoor origin.


Recent studies associate particulate air pollution with adverse health effects; however, the exposure to indoor particles of outdoor origin is not well characterized, particularly for individual chemical species. We conducted a field study in an unoccupied, single-story residence in Clovis, California to provide data and analyses to address
issues important for assessing exposure. We used real-time particle monitors both outdoors and indoors to quantify nitrate, sulfate, and carbon particulate matter of particle size 2.5 μm or less in diameter (PM-2.5). The results show that measured indoor ammonium nitrate concentrations were significantly lower than would be expected based solely on penetration and deposition losses. The additional reduction can be attributed to the transformation indoors of ammonium nitrate into ammonia and nitric acid gases, which are subsequently lost by deposition and sorption to indoor surfaces. A mass balance model that accounts for the kinetics of ammonium nitrate evaporation was able to reproduce measured indoor ammonium nitrate and nitric acid concentrations, resulting in a fitted value of the deposition velocity for nitric acid of 0.56 cm s⁻¹. The results indicate that indoor exposure to outdoor ammonium nitrate in Central Valley of California are small, and suggest that exposure assessments based on total particle mass measured outdoors may obscure the actual causal relationships for indoor exposure to particles of outdoor origin.

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This paper analyzes day-of-week variations in concentrations of particulate matter (PM) in California. Because volatile organic compounds (VOCs) and oxides of nitrogen (NOx) are not only precursors of ozone (O₃) but also of secondary PM, it is useful to know whether the variations by day of week in these precursors are also evident in PM data. Concentrations of PM less than or equal to 10 μm (PM10) and less than or equal to 2.5 μm in aerodynamic diameter (PM2.5) were analyzed. PM concentrations exhibit a general weekly pattern, with the maximum occurring late in the workweek and the minimum occurring on weekends (especially Sunday); however, this pattern does not prevail at all sites and areas. PM nitrate (NO₃⁻) data from Size Selective Inlet (SSI) samplers in the South Coast Air Basin (SoCAB) tend to be somewhat lower on weekends compared with weekdays. During 1988-1991, the weekend average was lower than the weekday average at 8 of 13 locations, with an average decrease of 1%. During 1997-2000, the weekend average was lower than the weekday average at 10 of 13 locations, with an average decrease of 6%. The weekend averages are generally lower than weekday averages for sulfates, organic carbon, and elemental carbon. Because heavy-duty trucks typically represent a major source of elemental carbon, the weekend decrease in heavy-duty truck traffic may also result in a decrease in ambient elemental carbon concentrations.


it will be many years before the recently deployed network of fine particulate matter with an aerodynamic diameter less than 2.5, μm (PM2.5) Federal Reference Method (FRM) samplers produces information on nonattainment areas, trends, and source impacts. However, data on PM2.5 and its major constituents have been routinely collected in California for the past 20 years. The California Air Resources Board operated as many as 20 dichotomous (dichot) samplers for PM2.5 and coarse PM (PM10-2.5). The California Acid Deposition Monitoring Program (CADMP) collected 12-h-average PM2.5 and PM10 from 1988 to 1995 at ten urban and rural sites and 24-h-average PM, at five urban sites since 1995. Beginning in 1994, the Children's Health Study collected 2-week averages of PM2.5 in 12 communities in southern California using the Two-Week Sampler (TWS). Comparisons of collocated samples establish relationships between the dichot, CADMP, and TWS samplers and the 82-site network of PM2.5 FRM samplers deployed since 1999 in California. PM mass data from the different monitoring programs have modest to high correlation to FRM mass data, fairly small systematic biases and negative proportional biases ranging from 7 to 22%. If the biases are taken into account, all of the programs should be considered comparable with the FRM program. Thus, historical data can be used to develop long-term PM trends in California.


Geographic and temporal variations in the concentration and composition of particulate matter (PM) provide important insights into particle sources, atmospheric processes that influence particle formation, and PM management strategies. In the nonurban areas of California, annual-average PM2.5 and PM10 concentrations range from 3 to 10 μg/m³ and from 5 to 18 μg/m³, respectively. In the urban areas of California, annual-averages
for PM2.5 range from 7 to 30 mug/m(3), with observed 24-hr peaks reaching levels as high as 160 mug/m(3). Within each air basin, exceedances are a mixture of isolated events as well as periods of elevated PM2.5 concentrations that are more prolonged and regional in nature. PM2.5 concentrations are generally highest during the winter months. The exception is the South Coast Air Basin, where fairly high values occur throughout the year. Annual-average PM2.5 mass, as well as the concentrations of major components, declined from 1988 to 2000. The declines are especially pronounced for the sulfate (SO42-) and nitrate (NO3-) components of PM2.5 and PM10 and correlate with reductions in ambient levels of oxides of sulfur (SOx) and oxides of nitrogen (NOx). Annual averages for PM10-2.5 and PM10 exhibited similar downwind trends from 1994 to 1999, with a slightly less pronounced decrease in the coarse fraction.


[1] Spatial variations in the partitioning of nitrate between gas phase nitric acid (HNO3) and particulate ammonium nitrate were observed using airborne measurements of trace gas mixing ratios, particle size distributions, and particle composition. During the Intercontinental Transport and Chemical Transformation experiment in April and May 2002 the NOAA WP-3 aircraft flew up to 8 km altitude on 11 research flights from Monterey, California. The formation of semivolatile aerosols was studied by examining the enhancement of fine-particulate ammonium nitrate and depletion of gas-phase HNO3 over the San Joaquin Valley, Los Angeles Basin, and Mojave Desert. Gas-phase particle precursors, HNO3 and ammonia (NH3), were converted to particulate ammonium nitrate at higher altitudes within the boundary layer. These particle layers were a consequence of lower ambient temperatures that caused a reduction of the dissociation constant for ammonium nitrate aerosol so that gas phase HNO3 was depleted and particle mass was formed. The resulting vertical gradients in particulate matter and HNO3 were observed in well-mixed boundary layers where other directly emitted trace gases (CO) and secondary pollutants (O-3) exhibited no vertical gradients. Hence the equilibrium between the gas and particle phases occurred faster than boundary layer mixing times and chemical rather than meteorological effects were responsible for the layers of enhanced particulate matter aloft. Coincident HNO3 depletion and ammonium nitrate formation was also observed downwind from regions characterized by large agricultural NH3 emissions in the Los Angeles Basin and San Joaquin Valley.


We report ozonesonde observations from the following four locations across the United States: Trinidad Head, California; Boulder, Colorado; Huntsville, Alabama; and Wallops Island, Virginia. These ozone profiles clearly indicate evidence of stratosphere-troposphere exchange, boundary layer pollution, and strong seasonal variations. Significant variation at the shortest interlaunch frequencies (typically weekly) appears in all seasons, at all stations throughout the troposphere. Activity near the tropopause dominates in the winter and spring, while boundary layer ozone maximizes in the summer. The vertical extent and maximum values of boundary layer ozone are larger at the eastern stations. Comparisons to the TOMS overpasses indicate agreement to within 2% for the total-column ozone at all stations, with station-to-station mean biases less than 2%. The seasonal variation of the total ozone column is essentially identical at Trinidad Head and Wallops Island, while the summertime values at Boulder are significantly smaller by comparison, and the amplitude of the annual cycle at Huntsville is smaller than the amplitude of the other three stations. The longitudinal character of upper tropospheric ozone shows amounts generally increasing westward from Huntsville, and in the lower troposphere, ozone decreases westward from Huntsville in all seasons. Values to the east of Huntsville increase at all altitudes and seasons, with the possible exception of August when Huntsville's boundary layer and free-tropospheric ozone dominate.


Volatile organic compounds emitted from an industrial dairy in Northern California were identified and quantified while simultaneously correlating them to odor. Sampling was performed using sorbent tubes that were then analyzed.
using thermal-desorption GC/MS with concurrent olfactometry. Using spectral information as well as verification with 110 authentic standards, a total of 35 compounds were identified and quantified and varied in concentration from 0.08 to 747.76 μg m⁻³. Compounds included acids, esters, alcohols, aldehydes, ketones, halogenates, amines and hydrocarbons. Few compounds exhibited offensive odors, and those that did were present at low concentrations. Sampling location within the dairy, temperature and relative humidity had no observable effect on the qualitative or quantitative composition of the samples. (C) 2003 Elsevier Science Ltd. All rights reserved.


Analyses of ambient measured ozone data were used in conjunction with the application of photochemical modeling to determine the technical feasibility of attaining the federal 8-hr ozone standard in central California. Various combinations of volatile organic compound (VOC) and oxides of nitrogen (NOx) emission reductions were effective in lowering modeled peak 1-hr ozone concentrations. However, VOC emissions reductions were found to have only a modest impact on modeled peak 8-hr ozone concentrations. NOx emission reductions generally lowered 8-hr ozone concentrations, but their effectiveness was partially or, in some cases, wholly offset by the increase in the number of NO cycles and, hence, in the ozone produced per NO. As a result, substantial NOx emission reductions-70 to 90%-were required to reduce peak 8-hr ozone concentrations to the level of the standard throughout the modeling domain. These modeling results provide a possible physical explanation for recent analyses that have reported more prominent trends in peak 1-hr ozone levels than in peak 8-hr ozone concentrations or in occurrences of mid-level (60-90 parts per billion by volume) ozone concentrations. The findings also have serious implications for the feasibility of attaining the 8-hr ozone standard in central California. Further efforts are needed to clarify the applicability of the modeling results to the full set of days with ozone levels exceeding the 8-hr ozone standard, as well as their applicability to other geographical areas.


Field measurements were conducted to determine atmospheric concentrations of nitrogen dioxide, nitric acid, formaldehyde, and hydrogen peroxide gases using two dual-channel tunable diode laser absorption systems. These measurements were made as part of the Central California Ozone Study (CCOS) and were conducted for a total of 28 days from July to September 2000 at the Kearney Agricultural Research Station in Parlier, California. All four trace gases exhibit marked diurnal cycles. Ranges of measured concentrations: 1-38 ppb NO₂, 0-26 ppb HNO₃, 1-17 ppb HCHO, and 0-1.2 ppb H₂O₂. Formaldehyde, nitric acid and hydrogen peroxide mixing ratios showed unusual behavior during the last intensive measurement period in September 2000. (C) 2003 Elsevier Science Ltd. All rights reserved.


Epidemiologic studies have shown that airborne particulate matter (PM) with a mass median aerodynamic diameter < 10 μm (PM10) is associated with an increase in respiratory-related disease. However, there is a growing consensus that particles < 2.5 μm (PM2.5), including many in the ultrafine (< 0.1 μm) size range, may elicit greater adverse effects. PM is a complex mixture of organic and inorganic compounds; however, those components or properties responsible for biologic effects on the respiratory system have yet to be determined. During the fall and winter of 2000-2001, healthy adult Sprague-Dawley rats were exposed in six separate experiments to filtered air or combined fine (PM2.5) and ultrafine portions of ambient PM in Fresno, California, enhanced approximately 20-fold above outdoor levels. The intent of these studies was to determine if concentrated fine/ultrafine fractions of PM are cytotoxic and/or proinflammatory in the lungs of healthy adult rats. Exposures were for 4 hr/day for 3 consecutive days. The mean mass concentration of particles ranged from 190 to 847 μg/m³. PM was enriched primarily with ammonium nitrate, organic and elemental carbon, and metals. Viability of cells recovered by bronchoalveolar lavage (BAL) from rats exposed to concentrated PM was significantly decreased during 4 of 6 weeks, compared with rats exposed to filtered air (p < 0.05). Total numbers of BAL cells were increased during 1 week, and neutrophil numbers were increased during 2 weeks. These observations strongly suggest exposure to enhanced concentrations
of ambient fine/ultrafine particles in Fresno is associated with mild, but significant, cellular effects in the lungs of healthy adult rats


Measurements of the biogenic hydrocarbons isoprene and 2-methyl-3-buten-2-ol (MBO), their first-, second-, and third-generation photooxidation products methacrolein (MACR), methyl vinyl ketone (MVK), acetone, 2-hydroxy-2-methylpropanal (2-HMPR), glycolaldehyde, hydroxyacetone, methylglyoxal, and glyoxal, and carbon monoxide (CO), were obtained above a ponderosa pine plantation, near the Blodgett Forest Research Station, California on 15-19 August and 11-15 September 2000. Diurnal cycles for all the compounds were similar, with maximum mixing ratios in the afternoon and minimum mixing ratios in the early morning. The diurnal cycles of the second-generation isoprene photooxidation products were similar to their precursors, while changes in 2-HMPR, a compound unique to MBO photooxidation, lagged behind corresponding changes in MBO. These observations are consistent with transport of isoprene and its photooxidation products from a strong source several hours upwind, and a predominantly local source of MBO with in situ photochemical production of 2-HMPR. Glycolaldehyde and hydroxyacetone mixing ratios exceeded the mixing ratios of their biogenic precursors on days with high CO, and were generally correlated more strongly with CO than with their biogenic precursors. The agreement between measured product ratios and ratios predicted by a box model improved when anthropogenic precursors were added to the model. Quantification of the source apportionment demonstrated that photooxidation of anthropogenic precursors contributed significantly to the mixing ratios of glycolaldehyde and hydroxyacetone measured in this rural environment. More research into the photochemistry and yields of multifunctional carbonyl compounds from hydrocarbon photooxidation is needed in order for models to accurately predict their role in tropospheric chemistry.


[1] The role of biogenic emissions in the production of ground-level ozone has been the subject of considerable scientific investigation. However, because existing studies generally draw their conclusions from simulations of episodes lasting days to a week, there is a need to evaluate the biogenic impact over a relatively long timescale. Moreover, the magnitude of synergistic interaction between anthropogenic and biogenic emissions should be carefully quantified, and this issue is not accounted for in most previous investigations. In this study, we performed a summer seasonal (June to August 1995) model evaluation of surface ozone across the continental United States. A three-dimensional regional climate, emissions, and air quality modeling system was used to do the simulations. The factor separation (FS) technique was applied to quantify the contributions from biogenic emissions alone and those from the synergy between anthropogenic and biogenic emissions. In the first step of this study, U. S. Environmental Protection Agency's National Emission Trends (NET) 1996 and 2020 "control case" raw anthropogenic emissions inventories were processed through Sparse Matrix Operator Kernel Emissions (SMOKE), an emissions model, to generate the speciated, gridded, and hourly emissions data needed for the air quality model. Next, six air quality simulations were carried out assuming zero emissions, biogenic only emissions, 1995 anthropogenic only emissions, biogenic plus 1995 anthropogenic emissions, 2020 anthropogenic only emissions, and biogenic plus 2020 anthropogenic emissions. The model results show that ground-level ozone concentrations decrease moderately under the EPA's 2020 emissions scenario for many areas within the continental United States, with large reductions in vast areas of the eastern United States. They also show that the 1995 summer average "total biogenic contribution" to daily maximum surface ozone concentrations can reach 34 ppb. Biogenic emissions are associated with at least 20% of surface ozone concentrations for the most areas of the continental United States, with the peaks reaching more than 40% in California coastal areas, the southeastern states, and northeastern areas. A sizable portion of this "total biogenic contribution," however, (up to 80% in some areas) is due to the synergy between anthropogenic and biogenic emissions and would thus be influenced by controls on anthropogenic source emissions.

Hydroxymethanesulfonate (HMS), an important component in fog and cloud systems, is identified in the negative ion mass spectra of individual particles sampled with an aerosol time-of-flight mass spectrometer (ATOFMS). The peak assignment at mass/charge (m/z)- 1 1 1 is confirmed by analyzing HMS particles produced in the laboratory. Individual particle mass spectra from a field campaign in Bakersfield, California reveal the presence of HMS in the ambient aerosol during isolated time periods near the dissipation phase of fog suggesting fog processing of the aerosol. The lifetime of HMS in the aerosol is limited to less than 12 h. Using the presence of HMS as a tracer for aqueous-phase fog processing, the size distribution indicates that particles with aerodynamic diameters greater than 0.7 


Little data exists on the determinants of agricultural dust exposure, particularly in dry climates. Annual exposure indices to inhalable and respirable dust were constructed by exposure estimates for specific tasks, task duration, and task frequency. The estimates of exposure levels were based on actual field measurements and subjective dust exposure ranking. The task duration and frequency data were obtained by questionnaire from 346 farm operators in California. Annual exposure indices were analyzed to determine which tasks were major contributors to chronic dust exposure. The important tasks were identified by comparisons of the cumulative distribution of exposures for all tasks and the cumulative distribution of exposures with one task deleted. Thirteen and 11 tasks were identified to be important to both inhalable and respirable dust exposures, respectively. Tasks identified to be important to agricultural exposure may be ascribed to exposure duration more than to exposure intensity. Information on task-specific exposure is important for developing control strategies in the agricultural workplace.


Pilot-scale tests for the land disposal of Se-enriched sediments from the San Luis Drain were performed in the San Joaquin Valley, California. Three test plots were instrumented and monitored on a dirt-road embankment near the sediment source area, providing an opportunity to measure Se oxidation and solubilization rates over a period of 2-3 yr. Soil, soil water, and groundwater data indicated that the amendment did not cause movement of dissolved Se below a depth of 15 cm. The low permeability of underlying sediments and the overall low Se solubility limit Se movement toward the groundwater table. Selenium remained in reduced forms and largely immobile at this site although in-situ Se oxidation was measurable. Soluble Se concentrations increased from less than 0.5% to approximately 2.5% in the first 207 d following sediment application. Minor Se solubilization occurred after 439 and 704 d. Changes in Se fractionation measured using sequential extractions and Se speciation based on X-ray spectroscopy (XANES) results were in qualitative agreement. XANES results indicated initially rapid oxidation of organo-Se and/or elemental Se to selenite during the first 207 d, followed by minor oxidation after 439 d. Further solubilization of the Se inventory is anticipated, but at a low rate of 1-2% per year, comparable to rates measured in other studies.

Zhang, Q., Anastasio, C., 2003. Free and combined amino compounds in atmospheric fine particles (PM2.5) and fog waters from Northern California. Atmospheric Environment 37 (16), 2247-2258.

Atmospheric fine particles (PM2.5) collected during August 1997-July 1998 and wintertime fog waters collected during 1997-1999 at Davis, California were analyzed for free and combined amino compounds. In both PM2.5 and fog waters, the average concentrations of combined amino compounds (CAC, e.g., proteins and peptides) were generally 4-5 times higher than those of free amino compounds (FAC, i.e., amino acids and alkyl amines).
Concentrations of total amino compounds (TAC=FAC+CAC) ranged from 1260 to 3650 pmol m(-3) air in PM2.5, and from 1620 to 5880 pmol m(-3) air in fog waters. Average values (+/-1sigma) were 2500+/−879 and 3400+/−1430 pmol m(-3) air, respectively. Concentrations of amino compounds in PM2.5 varied seasonally, with a peak during late winter and early spring. Ornithine was a major FAC component in both PM2.5 and fog waters (typically accounting for similar to 20% of FAC), but these sample types otherwise had fairly different FAC distributions. FAC in PM2.5 were enriched in protein-type amino species such as glycine/threonine, serine and alanine, while fog water FAC had significantly higher levels of non-protein species such as methylamine, gamma-aminobutyric acid and ethanolamine. The compositions of CAC in PM2.5 and fogs were fairly similar and were mainly protein-type. Mass concentrations of TAC in PM2.5 and fog waters were, on average, 302 and 399 ng m(-3) air, respectively. Amino compounds were an important component of the organic carbon pool for both fog and particles, with TAC accounting for an average of 13% of the dissolved organic carbon in fog waters and similar to 10% of the water-soluble organic carbon in PM2.5. At these levels amino compounds likely play important roles in the chemistry of fog drops and fine particles, for example by influencing their buffering capacity and basicity.


The high-value, large-scale crop production systems in the San Joaquin Valley (SJV) of California typically entail intensive tillage and large fertilizer and water inputs but few C additions to the soil. Such practices often contribute to a decline in soil quality. Our objective for this participatory study was to examine the effects of supplemental C management practices (SCMPs) on various soil quality indicators. To increase farmer participation, we conducted the study on farms using a variety of SCMPs, including cover crops, compost and manure amendments, and several different crop rotations common to the region. The SCMPs significantly changed a number of soil properties, including soil organic matter (SOM); total Kjeldahl N; microbial biomass C and N; exchangeable K; Olsen P; and extractable Fe, Mn, and Zn. A comparison including previously established, adjacent organic, conventional, and transitional fields in addition to the treatment fields at one farm revealed significant differences in 16 of 18 soil quality indicators. A soil quality index computed for this farm scored the established organic system significantly higher than the conventional system. Our results suggest that significant changes in several soil quality indicators occur with a variety of SCMPs. This is especially noteworthy considering the intensive tillage, irrigation, and hot, semiarid environment of the SJV, California, where increases in SOM and related soil properties are generally not expected in a 3-yr study.


Aircraft measurements of the Sacramento pollutant plume were obtained over the western Sierra Nevada on 7 days in the summers of 1995 and 1996. These measurements, as well as those documenting the meteorological setting and evolution of surface conditions, are summarized. High concentrations of residual ozone above the surface layer in the early morning hours appear to be necessary to produce afternoon concentrations in excess of 125 ppbv. The moderately polluted days were characterized by low residual pollutant concentrations aloft in the early morning and moderate to weak vertical stratification during the day. The cleanest days had good ventilation with deep layers of near neutral stratification and moderate to strong winds. Horizontal spatial variability of ozone concentrations within the mixed layer was often significant at scales less than or equal to 5 km. The maximum ozone concentrations were frequently observed in the afternoon, 40-80 km downwind of the city, but these decreased to about one-half those values at distances 120 km downwind. The measured oxides of nitrogen were generally just above detection limits (similar to 1 ppbv), except in the surface layer in the early morning hours.


This experiment shows that carbonate concentrations are negligible at most Interagency Monitoring of Protected Visual Environments (IMPROVE) monitoring sites. Even when present, carbonate does not cause significant biases in total carbon (TC), organic carbon (OC), and elemental carbon (EC) concentrations in the IMPROVE protocol. The analysis also shows that acidification to remove interferences from carbonates is not necessary when using a
thermal evolution method in which the highest temperature is less than 800 degreesC. Seventy-seven samples with
the highest calcium concentrations from 58 sites in the IMPROVE network were analyzed for carbonate by
acidification. Measured carbonate carbon concentrations at most sites were <100 ng m(-3), with many less than
lower quantifiable limits; the highest carbonate carbon of 420 ng m(-3) was measured at Guadalupe Mountains
National Park in western Texas. Comparison of EC measured at 800 &DEG;C with and without acidification
showed no consistent biases for the nonacidified analysis, even when carbonate levels were high. Acidification may
be advisable when sampling particle sizes larger than 2.5 &mu;m, when samples are acquired at locations where
carbonate carbon is expected to be high, or when >800degreesC temperatures are applied during thermal evolution
carbon analysis.

Chow, J.C., Bachmann, J.D., Wierman, S.S.G., Mathai, C.V., Malm, W.C., White, W.H., Mueller, P.K.,
of the Air & Waste Management Association 52 (9), 973-999

chemical composition of fogs and intercepted clouds in the United States. Atmospheric Research 64 (1-4), 29-
40.

Over the past decade, the chemical compositions of fogs and intercepted clouds have been investigated at more than
a dozen locations across the United States. Sampling sites have been located in the northeast, southeast, Rocky
Mountain, and west coast regions of the US. They include both pristine and heavily polluted locations.
Frontal/orographic clouds (warm and supercooled), intercepted coastal stratiform clouds, and radiation fogs have all
been examined. Sample pH values range from below 3 to above 7. Major ions also exhibit a wide concentration
range, with clouds at some locations exhibiting high sea salt concentrations, while composition at other locations is
dominated by ammonium and sulfate or nitrate. (C) 2002 Elsevier Science B.V. All rights reserved

Research Part D-Transport and Environment 7 (3), 197-211.

Increasing regional mobility demand amid rising roadway congestion has motivated plans for passenger ferry
expansion and modernization in many parts of the US. While this trend applies to ferry systems in Alaska, New
York, Boston, and Washington state, efforts to expand ferry service in the San Francisco Bay Area are unique in
scale and vision. Integrating ferry service into the regional, door-to-door transit system can significantly increase
water-crossing capacity for commuters. However, to realize this potential, the ferry industry must meet several
challenges associated with growth, including environmental impacts. In particular, concern over air pollution
emissions from marine engines is motivating new comparisons between ferries and other transportation modes in
terms of both mobility and air pollution. This paper describes the current debate about ferry system operation and
expansion, and presents a parametric analysis comparing existing, uncontrolled ferry emissions to automobiles.
Under all reasonable assumptions, we show that diesel-powered ferries without emissions controls will produce
more NO, and PM, but less CO per passenger-trip than if those people commuted by car under current conditions.
This paper also projects the emissions from the expanded ferry system proposed for the San Francisco Bay Area,
showing that a larger ferry fleet equipped with new engines meeting future EPA emissions standards could become
one of the major non-road NO, sources in the region. We conclude by outlining the alternatives and challenges to
reduce ferry emissions so that they are more comparable to automobile emissions. Policy implications of these
alternatives are also discussed. (C) 2002 Elsevier Science Ltd. All rights reserved

Destaillats, H., Spaulding, R.S., Charles, M.J., 2002. Ambient air measurement of acrolein and other
carbonyls at the Oakland-San Francisco Bay Bridge toll plaza. Environmental Science & Technology 36 (10),
2227-2235, DOI: 10.1021/es011394c.

together with the advancement of new catalysts and fleet turnover throughout the 1990s, are likely to account for
part of the gap between our determination and the 1996 levels. Interest in ambient concentrations of acrolein and
other alpha, beta-unsaturated aldehydes and dicarbonyls (e.g., crotonaldehyde, methyl glyoxal, glyoxal,
malonaldehyde (malondialdehyde)) is growing because either they exist at high levels in motor vehicle emissions or
they arise from photooxidation of other hydrocarbons emitted from mobile sources. In addition, their mutagenic,
genotoxic, or carcinogenic properties are well-established, and the results of a dispersion-modeling study regarding
the health risks posed by the 188 hazardous air pollutants in California attributes the highest noncancer risk to exposure to acrolein. Such modeling studies, conducted by the U.S. Environmental Protection Agency (U.S. EPA), also predict median ambient air concentrations of acrolein higher than 0.06 mug/m\(^3\), the chronic inhalation reference exposure level stipulated by the California Office of Environmental Health Hazard Assessment in counties surrounding the Oakland-San Francisco Bay Bridge. We measured acrolein and other potentially toxic carbonyls in air sampled at the San Francisco Bay Bridge toll plaza during rush hour traffic, which may be considered a "worst case scenario" for outdoor airborne carbonyls. We identified 36 carbonyls in the sample extracts, including 14 saturated aliphatic carbonyls, six unsaturated carbonyls, four aromatic carbonyls, six dicarbonyls, and six hydroxy carbonyls. Structural information to support tentative identification of carbonyls and hydroxycarbonyls was obtained by using a method that involves O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) and PFBHA/bis(trimethylsilyl)trifluoroacetamide (BSTFA) derivatization in concert with gas chromatography/ion trap mass spectrometry. Most notably, we report for the first time the presence of malonaldehyde in the ambient atmospheric environment. A relatively linear relationship between retention time and the molecular weight of the derivatives was established to assist in obtaining structural information about chemicals for which authentic standards are not readily available. Levels of acrolein exceeded the California reference exposure level during morning rush hour traffic. The measured values, however, were significantly lower than estimates of county-wide average acrolein concentrations predicted by a U.S. EPA modeling study based on 1996 data. Successful regulatory efforts such as the introduction of reformulated gasoline


Measurements of anthropogenic hydrocarbons, ozone, and meteorological variables were obtained during the summer of 1997 near the University of California Blodgett Forest Research Station on the western slope of the Sierra Nevada Mountains. These measurements and related observations obtained upwind in Sacramento and Folsom, California, by the California Air Resources Board and the National Weather Service demonstrate that the transport of the Sacramento plume is controlled by extremely consistent, terrain-driven winds that draw polluted air into the Sierra Nevada by day and flush the mountains at night with clean, continental background air. In effect the plume serves as a mesoscale (100 km) daytime flow reactor where the daily evolution of the Sacramento urban plume can be characterized as a Lagrangian air parcel transported from the urban core into the sparsely populated Sierra Nevada mountains. Using observations of slowly reacting anthropogenic hydrocarbons, we demonstrate that at the peak impact of the Sacramento plume the air at Blodgett Forest can be characterized as a mixture of 32% air from the urban core and 68% from the relatively clean background. From measurements of more reactive hydrocarbons we infer an average daytime OH concentration of 1.1 x 10(7) molecules cm(-3) during the transit of the urban plume.


Control of CO is one of the great air-quality management success stories of the past 20 years. This paper evaluates whether past progress will continue into the future and whether changes in microscale CO concentrations are comparable to reductions observed at the regional scale. Neighborhood and microscale CO concentrations were evaluated at six northern and southern California monitoring sites. The study also included a review of CO emission, concentration, and exposure trends and on-road motor vehicle-based CO emission control programs for California and the United States. Consistent with California and national trends, CO concentrations declined at each of the six study locations from 1988 through 1998. Microscale concentrations declined at the same rate as did neighborhood-scale concentrations. Rollback analyses demonstrated that microscale concentrations will continue to decline through at least 2010-2020. Within a few years, microscale violations of the CO National Ambient Air Quality Standards (NAAQS) will be unlikely in California except under extraordinary circumstances

Selenium stable isotope ratios are known to shift in predictable ways during various microbial, chemical, and biological processes, and can be used to better understand Se cycling in contaminated environments. In this study we used Se stable isotopes to discern the mechanisms controlling the transformation of oxidized, aqueous forms of Se to reduced, insoluble forms in sediments of Se-affected environments. We measured Se-80/Se-76 in surface waters, shallow ground waters, evaporites, digested plants and sediments, and sequential extracts from several sites where agricultural drainage water is processed in the San Joaquin Valley of California. Selenium isotope analyses of samples obtained from the Tulare Lake Drainage District flow-through wetland reveal small isotopic contrasts (mean difference 0.7%) between surface water and reduced Se species in the underlying sediments. Selenium in aquatic macrophytes was very similar isotopically to the NaOH and Na2SO3 sediment extracts designed to recover soluble organic Se and Se(0), respectively. For the integrated on-farm drainage management sites, evaporite salts were slightly (approximately 0.6%) enriched in the heavier isotope relative to the inferred parent waters, whereas surface soils were slightly (approximately 1.4%) depleted. Bacterial or chemical reduction of Se(VI) or Se(IV) may be occurring at these sites, but the small isotopic contrasts suggest that other, less isotopically fractionating mechanisms are responsible for accumulation of reduced forms in the sediments. These findings provide evidence that Se assimilation by plants and algae followed by deposition and mineralization is the dominant transformation pathway responsible for accumulation of reduced forms of Se in the wetland sediments.


Organic matter was studied in radiation fogs in the San Joaquin Valley of California during the California Regional Particulate Air Quality Study (CRPAQS). Total organic carbon (TOC) concentrations ranged from 2 to 40 ppm of C. While most organic carbon was found in solution as dissolved organic carbon (DOC), 23% on average was not dissolved inside the fog drops. We observe a clear variation of organic matter concentration with droplet size. TOC concentrations in small fog drops (< 17 mum) were a factor of 3, on average, higher than TOC concentrations in larger drops. As much as half of the dissolved organic matter was determined to have a molecular weight higher than 500 Da. Deposition fluxes of organic matter in fog drops were high (0.5-4.3 mug of C m(-2) min(-1)), indicating the importance of fog processing as a vector for removal of organic matter from the atmosphere. Deposition velocities of organic matter, however, were usually found to be lower than deposition velocities for fogwater, consistent with the enrichment of the organic matter in smaller fog drops with lower terminal settling velocities.


An accurate estimate of the magnitude of biogenic volatile organic compound (BVOC) emissions in California's airsheds is critical for formulating effective strategies to reduce concentrations of fine particles, ozone, and other secondary air pollutants which affect human health and reduce yields of agricultural crops. However, California's natural and urban landscapes contain more than 6000 species, and the BVOC emissions from only a small fraction of these species have been characterized by quantitative measurements. A taxonomic method has been proposed to assign BVOC emission rate measurements to unmeasured species, but data are needed for additional plant families and genera to further develop and test this taxonomic approach. In the present study, BVOC emissions from more than 250 plant species were measured through a semi-quantitative method employing calibrated portable analyzers with photoionization detectors (PID). Replicate samples of live foliage were placed in plastic bags, in both light and darkened conditions, and the BVOC emissions categorized as low, medium or high. To validate our approach, for 63 plant species we compared our PID-measured BVOC emissions with published values, based on gas chromatography (GC) or GC-mass spectrometry, and found them to be well correlated. The method employed was more suited for detecting compounds with relatively higher emission rates, such as isoprene, than compounds with low emission rates, which could include monoterpenes and oxygenated compounds. For approximately 200 plant species not previously measured, the results provide further evidence that plant taxonomy can serve as a useful guide for generalizing the emissions behavior of many, but not all, plant families and genera.

Attempts to characterize ozone formation as sensitive to either volatile organic compounds (VOC) or NOx within a region oversimplify a problem that shows spatial and temporal variation. California's Central Valley has some of the highest ozone levels in the country and a rapidly growing population, and air quality problems in this region can be influenced by interbasin transport of ozone and its precursors. An Eulerian photochemical airshed model is applied to the region for the period 3-6 August 1990. This episode spans a weekend, and the emission inventory incorporates revised motor vehicle emissions with day-specific activity patterns. Compared with the baseline inventory, the revised inventory contains higher VOC and lower NOx emissions from motor vehicles and different temporal patterns of these emissions. Revised estimates of biogenic emissions are greatly reduced. The baseline emission inventory used in previous modeling efforts appears to contain compensating errors, with high biogenic emissions making up for low motor vehicle emissions of VOC. Results suggest that heavily urbanized areas around and downwind of the San Francisco Bay and Sacramento are VOC-sensitive, while the more rural areas are NOx-sensitive. Ozone formation in the San Joaquin Valley, where progress in reducing ambient ozone concentrations has been slow, exhibits sensitivity to emissions of both VOC and NOx, and is influenced by emissions from the San Francisco Bay Area during this modeling episode.


Photochemical air pollution problems have proved difficult to understand and control in central California. A major source of uncertainty is the rate of precursor volatile organic compounds and NOx emissions, especially from motor vehicles. We develop alternative emissions estimates for on-road motor vehicles in 1990, using fuel sales data, emission factors measured in on-road studies, and ambient pollutant ratios, for a region that includes the San Francisco Bay and San Joaquin Valley air basins and Sacramento County. Fuel-based emissions estimates are compared with predictions of California's most recent motor vehicle emission factor model (EMFAC) and with an inventory that has been used in previous regional-scale photochemical modeling studies. The fuel-based inventory contains 10-50% less CO, 40-100% more nonmethane organic compounds, and 10-20% less NOx than estimated both by EMFAC and the photochemical modeling inventory. We also describe new temporal distributions of vehicle emissions by hour and day of week. Diesel trucks, a major source of NOx, have a broad midday peak in emissions on weekdays, in contrast to passenger vehicles, which show morning and afternoon commuter peaks. While passenger vehicle travel is similar on weekdays and weekends, diesel truck activity and emissions decrease by 70-80% on weekends. Vehicle emission rates and their temporal patterns are linked to a regional photochemical air pollution episode that spans a weekend in August 1990.


Ambient ozone concentrations vary by day of week in some locations, often with higher concentrations observed on weekends in urban and downwind areas. Emissions of ozone precursors appear to be lower on weekends, so the behavior of ozone concentrations on weekends may indicate the outcome of particular ozone control strategies. To examine the influence of day-of-week differences in motor vehicle emissions on ambient ozone concentrations, we combine a fuel-based motor vehicle emission inventory containing weekend-specific activity with an Eulerian photochemical airshed model applied to central California. Emissions of NOx on weekends are similar to 30% lower than on weekdays due to a large drop in heavy-duty diesel truck activity, and emissions of VOC are only slightly lower on weekends. In rural areas, passenger car traffic and the associated emissions are highest on Fridays and Sundays. The combination of VOC sensitivity and reduced emissions of NOx on weekends results in higher ozone concentrations on weekends. Changes in the timing of emissions also contribute to the weekend ozone effect, but sensitivity tests show that changes in emissions timing have a minor effect compared to changes in total mass of emissions on weekends. Even in situations where reductions in NOx emissions lead to higher ozone concentrations, NOx reductions may still be necessary for control of other air pollutants such as nitrogen dioxide, nitric acid, and aerosol nitrate.

Source sample extracts of vegetative detritus, motor vehicle exhaust, tire dust, paved road dust, and cigarette smoke have been silylated and analyzed by GC-MS to identify polar organic compounds that may serve as tracers for those specific emission sources of atmospheric fine particulate matter. Candidate molecular tracers were also identified in atmospheric fine particle samples collected in the San Joaquin Valley of California. A series of normal primary alkanols, dominated by even carbon-numbered homologues from C-26 to C-32, the secondary alcohol 10-nonacosanol, and some phytosterols are prominent polar compounds in the vegetative detritus source sample. No new polar organic compounds are found, in the motor vehicle exhaust samples. Several hydrogenated resin acids are present in the tire dust sample, which might serve as useful tracers for those sources in areas that are heavily impacted by motor vehicle traffic. Finally, the alcohol and sterol emission profiles developed for all the source samples examined in this project are scaled according to the ambient fine particle mass concentrations attributed to those sources by a chemical mass balance receptor model that was previously applied to the San Joaquin Valley to compute the predicted atmospheric concentrations of individual alcohols and sterols. The resulting underprediction of alkanol concentrations at the urban sites suggests that alkanols maybe more sensitive tracers for natural background from vegetative emissions (i.e., waxes) than the high molecular weight alkanes, which have been the best previously available tracers for that source


Two annular denuder samplers were evaluated for the determination of atmospheric nitric acid, SO2, and fine particulate sulfate and nitrate. One, the University Research Glassware (URG) sampler, used an elutriator-impactor to remove coarse particles prior to sampling the aerosol through the denuder sections for the removal of acid gases. The second, the Rupprecht and Patashnick (R&P) ChemSpec, removes the acid gases in diffusion denuder sections and then removes coarse particles prior to the collection of fine particles. Possible sampling artifacts examined included the removal of HNO3(g) by the inlet of the URG sampler before the collection of this gas-phase species by the diffusion denuder, resulting in the underestimation of HNO3(g) and the deposition of some coarse particles in the R&P denuders prior to the removal of these larger particles, and the collection of fine particles on a filter, resulting in the overestimation of HNO3(g) and SO2(g). Samples were collected in Riverside, CA, Bakersfield, CA, and Provo, UT. Both sampling artifacts were found to be present. However, the effect on the determination of HNO3(g) by the URG sampler and on the determination of particulate-phase sulfate and nitrate by the R&P ChemSpec were both small, on the order of a few tenths of a microgram per cubic meter.


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Few analytical methods exist that combine chemical and sensory analysis of odorous compounds in whole air. Volatile organic compounds were collected by sampling air downwind from a small dairy through sorbent-tubes of Tenax TA and Carboxen 569. Samples were analyzed by thermal desorption into a cryotrap and subsequent as:chromatographic separation, followed by simultaneous olfactometry and mass spectrometry. Because compounds are concentrated during sampling, sensory analysis encountered compounds at a concentration 40 times that in air, making this a useful method for identifying trace compounds participating in odor. Twenty odorous and nonodorous compounds were identified and quantified, including straight-chain and aromatic hydrocarbons, chlorinated compounds, alcohols, ketones, aldehydes, and organic acids, at air concentrations of 0.55-320.20 µg/m(3). Compound peaks were characterized by odors ranging from offensive to pleasant, demonstrating the integrative nature of olfaction. This method could be useful in studying many kinds of odors in air.


Despite the potential toxicity of respirable quartz to humans, little is known about the transport of airborne quartz from sources to receptors and how to distinguish anthropogenically generated quartz from natural background in a receptor sample. Airborne quartz emissions near a sand and gravel facility were determined using PM10 and PM2.5 filter samples collected at four downwind sites (D1: 22 m, D2: 62 m, D3: 259 m, and D4: 745 m from the facility) as well as one upwind site (U1: 1495 m) during summer sampling. X-ray diffraction was used to determine quartz concentration and elemental composition was analyzed using PIXE, XRF, PESA, and HIPS techniques. Elemental composition of the PM samples was used to determine the X-ray mass absorption coefficients that are essential for accurate quartz quantification by XRD. Elemental composition was found to be a useful tool to distinguish source and background crystalline silica. Both PM10 and PM2.5 samples collected at the D1, D2, and D3 sites contained more Si, Al, and Fe and less H, Na, and S, compared to those at the U1 site, whereas site D4 sample compositions were similar to those at the U1 site. A composite variable, SOIL(H+Na+S), where SOIL = 2.20Al + 2.49Si + 1.63Ca + 1.94Ti + 2.42Fe, was used to distinguish source materials from background. Average dry season quartz concentrations in replicate PM10 samples were 4.6 (+/- 0.9) µg m(-3) at U1, 60.6 (+/- 5.4) µg m(-1) at D1, 62.4 (+/- 3.6) at D2, 32.6 (+/- 2.1) µg m(-3) at D3, and 9.4 (+/- 0.9) µg m(-3) at D4. The mass fraction of quartz was the highest at the D1 site and decreased with increasing distance from the facility. The mass of PM2.5 samples was too low to determine quartz concentrations. These results identify the facility as the main source of quartz and other silicate minerals downwind of the plant and that the air quality of the most remote sampling site, located similar to 750 m downwind, was still impacted by the facility's activity.


In this study, we report on the distribution and mineralogy of micron-sized mineral aggregates formed in the top horizon of an acid sulfate soil. The distribution and oxidation state of arsenic (As) and selenium (Se) were also determined. The soil used in this study was formed from pyritic shale parent materials on the east side of the California Coast Range. Synchrotron-based X-ray fluorescence microprobe (mu-XRF) was used to generate elemental distribution maps of soil thin sections. Using the elemental distribution maps and optical micrographs, distinct mineral aggregates of iron oxide and iron sulfate were identified throughout the top horizon of the soil. These aggregates range in size from 10 to 100 gin in diameter and can be found only a few micrometers apart. The As and Se concentrations in the iron oxide aggregates were 5-10 times the concentrations in the iron sulfate aggregates and the weathered shale matrix. This suggests that the As and Se become preferentially associated with iron oxides during the weathering process. Using a focused micronsized beam, Fe, As, and Se X-ray absorption spectroscopy (XAS) data were collected from the submillimeter soil aggregates. The micro-extended X-ray absorption fine structure (mu-EXAFS) spectrum collected from the iron oxide aggregate revealed that its mineralogy was a combination of ferrihydrite (> 50%) and goethite. The mu-EXAFS spectra from the iron sulfate region suggest that these aggregates contain jarosite. Using micro-X-ray absorption near edge spectroscopy (mu-XANES), oxidation states of the As and Se were determined. Arsenic was present in the iron oxide aggregate as As(V). Selenium was present in the soil as both Se(IV) and Se(VI), with a higher percentage of Se(VI) in the jarosite aggregate than the iron oxide aggregate. These results provide direct evidence of the distribution, oxidation states, and speciation of As and Se in the solid phase of an unaltered native soil. Information on the weathering and
geochemistry of the pyritic materials, and the associated arsenic and selenium is useful for predicting the pedogenic processes of acid sulfate soils and the long-term fate of newly exposed pyritic materials (e.g., mine tailings and drained wetlands). (C) 2002 Elsevier Science B.V. All rights reserved


A study was conducted to measure atmospheric concentrations of PAHs and PCBs and estimate their fluxes between air and water in the northern San Francisco Estuary. Ambient air samples were collected once every 12 days at a single sampling site in Concord, CA, from June to November 2000, using a modified high-volume air-sampling device equipped with glass fiber filters and polyurethane foam. Concentrations of total PAHs and PCBs ranged from 5.7 to 56 and 0.17 to 0.32 ng/m(3), respectively. PAHs and PCBs in the ambient air were predominantly in the vapor phase (83-99%). Gaseous fluxes of PAHs in the estuary showed high seasonal variation, ranging from 110 ng(.)(m(-2).)(day(-1)) efflux in August to 1050 ng(.)(m(-2).)(day(-1)): influx in November. Gaseous PCBs showed consistent net, volatilization (2.2-24 ng(.)(m(-2).)(day(-1)) for this period. Particle settling contributed estimated net deposition fluxes of 45-960 ng(.)(m(-2).)(day(-1)) for PAHs and 0.39-2.1 ng(.)(m(-2).)(day(-1)) for PCBs. Combining these fluxes, PAHs were either deposited to or lost from the Estuary via the atmosphere, depending on the month. In contrast, there consistently was net emission of PCBs from the estuary to the atmosphere.


An observational data assimilation (ODA) technique was evaluated based on both its direct effect on meteorological model fields and its indirect effect on the results of two air quality models that input these meteorological fields: a Lagrangian particle model (LPM) and a photochemical model, the variable-grid version of the Urban Airshed Model (UAM-V). The purpose was to investigate the model performance improvements that are derived from using field-study observations with an ODA technique. The ODA technique, based upon Newtonian relaxation, was incorporated into the Colorado State University Regional Atmospheric Modeling System (RAMS). The technique was applied with rawinsonde, profiler, and sodar observations of winds, temperature, and moisture from an intensive field campaign during 3-7 August 1990 over the San Joaquin Valley in California. The RAMS meteorological fields, produced with and without the use of the ODA technique, and the results from the two air quality models using these two fields were evaluated and compared. The use of the ODA technique substantially reduced the gross errors of RAMS upper-air parameters but only produced minor reductions in the gross errors of RAMS surface-level parameters. The respective gross errors of RAMS upper-air results with and without ODA were 0.23 and 1.1 m s(-1) for wind speeds and 1.1 and 1.9 K for temperatures. For RAMS surface-level results, the respective gross errors with and without ODA were 0.76 and 0.78 m s(-1) for wind speeds and 3.4 and 3.8 K for temperatures. In both cases, the RAMS vector wind biases near the surface and aloft were less than 0.9 m s(-1). Both LPM simulations of the field-study tracer experiments produced particle distributions that were consistent with observations and that were similar to each other. However, the more accurate vertical temperature structure due to the use of ODA produced shallower planetary boundary layers and resulted in larger surface tracer concentrations. Both UAM-V simulations of ozone produced similar ozone results, with less than 22% normalized gross mean errors for observations greater than 40 ppb on the last two days of the simulations. The strong influence of the UAM-V boundary-condition values on the sensitivity of UAM-V to the two meteorological inputs is demonstrated. This influence suggests that errors in other UAM-V inputs may obscure improvements in ozone modeling results from the use of ODA in creating meteorological inputs.


Although it is estimated that salinity stress occurs in 50% of irrigated agroecosystems around the world, not much is known about its impact on C and N dynamics. This study was conducted to characterize the impact of salinity stress on natural abundance C-13 and N-15 (delta(13)C and delta(15)N) on a Lethent Clay Loam (fine, smectitic, thermic typic natrargid) in the San Joaquin Valley (California) for a nonhalophyte, C-3 plant and soil organic matter (SOM) fractions. A total of 101 plant (Littleseed Canarygrass, [Phalaris minor Retz.]) and soil samples were collected from a 10-ha area. Electrical conductivity in a 1:5 soil/ water paste (EC1:5) ranged from 2.7 to 8.9 dS m(-1). The delta(13)C(plant) values varied from -29.8 to -24.0parts per thousand, and delta(15)N from 2.2 to 19.1parts per
thousand. Average values for delta(13)C increased from 26.9 parts per thousand in the plant, to -25.3 parts per thousand in the light fraction (LF) and 24.1 parts per thousand in the SOM. Salinity explained 57% of variance in delta(13)C(plant), 16% of delta(13)C(LF) and 6% of delta(13)C(SOM). For WIN, these numbers were 41, 56, and 0%, respectively. There was a clear spatial pattern match between salinity, delta(13)C(plant), delta(15)N(plant), and delta(15)N(LF). The lack of any salinity-induced signature in total SOM probably indicates that the salinity was of recent origin. The high positive correlation between salinity and delta(15)N in crop and LF might be because of higher NH3 volatilization caused by high pH, combined with a relative increase of NH4+-uptake by the plant under saline conditions. Under certain conditions, delta(13)C and delta(15)N signatures of recalcitrant SOM fractions may be used to reconstruct historic salinity patterns.


A winter PM2.5 episode that achieved a maximum 24-h average of 138 mug m(-3) at the Fresno Supersite in California's San Joaquin Valley between 2 and 12 January, 2000 is examined using 5-min to 1-h continuous measurements of mass, nitrate, black carbon, particle-bound PAH, and meteorological measurements. Every day PM2.5 sampling showed that many episodes, including this one, are missed by commonly applied six-day monitoring, even though quarterly averages and numbers of US air quality standard exceedances are adequately estimated. Simultaneous measurements at satellite sites show that the Fresno Supersite represented PM2.5 within the city, and that half or more of the urban concentrations were present at distant, non-urban locations unaffected by local sources. Most of the primary particles accumulated during early morning and nighttime, decreasing when surface temperatures increased and the shallow radiation inversion coupled to a valleywide layer. When this coupling occurred, nitrate levels increased rapidly over a 10-30 min period as black carbon and gaseous concentrations dropped. This is consistent with a conceptual model in which secondary aerosol forms above the surface layer and is effectively decoupled from the surface for all but the late-morning and early afternoon period. Primary pollutants, such as organic and black carbon, accumulate within the shallow surface layer in urban areas where wood burning and vehicle exhaust emissions are high. Such a model would explain why earlier studies find nitrate concentrations to be nearly the same among widely separated sites in urban areas, as winds aloft of 1 to 6 ms(-1) could easily disperse the elevated aerosol throughout the valley.


The Fresno Supersite in Fresno, California, USA, acquires in situ 5- to 60-min average PM2.5 organic carbon (OC), elemental carbon (EC), and total carbon (TC) measurements by the following methods: (1) thermal evolution carbon analyzer for organic, elemental, and total carbon; (2) single-wavelength and seven-color aethalometer for black carbon (BC); and (3) photoionization for particle-bound polycyclic aromatic hydrocarbons. Twenty-four-hour average PM2.5 filter-based measurements include (1) nondenuded quartz filters with no backup filter in a PM2.5 Federal Reference Method (FRM) sampler; (2) quartz filters behind an organic carbon denuder with a quartz backup filter in a Reference Ambient Aerosol Sampler (RAAS); (3) nondenuded quartz filters with backup filter in a RAAS; and (4) nondenuded quartz filters with no backup filter in a sequential filter sampler. Filter samples are analyzed after sampling by the Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal/optical reflectance carbon analysis protocol. Collocated measurements are examined for year 2000. Measurement equivalence is found for PM2.5 mass, light transmission, and TC between the FRM and RAAS speciation samplers. The average ratios of front filter carbon between the denuded and nondenuded channels in the RAAS sampler are 0.83 +/- 0.19 for TC, 0.81 +/- 0.20 for OC, and 1.01 +/- 0.33 for EC. The average differences for TC and OC are low (1.2 to 1.4 mug m(-3)) and are comparable to the measurement uncertainties. Continuous thermal evolution carbon measurements are not comparable to filter measurements. Aethalometer BC and filter EC are highly correlated,
Filter EC is consistently 20-25% higher than continuous aethalometer BC. Pairwise comparisons show filter EC measurements acquired in this study are predictable from aethalometer BC measurements.


High-resolution sequence stratigraphy provides a framework to interpret unconformity-bounded depositional sequences in the stream-dominated Kings River alluvial fan, located near Fresno, California. Depositional units in the fan are analogous to systems tracts described from marine deposits. Fan sequences reflect changes in accumulation space (Blum and Tornqvist 2000) associated with Pleistocene glacial cycles in the Sierra Nevada and preservation space created by tectonic subsidence in the San Joaquin basin. Adjustments in accumulation space are driven by changes in the ratio of sediment supply to discharge during glacial advances and retreats. At the end of glacial periods and the beginning of interglacial periods, declines in the ratio of sediment supply to discharge led to fan incision, a basinward shift in the fan intersection point, and loss of accumulation space. In mid. and upper-fan settings, incised valleys and laterally extensive, moderately mature paleosols formed, marking the unconformable base of the depositional sequence. Throughout the interglacial period, relatively low accumulation space existed and deposition was confined to the distal areas of the fan. Rapid aggradation and, thus, accumulation space increase, in response to increased sediment supply during the next glacial event initially filled the incised valley with a fining-upward succession of relatively coarse-grained channel and overbank deposits that contain rare, immature paleosols. Upon filling of the incised valley, the intersection point stabilized near the fan apex. This led to unconfined, open-fan deposition, indicating that widespread accumulation space was available across most of the fan surface. These high-accumulation-space units consist of fluvial deposits from multiple, large glacial outwash channels that radiated outward from the proximally located intersection point. Sequence boundaries and units associated with accumulation-space cycles can be used to understand and predict facies distributions and stratigraphic packaging within glacially influenced fans similar to the Kings River alluvial fan


Particle and meteorological instrumentation were used to characterize ambient atmospheric conditions, aerosol size distributions, aerosol mass concentrations, and single particle size and chemical composition in Bakersfield, CA for the period January 9, 1999 through January 28, 1999. The sampling period included four distinct meteorological periods of stagnation, clearing, haze, and rain. Particle number and mass concentrations were the highest during the stagnation episode when a heavy and extensive fog developed. Mass and number concentrations also approached these high levels during the haze period. Single particle size and composition data from an aerosol time-of-flight mass spectrometer (ATOFMS) are used to provide unique continuous information on the diversity in types of particles present, the effects of meteorology on particle size and composition, and the distribution of important chemical species within individual particles. Aerosol composition and mixing state are found to vary with meteorological conditions, Single particle data show that carbonaceous aerosol with secondary ammonium, nitrate, and sulfate dominate the aerosol concentration during a stagnation period with a dramatic composition shift occurring to sodium type particles during the haze period. The aerosol is internally mixed with respect to carbon, nitrate, sulfate, and ammonium during the stagnation period. The mixing state changes significantly over the haze period when much greater diversity in the associations of chemical species within individual particles occurs


Geologic materials are an important source of airborne particulate matter less than 10 mum aerodynamic diameter (PM10), but the contribution of contaminated soil to concentrations of Pb and other trace elements in air has not been documented. To examine the potential significance of this mechanism, surface soil samples with a range of bulk soil Pb concentrations were obtained near five industrial facilities and along roadsides and were resuspended in
a specially designed laboratory chamber. The concentration of Pb and other trace elements was measured in the bulk soil, in soil size fractions, and in PM10 generated during resuspension of soils and fractions. Average yields of PM10 from dry soils ranged from 0.169 to 0.869 mg of PM10/g of soil. Yields declined approximately linearly with increasing geometric mean particle size of the bulk soil. The resulting PM10 had average Pb concentrations as high as 2283 mg/kg for samples from a secondary Pb smelter. Pb was enriched in PM10 by 5.36-88.7 times as compared with uncontaminated California soils. Total production of PM10 bound Pb from the soil samples varied between 0.012 and 1.2 mg of Pb/kg of bulk soil. During a relatively large erosion event, a contaminated site might contribute approximately 300 ng/m(3) of PM10-bound Pb to air. Contribution of soil from contaminated sites to airborne element balances thus deserves consideration when constructing receptor models for source apportionment or attempting to control airborne Pb emissions.


The aqueous-phase photoformation of hydroxyl radical ((OH)-O-. ) and singlet molecular oxygen (O-2((1)Delta (g)) or O-1(2)*) was characterized in winter fog waters collected in Davis, California. All of the samples studied formed (OH)-O-. and O-1(2)* upon illumination with simulated sunlight. Nitrite photolysis was a major source of (OH)-O-. in these samples, accounting for 47-100% of (OH)-O-. photoformation. Compared to calculated rates of gas-to-drop partitioning, in situ photoformation was a significant source of (OH)-O-. to all but the smallest fog drops, and was the dominant source of aqueous-phase IO(2)(*). Measured lifetimes of (OH)-O-. in the fog drops ranged from 0.38 to 1.5 mus. These values are significantly shorter than those predicted based on known drop constituents, indicating that uncharacterized compounds - likely organic - are significant sinks for (OH)-O-. in fog waters. Based on measured steady-state concentrations, both (OH)-O-. and O-1(2)* are likely to play significant roles in the transformations of trace species in fog drops. Hydroxyl radical appears to be a relatively significant sink for refractory compounds and a minor sink for reactive trace species. Conversely, IO(2)(*) will be a minor sink for refractory compounds but a significant sink for certain electron-rich reactive trace species.


The threshold values of indicator species and ratios delineating the transition between NOx and VOC sensitivity of ozone formation are assumed to be universal by various investigators. However, our previous studies suggested that threshold values might vary according to the locations and conditions. In this study, threshold values derived from various model simulations at two different locations (the area of Switzerland by UAM Model and San Joaquin Valley of Central California by SAQM Model) are examined using a new approach for defining NOy and VOC sensitive regimes. Possible definitions for the distinction of NO, and VOC sensitive ozone production regimes are given. The dependence of the threshold values for indicators and indicator ratios such as NOy, O-3/NOz, HCHO/NOy, and H2O2/HNO3 on the definition of NOx and VOC sensitivity is discussed. Then the variations of threshold values under low emission conditions and in two different days are examined in both areas to check whether the models respond consistently to changes in environmental conditions. In both cases, threshold values are shifted similarly when emissions are reduced. Changes in the wind fields and aging of the photochemical oxidants seem to cause the day-to-day variation of the threshold values. O-3/NOz and HCHO/NOy indicators are predicted to be unsatisfactory to separate the NOx and VOC sensitive regimes. Although NOy and H2O2/HNO3 provide a good separation of the two regimes, threshold values are affected by changes in the environmental conditions studied in this work. (C) 2001 Elsevier Science Ltd. All rights reserved


We present a study of the impact of initial concentrations on the modeling of photochemical oxidants. A simple impact model is employed, and an impact factor is defined which describes the ratio between the initial concentration and the time-dependent model concentration. The calculations have been carried out with data from a box model and a comprehensive three-dimensional (3-D) model. Results are for three different sites in the California San Joaquin Valley. By using data from the chemical box model a very active chemistry and rather high
concentrations are obtained since no transport processes are included. The impact of the initial concentrations is small already after 24 hours of model integration under such conditions. Results from the more realistic 3-D data show that the impact factor is reduced to less than 10% within the planetary boundary layer after 48 hours for nearly all chemical components studied. An exception is the sum of selected grouped species of O-x + NO2 + NO3 + N2O5 + HNO3 + PAN (sum of reservoir species for O-3) which is not below 10% before approximately after 3 days at the two least polluted sites. In the free troposphere the impact factors of the initial concentrations are large even after 3 days for paraffin, ethene, and isoprene. For selected grouped species of O-x + NO2 and O-x + NO2 + NO3 + N2O5 + HNO3 + PAN, large impact factors are still found after 3 days. The large impact of the initial concentrations in the free troposphere strongly complicates any model evaluation by use of measurements.


Comparisons were made between the predictions of six photochemical air quality simulation models (PAQSMs) and three indicators of ozone response to emission reductions: the ratios of O-3/NOz and O-3/NOy and the extent of reaction. The values of the two indicator ratios and the extent of reaction were computed from the model-predicted mixing ratios of ozone and oxidized nitrogen species and were compared to the changes in peak 1 and 8 h ozone mixing ratios predicted by the PAQSMs. The ozone changes were determined from the ozone levels predicted for base-case emission levels and for reduced emissions of volatile organic compounds (VOCs) and oxides of nitrogen (NOx). For all simulations, the model-predicted responses of peak 1 and 8 h ozone mixing ratios to VOC or NOx emission reductions were correlated with the base-case extent of reaction and ratios of O-3/NOz and O-3/NOy. Peak ozone values increased following NOx control in 95% (median over all simulations) of the high-ozone (>80 ppbv hourly mixing ratio in the base-case) grid cells having mean afternoon O-3/NOz ratios less than 5:1, O-3/NOy less than 4:1, or extent less than 0.6. Peak ozone levels decreased in response to NOx reductions in 95% (median over all simulations) of the grid cells having peak hourly ozone mixing ratios greater than 80 ppbv and where mean afternoon O-3/NOz exceeded 10: 1, O-3/NOy was greater than 8 : 1, or extent exceed 0.8. Ozone responses varied in grid cells where O-3/NOz was between 5:1 and 10:1, O-3/NOy was between 4: 1 and 8: 1, or extent was between 0.6 and 0.8. The responses in such grid cells were affected by ozone responses in upwind grid cells and by the changes in ozone levels along the upwind boundaries of the modeling domains.


Ambient aerometric data were used to predict whether ozone formation at specific times and locations in central California was limited by the availability of volatile organic compounds (VOC) or oxides of nitrogen (NOx). The predictions were compared with differences between mean weekday and weekend peak ozone values. The comparison with weekend and weekday ozone levels provided a means for empirically investigating the effects of VOC and NOx reductions on ozone formation, because the relative proportions and levels of ozone precursor species were significantly different on weekends than on weekdays. Weekend NOx levels averaged 27 percent lower than weekday levels at the time of the peak ozone hour. Daytime weekend levels of VOC species were also consistently lower than weekday values throughout the region, though the differences between weekends and weekdays were not always statistically significant (p<0.05). Site-to-site differences between weekend and weekday mean peak hourly ozone were related to whether ozone formation was VOC- or NOx-limited.


Fugitive dust emissions contribute a large fraction to the ambient PM10 concentrations in California's San Joaquin Valley. Some of the major sources of this dust include agricultural activities, construction sites, paved and unpaved roads, and wind erosion. The predictive equations recommended by USEPA to estimate fugitive dust emissions from soil sources were developed through empirical relationships between measured emission rates and the soil's dry silt content (the fraction less than 75 mum physical diameter by dry sieving). The soil's dry silt content is not readily available, though, so this parameter is not widely useful for estimating PM10 emission potential. The goal of the research described here is to develop a method that will improve predictions of PM10 emissions from soils. A
method was developed to measure the potential for PM10 dust production from soil using samples collected in California's San Joaquin Valley and a dust resuspension chamber. The PM10 index is highly correlated to the soil's sand or clay content. In fact, the clay content of the soil is an excellent predictor of the PM10 index; thus, it is a useful measure of the ability of soil to emit PM10.


Maps of temporal and spatial values of annual averages of daily particulate matter (PM10) concentrations were generated throughout the state of California using uncertain forms of physical data. The PM10 estimates were derived in an integrated space/time domain using the Bayesian maximum entropy (BME) mapping approach of modern spatiotemporal geostatistics. The approach possesses some interesting features which allow an insightful analysis of the PM10 space/time distribution. A complete stochastic characterization of the pollutant involves the probability density function of the PM10 map, which is the result of a rigorous knowledge-integration process. This process is considerably flexible, it can account for several physical knowledge bases and sources of uncertainty, and it may involve Bayesian or material conditionalization rules. Taking advantage of BME's flexibility, PM10 estimates were chosen which offered an appropriate representation of the real distribution in space/time, and a meaningful assessment of the representation accuracy was derived. Depending on the space scales/timescales considered, the PM10 distributions depicted considerable levels of variability, which may be associated with topographic features, climatic changes, seasonal patterns, and random fluctuations. The importance of integrating soft information available at surrounding sites as well as at the estimation points themselves was discussed. Comparisons were designed which demonstrated the usefulness of the BME-based maps to represent PM10 distributions in space/time. Areas were identified where the annual PM10 geometric mean reached or exceeded the California standard, which is valuable information for regulatory purposes.


Measurements collected using five real-time continuous airborne particle monitors were compared to measurements made using reference filter-based samplers at Bakersfield, CA, between December 2, 1998, and January 31, 1999. The purpose of this analysis was to evaluate the suitability of each instrument for use in a real-time continuous monitoring network designed to measure the mass of airborne particles with an aerodynamic diameter less than 2.5 μm (PM2.5) under wintertime conditions in the southern San Joaquin Valley. Measurements of airborne particulate mass made with a beta attenuation monitor (BAM), an integrating nephelometer, and a continuous aerosol mass monitor (CAMM) were found to correlate well with reference measurements made with a filter-based sampler. A Dusttrak aerosol sampler overestimated airborne particle concentrations by a factor of similar to 3 throughout the study. Measurements of airborne particulate matter made with a tapered element oscillating microbalance (TEOM) were found to be lower than the reference filter-based measurements by an amount approximately equal to the concentration of NH4NO3 observed to be present in the airborne particles. The performance of the Dusttrak sampler and the integrating nephelometer was affected by the size distribution of airborne particulate matter. The performance of the BAM, the integrating nephelometer, the CAMM, the Dusttrak sampler, and the TEOM was not strongly affected by temperature, relative humidity, wind speed, or wind direction within the range of conditions encountered in the current study. Based on instrument performance, the BAM, the integrating nephelometer, and the CAMM appear to be suitable candidates for deployment in a real-time continuous PM2.5 monitoring network in central California for the range of winter conditions and aerosol composition encountered during the study.

Two collected micro-orifice uniform deposit impactors (MOUDIs) and a filter-based sampler were used to measure the size distribution and chemical composition of atmospheric particulate matter at Bakersfield, CA, between January 14 and 23, 1999. The peak number concentration of airborne ultrafine particles measured was $1.45 \times 10^{11}$ m$^{-3}$, which is a factor of approximately 3 higher than the peak airborne ultrafine particle number concentration measured previously in Pasadena, CA. Chemical analysis revealed that airborne ultrafine particles ($D_p < 0.1$ micron) at Bakersfield contained significant amounts of water-soluble species, including calcium, sodium, ammonium ion, nitrate, and sulfate. Other chemical species detected in the ultrafine size range included potassium, iron, copper, zinc, and strontium. A balance of aqueous ions showed that ultrafine particles were alkaline in nature with calcium acting as the dominant cation. Bulk samples of airborne particles with diameter less than 2.0 microns (PM2.0) were essentially neutral, but particle acidity was found to be a strong function of particle size. The results of this experiment suggest that areas deep in the human lung that preferentially collect particles in the ultrafine size range could be exposed to locally acidic or alkaline conditions even if the integrated airborne particle complex is essentially neutral.


Mesoscale meteorological models are being used to provide inputs of winds, vertical temperature and stability structure, mixing depths, and other parameters to atmospheric transport and dispersion models. An evaluation methodology is suggested and tested with simulations available from four mesoscale meteorological models (Fifth-Generation Pennsylvania State University-National Center for Atmospheric Research Mesoscale Model, Regional Atmospheric Modeling System, Coupled Ocean-Atmosphere Mesoscale Prediction System, and Operational Multiscale Environmental Model with Grid Adaptivity). These models have been applied by others to time periods of several days in three areas of the United States (Northeast, Lake Michigan area, and central California) and in Iraq. The authors' analysis indicates that the typical root-mean-square error (rmse) of hourly averaged surface wind speed is found to be about 2-3 m s$^{-1}$ for a wide range of wind speeds for the models and for the geographic regions studied. The rmse of surface wind direction is about 50 degrees for wind speeds of about 3 or 4 m s$^{-1}$. It is suggested that these uncertainties in wind speeds and directions are primarily due to random turbulent processes that cannot be simulated by the models and to subgrid variations in terrain and land use, and therefore it is unlikely that the errors can be reduced much further. Model simulations of daytime mixing depths are shown to be often within 20% of observations. However, the models tend to predict weaker inversions than are observed in interfacial layers capping the mixing depth. The models also underestimate the vertical temperature gradients in the lowest 100 m during the nighttime, which implies that the simulated boundary layer stability is not as great as that observed, suggesting that the rate of vertical dispersion may be overestimated. The models would be able to simulate better the structure of shallow inversions if their vertical grid sizes were smaller.


A series of twelve intensively monitored 1-hr CO dispersion studies were conducted near Davis, CA, in winter 1996. The experimental equipment included twelve CO sampling ports at elevations up to 50 m, three sonic anemometers, a tethered station, aircraft measurements of wind and temperature profile aloft, and a variety of conventional meteorological equipment. The study was designed to explore the role of vehicular exhaust buoyancy during worst-case meteorological conditions, such as low winds oriented in near-parallel alignment with the road during a surface-based nocturnal inversion. From the study, field estimates of the CO emission factor (EF) from a California vehicle fleet were computed using two different methods. The analysis suggests that the CT-EMFAC/EMFAC (EMission FACtor) models currently used to conduct federal conformity modeling significantly overpredict CO emissions for high-speed, free-flowing traffic on California highways.


Vertical profiling with point samplers is an accepted method for quantifying the fluxes of PM$_{10}$ from point-point fugitive dust sources, but is limited by uncertainty in estimates of the actual height of the dust plume, especially for
plumes that exceed the highest sampling height. Agricultural land preparation operations in the San Joaquin Valley were monitored using upwind-downwind vertical PM10 profiles and data collected during the first successful experiment to include light detection and ranging (lidar), in 1998, were analyzed to provide modeling criteria for the 1996 and 1997 data. A series of six comprehensive PM10 tests with concurrent lidar data was examined to: (a) develop a framework for analyzing upwind-downwind point PM10 concentration profiles of land preparation operations (disking, listing, root cutting, and ripping) and (b) identify conditions under which the field sampling strategies affect the reproducibility of PM10 concentration measurements. Lidar data were used to verify that the plume heights and shapes extrapolated from the point sampler vertical profiles adequately described the plumes. The shortcomings of the vertical profiling technique and lidar methods are discussed in the light of developing efficient robust methods for accurate PM10 emissions quantification from complex non-point sources. (C) 2001 Elsevier Science Ltd. All rights reserved


Emission factors for agricultural operations are needed in order to develop reliable PM10 emissions inventories and air quality models for air basins with significant agricultural land use. A framework was developed to analyze the PM10 vertical profiles collected downwind of tilling operations in the San Joaquin Valley. The methods calculate emission factors on the basis of profile shape and assign quality ratings to each land preparation test. Uncertainties in the calculated emission factors and plume heights were used as one criterion for evaluating the relative quality of the reported emission factor. Other quality ratings were based on the magnitude of the difference in measured up- and downwind concentrations, wind direction, whether the tests were conducted near the edges of the field, and how well the proposed model fit the profile data. The emission factors from different operations were compared taking the quality of the emission factor into account. Plume heights and emission factors for 24 valid test profiles ranged from 2 to 20m (mean = 9.8; SD = 3.6; median = 9.8) and zero to 800 mg m(-2) (mean = 152; SD = 240; median = 43), respectively. Key environmental properties governing PM10 emission from these operations include relative humidity, soil moisture and vertical temperature gradient. Surprisingly, no discernable relationships were found between implement type or wind speed and the measured emission factors. (C) 2001 Elsevier Science Ltd. All rights reserved


A model that treats nesting of gas, size- and composition-resolved aerosol, radiative, and meteorological parameters from the global through urban scales (<5-km grid spacing) was developed. The model treats multiple one-way-nested layers and multiple air quality and meteorological domains in each layer between the global and the urban scales. This latter feature allows forecast of air pollution and weather at several urban or regional sites during the same simulation. Regardless of the number of domains used during a single continuous simulation, the central memory required never exceeds 1.5 times and 2.1 times that of the largest domain for gas and gas/aerosol simulations, respectively. A submodule was developed for all domains to treat ground temperatures, latent heat fluxes, and sensible heat fluxes over subgrid soil types (with and without vegetation), water, sea ice, and urban areas. Urban areas are divided into road surfaces, rooftops, vegetation, and bare soil. Snow is treated over all surface types. The global-through-urban model is applied in a companion paper to study elevated ozone, ozone in national parks, and weather during a field campaign in northern and central California


The GATORG-GCMM global- through urban-scale nested air pollution/weather forecast model was applied to study ozone layers aloft, ozone in national parks, and weather during the August 3-6, 1990, SARMAP field campaign in northern and central California. Predictions of meteorological variables and mixing ratios of 20 gases were compared with observations. With nesting, the normalized gross error in predicted near-surface Kelvin temperatures was 1.02% and that in near-surface ozone above 50 ppbv was 22.5%. Statistics from outer nested domains indicated
that the coarser the grid spacing, the greater the underprediction of ozone. In the absence of nesting, statistics
deteriorated but not a lot. The model simulated observed nighttime ozone layers aloft and daytime ozone mixed
layers in the San Joaquin Valley and San Francisco Bay Area. It also simulated observed daytime and nighttime
ozone layers aloft over the San Francisco Bay near Hayward. The formation mechanism of these layers is discussed.
The model was used to estimate that about 47-57% of peak daytime ozone in Sequoia and Yosemite National Parks
during SARMAP was produced by anthropogenic gases, 13-3% was produced by biogenic hydrocarbons, and the
rest (about 40%) was background.

Kahn, R., Banerjee, P., McDonald, D., Martonchik, J., 2001. Aerosol properties derived from aircraft

The first generic and climatological aerosol retrievals using AirMISR data are presented. Multiangle observations at
672 and 867 nm, in a cloud-free region over dark water in Monterey Bay on June 29, 1999, yield complementary
generic and climatological results. The generic retrieval produces cross-section-weighted, column-mean aerosol
properties: midvisible aerosol optical depth between 0.05 and 0.10, with a preference for values on the low side of
the range, particle number-mean characteristic radius between 0.25 and 0.45 μm, and imaginary index of refraction
<0.004, with 0.0 as the most likely value. These properties correspond to a "medium-to-large, spherical" column-
average particle. The climatological retrieval identifies a maritime air mass, having a total aerosol optical depth
about 0.1, and mixing ratio for sea-salt particles (large, spherical) of 50%, based on optical depth in MISR Band 2,
and 40% for the sulfate plus carbonaceous (medium, spherical) components, to an accuracy of about +/- 15%. These
results are in good agreement with the limited nearby surface-based and aircraft observations available. The analysis
also shows that over dark water, pixel-to-pixel scene variability can contribute more to the retrieval uncertainty than
camera calibration and that high spatial variance of the reflectance, in addition to geometric considerations, is a
better indicator of Sun glint contamination than geometry alone. This work represents an early step toward the goal
of using MISR multiangle data to add spatial detail and information about temporal variability to the global aerosol
climatology.

Kirchstetter, T.W., Corrigan, C.E., Novakov, T., 2001. Laboratory and field investigation of the adsorption
of gaseous organic compounds onto quartz filters. Atmospheric Environment 35 (9), 1663-1671.

A common method for measuring the mass of organic carbon in airborne particulate matter involves collection on a
quartz filter and subsequent thermal analysis. If unaccounted for, the adsorption of organic gases onto quartz filters
will lead to the overestimation of aerosol organic carbon concentrations (positive artifact). A recommended method
of correction for the positive artifact involves sampling with a backup filter. Placed behind either the primary quartz
filter, or behind a Teflon filter and collected in parallel with the primary quartz filter, the carbon content of the
quartz backup filter is a measure of the adsorbed organic material on the primary quartz filter. In this paper, we
illustrate the application of this technique to samples collected in Berkeley, California. While the tandem quartz
filter method can be successfully applied to correct for the positive artifact, we discuss two cases when this method
will fail. We have found that the capacity for adsorption of organic gases is not uniform for all filters. Instead, filters
manufactured by the same company, but having different lot numbers, exhibit variable adsorption capacity. Thus, a
filter pair composed of filters from different lots may lead to significant under- or overestimation of particulate
organic carbon concentration. Additionally, we have observed that the tandem filter method under-corrects for the
positive artifact if the sampling time is short (few hours). Laboratory experiments with vapors of single organic
compounds corroborate results based on ambient samples. The evolution of adsorbed organic gases, particularly
polar compounds, during thermal analysis indicates that a single compound may experience two distinct adsorbent-
adsorbate binding energies. Adsorbed gases may co-evolve with particles at temperatures in excess of 250 degreesC.

Koracin, D., Dorman, C.E., 2001. Marine atmospheric boundary layer divergence and clouds along

The authors have performed a numerical experiment using Mesoscale Model 5 (MM5) with a horizontal resolution
of 9 km to simulate hourly atmospheric dynamics and thermodynamics along the U.S. California coast for all of
June 1996. The MM5 results were evaluated using more than 18 000 data points from wind profilers, radiosondes,
buoys, and land stations; the results support the use of modeled dynamics for reliable monthly statistics and
calculation of diurnal variations. Month-long mesoscale simulations of the marine atmospheric boundary layer
(MABL) and satellite observations have been used to investigate the diurnal variation of near-shore and farther
offshore clouds along the U.S. California coast. The authors extended the usual model evaluation with respect to
time series and power spectrum analysis to investigate a link between the evaluated dynamics and satellite-derived
cloudiness. Two distinct types of cloudiness variation were revealed. One is in the near-shore zone, extending
approximately 100 km in the offshore direction, where the diurnal variation of cloudiness develops in response to
the formation of MABL wind divergence and convergence fields. Each of the five major capes between southern
Oregon and southern California has a satellite-derived, low-cloud maximum albedo on the leeward side and a
minimum on the windward side that closely corresponds to "expansion fans" and "compression bulges." The
expansion fan is associated with a divergence field of fast horizontal winds, shallow MABL, and high Froude
number. The compression bulge is associated mainly with relatively weak winds (convergent or slightly divergent),
a deeper MABL, and smaller Froude number. Simulated divergence in the expansion fan areas shows a significant
diurnal trend with the maximum during the late morning through early afternoon. In the compression bulge, either
the divergence is an order of magnitude less, or the flow becomes convergent. Going westward, the MABL
divergence becomes an order of magnitude less at distances of 30-40 km from the coastline. Since the expansion fan
is characteristic of the MABL, the effect of the divergence field decays rapidly in the vertical and, due to mass
continuity, reverses into a convergent flow above the MABL. Farther offshore, the cloudiness variation is at a
minimum around midday as well, but that is mainly a consequence of radiative heat transfer effects within the cloud.
Marine atmospheric boundary layer divergence does not have a significant diurnal trend in that area. Daytime
offshore cloud clearing begins first in the northern domain, where the marine layer and clouds are shallower. The
clearing propagates southward until the marine layer and clouds are too deep; generally the clouds persist
throughout the entire day. The study shows the importance of dynamics on the evolution of observed cloudiness and
constitutes an approach to indirectly evaluate modeled dynamics using satellite-derived cloudiness


California's Phase 2 Reformulated Gasoline (CaRFG), introduced early in 1996, represents an important step toward
attainment of ozone standards. Studies of vehicle emissions and ambient air quality data have reported substantial
reductions of ozone precursors due to CaRFG. This study uses daily measurements of regional ozone and
meteorology to estimate the effect of CaRFG on ozone concentrations in three areas of California. In each area, a
regression model was used to partially account for the daily effects of meteorology on area-wide ozone maxima for
May-October. The statistical models are based on combinations of air temperature aloft (similar to 5000 ft), surface
air temperatures, and surface wind speeds. Estimated ozone benefits were attributed to CaRFG after accounting for
meteorology, which improved the precision of the estimates by approximately 37-57% based on a resampling
analysis. The ozone benefits were calculated as the difference in ozone times the proportion of the reductions of
hydrocarbons and nitrogen oxides attributed to CaRFG by the best available emission inventories. Ozone benefits
attributed to CaRFG (with similar to 90% confidence) are 8-13% in the Los Angeles area, -2-6% in the San
Francisco Bay area overall with greater benefits in two major subregions, and 3-15% in the Sacramento area

Fresno Exposure Studies as functions of size, season, and meteorology. Aerosol Science & Technology 34 (1),
66-74.

Two 1999 Fresno exposure studies took place in February (winter season) and April/May (spring season) for
periods of four weeks each. During that time, nearly continuous measurements of outdoor aerosol concentrations
were made with a TSI Scanning Mobility Particle Sizer (SMPS) and a PMS optical particle counter (LASX). These
instruments provide particle size distribution information from about 0.01 to 3 mum. Although the primary
concentration measurements were performed with integrated samplers, the SMPS/LASX combination provided
useful information on the real-time variations of concentration and particle size distributions. This paper describes
the agreement between the real-time instrumentation and the integrated measurements and examines some of the
information available from the SMPS/LASX combination. In particular, two different types of aerosols contributing
to PM2.5 were deduced from the instrumental data.

the California coastal zone by dynamic initialization of the marine boundary layer. Monthly Weather Review
129 (2), 275-294.
Few data are available over the world's oceans to characterize the initial atmospheric state in numerical models. Objective analysis in these regions is largely based on forecast fields obtained from a global model and used as the background (“first guess”). Unfortunately, global models often do not resolve the marine boundary layer (MBL) structure, which is important for simulating stratus clouds, coastal zone circulations, and electromagnetic wave propagation. Furthermore, initialization of the MBL in the coastal zone and data-sparse oceanic regions poses a challenging mesoscale modeling problem. The goal of this study, therefore, is to improve warm-season short-term mesoscale numerical prediction of California coastal zone meteorology by improving the model initial conditions in the coastal zone and offshore data-void regions. Initialization strategies tested include standard static and dynamic techniques and a new marine boundary layer initialization scheme that uses a dynamic initialization based on the remarkably consistent summertime marine-layer climatology of the eastern Pacific Ocean. The model used in this study is the Pennsylvania State University-National Center for Atmospheric Research fifth-generation Mesoscale Model (MM5). Experiments were performed for a typical summertime case (3-4 Aug 1990) to determine an initialization strategy suitable for coastal one forecasting over the northeast Pacific. The meteorology in this case was dominated by quasi-stationary synoptic-scale high pressure over the ocean. Results from the model experiments were verified using 6-hourly coastal rawinsonde observations and visible range satellite cloud imagery. More accurate initial conditions were obtained by using dynamic initialization compared to static initialization. The most accurate initialization and short-range model forecasts were produced by assimilating a combination of observed data over land and climatological information offshore during the 12-h preforecast period. Through the 24-h forecast period, errors in the coastal zone PBL depth and marine inversion strength were reduced by 65% and 41%, respectively, compared to the static-initialization control experiments. Without proper initialization of the offshore MBL, coastal zone forecasts degraded with time due to the long timescale of physical processes responsible for generating the MBL structure over cold, low-latitude oceans. Therefore, improvement of the model initial conditions in the California coastal zone by assimilation of climatological information offshore in combination with observed conditions near the coast proved to be an effective strategy for increasing short range forecast accuracy.


The diesel engine is the most efficient prime mover commonly available today. Diesel engines move a large portion of the world's goods, power much of the world's equipment, and generate electricity more economically than any other device in their size range. But the diesel is one of the largest contributors to environmental pollution problems worldwide, and will remain so, with large increases expected in vehicle population and vehicle miles traveled (VMT) causing ever-increasing global emissions. Diesel emissions contribute to the development of cancer; cardiovascular and respiratory health effects; pollution of air, water, and soil; soiling; reductions in visibility; and global climate change. Where instituted, control programs have been effective in reducing diesel fleet emissions. Fuel changes, such as reduced sulfur and aromatics content, have resulted in immediate improvements across the entire diesel on- and off-road fleet, and promise more improvements with future control. In the United States, for example, 49-state (non-California) off-road diesel fuel sulfur content is 10 times higher than that of national on-road diesel fuel. Significantly reducing this sulfur content would reduce secondary particulate matter (PM) formation and allow the use of control technologies that have proven effective in the on-road arena. The use of essentially zero-sulfur fuels, such as natural gas, in heavy-duty applications is also expected to continue. Technology changes, such as engine modifications, exhaust gas recirculation, and catalytic aftertreatment, take longer to fully implement, due to slow fleet turnover. However, they eventually result in significant emission reductions and will be continued on an ever-widening basis in the United States and worldwide. New technologies, such as hybrids and fuel cells, show significant promise in reducing emissions from sources currently dominated by diesel use. Lastly, the turnover of trucks and especially off-road equipment is slow; pollution control agencies need to address existing emissions with in-use programs, such as exhaust trap retrofits and smoke inspections. Such a program is underway in California. These and other steps that can be continued and improved will allow the use of the diesel engine, with its superior fuel consumption, to continue to benefit society while greatly reducing its negative environmental and health impacts. The next ten years can and must become the "Decade of Clean Diesel."


Although amino compounds are seemingly ubiquitous in atmospheric particles and deposition, little is known of their fate in the troposphere. We report here on the fate of 21 amino acids and alkyl amines in fog waters from Davis, California, illuminated with simulated sunlight or monochromatic light. In all experiments four amino acids - histidine (His), methionine (Met), tryptophan (Trp), and tyrosine (Tyr) - consistently decayed, with half-lives that ranged from similar to 1 h (Met) to similar to 23 h (Tyr) in midday, winter-solstice sunlight at Davis, CA (solar zenith angle = 62 degrees). Half-lives for the remaining amino compounds examined were typically > 45 h in our experiments. Reactions with photoformed hydroxyl radical ((OH)-O-) and singlet molecular oxygen (O-2((1)Delta (g)) or O-1(2)*) accounted for essentially all of the loss of His and Tyr, the less reactive of the four amino acids that consistently decayed, but were minor sinks for the more reactive compounds (Met and Trp). Additional experiments revealed that methionine sulfoxide (MetSO) was formed with a yield of 58-88% during the oxidation of methionine, suggesting that the ratio of MetSO to Met might be a useful chemical marker for the age of atmospheric particles and drops. Other products expected from the transformation of amino compounds include ammonia, organic acids, and possibly mutagenic nitrosoaromatics.

To complement our laboratory experiments, we also calculated rates of transformations of amino acids in near-neutral pH fog drops under ambient conditions. These calculations reveal that ozone should be a major sink for amino acids and that half-lives for many amino acids in ambient fog drops will be much shorter than those determined in our photochemistry experiments. Overall, our results indicate that reactions in atmospheric condensed phases will transform amino nitrogen compounds (including free amino acids as well as proteins and peptides) and, consequently, increase the bioavailability of nitrogen in atmospheric deposition.


A challenging problem in numerical weather prediction is to optimize the use of meteorological observations in data assimilation. Even assimilation techniques considered "optimal" in the "least squares" sense usually involve a set of assumptions that prescribes the horizontal and vertical distributions of analysis increments used to update the background analysis. These assumptions may impose limitations on the use of the data that can adversely affect the data assimilation and any subsequent forecast. Virtually all widely used operational analysis and dynamic-initialization techniques assume, at some level, that the errors are isotropic and so the data can be applied within circular regions of influence around measurement sites. Whether implied or used directly, circular isotropic regions of influence are indiscriminate toward thermal and wind gradients that may reflect changes of air mass. That is, the analytic process may ignore key flow-dependent information available about the physical error structures of an individual case. Although this simplification is widely recognized, many data assimilation schemes currently offer no practical remedy. To explore the potential value of case-adaptive, noncircular weighting in a computationally efficient manner, an approach for structure-dependent weighting of observations (SWOBS) is investigated in a continuous data assimilation scheme. In this study, SWOBS is used to dynamically initialize the PSU-NCAR Mesoscale Model using temperature and wind data in a series of observing-system simulation experiments. Results of this heuristic study suggest that improvements in analysis and forecast skill are possible with case-specific, flow-dependent, anisotropic weighting of observations.


Coast-parallel low-level jets are commonplace in the marine boundary layer off the west coast of the United States during summer. A field study was conducted in early summer of 1997 to document the forcing of boundary layer winds in the near-coastal environment off California. On 8 June 1997 the Wyoming King Air collected data along a 350-km stretch of coastal margin from Cape Mendocino to San Francisco in order to examine the interaction between the coastal topography and the low-level jet. During the course of the flight, 32 soundings were conducted. The maximum speed of the coastal jet was found near the top of the marine boundary layer at altitudes from 200 to 600 m. Analysis of the data revealed a westward increase in the height of the marine boundary layer and maximum jet wind speeds. Strongest jet winds were observed southwest of Cape Mendocino with a maximum speed of 28 m s(-1). The coastal jet was characterized by a broad horizontal extent. Wind maxima were found at distances approximately 30 km to more than 100 km offshore. Hydraulic features such as jumps and expansion fans have previously been observed downwind of coastal capes and points along the California coast. The flow upwind of Cape Mendocino and Point Arena was found to be supercritical, but the King Air data showed that accelerations
associated with possible expansion fan phenomena were minimal. It is proposed that the sloping inversion at the top of the marine boundary layer and attendant coastal jet are fundamentally the result of a geostrophic adjustment process arising because of the horizontal temperature contrast between the cool ocean and warm continent. This view emphasizes that the coastal jet is a ubiquitous, large-scale feature of the summertime coastal environment. Terrain-induced wind speed variations associated with expansion fans and hydraulic jumps only modulate the primary jet structure.


The formation of secondary ammonium nitrate during the 1995 Integrated Monitoring Study (IMS95) in San Joaquin Valley, CA was investigated using a box model that simulates the atmospheric chemistry and gas/particle partition of inorganic compounds. The concentration of particulate matter (PM) nitrate was found to be sensitive to reductions in VOC emissions. Nitric acid, rather than ammonia, was the limiting reagent in the formation of PM nitrate. The formation of nitric acid was more sensitive to the availability of oxidants than that of NOX. Oxidant chemistry in wintertime conditions in the San Joaquin Valley was shown to be VOC-sensitive. In fact, a decrease in NOx emissions may have the counter-intuitive effect of increasing PM nitrate.


Few data are available on the ammonia emissions of large-scale outdoor animal facilities in arid climates such as those found in California’s San Joaquin Valley. Passive samplers provide an ideal tool for studying such large and heterogeneous area sources, because they are inexpensive, portable, and fully self-contained. UC Davis passive ammonia samplers incorporate modifications on a previous design, the Willems Badge, for ease of analysis. Citric acid was chosen as a coating medium though it performed as well as oxalic, sulfuric, and tartaric acids. Zefluor PTFE prefilters were used instead of Teflo though both showed the same resistance to diffusion. Citric acid-coated filters were stable for up to 10 weeks, though more so if stored in Petri dishes rather than in the sampling cassettes themselves. The most effective sampler position was found to be in a face-down configuration fixed into the wind to avoid debris and sensitivity to wind shifts. A new method of rinsing the filters within the cassettes by dropwise elution proved highly effective, with 85% of the ammonium being removed in the first 3 mL of the 10-mL rinse volume. Application of the sampler at a dairy in the Joaquin Valley revealed large variations in concentrations at different locations along the downwind fenceline, which correlated with animal populations and activities directly upwind. In addition, large variations in ammonia concentrations were observed in relation to time of day and animal activity. Field blank loadings were of 1.40 mug NH4-N/filter (SD = 0.74 mug NH4-N/filter). Replicate passive samplers placed side-by-side during sampling episodes agreed with a slope of 1.010 (standard error = 0.028). Impingers were used as a reference method to obtain the correlation between filter loadings and air concentrations, yielding an "effective sampling rate" for the passive samplers of 6.18 L/h (error = 0.23 L/h) Using a theoretical calculation that "effective flow rate" was calculated to be 6.29 L/h. The method's limit of detection was found to be 82.5 mug NH4- N/m(3). Wind speed was found to theoretically affect linearity of sampler response only for speeds less than 0.92 m/s.


Six radiation fog episodes were sampled in the Central Valley of California during winter 1998/1999. Drop size-resolved fog samples were sampled using a size-fractionating Caltech active strand cloudwater collector (sf-CASCC). The sf-CASCC collects a large fog drop sample, comprised mainly of drops larger than 17 mum diameter, and a small fog drop sample, comprised mainly of drops with diameters between 4 and 17 mum. The fog pH was found to vary between approximately pH 5.3 and 6.8, with the pH of the large fog drop sample typically several tenths of a pH unit higher than the simultaneously collected small fog drop sample. At these high pH values, dissolved sulfur dioxide can be rapidly oxidized by a variety of chemical pathways and also can react quickly with dissolved formaldehyde to form hydroxymethanesulfonate. The amount of sulfate produced by aqueous-phase oxidation during each fog episode was determined by application of a tracer technique. The ratio of large: small drop
S(IV) oxidation was compared with theoretically predicted ratios of large: small drop S(IV) oxidation rates. Although the higher pH of the large fog drops should promote more rapid S(IV) oxidation by ozone, finite rates of mass transport into the large drops and an increasing rate of complexation of S(IV) by formaldehyde at high pH combine to depress theoretically predicted rates of aqueous sulfate production in large fog drops below rates expected for small fog drops. This prediction is supported by the tracer results that indicate the concentration of sulfate resulting from aqueous-phase S(W) oxidation in small drops generally exceeded the concentration formed in large drops. These findings stand in sharp contrast to observations in acidic clouds at Whiteface Mountain, New York, where hydrogen peroxide was determined to be the dominant S(IV) oxidant and the rate of S(IV) oxidation was found to be independent of drop Size.


Acidity in crude oils has long been a problem for refining. Knowledge of the detailed chemical composition of the acids responsible for corrosion can facilitate identification of problem crude oils and potentially lead to improved processing options for corrosive oils. A highly aerobically biodegraded crude from the San Joaquin Valley, which has a long history of causing corrosion problems during refining was the subject of this study. The oil was first extracted with base, then acidified and extracted with petroleum ether. A portion of the resulting acid fraction was methylated. The unmethylated extract was analyzed by FTIR, NMR, and the methylated sample was analyzed by high-resolution mass spectrometry (HRMS). Over 96% of the ions observed in HRMS have been assigned reliable formulas. Considerably greater functionality is seen in this sample than would be presumed from the "naphthenic acid" title typically assigned to these species. Although over 60% of the compounds contained two or more oxygens, compounds containing only oxygen heteroatoms accounted for less than 10% of the acidic compounds identified. Approximately one-half of the species contained nitrogen and about one-fourth contained sulfur. It is believed that microbial degradation is a major source of these acidic components. It was also observed that acid species with higher degrees of heteroatom substitution generally also had a higher degree of saturation than those species having less heteroatoms, possibly due to impeded migration of highly substituted, less-saturated species.


Particle size distributions were measured indoors and outdoors of a single, detached residence during the Fresno particulate matter exposure studies in winter (February 1-28, 1999) and spring (April 18-May 16, 1999). Data was collected for particle sizes ranging from about 0.01 to 2.5 µm. These data were used to investigate the temporal relationships between indoor and outdoor aerosol concentrations and to determine particle deposition rates and penetration factors for discrete particle sizes. Indoor/outdoor aerosol concentration ratios for particle sizes >1 µm were diurnally variable with highest ratios occurring during daytime (6:00-18:00) due to resuspension from indoor activities. Daytime and nighttime (19:00-7:00) aerosol concentration ratios were very similar for particle sizes <1 µm. Particle deposition rates were determined by measuring the decay in indoor aerosol concentrations after indoor levels were elevated by infiltration of native ambient aerosols, Deposition rates varied depending on particle size and were consistent with model results up to about 0.4 µm. The experimentally determined deposition rates were considerably higher than model results at larger particle sizes, suggesting the possibility of an additional indoor loss mechanism. Penetration factors were determined to be less than unity for all particle sizes and ranged from 0.5 to 0.9.


The chemical mass balance (CMB) receptor model has apportioned volatile organic compounds (VOCs) in more than 20 urban areas, mostly in the United States. These applications differ in terms of the total fraction apportioned, the calculation method, the chemical compounds used in the calculation, the apportionment units, and the source profiles applied. Nevertheless, they show similar results for VOC fractions contributed by different sources. Gasoline vehicle exhaust, liquid gasoline, and gasoline evaporation contribute up to 50% or more of the ambient VOCs in many of these studies. Relative motor vehicle source contributions determined by CMB were similar to or larger than their proportions in emissions inventories. Coatings and solvent contributions from CMB were much
lower than the proportions attributed to these sources in current emissions inventories. Several measurement and reporting conventions would facilitate CMB analyses of VOC data sets.


Although organic nitrogen (ON) has been found to be a ubiquitous and significant component in wet and dry deposition, almost nothing is known about its concentration or composition in fog waters. To address this gap, we have investigated the concentration and composition of ON in fog waters collected in Davis, in California's Central Valley. Significant quantities of dissolved organic nitrogen (DON) were found in these samples, with a median concentration of 303 μM N (range = 120-1630 μM N). DON typically represented approximately 16% of the total dissolved nitrogen (inorganic + organic) in Davis fog waters. The median concentration of nitrogen in free amino acids and alkyl amines was 16 μM N (range = 3.8-120 μM N), which accounted for 3.4% of the DON in Davis fogs. Thus, although the absolute concentrations of free amino compounds were significant, they were only a minor component of the DON pool. Combined amino nitrogen (e.g., proteins and peptides) was present at higher concentrations and accounted for 6.1-29% (median = 16%) of DON. Overall, free and combined amino compounds typically accounted for a median value of 22% of DON in the fog waters. The high concentrations of DON found, and the fact that amino and other N-containing organic compounds can serve as nitrogen sources for microorganisms and plants, indicate that atmospheric ON compounds likely play an important role in nitrogen cycling in the Central Valley. In addition, due to the basicity of some N functional groups, ON compounds likely contribute to the previously observed acid buffering capacity of Central Valley fog waters. Finally, a comparison of fog waters with fine particles (PM2.5) collected from the same site during the same period of time indicated that the median concentrations (mol N m(-3)-air) of total water-soluble ON, free amino nitrogen and total amino nitrogen were very similar in the fog water and PM2.5. Given the high water solubility of many organic N compounds, this result suggests that ON might contribute to the hygroscopic properties of atmospheric particles.


A thermodynamic equilibrium model was used to investigate the response of aerosol NO3 to changes in concentrations of HNO3, NH3, and H2SO4. Over a range of temperatures and relative humidities (RHs), two parameters provided sufficient information for indicating the qualitative response of aerosol NO3. The first was the excess of aerosol NH4+ plus gas-phase NH3 over the sum of HNO3, particulate NO3, and particulate SO42- concentrations. The second was the ratio of particulate to total NO3 concentrations. Computation of these quantities from ambient measurements provides a means to rapidly analyze large numbers of samples and identify cases in which inorganic aerosol NO3 formation is limited by the availability of NH3. Example calculations are presented using data from three field studies. The predictions of the indicator variables and the equilibrium model are compared.


Changes in gasoline formulation will be required as use of methyl tert-butyl ether (MTBE) is phased out. Changes in evaporative emissions of volatile organic compounds (VOCs) may be of concern in cases where ethanol is added to gasoline to replace MTBE. Regular, mid-, and premium grade gasoline samples containing ethanol were collected in the San Francisco Bay area during May 1999. The compositions of the liquid fuel samples and their headspace vapors were measured. Ethanol contents ranged from 3.25 to 9.65 wt % in the liquid fuel samples. Four compounds (n-butane, n-pentane, 2-methylbutane, and ethanol) together accounted for >50% of the total headspace vapor mass. The partial pressure of ethanol in headspace vapors increased only modestly, despite a 5-fold increase in ethanol in the liquid samples of premium vs regular grade gasoline. Reactivity with respect to ozone formation of the liquid fuel samples was dominated by aromatics, whereas the reactivity of headspace vapors was dominated by alkanes and cycloalkanes. The olefin and sulfur contents of the liquid fuel samples were unusually low. Equilibrium headspace vapor composition was predicted using measured liquid fuel composition, pure liquid vapor pressures of each fuel constituent, and activity coefficients derived from equilibrium P, T, x, and y measurements for ethanol in solution with gasoline hydrocarbons. Weight fractions of the 13 most abundant species in gasoline headspace vapors were predicted to within +/-15% of measured values, except for n-butane which was overpredicted by 22%. Alternate predictions of headspace vapor composition using the universal functional-group activity coefficient (UNIFAC) model were generally less accurate, especially for ethanol.


A field study was conducted in September 1995 to measure the ambient atmospheric concentrations of methyl bromide (McBr) in the Salinas Valley, California. Air concentrations of McBr were measured at 11 sites located on the adjacent mountains, valley floor and at the Pacific Ocean coast over a 4-d period. The concentrations ranged up to 8.98 pg m\(^{-3}\) Industrial Source Complex Short Term 3 (ISCST3) and CALPUFF dispersion model simulations were performed with several fumigated fields serving as sources, using two estimates of source strengths from published flux values. CALPUFF was driven by 3D meteorology from CALMET. With the lower of the two estimates, the ISCST3 model underpredicted concentrations for 76% of data and averaged 66% of measured, and the CALPUFF model also underpredicted concentrations for 60% of observations and averaged 84% of measured. With the higher of the two estimates the ISCST3 model overpredicted by a factor of two For 67% of data, and CALPUFF overpredicted concentrations by a factor of 1.6 for over 50% of data. Between the model predicted and measured concentrations, the coefficient of determination, R\(^2\), was approximated to 0.7 for both source strengths with ISCST3 model. The R\(^2\) with CALPUFF model was 0.55 and 0.82 with source strength estimated from two prior flux studies. The margin of exposure (MOE) for the population of the city of Salinas was calculated based on the measured ambient concentrations and compared with the current benchmark used by US-EPA and California Department of Pesticide Regulation for acceptable human health risk. Based on the models predicted worst-case exposure concentration, the MOE for acute effects was approximately 10,000. For chronic effects it was approximately 100, indicating a need for attention to exposure to McBr in areas of intense methyl bromide use. (C) 2000 Elsevier Science Ltd. All rights reserved.


In population exposure studies, personal exposure to PM is typically measured as a 12- to 24-hr integrated mass concentration. To better understand short-term variation in personal PM exposure, continuous (1-min averaging time) nephelometers were worn by 15 participants as part of two U.S. Environmental Protection Agency (EPA) longitudinal PM exposure studies conducted in Baltimore County, MD, and Fresno, CA. Participants also wore inertial impactor samplers (24-hr integrated filter samples) and recorded their daily activities in 15-min intervals. In Baltimore, the nephelometers correlated well (R\(^2\) = 0.66) with the PM2.5 impactors. Time-series plots of personal nephelometer data showed each participant's PM exposure to consist of a series of peaks of relatively short duration. Activities corresponding to a significant instrument response included cooking, outdoor activities, transportation, laundry, cleaning, shopping, gardening, moving between microenvironments, and removing/putting on the instrument. On average, 63-66% of the daily PM exposure occurred indoors at home (about 2/3 of which occurred during waking hours), primarily due to the large amount of time spent in that location (an average of 72-77%).

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Although not a reference method for measuring mass concentration, the nephelometer did help identify PM sources and the relative contribution of those sources to an individual's personal exposure.


The global continental haze pattern was evaluated based on daily average visibility data at 7000 surface weather stations over five years, 1994-98. The data processing consisted of three broad categories of filters: (1) validity of individual data points, (2) filters based on statistics for specific stations, and (3) filters based on spatial analysis. The data are presented as the aerosol extinction coefficient (Bext or haze) at the surface, seasonally aggregated over five years. The data reveal that the continental haze is concentrated over distinct aerosol regions of the world. The haziest regions of Asia are the Indian subcontinent, eastern China, and Indochina where the 75 percentile seasonal Bext exceeds 0.4 km(-1). In Africa, the highest year around extinction coefficient > 0.4 km(-1) is found over Mauritania, Mali, and Niger. During December, January, February, the savanna region of sub-Saharan Africa shows similar values. The haziest region of South America is over Bolivia, adjacent to the Andes mountain range, with a peak during August-November (0.4-0.6 km(-1)). In North America and Europe, there are isolated haze pockets, such as the San Joaquin Valley in California and the Po River Valley in the northern Italy. In many regions of the world the size, shape, and intensity of hazy pockets is determined by the topographic barriers. A major qualification of this work is that the haze maps are based on daily average visibility which emphasizes humid regions with hygroscopic aerosols (nighttime peak Bext) and de-emphasizes arid, dusty regions with daytime maximum extinction. Regional haze episodes over several continental aerosol regions are illustrated by truecolor rendering of the reflectance data from the SeaWiFS satellite.


An automated system has collected meteorological data hourly in the San Francisco Bay Area since October 1995. Data from sites operated by the National Weather Service, Federal Aviation Administration, U.S. Navy, U.S. Air Force, the San Francisco Bay Area Air Quality Management District, and others have been integrated into a common database and archived by the U.S. Geological Survey. Data for 0300 and 1500 UTC during 1996 were taken from that archive and used to evaluate the performance of the Winds on Critical Streamline Surfaces objective analysis code in this area of complex terrain, where altitudes range from 0 to over 1000 m above mean sea level. The comparisons of observed and modeled winds are for a longer time period and a wider variety of meteorological conditions than are available from limited-duration held studies. The authors chose 4-, 7-, and 11-station "networks" for analysis: there were 461 h when data were available from all the sites in the 4-station network, 439 h for the 7 stations, and 343 for the 11 stations. The essential features of the model are described, and tramples are given to show how changing some of the features affects the comparisons between modeled and observed winds. The effects of increasing the number of stations used for the analyses also are discussed. The model evaluation techniques described here can be applied to wind analyses from any source, but application certainly is more feasible with simple diagnostic models that can be run repeatedly so that sensitivities and performance changes can be examined. The performances of more complex models also can be compared with these results to determine if their greater complexity produces significant improvements.


We examined the relationship between intrapulmonary particle distribution of carbonaceous and mineral dusts and remodeling of the airways along anatomically distinct airway paths in the lungs of Hispanic males from the central valley of California. Lung autopsy specimens from the Fresno County Coroner's Office were prepared by intratracheal instillation of 2% glutaraldehyde at 30 cm H2O pressure. Two distinct airway paths into the apico-posterior and apico-anterior portions of the left upper lung lobe were followed. Tissue samples for histologic analysis were generally taken from the intrapulmonary second, fourth, sixth, and ninth airway generations. Parenchymal tissues beyond the 12th airway generation of each airway path were also analyzed. There was little evidence of visible particle accumulation in the larger conducting airways (generations 2-6), except in bronchial-associated lymphoid tissues and within peribronchial connective tissue. In contrast, terminal and respiratory
bronchioles arising from each pathway revealed varying degrees of wall thickening and remodeling. Walls with marked thickening contained moderate to heavy amounts of carbonaceous and mineral dusts. Wall thickening was associated with increases in collagen and interstitial inflammatory cells, including dust-laden macrophages. These changes were significantly greater in first-generation respiratory bronchioles compared to second- and third-generation respiratory bronchioles. These findings suggest that accumulation of carbonaceous and mineral dust in the lungs is significantly affected by lung anatomy with the greatest retention in centers of lung acini. Furthermore, there is significant remodeling of this transitional zone in humans exposed to ambient particulate matter.


Ambient air monitoring for organic acids in PM$_{2.5}$, was conducted at several locations in California. During the study, it was found that oxalic acid (ethanedioic acid) was the most abundant organic acid found in the PM$_{2.5}$ fraction. Samples from Azusa (in southern California), San Jose (in the San Francisco Bay area), and Fresno (in central California), a PM$_{2.5}$ Super Site, were collected in 1999 and analyzed. The results for oxalic acid concentrations during this monitoring effort are presented.


Data from the 1990 San Joaquin Valley Air Quality Study/Atmospheric Utility Signatures, Predictions, and Experiments (SJVAQS/AUSPEX) field program in California's San Joaquin Valley (SJV) suggest that both urban and rural areas would have difficulty meeting an 8-hr average O-3 standard of 80 ppb. A conceptual model of O-3 formation and accumulation in the SJV is formulated based on the chemical, meteorological, and tracer data from SJVAQS/AUSPEX. Two major phenomena appear to lead to high O-3 concentrations in the SJV: (1) transport of O-3 and precursors from upwind areas (primarily the San Francisco Bay Area, but also the Sacramento Valley) into the SJV, affecting the northern part of the valley, and (2) emissions of precursors, mixing, transport (including long, orange transport), and atmospheric reactions within the SJV responsible for regional and urban-scale (e.g., downwind of Fresno and Bakersfield) distributions of O-3. Using this conceptual model, we then conduct a critical evaluation of the meteorological model and air quality model. Areas of model improvements and data needed to understand and properly simulate O-3 formation in the SJV are highlighted.


Two chemical mass balance receptor models are developed which can determine the source contributions to atmospheric pollutant concentrations using organic compounds as tracers. The first model uses particle-phase organic compounds to apportion the primary source contributions to atmospheric fine particulate organic carbon concentrations and fine particle mass concentrations. The second receptor model simultaneously uses both volatile gas-phase hydrocarbons and particle-phase organic compounds as tracers to determine source contributions to non-methane organic gases in the atmosphere. Both models are applied to data collected in California's San Joaquin Valley during two severe wintertime air pollution episodes. Source contributions to fine particle air quality are calculated for two urban sites, Fresno and Bakersfield, and one background site, Kern Wildlife Refuge. Primary particle emissions from hardwood combustion, softwood combustion, diesel engines, meat cooking, and gasoline-powered motor vehicles contribute on average 79% of the airborne fine particle organic compound mass at the urban sites during both episodes with smaller but still measurable contributions from fine particle road dust and natural gas combustion aerosol. Anthropogenic primary particle sources contribute less than 10% of the fine particle mass concentration at the background site. The combined gas-phase and particle-phase organic compound receptor model shows that gasoline-powered motor vehicle exhaust and gasoline vapors are the largest contributors to nonmethane organic gases concentrations followed by natural gas leakage. Smaller but statistically significant contributions to organic vapors from wood combustion, meat cooking, and diesel exhaust also are quantified.


During the past decade, nearly 600 million dollars were invested in more than 30 major held studies in North America and Europe examining tropospheric ozone chemistry, meteorology, precursor emissions, and modeling. Most of these studies were undertaken to provide new or refined knowledge about ozone accumulation and to assist in the development of economical and effective emissions management practices for ozone. In this paper, we describe a selection of field research programs conducted under a wide range of geographical and climatological conditions in North America and Europe. The designs of these studies were generally similar, employing a combination of ground-based observation networks, upper-air sampling, and meteorological observations. Analysis and interpretation of the resulting data were combined with improved inventories of ozone precursor emissions and air quality modeling to develop new or enhanced knowledge about photochemical processes under various tropospheric conditions. The scientific results from these studies contained few surprises; in fact, they generally affirmed the conclusions in the review by the US National Research Council (NRC, 1999). Key findings include: (1) reaffirmation that tropospheric ozone is a multi-scale phenomenon extending to continental boundaries; (2) aerometric conditions aloft are important to ground-level ozone; (3) biogenic sources make important contributions to VOC and NOx emissions in parts of eastern North America and southern Europe; (4) emissions estimates are among the more uncertain components of predictive models for ozone; (5) recirculating flow over complex terrain and large water bodies are universally important factors affecting accumulation of ozone at the ground; (6) nonlinearities in ozone response to precursor changes create important degrees of freedom in management strategies - VOC and NOx sensitivities vary extensively in urban and rural areas, making decisions about emissions management complicated; (7) measurement methods for many precursors, intermediates, and products of photochemical reactions have improved greatly; and (8) additional analysis and interpretation of existing data from many of these field studies should pay handsome dividends at relatively modest cost. Published by Elsevier Science Ltd


This paper describes a new methodology developed to provide objective guidance for cost-effective siting of meteorological observations on the mesoscale for air quality applications. This field-coherence technique (FCT) is based on a statistical analysis of the mesoscale atmospheric structure defined by the spatial and temporal "coherence" in the meteorological fields. The coherence, as defined here, is a measure of the distance scale over which there is temporal consistency in the spatial structure within a variable field. It indicates how well a measurement taken at one location can be used to estimate the value of that field at another location at a given analysis time. The FCT postulates that, the larger the field coherence is, the fewer measurement sites are needed to resolve adequately the dominant characteristics of that field. Proof of concept was demonstrated using real data from an extensive field-program database over the San Joaquin Valley in the summer of 1990. The FCT next was applied to numerical model results for the same period, which produced similar guidance. The transferability of the methodology from real data to numerical model results having been demonstrated, the FCT then was applied in a model-based study over California's South Coast Air Basin to contribute in the design of a new field program, the Southern California Ozone Study (SCOS97). Interpretation of the FCT results mostly corroborated a preliminary field-program design produced by the design team and based on past experience, subjective evaluation of historical datasets, and other considerations. However, the FCT results also led the design team to make several changes, which were confirmed by experts familiar with the meteorological behavior of the region and were included in the final SCOS97 field-program plan


A new method has been developed to assess the aerosol particle formation reactivity of nitrogen oxide (NOx) emissions. The method involves using a photochemical box model with gas-phase photochemistry, aerosol production and deposition to calculate the ammonium nitrate particle equivalent of NOx emissions. The yields of ammonium nitrate particles used in the box model were determined from parametric simulations made with an
equilibrium model that calculated the fraction of nitric acid that reacts to produce ammonium nitrate from the temperature, relative humidity and ammonium-to-nitrate ratios. For the wintertime conditions of emissions and meteorology in the San Joaquin Valley of central California, approximately 80% of the moles of nitric acid produced was found to be in the particulate nitrate phase and about 33% of the moles of emitted NOx was converted to particulate nitrate. The particle equivalent of NOx emissions was found to be on the order of 0.6 g of ammonium nitrate for each gram of NOx emitted (the mass of NOx calculated as NO2). This estimate is in reasonable agreement with an analysis of field measurements made in central California. (C) 2000 Elsevier Science Ltd. All rights reserved


In Part I of this paper, a held-coherence technique (FCT) was developed to provide objective guidance for cost-effective siting of meteorological observations on the mesoscale for air quality applications. The FCT is evaluated here in Part II using the Fifth-Generation Pennsylvania State University-National Center for Atmospheric Research Mesoscale Model (MM5) and the rich datasets of the San Joaquin Valley Air Quality Study (SJVAQS) and the Atmospheric Utility Signatures, Prediction, and Experiments (AUSPEX), which were combined in the SJVAQS-AUSPEX Regional Modeling Adaptation Project (SARMAP). The FCT is used to define a data-starvation Observing System Experiment in which the size of the SARMAP meteorological dataset used for four-dimensional data assimilation (FDDA) in the mesoscale model is reduced optimally by about half. The Meteorological conditions for the 2-7 August 1990 period are simulated using the FCT-based reduced-data distribution (partial FDDA). all available data (full FDDA), and no data from the study (no FDDA). The three meteorological simulations then are used as input to the SARMAP Air Quality Model to simulate the 3-6 August 1990 ozone episode in the San Joaquin Valley. It was demonstrated that the MM5 simulation using partial FDDA produces results very similar to those obtained from the full FDDA, and the two FDDA assisted meteorological datasets are significantly more accurate than that obtained with no FDDA for the 5-day period. The results obtained from the three associated air quality simulations were compared with each other and with ozone and precursor measurements. It was found that the partial-FDDA meteorological input produces air quality model results very similar to those obtained from the full-FDDA input and closer to the observations than results from input based on no FDDA. These findings confirm that the FCT can provide guidance for a more test-effective field-program design in terms of both the meteorological behavior and the air quality based on that meteorological behavior


The Fresno Supersite intends to 1) evaluate non-routine monitoring methods, establishing their comparability with existing methods and their applicability to air quality planning, exposure assessment, and health effects studies; 2) provide a better understanding of aerosol characteristics, behavior, and sources to assist regulatory agencies in developing standards and strategies that protect public health; and 3) support studies that evaluate relationships between aerosol properties, co-factors, and observed health end-points. Supersite observables include in-situ, continuous, short-duration measurements of 1) PM2.5 PM10, and coarse (PM10 minus PM2.5) mass; 2) PM2.5 SO4-2, NO3-, carbon, light absorption, and light extinction; 3) numbers of particles in discrete size bins ranging from 0.01 to similar to 10 mu m; 4) criteria pollutant gases (O-3, CO, NOx); 5) reactive gases (NO2, NOy, HNO3, peroxyacetyl nitrate [PAN], NH3); and 6) single particle characterization by time-of-flight mass spectrometry. Field sampling and laboratory analysis are applied for gaseous and particulate organic compounds (light hydrocarbons, heavy hydrocarbons, carbonyls, polycyclic aromatic hydrocarbons [PAH], and other semi-volatiles), and PM2.5 mass, elements, ions, and carbon. Observables common to other Supersites are 1) daily PM2.5 24-hr average mass with Federal Reference Method (FRM) samplers; 2) continuous hourly and 5-min average PM2.5 and PM10 mass with beta attenuation monitors (BAM) and tapered element oscillating microbalances (TEOM); 3) PM2.5 chemical speciation with a U.S. Environmental Protection Agency (EPA) speciation monitor and protocol; 4) coarse particle mass by dichotomous sampler and difference between PM10 and TEOM measurements; 5) coarse particle chemical composition; and 6) high sensitivity and time resolution scalar and vector wind speed, wind direction, temperature, relative humidity, barometric pressure, and solar radiation. The Fresno Supersite is
coordinated with health and toxicological studies that will use these data in establishing relationships with asthma, other respiratory disease, and cardiovascular changes in human and animal subjects.


Daily measurements of PM10 mass and chemical composition were obtained for the period 1-14 November 1995 from a saturation monitoring network around Corcoran, and for varying portions of the period 9 December 1995-6 January 1996 for three networks around Bakersfield, Fresno, and the Kern Wildlife Refuge, in California's San Joaquin Valley. During the latter period, monitoring locations were also operated along the boundaries and across the width of the Valley. The Corcoran, Bakersfield, and Fresno networks consisted of 12-25 sites, located in areas of about 300-800 km(2). Each network also included one core site, situated at a pre-existing monitoring location, with more extensive and more temporally resolved measurements. Mean concentrations of PM10 and its constituents varied from core-site concentrations by 20% or more over distances ranging from 4 to 14 km. Local source influences were observed to affect sites over distances of less than 1 km, but primary particulate emissions were also transported over urban or sub-regional scales of approximately 10-30 km during the winter and greater than 30 km in the fall. During winter, gas-phase precursors of secondary aerosol may have been transported over distances of approximately 100 km, but little evidence was found for transport of primary PM on such a scale. (C) 1999 Published by Elsevier Science Ltd. All rights reserved.


The spatial and temporal distributions of particle mass and its chemical constituents are essential for understanding the source-receptor relationships as well as the chemical, physical, and meteorological processes that result in elevated particulate concentrations in California's San Joaquin Valley (SJV). Fine particulate matter (PM2.5), coarse particulate matter (PM10), and aerosol precursor gases were sampled on a 3-hr time base at two urban (Bakersfield and Fresno) and two non-urban (Kern Wildlife Refuge and Chowchilla) core sites in the SJV during the winter of 1995-1996. Day-to-day variations of PM2.5 and PM10 and their chemical constituents were influenced by the synoptic-scale meteorology and were coherent among the four core sites. Under non-rainy conditions, similar diurnal variations of PM2.5 and coarse aerosol were found at the two urban sites, with concentrations peaking during the nighttime hours. Conversely, PM2.5 and coarse aerosol peaked during the morning and afternoon hours at the two non-urban sites. Under rainy and foggy conditions, these diurnal patterns were absent or greatly suppressed. In the urban areas, elevated concentrations of primary pollutants (e.g., organic and elemental carbons) during the late afternoon and nighttime hours reflected the impact from residential wood combustion and motor vehicle exhaust. During the daytime, these concentrations decreased as the mixed layer deepened. Increases of secondary nitrate and sulfate concentrations were found during the daylight hours as a result of photochemical reactions. At the non-urban sites, the same increases in secondary aerosol concentrations occurred during the daylight hours but with a discernable lag time. Concentrations of the primary pollutants also increased at the non-urban sites during the daytime. These observations are attributed to mixing aloft of primary aerosols and secondary precursor gases in urban areas followed by rapid transport aloft to non-urban areas coupled with photochemical conversion.


Although several chemical pathways exist for S(IV) oddation in fogs and clouds, many are self-limiting: as sulfuric acid is produced and the drop pH declines, the rates of these pathways also decline. Some of the acid that is produced can be buffered by uptake of gaseous ammonia. Additional internal buffering can result from protonation of weak and strong bases present in solution. Acid titrations of high pH fog samples (median pH = 6.49) collected in California's San Joaquin Valley reveal the presence of considerable internal acid buffering. In samples collected at a rural location, the observed internal buffering could be nearly accounted for based on concentrations of ammonia and bicarbonate present in solution. In samples collected in the cities of Fresno and Bakersfield, however, significant additional, unexplained buffering was present over a pH range extending from approximately four to seven. The
additional buffering was found to be associated with dissolved compounds in the fogwater. It could not be accounted for by measured concentrations of low molecular weight (C-1-C-3) carboxylic acids, S(IV), phosphate, or nitrophenols. The amount of unexplained buffering in individual fog samples was found to correlate strongly with the sum of sample acetate and formate concentrations, suggesting that unmeasured organic species may be important contributors. Simulation of a Bakersfield fog episode with and without the additional, unexplained buffering revealed a significant impact on the fog chemistry. When the additional buffering was included, the simulated fog pH remained 0.3-0.7 pH units higher and the amount of sulfate present after the fog evaporated was increased by 50%. Including the additional buffering in the model simulation did not affect fogwater nitrate concentrations and was found to slightly decrease ammonium concentrations. The magnitude of the buffering effect on aqueous sulfate production is sensitive to the amount of ozone present to oxidize S(IV) in these high pH fogs. (C) 1999 Elsevier Science Ltd. All rights reserved


Fog was sampled at four locations in California's San Joaquin Valley (SJV) during December 1995 and January 1996 as part of the 1995 Integrated Monitoring Study (IMS95). The fog sampling campaign was conducted in two phases. During the first phase, fog was sampled at three southern SJV surface locations, two urban (Fresno and Bakersfield) and one rural (near the Kern Wildlife Refuge). Both bulk samples (representative of the entire fog drop spectrum) and size-fractionated samples were collected. During the second phase, bulk fog samples were collected at three elevations on a 430 m television transmission tower in the northern SJV, representing some of the first observations of vertical variations in fog composition. SJV fog was observed to be consistently alkaline. The median pH measured in the southern SJV was 6.49, with a range from 4.97 to 7.43. Dominant species in the fog water were ammonium (median southern SJV concentration of 1008 microequivalents/l (µ N)), nitrate (483 µ N), sulfate (117 µ N), acetate (117 µ N), formate (63 µ N), and formaldehyde (46 µ M). Concentrations of the inorganic ions were similar in the urban and rural fogs, although occasionally much higher spikes of S(IV) and sulfate were observed in Bakersfield fog. Acetate, formaldehyde, and total organic carbon, by contrast, were observed to be present in greater concentration in the urban fogs. Bakersfield IMS95 fog concentrations of most species were similar to those measured there in the early 1980s, although concentrations of S(IV) and sulfate were much lower in IMS95 fogs. Significant differences were found between the composition of large and small fog drops, with pH differences at times exceeding one pH unit. The chemical heterogeneity present among SJV fog drop populations is likely to result in significant enhancement of aqueous sulfate production rates over those expected from average fog properties. Significant vertical variations were also observed in fog composition. Liquid water content was observed to increase strongly with elevation, while major ion aqueous concentrations in fog drops decreased with altitude. The total amount of solute contained within the fog (per unit volume of air) was observed to increase with altitude. These observations form a unique data set to be used for model evaluation and for further analysis of aerosol processing by fogs. (C) 1998 Elsevier Science Ltd. All rights reserved


Basing the quantitative expression of environmental regulatory standards and associated compliance criteria on statistical principles has recently received attention in Europe, most visibly in a study by the UK Royal Commission on Environmental Pollution. These issues are timely for consideration in the USA, where a recent periodic review, of National Ambient Air Quality Standards (NAAQS) has led to revision of the regulatory standards for ambient ozone and particulate matter. Salient statistical issues include accounting for errors of the first and second kind due to sampling and measurement error. These issues appear routine statistically and also may seem absent from regulations, but neither is necessarily the case. This paper is directed towards developing a methodology for examining the problem of dealing with uncertainty and variation in environmental regulations and compliance criteria. Our approach is illustrated through statistical analysis of the (old) 1 hour and the (new) 8 hour standards for ambient ozone, based on intensive monitoring in California's San Joaquin Valley during summer 1990 performed under the SARMAP Project. This paper presents preliminary findings based on quantifying measurement error or precision in terms of small-scale spatial and temporal variability, laying the groundwork for future work.

The dynamics of ozone in the San Joaquin Valley of central California are studied by systematic diagnostic runs of the three-dimensional SARMAP Air Quality Model. Air quality in the San Joaquin Valley is the result of a complex combination of local and transported emissions. Simulations show that relatively brisk winds at points of inflow to the Valley produce a strong dependence of ozone in the Valley on upwind conditions. Furthermore, NOx influx from boundaries and local emissions has significantly greater impact on ozone production than ROG influx and emissions. (C) 1999 Elsevier Science Ltd. All rights reserved


Pollen analysis and nine radiocarbon dates of an 853-cm core from historically drained Tulare Lake, south-central California are reported prior to 7000 yr B.P., the vegetation of the southern San Joaquin Valley (central California) resembled that of the contemporary Great Basin, including abundant greasewood (Sarcobatus), which currently does not occur west of the Sierra Nevada. The early-Holocene pollen assemblage is dominated by Cupressaceae (>40%), Pinus (>20%), Quercus (5-20%), Artemisia (>15%), and Sarcobatus (>5%), suggesting pinyon-juniper-oak woodland in the uplands, with greasewood on the saltflats near the lake. Giant sequoia was widespread along the Sierra Nevada streams draining into Tulare Lake, prior to 9000 yr B.P. as Sequoiadendron pollen is greater than 4%. The pollen assemblages before 18,500 yr B.P. are similar to those of the early Holocene (Cupressaceae, Artemisia, and Sarcobatus), but a gap in sedimentation from ca. 18,500-10,500 yr B.P. prohibits characterization of full-glacial vegetation. The end of Great Basin-like pollen assemblages 7000 yr B.P. (demise of Sarcobatus) coincides with increased frequency of charcoal; i.e., greater fire frequency in the Holocene woodland and grassland. From 7000-4000 yr B.P. the pollen assemblage is dominated by Other Compositae and Chenopodiaceae-Amaranthus pollen, suggesting expansion of xerophytic steppe at the expense of oak woodland. Higher percentages of littoral pollen (Cyperaceae, Typha-Sparganium) and lower percentages of pelagic algae (Botryococcus + Pediastrum) during the middle Holocene indicate lake levels generally lower than during the early Holocene. The late Holocene begins with a cold-wet period 3500-2500 yr B.P. followed by progressive drying of the lake. Climate estimates based on modern pollen analogs confirm the climate implications of the vegetation and lake history. Early Holocene climate was cold and wet, and maximum Holocene temperature and drought occurred between 7000 and 4000 yr B.P. Cool-moist climate from 4000 to 2000 yr B.P. is followed by a return to aridity and high temperature ca. 1000 yr B.P. (C) 1999 Elsevier Science B.V, All rights reserved


The size, composition, and concentration of particulate matter (PM) var with location and time. Several monitoring/sampling programs are operated in California to characterize PM less than 2.5 and 10 μm in aerodynamic diameter (PM2.5 and PM10). This paper presents a broad summary of the spatial and temporal variations observed in ambient PM2.5 and PM10 concentrations in California. Many areas that have high PM10 concentrations also have relatively high PM2.5 concentrations, and data indicate that a significant portion of the PM10 air quality problem is caused by PM2.5. To develop effective plans for attaining the ambient PM standards, improved understanding of these unique problems is needed. Since 1989, pollution control efforts—whether specifically targeted for particulate matter or indirectly via controls on gaseous emissions—have caused annual average PM2.5 and PM10 concentrations to decline at most sites in California


A computational system that uses statistical equations to forecast hourly probabilities of marine stratus burnoff (via ceiling) at the San Francisco international Airport for 1-6-h lead times is developed. The system is based entirely upon surface and upper-air observations in the San Francisco Bay Area as predictors. A test of the product on a 3-yr independent sample shows a 6%-21% reduction in the mean square error (mse) compared with persistence "climatology." The amount of improvement is noteworthy, considering that a dearth of reliable observations exists upstream from the airport. Moreover, the inclusion of important upper-air predictors into the forecast equations can reduce the mse by 3% when compared with a system of equations derived solely from surface data. Paired-difference tests reveal that the upper-air data provide the greatest contribution for valid rimes that are nearest to the data's observational time. Ceiling forecasts are compared to Model Output Statistics (MOS) probabilistic ceiling forecasts for two different MOS lead times. When forecasts valid at 1500 UTC are verified, 3-h observation-based forecasts result in a 32% reduction in the mse over MOS forecasts having a 13- to 15-h lead time. When a more competitive 4- to 6-h MOS lead time is allotted (using an 1800 UTC valid time), 3-h observation-based forecasts result in an 8% reduction in the mse over MOS forecasts. Analysis of the predictive system's performance on the 3-yr independent sample reveals that a broad distribution of probabilistic forecasts is produced, in contrast with forecasts made from persistence climatology, which can offer only a limited probability distribution for each case. Because the probabilistic forecasts are shown to be unbiased, it is expected that similar systems designed for operational use would guide users toward more prudent decisions on the implementation or termination of air traffic delay programs.


Drop size-resolved measurements of fog chemistry in California's San Joaquin Valley during the 1995 Integrated Monitoring Study reveal that fog composition varies with drop size. Small fog drops were less alkaline and typically contained higher major ion (nitrate, sulfate, ammonium) concentrations than large drops. Small drops often contained higher concentrations of Fe and Mn than large drops while H2O2 concentrations exhibited no strong drop size dependence. Simulation of an extended fog episode in Fresno, California revealed the capability of a drop size-resolved fog chemistry model to reproduce the measured (based on two drop size categories) drop size dependence of several key species. The model was also able to satisfactorily reproduce measured species-dependent deposition rates (ammonium > sulfate > nitrate) resulting from fog drop sedimentation. Both the model simulation and direct analysis of size-resolved fog composition observations and measured gas-phase oxidant concentrations indicate the importance of ozone as an aqueous-phase S(IV) oxidant in these high pH fogs. Due to the nonlinear dependence of the rate law for the ozone pathway on the hydrogen ion concentration, use of the average fog drop composition can lead to significant underprediction of aqueous phase sulfate production rates in these chemically heterogeneous Fogs. (C) 1999 Elsevier Science Ltd. All rights reserved.


An updated assessment of fine particle emissions from light- and heavy-duty vehicles is needed due to recent changes to the composition of gasoline and diesel fuel, more stringent emission standards applying to new vehicles sold in the 1990s, and the adoption of a new ambient air quality standard for fine particulate matter (PM2.5) in the United States. This paper reports the measurement of emissions from vehicles in a northern California roadway tunnel during summer 1997. Separate measurements were made of uphill traffic in two tunnel bores: one bore carried both light-duty vehicles and heavy-duty diesel trucks, and the second bore was reserved for light-duty vehicles. Ninety-eight percent of the light-duty vehicles were gasoline-powered. In the tunnel, heavy-duty diesel trucks emitted 24, 37, and 21 times more fine particle, black carbon, and sulfate mass per unit mass of fuel burned than light-duty vehicles. Heavy-duty diesel trucks also emitted 15-20 times the number of particles per unit mass of
fuel burned compared to light-duty vehicles. Fine particle emissions from both vehicle classes were composed mostly of carbon; diesel-derived particulate matter contained more black carbon (51 +/- 11% of PM2.5 mass) than did light-duty fine particle emissions (33 +/- 4%). Sulfate comprised only 2% of total fine particle emissions for both vehicle classes. Sulfate emissions measured in this study for heavy-duty diesel trucks are significantly lower than values reported in earlier studies conducted before the introduction of low-sulfur diesel fuel. This study suggests that heavy-duty diesel vehicles in California are responsible for nearly half of oxides of nitrogen emissions and greater than three-quarters of exhaust fine particle emissions from on-road motor vehicles.


A fully automated gas chromatograph-flame ionization detector system was designed and built to measure ambient concentrations of C-2-C-10 volatile organic compounds, including many oxygenated compounds, without using liquid cryogen. It was deployed at Blodgett Forest Research Station in Georgetown, California, 38 degrees 53'42.9"N, 120 degrees 37'57.9"W, 1315 m elevation. More than 900 in situ measurements were made above a ponderosa pine canopy at 40-min intervals, continuously from July 2 through August 1, 1997. Factor analysis and observed temporal patterns were used to categorize sources for measured compounds as biogenic or anthropogenic or both. Compounds that were clearly biogenic included methylbutenol, isoprene and its oxidation products (methacrolein and methyl vinyl ketone), and terpenes (alpha-pinene, 3-carene, d-limonene). Other compounds were partially biogenic, including acetone, ethene, propene, hexanal, acetaldehyde, and methanol. Hydroxyl radical (OH) loss rates were dominated by the clearly biogenic compounds, accounting for 70% of the loss under mean midday conditions. The most important single compounds were isoprene (33%) and methylbutenol (21%). These two compounds were dominant under all conditions, including the coldest and most polluted days. Under the most polluted conditions, acetaldehyde became very important, accounting for 13% of the total. Total OH loss rates were highly correlated with temperature because emissions of biogenic compounds, which dominate OH loss, are strongly temperature dependent. Much of the research on biogenic volatile organic compounds has focused on isoprene and terpenes. Our results suggest that quantifying and understanding factors controlling biogenic emissions of other compounds such as methylbutenol, acetone, hexanal, methanol, and acetaldehyde are critical for improving our understanding of regional photochemistry.


A radiation fog physics, gas- and aqueous-phase chemistry model is evaluated against measurements in three sites in the San Joaquin Valley of California (SJV) during the winter of 1995. The measurements include for the first time vertically resolved fog chemical composition measurements. Overall the model is successful in reproducing the fog dynamics as well as the temporal and spatial variability of the fog composition (pH, sulfate, nitrate, and ammonium concentrations) in the area. Sulfate production in the fog layer is relatively slow (1-4 mu g m(-3) per fog episode) compared to the episodes in the early 1980s because of the low SO2 concentrations in the area and the lack of oxidants inside the fog layer. Sulfate production inside the fog layer is limited by the availability of oxidants in the urban areas of the valley and by SO2 in the more remote areas. Nitrate is produced in the rural areas of the valley by the heterogeneous reaction of N2O5 on fog droplets, but this reaction is of secondary importance for the more polluted urban areas. The gas-phase production of HNO3 during the daytime is sufficient to balance the nitrate removed during the nighttime fog episodes. Entrainment of air from the layer above the fog provides another source of reactants for the fog layer. Wet removal is one of most important processes inside the fog layer in SJV. We estimate based on the three episodes investigated during IMS95 that a typical fog episode removes 500-2000 mu g m(-2) of sulfate, 2500-6500 mu g m(-2) of nitrate, and 2000-3500 mu g m(-2) of ammonium. For the winter SJV valley the net fog effect corresponds to reductions in ground ambient concentrations of 0.05-0.2 mu g m(-3) for sulfate, 3-6 mu g m(-3) for total nitrate, and 1-3 mu g m(-3) for total ammonium. (C) 1999 Published by Elsevier Science Ltd. All rights reserved

The ambient PM10 and PM2.5 data collected during the fall and winter portions of the 1995 Integrated Monitoring Study (IMS95) were used to conduct Chemical Mass Balance (CMB) Modeling to determine source contribution estimates. Data from the core and saturation monitoring sites provided an extensive database for evaluating the spatial and temporal variations of contributing sources. Geological sources dominated fall samples, while secondary ammonium nitrate and carbonaceous sources were the largest contributors for winter samples. Secondary ammonium nitrate concentrations were uniform across all sites during both the fall and winter. Site-to-site variability was primarily due to differences in geological contributions in the fall, and carbonaceous source contributions in the winter. During the winter, diurnal profiles of particulate matter (PM) were driven by variations in carbonaceous sources at urban sites, and by variations in secondary ammonium nitrate at rural sites. Although records of day-specific PM activities were recorded during the study, no correlation was observed between 24-h CMB results and specific activities. The ambient data collected during IMS95 was also used to evaluate the adequacy of the emissions inventory. Comparison of ambient and emissions based ratios of NMHC/NOx, PM/NOx, CO/NOx, and SOx/NOx suggested that emissions of NMHC and CO in some locations may be underestimated, while emissions for PM and SO, may be overestimated. Comparison of fractional primary CMB source contribution estimates to corresponding fractional emissions estimates indicated that geological sources were overemphasized in the inventory, while carbonaceous sources were underrepresented.

Motallebi, N., 1999. Wintertime PM2.5 and PM10 source apportionment at Sacramento, California. Journal of the Air & Waste Management Association 49 (PM), PM25-PM34.

The chemical mass balance (CMB) model was applied to winter (November through January) 1991-1996 PM2.5 and PM10 data from the Sacramento 13th and T Streets site in order to identify the contributions from major source categories to peak 24-hr ambient PM2.5 and PM10 levels. The average monthly PM10 monitoring data for the nine-year period in Sacramento County indicate that elevated concentrations are typical in the winter months. Concentrations on days of highest PM10 are dominated by the PM2.5 fraction. One factor contributing to increased PM2.5 concentrations in the winter is meteorology (cool temperatures, low wind Speeds, low inversion layers, and more humid conditions) that favors the formation of secondary nitrate and sulfate aerosols. Residential wood burning also elevates fine particulate concentrations in the Sacramento area. The results of the CMB analysis highlight three key points. First, the source apportionment results indicate that primary motor vehicle exhaust and wood smoke are significant sources of both PM2.5 and PM10 in winter. Second, nitrates, secondarily formed as a result of motor-vehicle and other sources of nitrogen oxide (NOx), are another principal cause of the high PM2.5 and PM10 levels during the winter months. Third, fugitive dust, whether it is resuspended soil and dust or agricultural tillage, is not the major contributor to peak winter PM2.5 and PM10 levels in the Sacramento area.


Fine particulate matter emitted during wood combustion is known to contribute a significant fraction of the total fine aerosol concentration in the atmosphere of both urban and rural areas, in the present study, additional organic compounds that may act as wood smoke tracers in the atmosphere are sought. Polar organic compounds in wood smoke fine particulate matter are converted to their trimethylsilyl derivatives and analyzed by gas chromatography/mass spectrometry. Silylation enables the detection of n-alkanols, plant sterols, and a number of compounds derived from wood lignin that have not previously been reported in wood smoke samples, as well as levoglucosan and related sugar anhydrides formed during the combustion of cellulose. The concentrations of these compounds measured in source emissions are compared to the concentrations in atmospheric fine particle samples collected at a rural background site and at two urban sites in California's San Joaquin Valley. On the basis of this analysis, the sugar anhydrides galactosan and mannosan can be listed along with levoglucosan as being among the most abundant organic compounds detected in all samples.


Quantitative information from the 1995 Integrated Monitoring Study (IMS95) is used to develop a conceptual model, which describes the chemical characteristics and the physical processes responsible for the accumulation of PM in the San Joaquin Valley of California. One significant finding of the conceptual model is the sensitivity of ammonium nitrate (46% of winter PM2.5) and nitric acid to oxidants, which may be VOC-sensitive rather than
NOx-sensitive. Key gaps in current knowledge are identified using the conceptual model, e.g., the relative sensitivity of winter oxidants to VOC and NOx, mechanistic details of secondary organic aerosol formation, mechanisms of dispersion under calm conditions, and the importance of dry deposition. Some recommendations are also provided for the formulation of air quality models suitable to address the accumulation of PM in the San Joaquin Valley.


Optical, filter chemistry, and cascade impactor data collected during the winter intensive of the IMS95 Study in the San Joaquin Valley (SJV) of California were analyzed to determine the light-extinction efficiency of aerosol species. Regression of light scattering by particles (b(sp)) measured by a heated nephelometer without a size selective inlet against PM2.5 front filter mass gave a scattering efficiency of 3.67 +/- 0.05 m(2)/g with an R-2 (fraction of variance explained) of 0.94. Division of the aerosol into two components and applying two different corrections to the filter data for nitrate and organic carbon on the backup filter gave scattering efficiencies of 3.7 +/- 0.3 or 3.1 +/- 0.2 m(2)/g for the salts composed of sulfate: nitrate, and ammonium and 2.9 +/- 0.2 or 3.1 +/- 0.2 m2/g for all other species with R-2 of 0.985 and 0.986. The ambient b(sp) measured by an open nephelometer was a simple function of PM2.5 mass and relative humidity (RH), giving R-2 of 0.90 and 0.88 for two different RH sensors. Variations in PM2.5 size distribution and composition did not have an important effect on ambient b(sp). The RH data from each sensor were repeatable enough to show the existence of a simple dependence of aerosol water uptake on RH, but RH sensor calibration uncertainties prevented determining this dependence. Inversion of MOUDI cascade impactor data gave sulfate and nitrate mass median diameters (MMD) between 0.4 and 0.8 mu m. Mie scattering calculations based on MOUDI data provided humidity-dependent extinction efficiencies for the principal aerosol chemical species. These efficiencies combined with particle filter data showed that ammonium nitrate was the dominant contributor to wintertime light extinction. Source apportionment showed that light extinction was dominated by emissions sources contributing to the formation of secondary species, especially nitrate. These wintertime data are not expected to apply to summertime in the SJV.


Ship tracks are a natural laboratory to isolate the effect of anthropogenic aerosol emissions on cloud properties. The Monterey Area Ship Tracks (MAST) experiment in the Pacific Ocean west of Monterey, California, in June 1994, provides an unprecedented data set for evaluating our understanding of the formation and persistence of the anomalous cloud features that characterize ship tracks. The data set includes conditions in which the marine boundary layer is both clean and continentally influenced. Two case studies during the MAST experiment are examined with a detailed aerosol microphysical model that considers an external mixture of independent particle populations. The model allows tracking individual particles through condensational and coagulational growth to identify the source of cloud condensation nuclei (CCN). In addition, a cloud microphysics model was employed to study specific effects of precipitation. Predictions and observations reveal important differences between clean (particle concentrations below 150 cm(-3)) and continentally influenced (particle concentrations above 400 cm(-3)) background conditions: in the continentally influenced conditions there is a smaller change in the cloud effective radius, drop number and liquid water content in the ship track relative to the background than in the clean marine case. Predictions of changes in cloud droplet number concentrations and effective radii are consistent with observations although there is significant uncertainty in the absolute concentrations due to a lack of measurements of the plume dilution. Gas-to-particle conversion of sulfur species produced by the combustion of ship fuel is predicted to be important in supplying soluble aerosol mass to combustion-generated particles, so as to render them available as CCN. Studies of the impact of these changes on the cloud's potential to precipitate concluded that more complex dynamical processes must be represented to allow sufficiently long drop activations for drizzle droplets to form.

The temporary ineffectiveness of motor vehicle emission controls at startup causes emission rates to be much higher for a short period after starting than during fully warmed, or stabilized, vehicle operation. Official motor vehicle emission inventories estimate that excess emissions during cold-start operation contribute a significant fraction of all hydrocarbon, carbon monoxide (CO), and nitrogen oxide (NOx) emissions from California vehicles. In an effort to verify these estimates under real-world conditions, vehicle emissions were measured in an underground parking garage in Oakland, CA, during March 1997. Hot stabilized emissions were measured as vehicles arrived at the garage in the morning, and cold-start emissions were measured as vehicles exited in the afternoon; the incremental, or excess, emissions associated with vehicle starting were calculated by difference. Composite emissions from similar to 135 vehicles were sampled during each of six morning and six afternoon periods. Measured stabilized exhaust emissions were 19 +/- 2 g nonmethane hydrocarbons (NMHC), 223 +/- 17 g CO, and 8.6 +/- 1.3 g NOx per gal of gasoline consumed. Cold-start emissions of 69 +/- 2 g NMHC/gal, 660 +/- 15 g CO/gal, and 27.8 +/- 1.2 g NOx/gal were measured for vehicles spending an average of similar to 60 sec in the garage after starting in the afternoon. Using second-by-second emissions data from California's light-duty vehicle surveillance program, average fuel use during cold start was estimated to be similar to 0.07 gal, and the cold-start period was estimated to last for similar to 200 sec. When cold-start emission factors measured in the garage were scaled to represent the full 200-sec cold-start period, incremental start emission factors of 2.1 g NMHC, 16 g CO, and 2.1 g NOx per vehicle start were calculated. These emission factors are lower than those used by California's motor vehicle emission inventory model (MVEI 7G) by 45% for NMHC, 65% for CO, and 12% for NOx. This suggests that the importance of cold-start emissions may be overstated in current emission inventories. Overall, the composition of volatile organic compound (VOC) emissions measured during cold start was similar to that of hot stabilized VOC emissions. However, the weight fractions of unburned fuel and acetylene were higher during cold start than during hot stabilized driving.


This paper provides a brief overview of the 1995-Integrated Monitoring Study (IMS95) and serves as an introduction to this special issue. The papers that follow this overview present an integrated effort to address the major IMS95 science questions. This paper describes the objectives of IMS95, and how IMS95 fits into the larger California Regional PM10/PM2.5 Air Quality Study (CRPAQS). The components of IMS95 are briefly summarized as a reference for the other papers in this special issue, indicating the location of sites by site type and a table providing a general listing of measurements performed at each site type. Details of study planning, design, measurements performed, and post field activities can be found in Solomon and Magliano (1998, 1999).


The 1995 Integrated Monitoring Study (IMS95) is part of the Phase 1 planning efforts for the California Regional PM10/PM2.5 Air Quality Study. Thus, the overall objectives of IMS95 are to (1) fill information gaps needed for planning an effective field program later this decade; (2) develop an improved conceptual model for pollution buildup (PM10, PM2.5, and aerosol precursors) in the San Joaquin Valley; (3) develop a uniform air quality, meteorological, and emissions database that can be used to perform initial evaluations of aerosol and fog air quality models; and (4) provide early products that can be used to help with the development of State Implementation Plans for PM10. Consideration of the new particulate matter standards were also included in the planning and design of IMS95, although they were proposed standards when IMS95 was in the planning process. This paper describes the objectives, components, and measurements obtained during IMS95. Results are presented elsewhere and are referenced within.

The apportionment of ambient aerosol mass to different sources of airborne soil is a difficult problem because of the similarity of the chemical composition of crustal sources. However, additional information can be obtained using individual particle analysis. A novel approach based on the combination of two neural networks, the adaptive resonance theory-based neural network (ART-2a) and the back-propagation (BP) neural network with electron microscopy data, has been developed to apportion the mass contributions of the crustal sources to ambient particle samples. The crustal source samples were analyzed using computer-controlled scanning electron microscopy (CCSEM). CCSEM provides elemental compositions and size parameters for individual particles as well as estimates of the shape and density from which the volume and mass of each particle can be estimated. The ART-2a neural network was first used to partition particles into homogeneous classes based on the elemental composition data. After the different particle type classes were produced by ART-2a, their mass fractions were calculated. In this way, the source profiles for the crustal dust sources can be obtained in terms of the mass fractions for different particle types. Then the BP neural network was applied to build the model between the mass fractions of different particle types and the mass contributions. Using the three physical source samples prepared for this study, artificial ambient samples were generated by randomly mixing particles from the three source samples. These samples were then used to examine the proposed method. Satisfactory predictions for the mass contributions of the three sources to the ambient samples have been obtained, indicating the proposed method is a promising tool for the source apportionment of chemically similar soil samples.


Three different methods are used to predict secondary organic aerosol (SOA) concentrations in the San Joaquin Valley of California during the winter of 1995-1996 [Integrated Monitoring Study, (IMS95)]. The first of these methods estimates SOA by using elemental carbon as a tracer of primary organic carbon. The second method relies on a Lagrangian trajectory model that simulates the formation, transport, and deposition of secondary organic aerosol. The model includes a recently developed gas-particle partitioning mechanism. Results from both methods are in good agreement with the chemical speciation of organic aerosol during IMS95 and suggest that most of the OC measured during IMS95 is of primary origin. Under suitable conditions (clear skies, low winds, low mixing heights) as much as 15-20 μg C m⁻³ of SOA can be produced, mainly due to oxidation of aromatics. The low mixing heights observed during the winter in the area allow accumulation of SOA precursors and the acceleration of SOA formation. Clouds and fog slow down the production of secondary compounds, reducing their concentrations by a factor of two or three from the above maximum levels. In addition, it appears that there is significant diurnal variation of SOA concentration. A strong dependence of SOA concentrations on temperature is observed, along with the existence of an optimal temperature for SOA formation. (C) 1999 Elsevier Science Ltd. All rights reserved.


SJVAQS/AUSPEX acquired PM2.5, PM10, and gas samples at ten sites in central California during five ozone episodes over a period of 14 intensive sampling days. Four sample sets per day were collected for 5- and 7-hour durations during this period and analyzed for particulate mass, elements, ions, and organic and elemental carbon (OC and EC). Gaseous ammonia, nitric acid, and sulfur dioxide were collected with absorbing filters. Ozone (O₃), nitrogen oxides (NOx), and peroxyacetyl nitrate (PAN) were measured continuously. Concentrations varied by sampling site, time of the day, and ozone episode. The highest concentrations of most chemical species were found at sites in the southern San Joaquin Valley.

Nitrate occurred mainly in the gas phase during the daytime when temperatures exceeded 25 degrees C, and in the particulate phase during the nighttime when temperatures decreased to less than 10 degrees C. Significant amounts of nitrate volatilized from particles collected on quartz-fiber filters. Diurnal patterns of ozone, nitrogen oxides, PAN, nitric acid, and total particle citrate were similar at most of the sites, which were separated by hundreds of kilometers, showing evidence of both photochemical conversion and transport of polluted air masses.

A fuel-based method for estimating heavy-duty diesel truck emissions is described. In this method, emission factors are normalized to fuel consumption; vehicle activity is measured by the amount of diesel fuel consumed. For the San Francisco Bay Area during summer 1996, on-road heavy-duty diesel trucks were estimated at the upper bound to emit 110 x 10^3 kg/day of nitrogen oxides (NOx) and 3.7 x 10^3 kg/day of fine black carbon (BC) particles. These upper bound values were 2.3 and 4.5 times, respectively, the corresponding predictions of California's motor vehicle emission inventory model, MVEI 7G. Significant decreases in diesel truck activity and emissions, 70-80% below typical weekday levels, were observed in the Bay Area on weekends. Reductions in diesel NOx and BC particle emissions on weekends may contribute to higher ambient ozone concentrations and higher organic carbon (OC) to BC ratios observed on weekends. Heavy-duty truck traffic peaks on weekdays during the middle of the day and falls off before the afternoon rush hour. Therefore, the diurnal pattern of heavy-duty truck travel may contribute to increases in ambient OC/BC ratios observed during late afternoon hours.


This study estimates the benefits to agriculture and human health of reducing ozone in the San Joaquin Valley of California, and the costs of ozone control. The San Joaquin Valley's highly valued crops suffer from high ozone levels. Federal and state primary ozone standards are based on health effects, not effects on other sectors, and do not consider costs of attaining the standards. The methods here allow comparison of both total and marginal benefits and costs. The results suggest that net gains can be achieved for the entire valley by reducing ozone below 1990 levels, although results vary by region.


Previous model studies suggested that ambient measurements of key chemical species and ratios of species could be used to assess the sensitivities of ozone formation to reductions in precursor emissions. Threshold values of these indicator species and ratios, delineating the transition between VOC and NOx sensitivity, were proposed. Subsequently, measurement studies have assumed the universality of these threshold criteria and have compared local observed indicators with previously established criteria to assess ozone sensitivities. In this study the concept of indicator species is extended to combinations of observable species that are consistently associated with different site characteristics (e.g., ozone sensitivities and emissions features). The results of SARMAP Air Quality Model (SAQM) simulations in the San Joaquin Valley, California, are used to investigate the applicability of indicators to assess ozone sensitivities and emissions features. The use of three indicator ratios (O-3/(NOy-NOx), HCHO/NOy, and H2O2/HNO3) alone with SAQM-derived threshold criteria a found to be effective for identifying VOC- or NOx-sensitive regimes. NOy and (NOy-NOx)/NOy are found to be useful in describing emission features and threshold criteria are derived by SAQM prediction. SAQM-derived threshold criteria for assessing ozone sensitivities are found to differ from threshold criteria proposed by previous studies using different models and under different conditions. Such differences suggest that threshold criteria are likely to be dependent on locations and environmental conditions, including emission patterns and rates. Therefore local observed indicator species and ratios can be used to determine ozone sensitivities only if appropriate threshold criteria have been derived for the local conditions.


This paper reports the first power spectra of ozone (O-3) in the surface layer for which the data quality approaches that of high-quality spectra of meteorological properties. These results are employed in a surface layer scalar similarity study involving temperature, moisture, and O-3 measurements over cotton. All data were obtained during the California Ozone Deposition Experiment, in the San Joaquin Valley of California, during July and August, 1991. A detailed comparison of nondimensional scalar power spectra during unstable conditions showed that the three scalars behaved similarly, thereby providing the first completely general test of scalar similarity theory


Differences in total iron and manganese concentrations between large (d > 23 mu m) and small (4 < d < 23 mu m) cloud and fog drops were investigated at four locations in the United States. The study examined coastal stratus and stratuscumulus clouds in southern California and northern Oregon, frontal and orographic clouds at Mt. Mitchell, North Carolina, and radiation fogs in California's San Joaquin Valley. The speciation of iron as a function of drop size was also examined in some fog samples from the San Joaquin Valley. Total iron and manganese concentrations were generally higher in large drops than in small drops in clouds sampled at Mt. Mitchell and along the southern California coast. These species were typically enriched in small drops at the Oregon coast and San Joaquin Valley sites. Ratios of dissolved Fe(III) to total dissolved Fe ranged from 0.88 to 0.93 in small fog drops. Non-uniform, distributions of iron and manganese across the drop size spectrum can influence rates of metal catalyzed S(IV) autooxidation. Approximately 50% of the sampled clouds were calculated to experience autooxidation rate enhancements greater than 30% due to variations in drop acidity and catalyst concentrations with drop size


Samples of fog and cloud drops were collected by drop size from several locations around the United States. Sites were selected to represent a variety of cloud types (coastal stratus clouds, frontal clouds, and radiation fog) as well as both clean and polluted environments. A size-fractionating version of the Caltech Active Strand Cloudwater Collector (sf-CASCC) and a two-stage Eidgenossische Technische Hochschule (ETH) cloud impactor were each used to simultaneously collect small and large cloud drop fractions. The sf-CASCC is designed to collect drops > 23 mu m in diameter in the large fraction and drops between 4 and 23 mu m in the small fraction, while the ETH impactor is typically configured to collect drops > 10 mu m in diameter and drops between 3 and 10 mu m in diameter in its two size fractions. Concentrations of sulfate and ammonium were typically observed to be enriched in small cloud drops. A similar pattern was observed for nitrate at several locations. Coarse mode aerosol species were often observed to be enriched in large cloud drops. These findings suggest that the size-dependent chemical signature of the precursor aerosol particle size distribution is at least partially maintained in the cloud drop size spectrum. The observed size dependence of the cloud drop composition can enhance rates of aqueous phase sulfate production relative to expectations based on average cloud drop composition, bias efficiencies with which individual chemical species are incorporated into precipitation within clouds, and affect patterns of chemical deposition to plant canopies or within the respiratory tract.

Evaporation ponds in the San Joaquin Valley (SJV), CA, used for the disposal of irrigation drainage waters, contain elevated levels of uranium. The ponds are filled periodically and support algae which upon evaporation become incorporated in the sediments as layers of decaying organic matter. This rich source of organic matter promotes reducing conditions in the sediments. Our research was conducted to characterize oxidation/reduction reactions that affect soluble and sediment U(IV)/U(VI) concentrations in the SJV ponds. Studies were done to (I) determine soluble U(VI)/U(IV) in waters in contact with a pond sediment subjected to changes in redox status, (2) observe U solid oxidation state as a reducing pond sediment underwent (in vitro) oxidation, and (3) determine U solid oxidation state with respect to depth in pond surface sediment layers. Low pressure ion-exchange chromatography with an eluent of 0.125 M H2C2O4/0.25 M HNO3 was used for the separation of U(IV) and U(VI) oxidation states in the drainage waters. Soluble U(VI) and U(IV) coexisted in sediment suspensions exposed to changes in redox potential (Eh) (-260 mV to +330 mV), and U(VI) was highly soluble in the oxidized, surface pond sediments. X-ray near edge absorption spectroscopy (XANES) showed that the U solid phases were 25% U(IV) and 75% U(VI) and probably a mixed solid [U3O8(s)] in highly reducing pond sediments. Sediment U(IV) increased slightly with depth in the surface pond sediment layers suggesting a gradual reduction of U(VI) to U(IV) with time. Under oxidized conditions, this mixed oxidation-state solid was highly soluble. Copyright (C) 1997 Elsevier Science Ltd


Removal of tropospheric ozone from polluted airbasins by deposition to vegetation may be an important determinant of regional air quality. The physiological and physical processes that determine the magnitude of deposition, and the relative contributions of uptake by photosynthetic tissues versus ozone destruction on plant and soil surfaces, are not well understood. The California Ozone Deposition Experiment (CODE) demonstrated substantial deposition of ozone to several vegetated surfaces in the San Joaquin Valley. Using data collected during CODE, we examine the roles of stomatal conductance and leaf wetness from dew in mediating ozone deposition to an extensive field of irrigated cotton. Stomatal conductance, photon flux density, leaf area index (L), leaf wetness, ozone deposition, and canopy photon extinction coefficient (K) were measured. Single leaf measurements were scaled to canopy values of stomatal conductance to ozone (g(c)). Deposition velocity (V-d) and surface conductance (g(surf)) were strongly positively correlated with g(c). Under dry canopy conditions g(c) < g(surf) indicating a significant residual conductance of a non-stomatal pathway for ozone deposition (g(r)), possibly reflecting reaction of O-3 with nitric oxide emitted from fertilized soil. Dewfall reduced ozone deposition and eliminated g(r). However, g(r) may actually have been increased by dew in amphistomatous cotton, as it was in hypostomatous grape during CODE. If so, canopy wetness reduced the stomatal pathway (g(c)) by occlusion of adaxial pores sufficiently to offset both the nitric oxide titration and the true wetness enhancement of g(r). We conclude that ozone deposition to cotton is largely controlled by stomatal responses, Stomatal responses may readily be modelled, potentially providing sufficient information to infer ozone deposition. In contrast to the case for hypostomatous grape, ozone uptake (particularly by the stomatal pathway) is reduced by leaf surface wetness in amphistomatous cotton. Alternative models of single leaf stomatal conductance and expected errors of +/- 20% in model parameters did not affect these conclusions. (C) 1997 Elsevier Science B.V


Understanding the speciation of the multioxidation states of selenium is vital to predicting the mineralization, mobilization, and toxicity of the trace element in natural systems. A sequential extraction scheme (SES) was developed for identification of Se oxidation states that first employed 0.1 M (pH 7.0) K2HPO4-KH2PO4 (P-buffer) to release soluble selenite (Se(+IV)) and selenide (Se(+II)) and ligand-exchangeable selenite (Se(+IV)). The second
step involved oxidation of organic materials with 0.1 M K2S2O8 (90 degrees C) to release Se--II and Se+IV associated or occluded with organic matter. The final step used HNO3 (90 degrees C) to solubilize insoluble Se remaining in the sample. The solubilized Se compounds were speciated by a selective hydride generation atomic absorption spectrophotometry technique. Accuracy of the developed SES method (96-103% recovery) was verified by use of prepared Se compounds of known speciation, NIST standard reference materials, and existing seleniferous soils. The average precision (relative standard deviation) for the P-buffer extraction ranged from 5.5 to 7.7% (n = 12); the precision of the persulfate extraction ranged from 2.6 to 8.4% (n = 12); and the precision of the nitric acid extraction ranged from 2.8 to 7.4% (n = 12) for three soils extracted at four different time periods. The method was applied to analyze Se species in seleniferous plant, soil, and sediment samples.


Aircraft-based eddy correlation flux data obtained at a height of 30 m above irrigated and non-irrigated agricultural land in southern California have been analyzed in terms of the coherent structures that dominate the turbulent exchange of energy and gases during daytime conditions. The analysis focused on transport of sensible heat, moisture, carbon dioxide and ozone in the gradient modes, i.e. excess up or deficit down for heat and moisture, and deficit up or excess down for carbon dioxide and ozone. Results are presented for composition and size of the dominant structures, over water-stressed and non-water-stressed surfaces, and on the relative frequency with which structures carrying only a single scalar, or given combinations of scalars, were encountered along the flight paths. Interpretation of results provides further evidence for the existence of a second (non-physiological) sink for ozone. The relative preponderance of structures that carry moisture, carbon dioxide and ozone simultaneously, particularly in the gradient up mode, reflects the importance of vegetation as co-located source/sink for these scalars. Surface characteristics resulting in thermal buoyancy and water vapour density gradients appears to be responsible for about 85% of gradient up transport. Finally, the detrending procedures described here may help to define more effective separation between local and mesoscale events in biosphere-atmosphere interactions. (C) 1997 Elsevier Science B.V


Current meter data have been analyzed from seven moorings on the continental slope along the central California coast, from Point Piedras Blancas to Point Reyes. The goal was to examine the subtidal variability in the 100 m to 1000 m depth range, particularly with regard to alongshore propagating events and interactions with eddies and meanders of the California Current offshore. The 2-year time series available off Point Sur were first analyzed in conjunction with the local and remote surface wind stress and coastal synthetic subsurface pressure, and then correlated with shorter coincident current records moored at similar depths to the north and south. The poleward flowing California Undercurrent was the most prominent feature at all the moorings except at one site located well into the Monterey Submarine Canyon. The strongest poleward flows over the slope occurred in 3- to 4-month bursts, not phase locked with the seasons, with vector speeds exceeding 40 cm s(-1). South of the canyon, an approximately monthly signal was identified which propagated poleward, upward, and offshore. The behavior of this signal was consistent with that of an internal coastal Kelvin wave generated at the surface by remote wind stress to the south and was likely not of equatorial origin. The wave was apparently scattered by the abrupt topography of the canyon, since its energy persisted to the north of the canyon but with unstable phase. At least three eddy-meander interaction events were observed, These warm, deep (>1000 m), anticyclonic features reversed the flow over the slope to equatorward when they moved onshore and interrupted the flow of the undercurrent. One event forced anomalously strong (>15 cm s(-1)) onshore flows off Monterey flay and offshore flows off Point Sur. While quantitative transport estimates could not be made with this sparse data set, it seems apparent that such events play a significant role in the exchange of water properties between the shelf and the deep ocean.


Successful programmes were developed by Ahlstrom Development Ash Corporation and Air Products and Chemicals for using fluidized bed combustion ash as a substitute for agricultural lime on dairy farms in northern
New York state and on fruit and nut crops in the San Joaquin Valley of California. The companies developed these programmes by utilizing the methodology developed through USDA-ARS research and working closely with agricultural consultants and regulatory agencies to ensure that the ash applications were both agronomically and environmentally sound.


The data from two current meter moorings off Point Sur, California, were analyzed to examine the energy transfers over the continental slope in the California Current system (CCS). The method used was to calculate terms in the heat equation at intermediate depths between instruments, using the thermal wind relation to estimate the horizontal temperature gradients from the vertical shear. Time series of u, v, and T were collected for 17 months (May 1989 to October 1990) at site P2 on the 800-m isobath and for 12 months (May 1990 to May 1991) at site P3, 25 km farther offshore on the 1800-m isobath. Instrument depths were 100, 350, and 500 m at both moorings plus 1000 m at site P3. Mean values of the energy conversion terms were computed at sites P2 and P3 at 225 m depth and at site P2 at 425 m depth. The local change of eddy potential energy (EPE) was approximately balanced (partial derivative EPE/partial derivative t approximate to 0) for each case but the dynamics were quite different. At P2 225, the sources of EPE were advection by the mean flow and baroclinic instability, which converted mean potential energy (MPE) to EPE. The losses came from eddy advection out of the region and the vertical eddy heat flux (VEHF), which converted EPE to eddy kinetic energy (EKE). At P2 425, baroclinic instability provided the major source of EPE. This, plus a small positive contribution from the VEHF, was balanced by advection of EPE out of the region by both the mean flow and the eddies. At P3 225, mean advection and baroclinic instability were negligible, and the downward eddy heat flux (VEHF) was balanced by advection of heat out of the region by the eddies. Time series of terms in the EPE equation were used to examine high energy transfer events at both moorings. Events at P2 involved both horizontal and vertical processes and had longer timescales (several days to weeks) than those at P3, which had much shorter timescales (2-5 days) and were dominated by vertical processes. Compared to the Gulf Stream, the mean baroclinic instability at P2 (both depths) was smaller by at least a factor of 10. A term-by-term comparison between the mean values off Point Sur and the Kuroshio Extension showed different processes, with the eddies gaining strength at the expense of the mean flow off Point Sur and the opposite occurring in the Kuroshio Extension.

Wallace, L., Slonecker, T., 1997. Ambient air concentrations of fine (PM_{2.5}) manganese in U.S. national parks and in California and Canadian cities: The possible impact of adding MMT to unleaded gasoline. Journal of the Air & Waste Management Association 47 (6), 642-652


PM(10) aerosols were collected during 1989 every sixth day at six sites in Santa Barbara County, CA. Samples were analyzed for sulfate, nitrate, and ammonium ions, carbon, and elements. Chemical Mass Balance (CMB) receptor modeling was conducted to determine the sources of PM(10). Motor vehicles, road dust, and marine aerosol accounted for 30-42, 25-27, and 18-23% of PM(10), respectively, at three urban sites: Santa Barbara, Santa Maria, and Santa Ynez. The marine contribution was 55-63% of PM(10) at two marine background sites. Fresh marine aerosols were characterized by low levels of urban emissions, low concentrations of secondary sulfate and nitrate, and generally higher levels of acidity. Conversely, marine aerosols aged by contact with land-based emissions had higher concentrations of secondary ammonium sulfate and nitrate.


SJVAQS/AUSPEX acquired PM(2.5) and PM(10) samples at ten sites in Central California for five ozone episodes over 14 intensive sampling days. Four sample sets per day were acquired for 5 and 7 h durations and measured for
particle mass; elements; water-soluble chloride, nitrate, sulfate, ammonium, sodium, and potassium ions; and organic and elemental carbon. Gaseous ammonia, nitric acid, and sulfur dioxide concentrations were acquired with absorbent filter material. To guard against contamination of these gases after sampling, the filter packs were sealed and refrigerated prior to analysis. Crustal species such as aluminum, silicon, calcium, titanium, iron, and calcium, were found in coarse particles at most sites. Substantial amounts of sodium and chloride were detected in the coarse particle fraction at the coastal Point Reyes site. Organic carbon and sulfate were the most abundant species in the PM(2.5) fraction. Elemental carbon concentrations were low at all sites. Only one 24 h average PM(0) concentration exceeded the U.S. PM(10) standard of 150 μg m(-3) during the study period, and this occurred at the agricultural-oriented Buttonwillow site. The highest concentrations of most chemical species were found at sites in the Southern San Joaquin Valley.


The planning process and implementation of control measures required to meet the Clean Air Act mandate to attain and maintain Federal Ozone Standards are outlined and discussed. Actual efforts began in the early 1960s and progressed from stationary source controls to new motor vehicle emission reductions to transportation control measures to limit emissions from vehicles in use. Air quality measurements demonstrate the success that these approaches have had in bringing days over the standard from 70 in the late 1960s to 2 or 3 in the most recent years.

Grantz, D.A., Zhang, X.J., Massman, W.J., Delany, A., Pederson, J.R., 1996. Ozone deposition to a cotton (Gossypium hirsutum L.) field: stomatal and surface wetness effects during the California Ozone Deposition Experiment. Agricultural and Forest Meteorology


Steam-enhanced recovery methods have been the overwhelming EOR champions since their inception in the mid-1960's. About 6 of every 10 EOR barrels produced worldwide are the result of some steam process. Historically most well known in the San Joaquin Valley of California, large steam projects exist in countries around the world, including Venezuela, Canada, Colombia, Indonesia, China, and the CIS. Therefore, one would think that most of the basic problems, such as effective steam-distribution piping systems and accurate methods of metering steam into wells, would have been solved years ago. Unfortunately, this is not the case. In fact, this technology has been woefully lacking compared with its relative importance. This paper summarizes current efforts by the industry to improve metering and distribution of quality steam.


On 29 November 1991 a series of collisions involving 164 vehicles occurred on Interstate 5 in the San Joaquin Valley in California in a dust storm that reduced the visibility to near zero. The accompanying high surface winds are hypothesized to result from intense upper-tropospheric downward motion that led to the formation of a strong upper front and tropopause fold and that transported high momentum air downward to midlevels where boundary layer processes could then mix it to the surface. The objectives of the research presented in this paper are to document the event, to provide support for the hypothesis that both upper-level and boundary layer processes were important, and to determine the structure of the mesoscale circulations in this case for future use in evaluating the navy's mesoscale data assimilation system. The strong upper-level descent present in this case is consistent with what one would expect for jet streak and frontal circulations in combination with quasigeostrophic processes. During the period examined, upper-level data and analyses portray a strong upper-tropospheric jet streak with maximum winds.
initially in excess of 85 m s\(^{-1}\) (approximate to 170 kt) that weakened as it propagated southward around the base of a long-wave trough. The jet streak was accompanied by a strong upper front and tropopause fold, both of which imply intense downward motion. The vertical motion field near the time of the accidents had two maxima—one that was associated with a combination of quasigeostrophic forcing and terrain-induced descent in the lee of the Sierra and one that was associated with the descending branch of the secondary circulation in the jet streak exit region and the cold advection by both the geostrophic wind and the ageostrophic wind in the upper front. The 700-hPa wind speed maximum over and west of the San Joaquin Valley overlapped with the latter maximum, supporting the hypothesized role of downward momentum transport. Given the significant 700-hPa wind speeds over the San Joaquin Valley during daytime hours on the day of the collisions, boundary layer mixing associated with solar heating of the earth's surface was then able to generate high surface winds. Once the high surface winds began, a dust storm was inevitable, since winter rains had not yet started and soil conditions were drier than usual in this sixth consecutive drought year. Surface observations from a variety of sources depict blowing dust and high surface winds at numerous locations in the San Joaquin Valley, the Mojave and other desert sites, and in the Los Angeles Basin and other south coast sites. High surface winds and low visibilities began in the late morning at desert and valley sites and lasted until just after sunset, consistent with the hypothesized heating-induced mixing. The 0000 UTC soundings in California portrayed an adiabatic layer from the surface to at least 750 hPa, also supporting the existence of mixing. On the other hand, the high winds in the Los Angeles Basin began near sunset in the wake of a propagating mesoscale trough that appeared to have formed in the lee of the mountains that separate the Los Angeles Basin from the San Joaquin Valley.


The roadway is one of the most important microenvironments for human exposure to carbon monoxide (CO). To evaluate long-term changes in pollutant exposure due to in-transit activities, a mathematical model has been developed to predict average daily vehicular emissions on highways. By utilizing measurements that are specific for a given location and year (e.g., traffic counts, fleet composition), this model can predict emissions for a specific roadway during various time periods of interest, allowing examination of long-term trends in human exposure to CO. For an arterial highway in northern California, this model predicts that CO emissions should have declined by 58% between 1980 and 1991, which agrees fairly well with field measurements of human exposure taken along that roadway during those two years. An additional reduction of up to 60% in CO emissions is predicted to occur between 1991 and 2002, due solely to the continued replacement of older cars with newer, cleaner vehicles.


Ozone conducive meteorological conditions are identified based on statistics derived from local meteorological data of 31 eastern U.S. cities in a period of ten summers (1981-1990). A method of using ozone conducive meteorological conditions to construct a wind rose to site photochemical pollutant monitors is presented. The approach used to derive ozone conducive criteria appears to be quite robust, suggesting that the method may be applicable to site photochemical pollutant monitors in other areas of the United States.
Several recent large-scale experiments in land-surface climatology have used the combination of aircraft- and tower-based flux measurements. Within these experiments, much effort has been made to assess the potential of aircraft to serve as extended observation platforms for the scaling up from local (tower-based) to regional estimates of surface-atmosphere exchange. Data collected as part of the California Ozone Deposition Experiment (CODE), during a one-month period of consistent day-to-day wind and radiation conditions, were particularly conducive to such a study. Aircraft-based flux estimates obtained at 30 and 60 m above two vineyard sites of approximately 9 km(2) (site A, 6 km x 1.5 km and site B, 4.5 km x 2 km) were compared to tower-based measurements made at 9.4 m above a section of site A. This paper shows that over the measuring period the sum of sensible and latent heat Bur at 30 m, as measured with the aircraft-based system, was about 11% less than that measured with a tower-based system at 9.4 m. It also shows that fluxes at 30 m were on the average about 10% larger than those at 60 m. It documents the flux variability of CO2, sensible and latent heat and ozone observed over relatively homogeneous surfaces. Although aircraft-tower comparisons must be interpreted with caution, due to the dissimilar surface areas sampled by the stationary and moving sensors located at different elevations, the consistent relationship obtained between these two sampling systems demonstrates the complementary nature of such measurements. It confirms that very repeatable measurements can be obtained with aircraft-based systems over distances as short as a few kilometers. It also demonstrates that compositing data for several runs and for several days from aircraft- and tower-based measurements can provide diurnal patterns of fluxes of sensible and latent heat as well as CO2 and O-3 on a regional scale.


One of the major concerns in central California (San Joaquin Valley) is the level of selenium (Se) in evaporation ponds containing agricultural drainage water. The objective of this work was to determine if volatilization of Se could be used as a bioremediation program to detoxify a saline seleniferous sediment of a dewatered evaporation pond. The dewatered sediment was rototilled, divided into subplots, and amended with various organic materials including citrus (orange) peel, cattle manure, barley straw and grape pomace. Some of the subplots were fertilized with nitrogen [(NH4)(2)SO4] and zinc (ZnSO4). Selenium volatilization was monitored in the field with a flux chamber system utilizing alkaline peroxide to trap the gas. Overall, the greatest emission of gaseous Se was recorded in the summer months and the lowest emission during the winter months. The background emission of volatile Se averaged 3.0 μg Se h(-1) m(-2). The most effective organic amendment was cattle manure with an avg. Se emission of 54 μg Se h(-1) m(-2). Composite soil samples from each subplot (upper 15 cm) were analyzed for total Se on a monthly interval during the course of this field study. After 22 months, the application of water plus tillage alone removed 32.2% of the Se content while the cattle manure treatment removed 57.8%. Among the parameters which enhanced volatilization of Se were an available C source, aeration, moisture, and high temperatures. This field study indicates promising results in detoxifying seleniferous sediments via microbial volatilization once environmental conditions have been optimized.


The chemical mass balance (CMB) receptor model was applied to the nonmethane organic gas (NMOG) database acquired during the San Joaquin Valley Air Quality Study (SJVAQS)/Atmospheric Utility Signatures-Predictions and Experiment (AUSPEX) Regional Model Adaptation Project (SARMAP). During SARMAP, the major contributors to NMOG were vehicle exhaust, liquid gasoline, gasoline vapor, oil production, acetone and unidentified organic compounds. Oil production was the major contributor to NMOG in the southern SJV during the morning hours, ranging from about one-third to one-half of the total NMOG. Contributions of oil production were lower during the afternoon due to increased ventilation, and larger contributions from secondary organic compounds. In the afternoon, the combined fraction of acetone and unidentified or unexplained (difference between calculated and measured mass) NMOG, which is mostly of secondary origin, accounted for about half of the total NMOG at receptor sites. Only the Yosemite and Giant Forest sites showed significant contributions from biogenic
The fact that CMB did not detect significant contributions from biogenic sources in samples collected from sites in the SJV where estimated biogenic emission rates exceed those of either Yosemite or Giant Forest, suggests that biogenic emissions are overestimated in the SARMAP inventory. Source contribution estimates for total motor vehicle emissions averaged 75 and 70% of the total measured NMOG in urban areas during the 0800-1000 and 1200-1400 sampling periods, respectively, compared to the average daily emission inventory contribution of 44%. These results support recent studies which indicate that motor vehicle emissions have been seriously underestimated.


Selenium has evapoconcentrated to hazardous levels in agricultural evaporation ponds in the San Joaquin Valley of California. Microbial methylation and volatilization is one of the pathways by which high Se concentrations may be dissipated from these ponds. To obtain a more complete understanding of this potential remediation process, kinetic models are developed to evaluate the factors affecting Se biomethylation such as temperature and organic C sources (carbohydrates and proteins) using experimental data from the literature. By assuming that dimethylselenide (DMSe, (CH3)2Se) formation is irreversible and follows first-order kinetics, the experimental data are described reasonably well using temperature- and organic matter-characteristics, except deviations occurred at a higher temperature (35 degrees C). Proteins are known to stimulate Se volatilization dramatically as compared with carbohydrates as the energy source. This stimulatory property appears to depend on the ability of microorganisms to absorb protein hydrolysis products, a source of methyl groups. A coupled reaction mechanism is proposed in which proteins provide methyl groups for Se methylation to form volatile DMSe. The model fitted experimental data successfully. The volatility of DMSe through the air-water interface was evaluated using a two-layer film model. The predicted half-life of DMSe in water ranged from 1 to 3 d when assuming that wind speed was <3 m s(-1) and the water body was 1 m deep. An opportunity exists to enhance Se volatilization by fungi, bacteria, microalgae, and other indigenous microbes found in evaporation ponds as a remediation technique. Additional knowledge on the fate of DMSe both in the water and in the atmosphere, however, is needed to evaluate this dissipation strategy in high Se water bodies.


Surface deposition is an important sink that removes ozone from polluted air basins, and leads to crop damage and ecosystem decline. Physiological and physical processes controlling deposition to vegetated surfaces are incompletely understood. We investigate the relationship between ozone flux to trellised grape, F, and canopy stomatal conductance to ozone, g(c), under dew-wetted and dry conditions. Empirically measured stomatal conductance was scaled to g(c) using empirical measurements of leaf area index, L, single leaf stomatal response to photon flux density, I, and bulk canopy radiation extinction coefficient, K. Leaf wetness was determined with surrogate leaves covered with electrical impedance grids. Deposition velocity, V-d, and surface conductance, g(surf), were positively and highly significantly related to g(c). Surface wetness substantially increased V-d and g(surf). Under all conditions, g(c) < g(surf), suggesting a significant non-stomatal (residual) pathway for ozone deposition, g(r). This residual term, g(r), was increased under wet conditions by a constant amount over the full range of g(c). Expected errors of +/- 20% in the single leaf model, in L, or in K, did not influence these conclusions. We conclude that V-d and g(surf) were dominated by g(c), which may be used effectively to predict ozone deposition to physiologically active vegetated surfaces. Dew formation enhanced ozone deposition to the hypostomatous leaves of this grape canopy by a nonstomatal pathway.


The interplay between surface uptake and atmospheric chemistry makes aircraft-measured ozone fluxes near the surface complex to interpret over such surfaces as recently, cultivated bare soil, newly cut hay, cities and near highways in the San Joaquin Valley of California (the California Ozone Deposition Experiment, 1991). In this study, a simple partitioning scheme is proposed, based on the estimation of the ozone surface-uptake rate by a regressional
fit of ozone flux vs latent heat flux and a vegetation index, over well-irrigated vegetative surfaces, by assuming that ozone flux residuals are due to atmospheric chemistry. The contributions to ozone fluxes by atmospheric chemistry over surfaces other than well-irrigated vegetative surfaces can then be estimated from the difference between the estimated ozone surface-uptake rate and the measured ozone flux. The estimates indicate that chemical contributions are more significant than surface-uptake and that the chemical contributions are dominated primarily by ozone destruction over recently cultivated bare soil, newly cut hay, city and near highway. The dominant sink for ozone destruction is analytically shown to be caused by NO concentrations in excess of the photostationary state, which are believed to be linked to the strong NO emissions from the surfaces.


Fluxes of sensible heat, latent heat, CO\textsubscript{2} and ozone over a variety of land surfaces, based on 5 km-averaged near-surface airborne data, are examined within the 1991 California Ozone Deposition Experiment (CODE) in the San Joaquin Valley of California. It is found that the fluxes of sensible heat, latent heat and CO\textsubscript{2} are well correlated and correspond significantly to the surface greenness index over all selected surface types, which indicates that the three fluxes are primarily driven by the surface biological (physiological) processes. However, a significant correspondence between ozone flux and the surface greenness index is found only over the vegetative surfaces. The nonvegetative surfaces are composed of recently cultivated bare soil and newly cut hay, where the rapid chemical reactions of ozone with its precursors originating from soil microbial activities might become an important controlling factor. This suggests that ozone flux may be controlled by a combination of the surface uptake process dominant over the vegetative surfaces and the atmospheric chemical process dominant over the nonvegetative surfaces. The two kinds of processes may mask each other's effects, and lead to the poor and confusing correspondence between ozone flux and the surface greenness index.


In this study, the authors have conducted a series of numerical experiments to investigate the how circulations in the Central Valley of California and the formation mechanisms of the Fresno eddy. The authors have found the following: Under an adiabatic northwesterly, low-Froude number flow over the Central Valley, two cyclonic vortices form in the basin. One is located on the lee slope of the northern Coastal Range, while the other is located to the south of the San Joaquin Valley. The first may be identified as the Sacramento eddy, while the second may be identified as the Fresno eddy, although the Fresno eddy is located slightly farther to the south. The formation of the Sacramento eddy may be explained by either the generation of potential vorticity (Smith) or the generation of vorticity due to baroclinicity (Smolarkiewicz and Rotunno) on the lee slope in a low-Froude number dow. The Sacramento eddy may also be classified as a lee mesocyclone since it is collocated with a lee mesolow (Lin et al.). In addition, a northwesterly jet forms at the gap of the Coastal Range due to the channeling effect. The Fresno eddy forms when the low-Froude number northwesterly flow meets the return flow from the Tehachapi Mountains in a rotating fluid system and is strengthened and expands farther to the north due to the effects of nocturnal radiative cooling. The northwesterly jet in the Central Valley, the southeasterly wind from the foothills of the Sierra Nevada, and the blocking effect due to the Tehachapi Mountains all play important roles in the formation of the Fresno eddy. The Sacramento eddy moves eastward to the foothills of the Sierra Nevada, while the jet at the gap of the Coastal Range is suppressed when nocturnal radiative cooling is present. The nocturnal drainage flow over the western slope of the Sierra Nevada is weakened by the southerly return flow from the Tehachapi Mountains. The simulations indicate that in the absence of nocturnal radiative cooling the Fresno eddy still forms but is weaker and is located near the southern end of the San Joaquin Valley. The Fresno eddy will form in an environment characterized by low-Froude number northwesterly wind. Suitable incoming flow speed and direction are among the major factors in determining the formation and strength of the Fresno eddy. The return flow from the southern boundary of the San Joaquin Valley plays an important role in the formation of the Fresno eddy. The Fresno eddy does not form in the absence of planetary rotation. The beta effect plays a negligible role in the formation of the Fresno eddy.

In the summer of 1991 the San Joaquin Valley Air Pollution Study Agency organized a four-week international field experiment to measure ozone concentrations and fluxes in the San Joaquin Valley of California. The field data are being used to improve the understanding of the exchange processes occurring between the atmosphere and various types of vegetation, and to develop a comprehensive computer model for ozone transport and deposition in the valley. The National Research Council of Canada (NRC) Twin Otter atmospheric research aircraft flew 24 flights in this program, measuring fluxes and deposition velocities adjacent to three highly instrumented tower facilities, each situated over a vegetation type significant to the area, i.e. cotton, grapes, and natural grassland. Having established a correlation between aircraft- and tower-measured fluxes at these reference locations, the aircraft was then used to measure fluxes at regional scales over several additional types of vegetation throughout the San Joaquin Valley. The paper will describe the instrumentation and flight procedures used to make these airborne flux measurements, with emphasis on ozone. Summary data will be presented on the correlation between ozone deposition velocity and the greenness index, the ratio of reflected infrared to red radiation which is an indication of the density of green vegetation beneath the aircraft. Sample results from several special studies will also be presented; these include repeated runs on a regional scale, a grid study, an overflight of the City of Fresno, runs made adjacent to Interstate-5, and repeated passes over the cotton site during the solar eclipse on 11 July 1991. More detailed results from the Twin Otter operations in this experiment are presented in a series of companion papers.


This study examines the spatial variability of ozone fluxes over flat heterogeneous terrain consisting of a patchwork of irrigated and nonirrigated surfaces. Fluxes of ozone and other quantities are computed from eight sequential flight legs of the Canadian Twin Otter research aircraft over the same track at 33 m above the surface for each of 2 days. The fluxes are composited over the eight runs to reduce the random flux error. The fluxes of heat, moisture, and carbon dioxide are closely related to spatial variations of surface vegetation. However, the ozone flux is affected by additional factors including reaction with NO released from point sources. This effect is illustrated here with two examples of irrigation pumping stations driven by diesel engines. We conclude that the ozone deposition to the surface cannot be estimated from the measured ozone flux without correction for the NO sources.


Stomatal uptake by vegetation is often the major sink for the destruction of tropospheric ozone. Using data obtained during the summer of 1991 at a grape vineyard and a cotton field in the San Joaquin Valley of California, we compare canopy (stomatal) conductances to ozone estimated (1) from eddy covariance ozone flux data (2) from eddy covariance evapotranspiration data and (3) by scaling leaf transpiration conductance to the canopy level using a canopy radiative transfer model. These simultaneous data, obtained at two levels of biological organization and for two trace gases, allow us to contrast the pathways for canopy-atmosphere exchange of water vapour and ozone, to evaluate limitations to scaling from leaf to canopy, and to predict ozone uptake parameters from those governing transpiration. At the vineyard site the eddy covariance ozone results underestimate the ET-based (eddy covariance and leaf scaling) approaches between 25% and 36%. At the cotton site the ozone-based results overestimate the ET-based approaches between 9% and 62%. A number of modelling and measurement uncertainties are of appropriate magnitude to reconcile these estimates. Some of the possible causes for these discrepancies that are discussed include NO effects, mesophyll resistances to ozone uptake and flaws in the K-theory (first-order closure) approach on which the canopy-scale analysis is based. Nevertheless, both canopy and single leaf measurements of conductance for water vapour provide acceptable estimates of conductance for ozone, but further experiments in which all are measured simultaneously are suggested.

Plants and soils act as major sinks for tropospheric ozone, especially during daylight hours when plant stomata are thought to provide the dominant pathway for ozone uptake. The present study, as part of the larger California Ozone Deposition Experiment, uses aircraft eddy covariance measurements taken during the summer of 1991 in the San Joaquin Valley of California to estimate the surface conductance for ozone uptake. To explore for possible sources of discrepancies between the aircraft-derived and tower-based surface conductances a comparison is first made between tower-based fluxes and aircraft fluxes at three tower-based sites. On the average the momentum and surface energy fluxes (sensible and latent heat) observed between 30 and 33 m altitude with an aircraft agreed to within +/- 10% with simultaneously measured tower-based fluxes (observed between 4 and 10 m at a vineyard, a cotton and a grassland site). However, comparisons of the aircraft- and tower-based ozone fluxes indicate that between about 4 and 33 m there is an average loss of ozone flux with height of about 18%. It is suggested that either (or both) soil NO emissions or entrainment of ozone free air at the top of the mixed layer may be responsible for this relatively larger discrepancy in the ozone fluxes. Nevertheless, in spite of any relatively larger uncertainties associated with the ozone flux, the tower-based and aircraft-based conductances are in good agreement. The aircraft-derived conductances display a similar magnitude and range of variation as the tower-based conductances and the regression coefficient between the two sets of conductances is 0.9 +/- 0.08. Therefore, results from this study suggest that the aircraft can be used to estimate surface conductances of ozone deposition; however, these conductances are subject to large uncertainties.


Grid-type flight patterns at an altitude of 30 m were executed in the summer of 1991 by the Canadian Twin Otter flux research aircraft over a 15 km x 16.1 km agricultural area, as part of the California ozone deposition experiment (CODE). This permitted the mapping, by eddy covariance techniques, of surface-atmosphere exchange for sensible heat, moisture, CO2 and ozone, in the form of GIS-interpolated flux maps and in the discrete form of those coherent structures of the turbulent transfer process that dominate these exchange processes. The magnitude of surface-related mesoscale contributions to the flux was also quantified. Flux observations were compared against radiometrically observed surface temperatures and vegetation indices (NDVI and VI), observed from aircraft and satellite, and surface characteristics obtained from ground surveys. Flux maps showed the expected close correspondence between greenness, evapotranspiration (ET) and CO2 exchange, but a weaker correspondence between these and ozone flux maps than would be expected if ozone uptake could consistently be scaled to stomatal conductance for moisture or CO2. Examination of the spatial coincidence between transporting structures for the various scalars (heat, moisture, CO2 and ozone), through the Jaccard coefficient of co-location, J, showed a lower overall value (0.45 < J < 0.55) for coincidence in transfer between ozone and moisture than between CO2 and moisture (0.6 < J < 0.7), and analysis of coincidence for the various crop types within the grid permits quantitative assessment of the potential error made when scaling ozone uptake to stomatal conductance. In general, the findings suggest the existence of two sinks for ozone only one of which is tied to stomatal conductance, and indicates a possible relative advantage for estimates of ozone uptake based on CO2 rather than moisture exchange.


The large volume of data measured during the 1990 summer San Joaquin Valley Air Quality Study/Atmospheric Utility Signatures, Predictions, and Experiments (SJVAQS/AUSPEX) provides a unique opportunity to examine the influence of meteorology on air quality for a variety of regions in central California. This paper provides a qualitative analysis of surface and upper-level meteorological and air quality data measured during 3-6 August 1990 in San Luis Obispo County (SLOC) and the southwestern side of the San Joaquin Valley (SJV). During this 4-day period, daytime and nighttime atmospheric mechanisms helped to transport ozone into layers aloft over the SJV. Air flowing out of the SJV in the afternoon transported elevated layers of ozone into SLOC. The daily onshore flow from the west opposed this outflow of air from the SJV. The onshore flow prevented the transported ozone from the SJV from reaching the surface and allowed some ventilation into the southwestern side of the SJV. However, on 5 August 1990, a strong ridge of high pressure over the western United States helped to weaken onshore flow and allowed outflow from the SJV to penetrate much further to the coast. These changes in the synoptic-scale meteorology increased transport of polluted air into the region and decreased overall circulations at the surface. As a
result, ozone levels exceeded the California state standard for ozone (>90 ppb) at two remote sites in the SJV on 5 August, and at one site in the SLOC on 6 August 1990. This paper discusses the synoptic meteorology and the surface and upper-level meteorological and air quality data. Also, it is revealed that ozone transport and other atmospheric processes that influence surface air quality caused the ozone exceedances


Evaporation ponds in California's San Joaquin Valley are an interim disposal solution for saline drainage waste water from irrigated agriculture. A water quality monitoring program was initiated to gauge the environmental fate of potential inorganic toxicants (As, B, Ma, and Se) upon evapoconcentration. Chemical composition is dominated by Na, Cl, and SO4, with electrical conductivities ranging from 8 to 34 dS/m in inflow and from 48 to 178 dS/m in pond waters. Trace element levels are largely determined by (1) geomorphic landscape position, (2) degree of evapoconcentration, and (3) chemical reactivity in the water column-sediment system. Cl-based evapoconcentration factors were calculated to evaluate trace element chemical reactivity. B was readily conserved, whereas As, Mo, and Se underwent loss from the water column. As, B, and Se approached or exceeded hazardous waste criteria.

Continued operation within environmental standards requires careful management


The California Ozone Deposition Experiment (CODE) is a program of observations and modeling to improve estimates of the rate of removal of tropospheric ozone at the earth's surface used in grid-based photochemical models of ozone production, transport, and removal. The purpose of CODE is to test, diagnose and improve treatment of dry deposition of ozone and other gaseous species. CODE supports a larger air quality measurement and modeling effort comprised of the San Joaquin Valley Air Quality Study (SJVAQS) and Atmospheric-Utilities Signatures: Predictions and Experiments (AUSPEX) joined as SJVAQS/AUSPEX Regional Model Adaptation Project (SARMAP). However, the CODE data are also applicable to a variety of boundary layer and turbulence problems. This paper describes the field methods and data collected during summer (10 July through 6 August) of 1991 in the San Joaquin Valley (SJV) of California and introduces several related papers. General comparisons and conclusions from all the participants are summarized. The core elements of the CODE field effort consisted of a research aircraft for spatial coverage and three ground sites located in a cotton field, grape vineyard, and very dry (senescent) annual grassland. A major portion of the SJV is represented by these three vegetation types. The eddy covariance method is used to compute the vertical fluxes of ozone, carbon dioxide, water vapor, sensible heat and momentum. For the first half of the study period, flights were made mainly for comparison with tower-based fluxes. Subsequent flights were over other vegetation types and to conduct special studies. In addition to the vertical fluxes, the ground-site data include individual leaf measurements of stomatal conductance, radiative leaf temperature, wetness of surrogate leaves, soil temperature profiles and heat flux, soil composition and water content, mean nitrogen oxide and ozone concentrations, solar and net radiation, photosynthetically active radiation, and vertical profiles of wind, temperature, ozone and water vapor. Aircraft data also include reflected short-wave radiation, surface greenness index and radiative surface temperature. Several factors simplify analyses: a nearly constant synoptic situation, lack of cloud cover, low-level (30 m) flights and land use characterized by extensive homogeneous areas with well defined interfaces. Repeated five-km aircraft runs, necessary for a representative flux calculation, were commonly made over a single crop type. In addition, a partial (60%) solar eclipse on 11 July provides an opportunity to examine the influence of light intensity upon the plant-atmosphere exchange of carbon dioxide and ozone via stomatal activity


This paper presents results of numerical simulations made with a high-resolution multiscale four-dimensional data assimilation system applied over California during two episodes associated with high ozone concentrations in the
San Joaquin Valley. The model used here is the nonhydrostatic Pennsylvania State University-National Center for Atmospheric Research Mesoscale Model (MM5). The focus of the paper is the objective validation of the regional (mesoalpha scale) meteorological results. The multiscale data assimilation approach produces highly reliable simulations of the wind, temperature, mixed-layer depth, and moisture, each of which is vital to air quality modeling and a host of other mesoscale applications. The significance of this research is threefold. First, it is the first evaluation of this multiscale assimilation system in strongly heated summertime conditions and with comparatively fine grid resolution (4-km inner mesh). Second, the assimilation system has been extended so that temperature soundings can be used to effectively reduce model errors for the simulated mixed-layer depth (which is crucial for correctly simulating boundary layer mixing and air chemistry processes). Third, by withholding half of the special data for use in model verification, it is shown that assimilation of observations at the mesoscale is, indeed, effective. Numerical errors are reduced over the intervening regions between the sites where data are assimilated. By establishing interobservation accuracy, we demonstrate that the data-assimilating model produces spatially consistent solutions without serious distortion of the active dynamical processes. In other words, the model and the observations are each able to contribute to the final numerical solution in a way that reduces error growth and does not disrupt the intervariable consistency among the primitive variable fields.


Differential optical absorption spectroscopy (DOAS) was used to measure the concentrations of the nitrate radical (NO3) and nitrogen dioxide (NO2), as part of the San Joaquin Valley Air Quality Study in central California. During 27 nights of measurements in July and August, 1990, the NO3 concentration was found to be highly variable with a maximum of 80 parts per trillion by volume (ppt). The average nighttime NO3 concentration profile, taken from 15 nights of continuous measurements, exhibits a maximum of 31 ppt about an hour after sunset, and then decreases slowly to sunrise. These concentrations of NO3 indicate that the nighttime oxidation of many organic compounds may be at least as fast as their oxidation by the hydroxyl radical (OH) during daytime. The atmospheric lifetime of NO3 was less than 10 min, with an average value of about 3 min. This short lifetime is most likely caused by the heterogeneous loss of nitrogen pentoxide (N2O5) onto moist aerosols, supplemented by the reactions of NO3 with olefinic hydrocarbons. These pathways make a significant contribution to the removal of nitrogen oxides from the lower troposphere.


To be aware of the influence that instrumentation, siting, data processing, and sensor exposure have upon the measurements. A unique opportunity arose to study this influence when in summer 1990, as part of the collaborative San Joaquin Valley Air Quality Study/Atmospheric Utility Signatures, Predictions and Experiments study (SJVAQS/AUSPEX), a vast meteorological measurement network was established for the central one-third of the state of California. Within the constraints of available resources, a variety of instruments, sites, site densities, sensor exposures, and data processing techniques were involved in the study. Based on the dataset from SJVAQS/AUSPEX, this paper was written to identify and quantify some common measurement influences for the benefit of users of the SJVAQS/AUSPEX data as well as the designers and users of other networks and datasets. To characterize and quantify measurement influences, comparisons were made of data associated with different instrument types, sites, measurement heights, and temporal averaging methodologies. Comparative statistics were then developed and summarized. Little variability existed among the characteristics of surface instrumentation, but sounding instrumentation varied greatly in the degree to which atmospheric vertical structure was resolved. Vertical sampling resolutions ranged from 4.5 to 300 m, and winds were averaged over layer depths ranging from 15 to 600 m. The spatial location of measurements had a great influence on the measured direction of the wind. Hourly wind directions at neighboring surface sites differed by an average of 18 degrees over the network with an rms variability of 55 degrees. Upper-air values of these same statistics were 12 degrees and 64 degrees, respectively. A functional dependence of wind variability on site separation distance was apparent from the data. The influence of sensor exposure height on wind speed measurements, when comparing neighboring sites with different measurement heights, was less than expected. The average ratio in wind speed for such site pairs was only 1.18 (1.06 by day and...
1.34 at night) for 10-m versus 2-m measurements. Temporal averaging methodology greatly influenced hourly wind values, especially for wind speeds less than 5 m s\(^{-1}\). Large differences were observed in hourly wind speed averages from scalar versus vector averaging, as well as in hourly wind direction averages from resultant versus unit vector averaging.


The spatial variability of ozone climatology is described for six remote sites on the western slope of the Sierra Nevada. A statistical analysis was applied to determine relationships between ozone concentrations and atmospheric variables, as well as relationships among sites. The sites, whose locations vary in latitude, elevation, and topography, show considerable variability in climatological patterns and statistics. However, the stations fall into two general groups: those with a distinct diurnal ozone pattern and those with a flat diurnal ozone pattern. Diurnal variations among sites appear to depend primarily on topographic setting rather than on remoteness from urban sources.


A geostatistical analysis of soil salinity in an agricultural area in the San Joaquin Valley included measurements of electrical conductivity of soil paste extract (EC\((e)\)) and water content of soil samples supplemented by surface measurements of apparent electrical conductivity (EM\((H)\)). Prediction of soil salinity at unsampled points by cokriging log\((e)\)EC\((e)\) and EM\((H)\) is worthwhile because EM\((H)\) measurements are quicker than soil sampling. This work studies how patterns of log\((e)\)EC\((e)\) predicted by cokriging with EM\((H)\) are influenced by variation in gravimetric water content (W). The data are mean EM\((H)\) = 1.00 +/- 0.13 dS m\(^{-1}\) for 2378 locations, mean log\((e)\)EC\((e)\) = 1.40 +/- 0.29 dS m\(^{-1}\), and mean gravimetric W = 0.260 +/- 0.003, both averaged for four samples from 0.3-m intervals to 1.2-m depth for 315 locations. The coefficient of determination (R\(^2\)) for EM\((H)\) vs. log\((e)\)EC\((e)\) increased with depth from 0.05 to 0.54 whereas the R\(^2\) for EM\((H)\) vs. W decreased from 0.48 to 0.28. A gray-scale EM\((H)\) map contained nine out of 56 quarter-section boundaries coinciding with step variations in EM\((H)\). The t-statistics for differences in mean W were six of nine significant at 0.001 and nine of nine at 0.05, but mean log\((e)\)EC\((e)\) had only two of nine at 0.05, implying that W caused EM\((H)\) steps. Water-affected EM\((H)\) impaired prediction of EC\((e)\) at depth by cokriging, because near-surface variations in W masked EC\((e)\). Two subareas were defined, one where management factors, such as irrigation, controlled EM\((H)\), causing steps, and one where near-surface W varied less, making cokriging predictions more reliable.


Fog water and interstitial particles were sampled at Berkeley, California, during foggy periods in the summer of 1986. The sampling site received marine fog advected from the San Francisco Bay. Samples of ambient particulate material (total aerosol) were collected using a filter sampler with a heated inlet. Concentrations of Na+, K+, NH4+, Cl-, NO3-, and SO42- were measured in the particles and fog water, for which pH was also measured. Black carbon aerosol was determined on the filter samples using optical attenuation.

The marine fog showed the influence of mixing and chemical reaction with anthropogenic pollutants. Twenty-six percent of the black carbon was present in fog droplets, indicating that incorporation of combustion particles into fog droplets had occurred. Anthropogenic particulate species were not scavenged by fog water as efficiently as sea-salt components. Non-sea-salt SO42- was enhanced in the total aerosol during fog compared to dry conditions, and this observation has been interpreted as evidence for heterogeneous production of SO42- in fog. The fog had elevated SO42- and NO3- levels compared to sites closer to the ocean. Sufficient NH3(g) was available to neutralize the increased acidity from anthropogenic H2SO3 and HNO3 so that the median pH was 4, as compared to pH 2.2 observed in Los Angeles fog water under more polluted conditions. Loss of Cl- from the fog or its precursor aerosol was enhanced compared to other measurements of San Francisco Bay Area fog at more remote locations.


We examine hourly ozone data collected in connection with a model evaluation study for ozone transport in the San Joaquin Valley of California. A space-time analysis of a subset of the data, 17 sites concentrated around the Sacramento area, indicates a relatively simple spatial covariance structure at night-time, while the afternoon readings show a more complex spatial covariance, which is partly explained by observations from a single station with suspicious data. Simple separable space-time covariance models do not appear applicable to these data.


Populations of Thielaviopsis basicola in naturally infested cotton field soils in the San Joaquin Valley of California were determined in 1992 with modified Specht's T. basicola-carrot-etrnidiazol-nystatin medium. In cotton fields in Kings County, CA, the pathogen was detected in 24 (88%) of the 27 fields surveyed, with a mean population density of 77.6 cfu/g of soil and a range of 1 to 220 cfu/g of soil. Black rot was detected in 79% of the fields where plants also were sampled. Disease severity was positively correlated with inoculum density, and pathogen populations were positively correlated with the number of years fields were planted to cotton. T basicola was found less frequently and at lower population densities in fields where crop rotation or summer flooding had been practiced, compared with fields planted continuously to cotton.


Homogeneous nucleation of sulfuric acid and water associated with urban fogs was examined. We approached the problem by analyzing the factors determining the gas-phase sulfuric acid concentration, and thereby identifying the ambient conditions where new particle production is expected to occur. We showed that H2SO4(g) concentration is in steady state with respect to its production and depletion via condensation in urban environment. Based on this, a simple formula was derived for estimating the nucleation probability from temperature, fine dry aerosol mass, and SO2(g) concentration and its oxidation rate during the post-fog conditions. The major uncertainty is associated with the value of the accommodation coefficient for sulfuric acid condensation on water. Nucleation was shown to be most favorable around 90% relative humidity after the dissipation of fog. We calculated a very high nucleation probability associated with fog observed in the San Joaquin Valley of California. In the South Coast Air Basin of Los Angeles, post-fog nucleation was predicted to occur frequently in Hawthorne and Long Beach, and occasionally at several other locations.


Plants and soils act as major sinks for the destruction of tropospheric ozone, especially during daylight hours when plant stomata open and are thought to provide the dominant pathway for the uptake of ozone. The present study, part of the California Ozone Deposition Experiment, compares predictions of the regional acid deposition model ozone surface conductance module with surface conductance data derived from eddy covariance measurements of ozone flux taken at a grape, a cotton, and a grassland site in the San Joaquin Valley of California during the summer of 1991. Results indicate that the model (which was developed to provide long-term large-area estimates for the eastern United States) significantly overpredicts the surface conductance at all times of the day for at least two important types of plant cover of the San Joaquin Valley and that it incorrectly partitions the ozone flux between transpiring and nontranspiring components of the surface at the third site. Consequently, the model either overpredicts or inaccurately represents the observed deposition velocities. Other results indicate that the presence of dew does not reduce the rate of ozone deposition, contradicting model assumptions, and that model assumptions involving the dependency of stomata upon environmental temperature are unnecessary. The effects of measurement errors and biases, arising from the presence of the roughness sublayer and possible photochemical reactions, are also discussed. A simpler model for ozone surface deposition (at least for the San Joaquin Valley) is proposed and evaluated.


As part of an extensive effort to characterize biogenic hydrocarbon emission rates in the San Joaquin Valley and surrounding areas during the SJVAQS/AUSPEX field experimental period, July-August 1990, measurements were made for the first time of isoprene, terpene, and other VOC emission rates from blue oak (Quercus douglasii), foothill pine (Pinus sabiniana), and a ground cover plant called tarweed (Holocarpha sp.) at a rural site near Mariposa, CA. A flow-through plant enclosure method was used to measure the emission flux rates from these species; the plant limb or whole plant was flushed with clean air just prior to hydrocarbon sampling. Samples of the plant emissions were collected on Tenax GC or Tenax GC-Carbosieve S-II cartridges and analysed by gas chromatography-Fourier transform infrared-mass spectrometry (GC-FTIR-MS). Quantifiable biogenic emissions from two blue oak specimens consisted only of isoprene, with an average emission rate of 8.4 mug g⁻¹ dry biomass h⁻¹. Emission rates (above the detection of about 0.05 mug g⁻¹ h⁻¹) from two foothill pine specimens consisted mostly of alpha-pinene; an average emission rate of 0.64 mug g⁻¹ h⁻¹ of alpha-pinene was observed. The tarweed species emitted both alpha- and beta-pinenes, along with other terpene and oxygenated species, some of which have been tentatively identified. The emission rates of biogenic hydrocarbons from foothill pine and blue oak species as determined in this study make these species potentially significant contributors to summertime VOC levels in the San Joaquin Valley of California, based on vegetation classification data and the predominant summer meteorology.

Troiano, J., Johnson, B.R., Powell, S., Schoenig, S., 1994. Use of cluster and principal component analyses to profile areas in California where ground water has been contaminated by pesticides. Environmental Monitoring and Assessment 32 (3), 269-288

This paper describes the development and evaluation of a computationally efficient semiempirical photochemical model that can be used as a screening tool to obtain quick estimates of the effect of a large number of VOC and NOx emission control strategies on ozone concentrations. Selected control strategies can subsequently be examined with a more complex model. The model is one component of an ozone management system, the regional ozone decision model (RODM), designed to examine the costs and environmental consequences of alternate ozone abatement strategies. The model was developed by systematic simplification of a detailed photochemical model. At each step of the simplification, the simplified model was tested against observations and against results from the detailed model. The first major simplification was the introduction of a highly parameterized chemistry mechanism, originally developed by Azzi et al. (1992 Proc. 11th Int. Clean Air Conf., 4th Regional IUAPPA Conf.). This modification resulted in a factor of 5 improvement in the computational efficiency of the model. The model with the simplified chemistry was then tested by applying it to a photochemical oxidant episode in the San Joaquin Valley of California. Further improvements in computational speed and efficiency were obtained by uncoupling the chemistry from the transport of VOC and NOx.


A simple time-dependent one-dimensional model of the planetary boundary layer (PBL) is described and used to examine the degree to which model design decisions affect model output variables. The model's sensitivity to changes in the environmental conditions is also explored. Averages of the surface fluxes, near-ground wind speeds and other PBL properties from 48 h simulations are compared to control runs. The model-calculated surface fluxes are most sensitive, in decreasing order of importance, to the vertical grid spacing, the form of closure between the surface temperature and the atmosphere, the use of vertical diffusivity smoothing, the choice of maximum time step and choice of turbulence closure scheme. These fluxes are relatively insensitive to mixing-length scaling or choice of implicit time step weighting factor. Sensitivity to changes in soil type exceeds any of the design criteria tested. The modeled fluxes are moderately sensitive to small variations in the horizontal pressure gradient, to unsteadiness in the geostrophic wind and to variations in surface roughness. They are relatively insensitive to uncertainties in local vertical velocities and small (25%) variations applied separately to soil thermal diffusivity or heat capacity. The sensitivity of the average PBL depth (Z(i)) to model and environmental changes are similar to those of surface fluxes except that Z(i) is more sensitive to changes in mixing length, albedo and imposed vertical velocity then are the surface fluxes.


An aerosol sampling study was carried out at six monitoring sites in California's San Joaquin Valley from June 14, 1988 through June 9, 1989. Concentrations of PM10 (particles < 10 mum in aerodynamic diameter) and PM2.5 (particles < 2.5 mum in aerodynamic diameter) mass, elements, water-soluble nitrate, sulfate, ammonium, sodium, potassium, and organic and elemental carbon were determined in 24-h aerosol samples collected during this period. Federal and state standards for PM10 were exceeded at both urban and nonurban sites. PM10 concentrations were generally highest during winter and were dominated by PM2.5 during this time. The coarse (PM10 minus PM2.5) aerosol fraction constituted more than half of PM10 mass during the summer and fall. PM10 concentrations of secondary ammonium nitrate were elevated during the winter at all sites. Conversely, concentrations of coarse particle iron, indicative of geologically related dust, were higher under less humid conditions during the summer and fall. Region-wide meteorological and chemical transformation processes influence the secondary (nitrate and sulfate) components of PM10. Elevated concentrations of coarse-particle dust,
however, appear to originate from local emissions, such as agricultural and transportation-related activities, as well as region-wide emissions.


Unusual air particulates are linked to recent heavy infestations of the ash whitefly in California using high-performance liquid chromatography, scanning electron microscopy, optical and infra-red microscopy, ion chromatography and X-ray fluorescence spectrometry. The unusual particles apparently are microdroplets of ash whitefly honeydew. Most of the suspended honeydew is in microdroplets with diameters between about two and twenty microns. The microdroplets were found to contain substantial amounts of sugars, primarily the oligosaccharides stachyose and raffinose. They also contain about 1 percent potassium, mainly as K+. The unusual microdroplets have been found in samples of air particulates taken in many areas of California after 1988. Using a receptor model, the suspended honeydew was calculated to add as much as 40 microgm/M3 to PM10 mass. The highest levels of suspended honeydew occurred between late August and early November.


This paper reports the results of measurements of formic and acetic acid at four sites located along the western slope of the Sierra Nevada and compares the results with those of earlier studies. Formic acid concentrations ranged from approximately 1 to 40 ppb; those of acetic acid ranged from approximately 0.5 to 13 ppb. Mean formic acid concentrations were 18 ppb at Tehachapi, located at the southern extremity of the range, and between 12 and 13 ppb at the three other sites. Mean acetic acid concentrations ranged from 3.9 ppb at Blodgett Experimental Forest, located at the northern extremity, to 8.0 ppb at Yosemite. Comparison with previous studies indicates that carboxylic acid levels measured in the Sierra Nevada are higher than those measured in past studies, and in many cases average concentrations of both formic and acetic acids observed during this study were greater than the previously reported maxima. Comparisons were also made to nitric acid concentrations measured at Yosemite and Giant Forest from October 1986 to September 1987. At Yosemite, annual nitric acid concentrations averaged 0.20 ppb during the day, and 0.06 ppb at night; and at Giant Forest, nitric acid averaged 0.17 ppb during the day, and 0.05 ppb at night. Thus, the high formic and acetic acid concentrations observed in this study suggest that carboxylic acid are major contributors to the overall flux of ambient acid deposition in the western Sierra Nevada.


An observational and modeling study of the microclimate of a suburban area, as related to the physical and biological nature of the site, is presented. The measurements and calculations are made in comparison with a nearby open agricultural location or "control site". The measurement program was conducted during the summer of 1981 in Davis, CA, and consisted of paired observations in which simultaneous measurements were made at a control site, located in a nearby rural area and one suburban site at a time. Results indicate that this methodology was generally successful. The various suburban sites were as often cooler than the rural site as they were warmer. In one case, a suburban site was found to be substantially cooler, averaging 7.38-degrees-C over a 5 day period, than the rural site. This special case was observed to be associated with unusually dry environmental air resulting in large evaporative cooling in the plant canopy. Comparison between the suburban temperature deficit and the physical nature of the various sites reveals that canopy height explained most of the variance of this data set. Two generally important mechanisms are hypothesized to be operating in this system: the effect of canopy size on turbulent mixing and on site shading, especially of paved areas. A simple energy balance model was applied to study the processes that control the daytime suburban temperature deficit. In particular, it is found that suburban sites can be as cool as
observed when the following conditions are obtained: low-canopy humidity, large canopy size, low wind speed and high radiation load. The model simulated the overall average suburban temperature deficit of all sites for physically reasonable choices of model parameters. It is pointed out that the fact that suburban areas may be cooler than surrounding rural areas may have significance to the problem of assessing the role of the urban heat island in relation to possible global warming.


Based on controlled experiments and simulation modeling, ozone (O3) has been estimated to cause significant yield losses to cotton. The study reported here was conducted to verify losses for 'Acala' cotton (Gossypium hirsutum L. 'SJ2') along a gradient of ambient O3 concentrations across the San Joaquin Valley in California. Cotton was grown in nonfiltered (NF) and charcoal-filtered (CF) open-top chambers, and ambient air (AA) at four sites during the 1988 and 1989 summer growing seasons. Cotton yields (weights of mature bolls m-2) were reduced in NF compared with CF air in general proportion to O3 concentrations across all sites and years. Greatest cotton yield losses were as Shafter in the southern part of the San Joaquin Valley (20% in 1989), and lowest losses were at Five Points in the western part of the valley (none in 1989). Ozone injury symptoms on cotton were most noticeable in areas with greatest yield losses. Linear O3 exposure vs. predicted relative yield loss models using four common exposure indices were constructed for each site and year based on the NF, CF, and AA data. All models except the second highest daily maximum concentration (2ndHDM, the current ambient air quality standard for O3) predicted yield losses comparable to those predicted with previously published models for cotton in the San Joaquin Valley. Ozone exposure indices giving more weight to higher O3 concentrations or the 7-h daytime mean better predicted cotton yield responses over the growing season than 2ndHDM.


Sampling was conducted at a station near Parlier, CA, in the winter, 1989, to assess the airborne concentrations of organophosphorus (OP) insecticides used as dormant sprays on deciduous fruit and nut orchards in the general region. For 24-h air samples, concentrations ranged to above 100 ng/M3 for parathion, chlorpyrifos, and diazinon, and somewhat less (maximum ca. 30 ng/m3) for methidathion. Night time air residues were generally higher than daytime residues, perhaps reflecting a lowered inversion boundary layer and calmer wind conditions at night. Oxons of the four OPs tended to be in higher amounts relative to the parent thions in day vs night samples, suggesting photochemical oxidant involvement in their formation. Fogwater sampled during the same general period contained residues of all four OPs and their oxons whether sampled with a Teflon-brand strand fog collector or by collecting tree drip moisture. Oxons tended to be higher in the tree drip, suggesting involvement of the tree surface in their formation. Potted parsley plants set out during the period contained measurable OP residues, suggesting deposition by wet processes or dry vapor exchange. The reported residue content of red-tailed hawks collected in the general vicinity suggested that deposition to a non-target wildlife organism also may have occurred.


Net radiation (R$_n$) is an important component of the modified Penman equation used to calculate reference evapotranspiration (ET$_o$). Net radiometers, however, require continual maintenance to ensure that the data they generate are reliable. An equation is developed that estimates hourly R$_n$ over well-watered grass from meteorological data, such as solar radiation, vapor pressure, and air temperature, collected by weather stations in various regions in California. The equation is based on Monteith's daily net radiation equation. Empirical equations are also developed to quantify surface albedo and clear sky global transmissivity. The modified Monteith formula for net radiation is tested in coastal, desert, mountain, and interior valley regions within California. After examining the 1984-1989 data from weather stations in the various regions, the absolute mean error of calculated hourly R$_n$ is within 10% of the measured hourly R$_n$. The absolute mean error of daytime R$_n$ during THETA > 10 degrees is within 8% of the measured R$_n$. These errors represent an even smaller error in ET$_o$ estimates. The modified Monteith equation for R$_n$ does not require site specific correction factors.


The Nitrate Management Program of the California Department of Food and Agriculture is helping improve farming practices, while reducing nitrate contribution to groundwater. The program facilitates and coordinates the development of local nitrate management programs by: (a) providing technical assistance and funding to carry out nitrate management research, demonstration and education efforts; and (b) improving access of local entities to federal, state and other resources by serving as a clearinghouse of information and funding sources. Program activities are directed to serving growers, public agencies, agricultural supply and service organizations, extension personnel, resource conservation and irrigation districts, the general public and other interested parties. The NMP has helped secure funding and technical expertise to start field work on projects to reduce agriculture's nitrate contribution to groundwater. Initial project sites have been chosen in the Salinas Valley, the east side of the San Joaquin Valley, and the Fall River Basin.


Measurements of Nd-Sr isotopes, major and trace elements, and model mineralogy were made on Upper Jurassic and Cretaceous Great Valley forearc sedimentary rocks to test models for the temporal and spatial evolution of Sierra Nevada arc sources. Isotopes and major and trace elements are sensitive provenance indicators because of the large west-east isotopic, geochemical, and age gradients in the plutonic rocks of the Sierra Nevada batholith, and because petrographic models indicate that source areas moved east during the Cretaceous. Isotopic and chemical variations are correlated in the forearc sandstone; as epsilon(Nd) decreases, Th, U, La, Nb, Zr, Hf, Pb, Rb, SiO$_2$, and K2O concentrations increase, and FeO, MgO, TiO$_2$, Ni, and Cr concentrations decrease. This relation is the same as that observed in the plutonic rocks and indicates that the arc was the primary source of sediment and that the sandstone chemistry was not disturbed by sedimentary processes. The epsilon(Nd)-epsilon(Sr) relation of San Joaquin Valley sandstone is the same as the plutonic rocks, but Sacramento Valley sandstone is elevated in
epsilon(Sr) because of seawater exchange, weathering, and diagenesis. Whole-rock sandstone decreases in epsilon(Nd) from +7 to -5 and increases in Sr-87/Sr-86 from 0.7045 to 0.7073 with decreasing stratigraphic age. The Nd-Sr isotopic composition is correlative with the plagioclase to feldspar ratio and indicates that source areas moved inland during the Cretaceous. Upper Cretaceous San Joaquin Valley shale is similar in epsilon(Nd) to the sandstone, indicating that sandstone and shale were derived from the same source and that the Nd isotopic composition is independent of grain size. The shale is higher in Sr-87/Sr-86 than the sandstone, possibly due to concentration of biotite in the fine fraction during transport and subsequent Rb loss during diagenesis. Nd-Sr isotopes were used to construct models to locate source areas. Parameters include lithology, drainage basin geometry, and erosion rate. The age and isotopic compositions of the calculated igneous component of the sandstone correspond to the age and isotopic compositions of the plutonic rocks of the batholith; this correspondence indicates that (1) the isotopic composition of the plutonic rocks and the coeval volcanic cover were similar, (2) the volcanic front was denuded within a few million years, and (3) the sediment was derived from the head of the drainage basin, located at the migrating volcanic front.


Uniform nursery stock of five almond cultivars [Prunus dulcis (Mill) D.A. Webb syn. P. amygdalus Batsch, cv. Butte, Carmel, Mission, Nonpareil, and Sonora] propagated on peach (P. domestica L. Batsch.) rootstock were exposed to three different atmospheric ozone (O3) partial pressures. The trees were planted in open-top fumigation chambers on 19 Apr. 1989 at the University of California Kearny Agricultural Center located in the San Joaquin Valley of California. Exposures of the trees to three atmospheric O3 partial pressures (charcoal filtered air, ambient air, or ambient air + O3) lasted from 1 June to 2 Nov. 1989. The mean 12-h [0800-2000 h Pacific Daylight Time (PDT)] O3, partial pressures measured in the open-top chambers during the experimental period were 0.038, 0.060, and 0.112-mu-Pa Pa-1 O3 in the charcoal filtered, ambient, and ambient + O3 treatments, respectively. Leaf net CO2 assimilation, trunk cross-sectional area growth, and root, trunk, foliage, and total dry weight of Nonpareil were reduced by increased atmospheric O3 partial pressures. Mission was unaffected by O3 and Butte, Carmel, and Sonora were intermediate in their responses. Foliage of Nonpareil also abscised prematurely in the ambient and ambient + O3 treatments. The results indicate that there are almond cultivars that are sensitive to O3 exposure.


Patterns of microearthquakes and Quatemary surface deformation suggest that the tectonic setting of the SW Sacramento Valley is similar to areas of the western San Joaquin Valley known to be underlain by seismogenic blind thrust faults. On the basis of previous work and analysis of geologic and seismic reflection data, the following late Cenozoic tectonic features and processes are identified: (1) uplift of the northern Coast Ranges beginning approximately 3.4 Ma, and eastward propagation of uplift into the southwestern Sacramento Valley by 1.0 Ma; (2) uplift and homoclinal flexure of Plio-Pleistocene strata at the eastern Coast Ranges mountain front; (3) uplift and folding above blind thrusts approximately 15 km east of the mountain front in the southwestern Sacramento Valley. Similar associations of structures and processes have been observed in thrust belts in Pakistan, the Peruvian Andes, and the Canadian Cordillera and are commonly attributed to thrusting within an intercutaneous wedge or triangle zone. By using other thrust belts as analogs, the propagation of an eastward tapering triangle zone is interpreted to be the principal mechanism for uplift and homoclinal flexure at the eastern Coast Ranges mountain front. Seismic reflection profiles reveal that (1) the triangle zone consists primarily of east-vergent blind thrusts and (2) west-vergent backthrusts exposed in the eastern Coast Ranges and southwestern Sacramento Valley are rooted in the east-vergent thrusts. Transfer of slip from the east-vergent blind thrusts to the west-vergent backthrusts occurs locally beneath the southwestern Sacramento Valley. Fault-bend folding in the hanging walls of the backthrusts has created a north-northwest striking chain of low hills approximately 15 km east of the mountain front. The folds deform 3.4-1.0 Ma fluvial sediments and thus are middle Pleistocene in age or younger. Local variations in strike suggest that the fold chain is segmented, like the New Idria-Coalinga-Kettleman Hills segmented fold chain in the southwestern San Joaquin Valley (Stein and Ekstrom, 1989). These data have implications for seismic hazard assessment.
Anecdotal accounts indicate that two $M = 6.0+$ events of the 1892 Winters-Vacaville earthquake sequence probably occurred beneath the eastern Coast Ranges (Dale, 1977; Toppozada et al., 1981). Ground cracking was observed following the main shocks along the mountain front in the southwestern Sacramento Valley. We propose that the earthquakes were generated by slip on a blind thrust beneath the Coast Ranges, and that the ground cracking in the valley represents propagation of the eastward tapering triangle zone. The 1892 earthquake sequence suggests that blind thrusts beneath the southwestern Sacramento Valley are active and capable of generating moderate to large magnitude earthquakes.


More than a dozen monoterpenes have been identified as emissions from agricultural and natural plant species occupying large acreages in the Central Valley of California, including as dominant emissions carvone, 2-carene, DELTA-3-carene, limonene, myrcene, trans-ocimene, beta-phellandrene, alpha-pinene, beta-pinene, sabinene, gamma-terpinene, and terpinolene. Isoprene was not a significant emission from any of the crop species examined but was emitted by a Valley Oak. In addition to the monoterpenes, sesquiterpenes were emitted from approximately one third of the species investigated, in some cases at higher levels than the monoterpene emissions from the same plant. The possible contributions of these biogenic emissions to the ozone exceedances in the Central Valley should be considered in planning future emission control strategies.


Spatial and temporal variations in patterns of precipitation and cloud interception were studied for a period of 14 months in the Sierra Nevada of central California. 14 fully automated sampling stations, located at elevations from 800 to 2400 m, were utilized in the study. Both precipitation and cloud interception were observed to increase with elevation. Cloudwater deposition increased at higher elevations due both to a greater frequency of cloud interception and higher wind speeds. Cloudwater deposition, caused primarily by the interception of clouds associated with cold fronts approaching from the north or north-west, is most important at elevations above 1500 m; however, the interception of highly polluted winter "Tule" fogs, lifting above the floor of the San Joaquin Valley, appears to be an important mechanism for cloudwater deposition at lower elevation sites. Observed and estimated hydrological and chemical inputs to the passive cloudwater collectors used in the study were substantial, suggesting that cloud interception may contribute significantly to the same inputs for exposed conifers in the region.


Nursery stock of peach (Prunus persica L. Batsch, cv. O'Henry), nectarine (P. persica L. Batsch, cv. Fantasia), plum (P. salicina Lindel., cv. Casselman), apricot (P. armeniaca L., cv. Tilton), almond (P. dulcis Mill., cv. Nonpareil), prune (P. domestica L., cv. Improved French), cherry (P. avium L., cv. Bing), oriental pear (Pyrus pyrifolia Rehd., cv. 20th Century), and apple (Malus pumila Mill., cv. Granny Smith) were planted in open-top chambers on April 1, 1988 at the University of California's Kearney Agricultural Center located in the San Joaquin Valley (30-degrees-40'N 119-degrees-40'W). Trees were exposed to three atmospheric ozone partial pressures (charcoal-filtered air (C), ambient air (A), or ambient air + ozone (T) from August 1 to November 17, 1988. The mean 12-h (0800 to 2000 h) ozone partial pressures measured in open-top chambers during the experimental period were 0.030, 0.051, and 0.117-μPa Pa⁻¹ in the C, A and T treatments, respectively. Leaf net CO₂ assimilation rate decreased linearly with increasing 12-h mean ozone partial pressure for the almond, plum, apricot, prune, pear, and apple cultivars. Stomatal conductances of apricot, apple, almond, and plum decreased linearly with increasing ozone partial pressure. Cross-sectional area relative growth rates of almond, plum, apricot, and pear decreased linearly with increasing ozone partial pressure. Net CO₂ assimilation rate, stomatal conductance, and trunk growth of cherry, peach and nectarine were unaffected by the ozone treatments. Reduced leaf gas exchange probably contributed to ozone-induced growth reduction of the susceptible species and cultivars. Several of the commercial fruit tree species and cultivars studied were relatively tolerant to the ozone treatments.


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