

Mobile Laboratory with Rapid Response Instruments for Real-Time Measurements of Urban and Regional Trace Gas and Particulate Distributions and Emission Source Characteristics

CHARLES E. KOLB,^{*,†,‡}
 SCOTT C. HERNDON,[†]
 J. BARRY MCMANUS,[†]
 JOANNE H. SHORTER,[†]
 MARK S. ZAHNISER,[†] DAVID D. NELSON,[†]
 JOHN T. JAYNE,[‡]
 MANJULA R. CANAGARATNA,[‡] AND
 DOUGLAS R. WORSNOP[‡]

*Center for Atmospheric and Environmental Chemistry and
 Center for Aerosol and Cloud Chemistry, 45 Manning Road,
 Aerodyne Research Inc., Billerica, Massachusetts 01821-3976*

Recent technological advances have allowed the development of robust, relatively compact, low power, rapid response (~1 s) instruments with sufficient sensitivity and specificity to quantify many trace gases and aerosol particle components in the ambient atmosphere. Suites of such instruments can be deployed on mobile platforms to study atmospheric processes, map concentration distributions of atmospheric pollutants, and determine the composition and intensities of emission sources. A mobile laboratory containing innovative tunable infrared laser differential absorption spectroscopy (TILDAS) instruments to measure selected trace gas concentrations at sub parts-per-billion levels and an aerosol mass spectrometer (AMS) to measure size resolved distributions of the nonrefractory chemical components of fine airborne particles as well as selected commercial fast response instruments and position/velocity sensors is described. Examples of the range of measurement strategies that can be undertaken using this mobile laboratory are discussed, and samples of measurement data are presented.

Introduction

Most in situ atmospheric chemistry research measurements and routine trace gas and aerosol particulate monitoring are conducted by periodically sampling air at a relatively small number of fixed sites. This strategy originated when most chemical environmental parameters were determined by collecting samples at fixed locations and returning them to a laboratory for analysis, a strategy so time-consuming and expensive that only sparse sampling grids could be utilized. The development of field deployable environmental instruments allowed fixed monitoring sites to produce more continuous data but still on sparse spatial scales.

These fixed site monitoring stations are valuable for assessing the local state of the environment and for specifying slowly varying parameters, such as remote concentrations of the long-lived greenhouse gases or atmospheric halocarbons, where relatively few stations can accurately describe large scale spatial distributions and their temporal trends. Unfortunately, the cost of equipping and maintaining fixed site monitoring stations usually means that too few are available to adequately describe the spatial and temporal variations of environmental parameters with more rapid rates of change, leading to significant under sampling.

One important strategy for overcoming this under sampling problem is to deploy fast response in situ (or short range remote) instruments on mobile platforms. By measuring rapidly, compared to the platform's rate of travel over the characteristic spatial dimensions of the target parameters, spatial distributions of the parameters of interest can often be mapped over a time interval short enough to ensure that the measurements are useful "snapshots" of the environment. Because one mobile suite of instruments may replace those from several fixed sites, it is often possible to invest in faster, more sensitive, and/or more specific instruments and to add instruments or extend instrumental capabilities to measure additional parameters. Mobile instrument platforms can include the following: vans, trailers, trucks, boats/ships, trains, balloons/blimps, and both piloted and unoccupied (remotely piloted) airplanes. Most mobile platforms have space, weight, and power constraints, placing a premium on small, lightweight, low power instruments capable of autonomous operation. Fortunately, recent advances in a wide range of technologies have made development of smaller, lower power, fast response, autonomous instruments feasible.

One notable early example was the deployment of NASA's high altitude ER-2 aircraft (a research version of the U-2 spy plane) equipped with autonomous, real-time sensors to investigate the causes of stratospheric ozone depletion (1). The success of the ER-2 airborne instrument suite in determining and characterizing the mechanisms that created the Antarctic ozone hole led to a large number of the United States and European aircraft with fast response instrument suites that have supplied much of our current knowledge about the composition and chemical evolution of the lower stratosphere and free troposphere. In addition, airborne suites of fast instruments have been used to characterize and to quantify urban area pollutant emissions and to investigate the impact of urban pollution plumes as they disperse into the surrounding regions (2–4). More recently, the development of relatively inexpensive autonomous sensors for a few important atmospheric trace species (e.g., water vapor and ozone) has allowed selected commercial aircraft to acquire useful trace gas distribution and trend data (5, 6).

Over more than a decade, Aerodyne Research, Inc. (ARI) staff, in collaboration with colleagues from Washington State University (WSU) and the University of New Hampshire (UNH), have used a mobile laboratory equipped with instruments to quantify emissions of greenhouse gases (primarily CH₄ and CO₂) from a variety of urban/industrial point and area emission sources, including components of natural and town gas production, transmission, and distribution systems, landfills, and even small towns and sections of cities (7–12). We have also used mobile laboratory techniques to determine emissions of the greenhouse gas, N₂O, from urban on-road mobile sources (13), measured ambient urban pollutant distributions in Boston (14, 15), and on-road heavy duty vehicle emissions in New York City (16, 17) in collaboration with colleagues from WSU, UNH,

* Corresponding author phone: (978)663-9500; fax: (978)663-4918; e-mail: kolb@aerodyne.com.

[†] Center for Atmospheric and Environmental Chemistry.

[‡] Center for Aerosol and Cloud Chemistry.

the Massachusetts Institute of Technology (MIT), and the State University of New York at Albany (SUNY Albany).

There is a critical distinction to be made between truly mobile laboratories, that function just as well while in transit as when parked and portable laboratories outfitted in vans, trucks, or trailers that are transported between fixed sites and are only designed to function while stationary. Portable laboratories, that have also been labeled mobile laboratories, have a long history of successful air quality measurements, even though they produce no data that could not be acquired by similarly instrumented fixed site stations. Several notable examples of portable ("mobile") laboratories being used to characterize urban aerosol particle loadings can be found in the literature (18–20). However, the studies using our mobile laboratory cited above in refs 7–17, all depend on measurements made while moving, and the advantages of truly mobile operation will be highlighted in this paper.

Recently, several other groups have developed mobile laboratories to address urban and regional air quality issues. European groups have recently reported the use of mobile laboratories to characterize ambient gaseous and fine particle pollutant distributions in and around Zürich (21), to characterize the dispersion of gaseous vehicle exhaust emissions from a roadway in Leeds (22), and to measure in-use vehicle exhaust emissions on a high-speed test track (23). Other U.S. researchers have reported using a tractor trailer mounted mobile laboratory to characterize on-road, heavy duty diesel truck emissions (24).

Urban/industrial air quality problems are characterized by complex emissions patterns and rapidly changing pollutant and pollutant precursor concentrations. The use of novel experimental strategies, including those exploiting mobile laboratories, to better characterize urban ambient pollutant distributions and quantify emissions fluxes are required to understand and address the air quality problems they create. This is particularly true in the burgeoning megacities of the developing world, where the temporally and spatially undersampled data from conventional fixed air quality measurement sites is either limited or unavailable and emissions inventories, where they exist, are often based on dubious extrapolations from those used for cities in the developed world.

In the following sections we present a description of our mobile laboratory and the associated fast response instrumentation we have developed and deployed to address urban/regional air quality issues. We further describe the experimental strategies we have developed and present representative urban ambient concentration and emission flux measurements to demonstrate their utility.

Mobile Laboratory Description

We have developed two van-based mobile laboratories in the past 14 years. Our original mobile laboratory was constructed in 1990 on a 1989 Ford Econoline 350 chassis powered by a gasoline engine. The laboratory was built into a van "box" approximately 4.3 m L \times 2.1 m W \times 1.8 m H with a step entry into the front driver/passenger compartment. This mobile lab accommodated three people: a driver, a front seat operator, and an instrument operator in the rear. When in motion the instrumentation was powered by one or two 3–5 kW Honda gasoline generators mounted on the rear bumper. In both versions dedicated laboratory section air conditioning, powered by the engine's alternator when moving, manages instrument and solar induced thermal loads. Although classified as a truck (gross weight of 4853 kg) the original mobile lab was sufficiently small and maneuverable enough to traverse one-lane roads and alleys and to track behind target vehicles on city streets as well as major roadways. After a dozen years of service our original mobile lab was retired in early 2003 and replaced with a new, second

generation vehicle, a 5.5 m L \times 2.1 m W \times 2.1 m H Union City Walk-in Van body on a 2002 5.5 m Workhouse F.C. chassis purchased from GMC. The new, slightly larger, mobile lab has 12 kW of built in generator power for instrumentation and air conditioning. It will accommodate a driver, a front operator, and up to two rear operators. With a full instrument load it has a gross weight of about 5000 kg.

When stationary the instrumentation and air conditioning are powered by 120 V AC lines plugged into the labs power grid to avoid ambient contamination from the generator and/or vehicle exhaust. Uninterruptible power supplies (UPSs) allow continuous operation while changing from plug to mobile generator power. Methods to characterize and avoid self-contamination during mobile measurements from the laboratory's drive train and generator are discussed below.

Inlet systems for our mobile laboratories have been specifically configured to accommodate the type of measurements required and the instrument suite to be employed in specific field campaigns. In general, inlets are situated well above and forward of the van engine and generator exhaust outlets. Inlets for instruments sampling "sticky", surface active gaseous species such as ammonia and nitric acid vapor are designed to be short and fast flowing and are internally coated to reduce surface losses. Flow times to various instruments sharing a common inlet are carefully measured so that concentrations of species measured with various real-time instruments can be correlated to within a second. Two inlet configurations used in recent deployments are described in detail in ref 17.

Mobile Laboratory Instrumentation

Instrumentation suites deployed in our mobile lab are typically composed of both research grade and more traditional commercial instrumentation, with an emphasis on rapid response (\sim 1 s) measurement times. A variety of trace gaseous pollutants can be quantified in real time with a dual tunable infrared laser differential absorption spectroscopy (TILDAS) instrument utilizing lead salt diode lasers (16, 25), including NO, NO₂, HONO, CO, N₂O, CH₄, C₂H₆, SO₂, and H₂CO. Recently, quantum cascade laser TILDAS systems which are more compact and do not require cryogenic cooling of the tunable lasers have been developed for mobile lab deployment with an initial emphasis on detection of NO and NH₃ (26, 27). Typical TILDAS sensitivities using ARI proprietary astigmatic multipass absorption cells with total absorption paths of 100–300 m are in the 0.3–1.0 ppbv range for a 1 s measurement. Maintaining 1 s instrument response times requires sufficient pumping speed to change the gas charge in the multipass cell each second; square wave injections of very sticky trace gases such as HNO₃ or NH₃ do show some residual signal, but cell design can reduce this effect (25). An electron capture fast response SF₆ detector developed by WSU is used to detect and quantify tracer flux plumes.

We have also deployed selected fast response commercial instrumentation. A LICOR nondispersive infrared unit (LI-6262) provides 1 s CO₂ measurements. A commercial proton transfer reaction mass spectrometer (PTR-MS) fielded by Montana State University (MSU) has been used to measure selected unsaturated and partially oxygenated organic compounds with time resolution of 2–3 s. A TSI Model 3022 condensation particle counter (CPC) provides 1 s total number densities for particles with diameters between 7 and 1000 nm. Slower response (10–30 s) commercial air quality instruments measuring CO, O₃, SO₂, and NO/NO₂ provided by WSU have also been successfully utilized, particularly for fixed site measurements. A commercial total nitrogen oxide (NO_x) analyzer provided by MIT has been successfully used in both 1 and 10 s measurement modes. Both the commercial

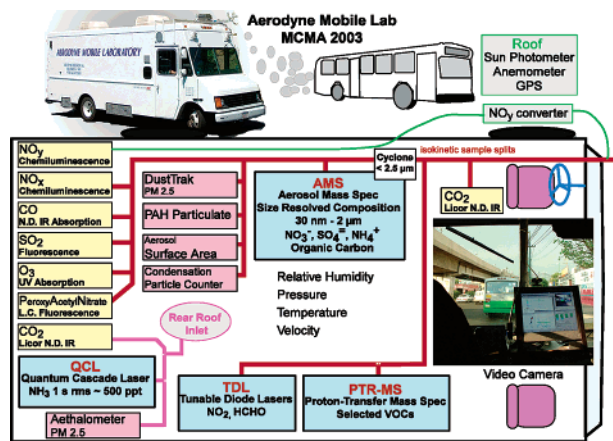


FIGURE 1. Schematic of the second generation ARI mobile laboratory as instrumented for the Spring 2003 Mexico City Metropolitan Area (MCMA) Measurement Campaign.

NO/NO_2 and NO_y instruments are based on O_3/NO chemiluminescence and a molybdenum converter.

Fast response fine particulate measurements of non-refractory chemical composition as a function of particle size are made with a proprietary ARI aerosol mass spectrometer (AMS). The Aerodyne AMS has been described in detail elsewhere (17, 28–30). It uses an aerodynamic lens to sample submicron particles (between 30 and ~1500 nm vacuum aerodynamic diameter) into a particle beam where they are aerodynamically sized, vaporized on a heated surface, and the resultant vapor phase species are chemically analyzed via electron impact ionization quadrupole mass spectrometry. The AMS is operated in two modes at time resolutions down to 1–2 s. In the time-of-flight (TOF) mode, aerosol size distributions are determined for selected ions using a particle beam-chopping technique. In the mass spectrum (MS) mode, the chopper is used to intermittently block and open the particle beam and ensemble mass spectra (m/z 0–300) are obtained for the sampled aerosol particles.

A video camera directed out the front windshield provides a multipurpose record of the mobile labs forward view, including current or potential emission sources. An onboard Trimble Pro XR Global Positioning System (GPS) provides a highly accurate record of the lab's position, while a shaft rotation counter attached to the driveshaft measures the mobile lab speed. A forward looking laser range finder can be deployed to measure the separation between the mobile lab and a target vehicle whose emissions are being sampled. A roof-top three axis sonic anemometer is mounted vertically for fixed site measurements and horizontally, facing forward, for mobile measurements. The latter arrangement allows measurement of the effective wind direction near the primary sampling inlet, flagging "tailwind" situations where mobile laboratory generator and/or motor exhaust might contaminate samples. Data from each individual instrument are logged on a central onboard computer, enabling all data streams to be viewed in real-time and stored synchronously.

A schematic layout of our second generation mobile laboratory with a representative fast response instrument suite is shown in Figure 1.

Mobile Laboratory Measurement Modes

The deployment of research grade fast response instruments in a mobile laboratory allows a wide range of measurement strategies to address urban and industrial emissions and ambient air quality issues. We have utilized three principle measurement modes: stationary sampling, mobile sampling and mapping, and vehicle chase. These measurement modes are summarized in Table 1. In the following sections we

TABLE 1. Mobile Laboratory Measurement Modes

Stationary Sampling
high time resolution point sampling
quality assurance for conventional fixed site air monitors
Mobile Sampling/Mapping
aggregate (fleet) motor vehicle pollutant emission ratios
point and area emission plume source location and dispersion measurements
stationary source plume tracer flux ratio emission measurements
high spatial resolution ambient background pollution distributions
Chase
on-road vehicle emissions quantification by vehicle and operating condition

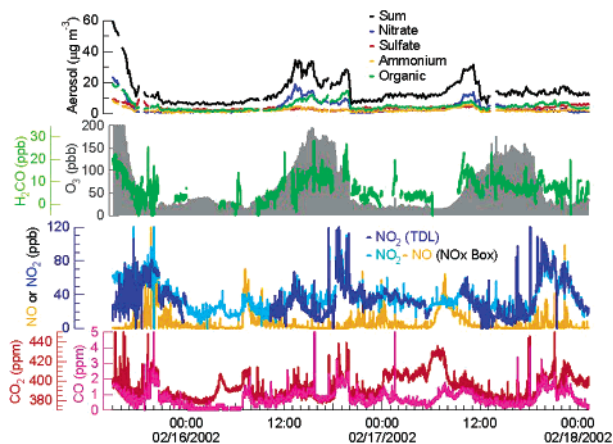


FIGURE 2. Multipollutant time series measured at the Pedregal, Mexico City air quality monitoring site in February 2002.

present examples of the data obtained utilizing each mode, focusing on the five modes that require true mobile operation.

Stationary Sampling. Like the portable laboratories, described in refs 18–20, our mobile laboratory can be deployed at fixed sites, serving as an additional air quality measurement site, with the advantages of flexible site selection. Using ~1 s response instruments, it can often provide much higher time resolution measurements than commercial air quality instruments to help identify transient plumes, correlate pollutants, and quantify plume impacts on time averaged pollution levels. The mobile lab can also be deployed at conventional fixed site air monitoring stations, where the research grade instruments can be intercompared with the site's commercial instruments. The high time resolution data from the mobile lab can provide insights into the pollutant fluxes influencing the site's time averaged ambient measurements as noted above. Figure 2 shows 2.5 days of photochemical activity from February 2002 at the Pedregal air quality monitoring site in Mexico City. High time resolution TILDAS measurements of formaldehyde and nitrogen dioxide, LICOR NDIR carbon dioxide, and aerosol mass spectrometer measurements of chemically speciated fine particles (~50–1000 nm, mode peak at ~500 nm) are displayed along with commercial monitor data for carbon monoxide, nitric oxide, nitrogen dioxide, and ozone. Afternoon peaks of photochemically produced ozone are strongly correlated with high loadings of fine secondary aerosol composed primarily of ammonium nitrate and oxygenated organics. The data in Figure 2 can be acquired without using a mobile laboratory, but we feel it is worth noting the range of simultaneous data that can be acquired from equipping a relatively small vehicle with modern, compact instrumentation.

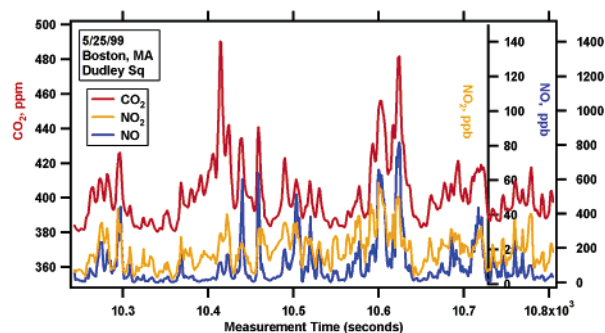


FIGURE 3. Typical segment of mobile on-road concentration data showing coincident peaks of CO₂, NO, and NO₂.

TABLE 2. Molar Fleet Emission Ratios for Gaseous Pollutants (Exhaust Pollutant Mixing Ratio/Exhaust CO₂ Mixing Ratio) for New England Cities

pollutant	city	date	venue	fleet emission ratio
NO	Boston	5/25/99	city roads	$3.7 (\pm 2.8) \times 10^{-3}$
			highway 1	$6.2 (\pm 2.9) \times 10^{-3}$
			highway 2	$3.6 (\pm 2.2) \times 10^{-3}$
N ₂ O	Manchester	6/18/98	city roads	$1.56 (\pm 0.03) \times 10^{-4}$
			highway	$1.09 (\pm 0.03) \times 10^{-4}$
CO	Manchester	6/18/98	city roads	$3.55 (\pm 0.94) \times 10^{-2}$
			highway	$2.92 (\pm 0.66) \times 10^{-2}$
CH ₄	Manchester	6/18/98	city roads	$1.49 (\pm 0.09) \times 10^{-3}$
			highway	$1.51 (\pm 0.58) \times 10^{-3}$

Mobile Fleet On-Road Emissions Ratio Measurements.

In heavy traffic, pollutant concentration levels are often dominated by partially diluted exhaust plumes from nearby vehicles which appear as sharp peaks in the mobile data record. For example, in Figure 3 we show NO, NO₂, and CO₂ levels found at rush hour in Dudley Square, Boston. The peaks for these three species are highly correlated indicating combustion sources, with CO₂, a major exhaust product, serving as an internal tracer. The measured ratios of "above background" plume NO/CO₂ and NO₂/CO₂ yield molar emissions ratios—e.g. moles of emitted pollutant/mole of exhaust CO₂. Assuming nominal fuel combustion stoichiometry, molar emission ratios can be converted with reasonable accuracy to fuel consumption emission ratios (e.g. g pollutant emitted/kg fuel consumed). Nonstoichiometry can be accounted for by simultaneously measuring CO and major exhaust VOCs or by assuming nominal exhaust CO and VOC mole fractions if direct measurements of these minority carbon species are not available. The aggregate emission ratios measured by moving through traffic can be influenced by mixing, especially for species, like NO₂, with rapid photochemical production/destruction mechanisms or for exhaust species with concentrations near background levels. However, strong isolated plumes are expected to accurately represent exhaust emission ratios.

We have previously published an analysis of aggregate emission ratios for nitrous oxide from motor vehicles in Boston and Manchester, NH (13). That study demonstrated that N₂O emission ratio distributions from U.S. motor vehicles sampled by chance with the mobile laboratory compare well with those from cross road, open path TILDAS remote sensing measurements of over 1400 individual vehicles. We have used the mobile laboratory technique to determine urban fleet emission ratio distributions for a variety of exhaust pollutants, including NO, NO₂, N₂O, CO, and CH₄ (13, 31), measured both on city roads and urban highways. A selection of typical fleet mean emissions ratios for various road types in New England cities is displayed in Table 2. In addition, we have measured fleet emission ratio distributions for NO, NO₂, CO,

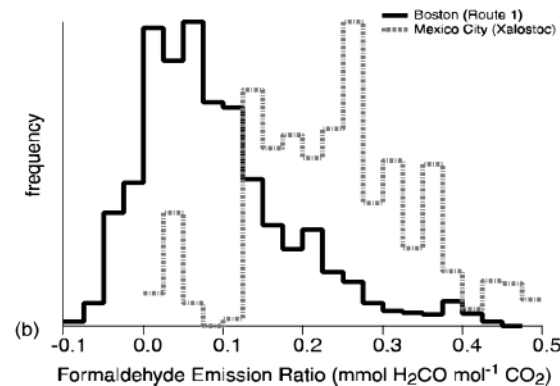
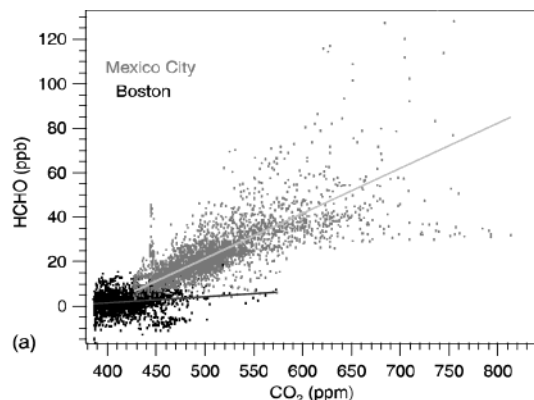


FIGURE 4. Mexico City and Boston metropolitan area aggregate on-road fleet (a) measured exhaust plume H₂CO/CO₂ emission ratios and (b) histogram of measured H₂CO/CO₂ (plume by plume). The average emission ratio shown by the fit lines in (a) for Mexico and Boston are 2×10^{-4} and 3×10^{-5} moles H₂CO per moles of CO₂.

and H₂CO in larger cities, including New York and Mexico City. Figure 4a compares correlations between on-road H₂CO and CO₂ exhaust plume data taken on cool, cloudy mornings with little photochemical H₂CO production in the Mexico City and Boston metropolitan areas. It can be seen that, in general, traffic exhaust plumes in Mexico City show a much higher H₂CO/CO₂ ratio than those in greater Boston. Figure 4b displays histogram plots of the data displayed in Figure 4a, clearly showing that while both metropolitan areas have a range of low to high H₂CO emitters, the fraction of high H₂CO emitters in Mexico City is much greater. The data displayed were taken in February 2002 in Mexico City, where the average plume H₂CO/CO₂ ratio was 2×10^{-4} , and March 2002 in Boston with a much lower mean H₂CO/CO₂ ratio of 3×10^{-5} . These data along with a much larger data set from more recent and extensive measurements in Mexico City are being prepared for separate publication.

The use of mobile real-time pollutant measurements of this type allow aggregate fleet emissions characterizations that are usually derived from tunnel studies (32), obtained from cross road remote sensing measurements (13, 33), or extrapolated from measurements of a small number of vehicles on dynamometers. However, an on-road mobile laboratory with rapid response instrumentation allows the equivalent of a "tunnel study" to be performed on nearly any city street. Further, unlike tunnel studies, but similar to cross road remote sensing studies, mobile laboratory on-road sampling studies determine representative distributions of emissions ratios as well as their mean. Also, while distributions of trace gas emission ratios appear to be quite similar for cross road remote sensing and on-road mobile laboratory sampling measurements (13), the mobile laboratory sampling strategy allows a greater variety of roadways and traffic speeds to be characterized, allows for exhaust particle chemical

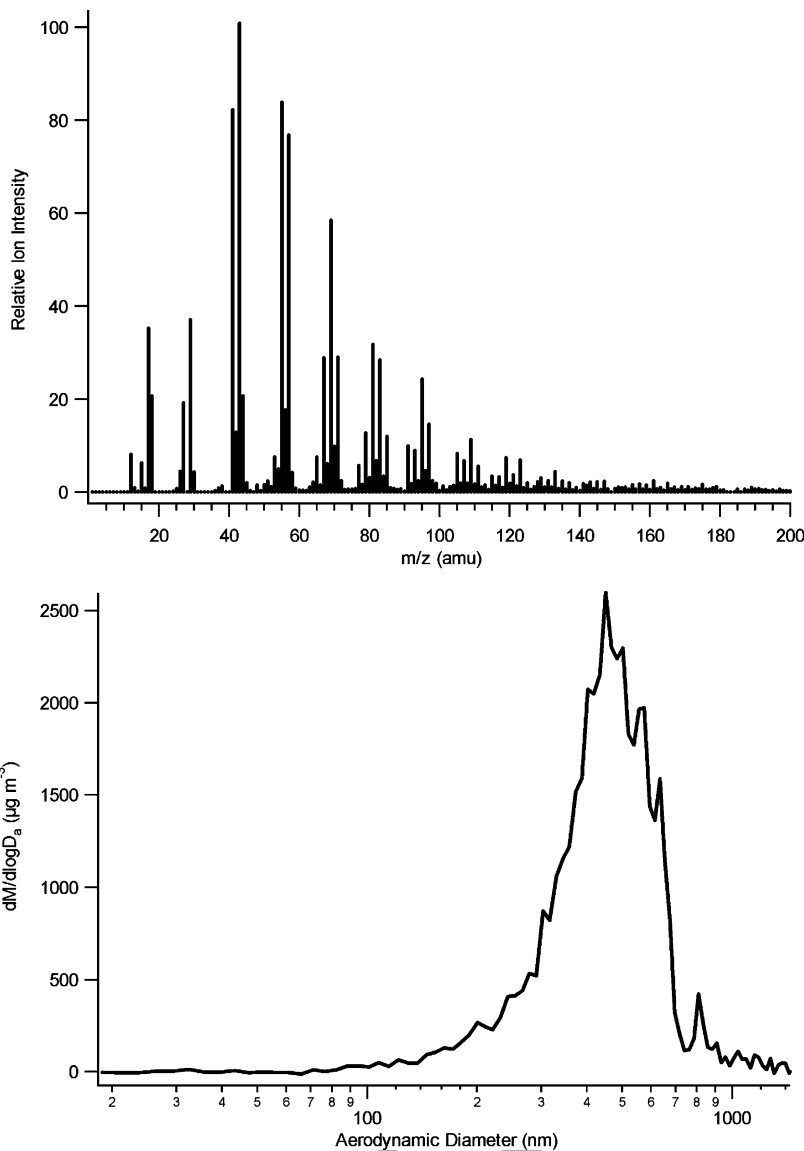


FIGURE 5. Average AMS mass spectrum (top panel) and organic aerosol size distribution (bottom panel) obtained while sampling the fumes generated by an asphalt paving operation encountered by the mobile laboratory in Queens, New York City. The sharp cutoff at particle diameters above 600 nm may be due to a drop in transmission efficiency for the aerodynamic lens used in this study (see Figure 11).

characterization as well as emission ratio measurements, and, at least for TILDAS trace gas measurements, and allows more accurate quantification of minor exhaust gas trace gas species such as H_2CO and N_2O (13).

Mobile Point and Area Emission Plume Characterization and Quantification. Mapping pollutant concentration patterns on a city district or neighborhood scale allows us to fill gaps in the undersampled urban atmosphere by providing better spatially resolved pollutant concentrations for comparison with air quality model predictions. Area mapping also allows characterization of plumes from strong area emission sources or from unique point sources. References 7–10 document the use of our mobile mapping techniques to detect and identify the sources of methane plumes from landfills, sewerage treatment plants, and components of natural or town gas distribution systems. Sometimes even transient plumes can be identified and characterized; Figure 5 shows AMS data for the fine particle size distribution and nonrefractory mass spectrum from a fume traced to a parking lot paving operation in the Queens section of New York City.

Emission fluxes from fixed point or area sources can be measured by utilizing an external tracer (e.g. SF_6) released at or near the pollutant source (8) or by utilizing an internal

tracer, like combustion produced CO_2 quantified by a known fuel consumption rate. Assuming the plume from a fixed source can be identified sufficiently far enough from the source that the plume dimensions are large compared to source dimensions, we can treat the source as pointlike and deduce pollutant fluxes from their ratios to the known tracer flux. Previous publications on mobile laboratory characterization of landfill and natural/town gas system component methane plumes have illustrated the basic methodology of tracer ratio plume flux quantification (8–12).

Mobile Mapping of Ambient Background Pollution Distributions. Urban mobile pollution mapping can also be used to determine variations in background pollutant distributions. These measurements are of interest for several reasons. First, the impact of pollutant exposures on human health or ecosystem viability may be nonlinear in pollutant concentrations, so evaluations of pollutant exposures may require detailed distributions of pollutant levels. Second, photochemical processes leading to oxidant and secondary aerosol particle formation are known to be nonlinear in precursor concentrations, so maps of both precursor and product distributions may allow better photochemical data analysis and model predictions.

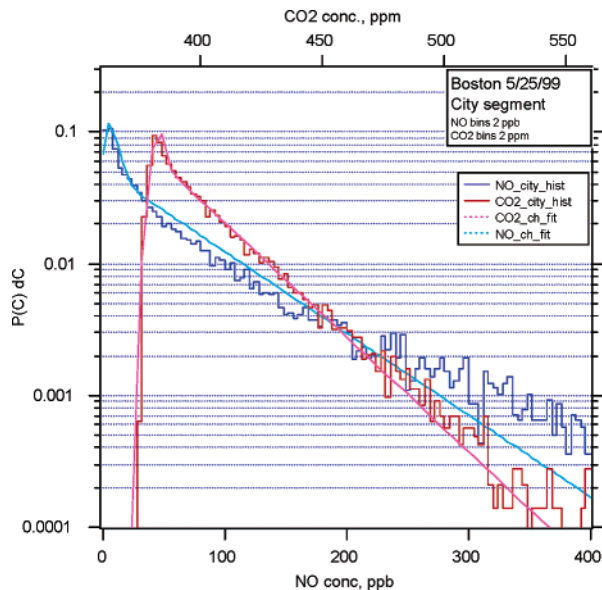


FIGURE 6. Concentration probability distributions for NO and CO₂ in Boston on May 25, 1999. The histograms have overlaid fits which are combinations of Gaussians and exponential tails.

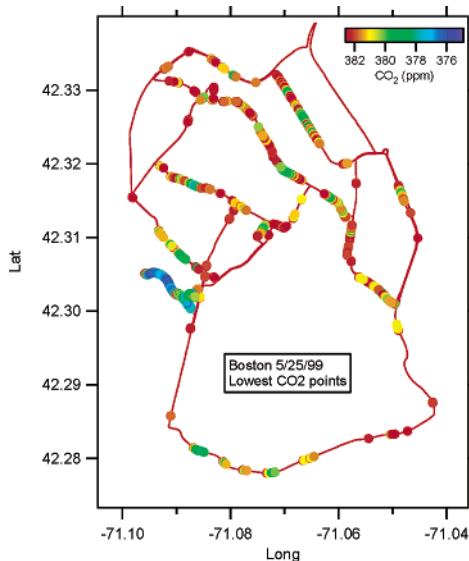


FIGURE 7. Points where CO₂ concentrations are below the maximum probability concentration, in Boston on May 25, 1999.

References 7 and 8 demonstrated that our mobile lab can be used to map relatively unreactive trace gases, like CH₄ and CO₂, in urban areas, especially under nighttime conditions with low mobile emissions and mild inversions that slow vertical mixing. We have more recently demonstrated that some measure of background pollutant distributions can be obtained in dense urban areas, even under conditions of moderate to heavy traffic and mid-day mixing.

As noted above, high resolution urban pollutant concentrations along measurement traverses taken during daytime or early evening are typically dominated by the many pollutant peaks due to local (on-road) sources. Late night or very early morning data are usually much less dominated by mobile source emissions allowing measurement of background distributions that more clearly show the influence of fixed point or areal sources (7, 8). For data with many discrete local source peaks, the underlying pattern of ambient pollutant concentrations is represented by the lower levels between the peaks. Observing general patterns of pollution from roadway traverses in moderate to heavy traffic levels

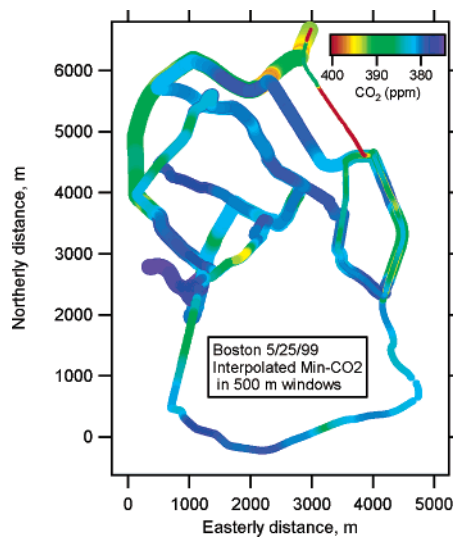


FIGURE 8. Interpolated minima in CO₂ concentrations over a range of ± 250 m during traverses on May 25, 1999 in Boston.

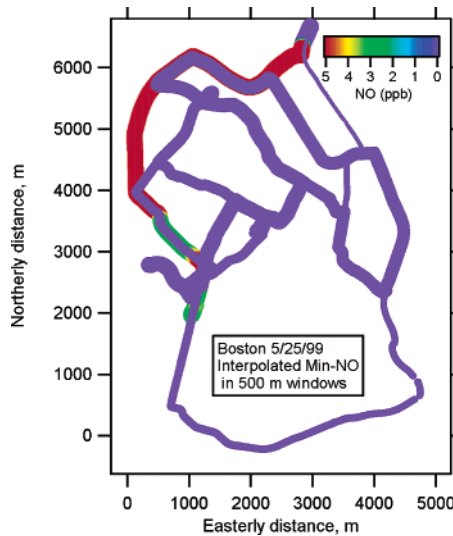
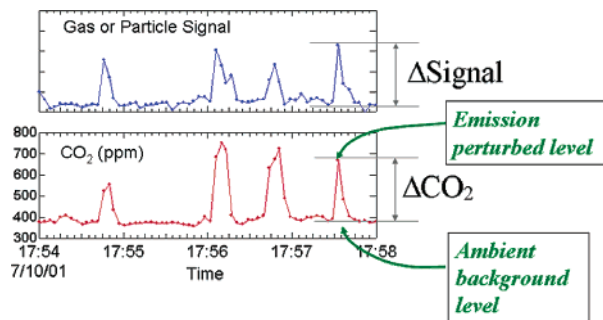


FIGURE 9. Interpolated minima in NO concentrations over a range of ± 250 m during traverses on May 25, 1999 in Boston.

is a problem analogous to seeing the forest floor between the trees. The lower concentration points are more typical of the well mixed urban air in the absence of local discrete sources.

We have developed two methods of deducing urban background pollution concentrations from daytime data exhibiting significant traffic exhaust signals (31). The first is to consider the probability distribution of concentrations measured during neighborhood to district scale traverses lasting about an hour or less. These typically have a low level Gaussian-like segment and a higher concentration exponential tail, as illustrated in Figure 6 for NO and CO₂ distributions in the Roxbury/Dorchester portion of Boston. We can select and plot the points in the low level Gaussian regime to visualize spatial patterns. An example of this process is shown in Figure 7, for daytime CO₂ concentrations on 5/25/99. We select the points that are below the concentration corresponding to the maximum probability as illustrated in Figure 6, where the probability has a Gaussian form. The map shows little structure, except the segment in Franklin Park (a large urban park represented by the spur in the center left of the figure with significantly lower concentrations than the low points on congested city roads, as expected).

The second method we have explored for presenting urban background pollution concentrations is to plot the inter-



$$\text{Emission Ratio} = \Delta\text{Signal}/\Delta\text{CO}_2$$

FIGURE 10. “In-plume” chase sampling marked normalized by above-ambient CO₂ levels; data shown are an AMS measure of hydrocarbon marker mass peak for diesel exhaust particles.

polated minima derived from a peak-background separation process (31). A “Rangemin” concentration data record is derived by replacing each point in the data with the minimum concentration encountered within a certain linear distance of that point. The resulting record also is smoothed to remove transition effects. While the primary purpose of the “Rangemin” procedure is to produce an automated background-subtracted peak segment for the vehicle exhaust emissions ratio analysis discussed above, the resulting background data records often reveal spatial patterns for ambient background pollutants.

We show two examples of Rangemin maps in Figures 8 and 9 for CO₂ and NO in Roxbury/Dorchester on 5/25/99. From these maps we see that the minimum levels were quite low, near 380 ppm for CO₂ and 0–5 ppb for NO. In these plots, the width of the trace decreases with distance traveled, to reveal different minima values derived at different times. The minima generally are not constant between different traverses on the same road; the relatively high level of NO seen on the northerly road (red in Figure 9) is not observed in a subsequent traverse. However, the background level of many pollutants is expected to change on the time scale of several tens of minutes required to repeat traverses of several km distance. Even so the range of deduced near ground level “background” pollution levels is instructive since the scale

of the mapped area is ~4 km × 5 km; near the size of a single grid box in a typical urban air quality model. Our mobile laboratory can provide thousands of data points per pollutant for typical grid cells, which could allow a systematic evaluation of the computational scale required to produce observed ambient background pollutant distributions.

Mobile Chase Measurements. We described the measurement of aggregate on road fleet emission ratios above. However, it is often desirable to characterize emissions from specific classes of vehicles in order to construct or verify emission inventories or to determine the effects of specific engine or exhaust conditioning technologies on real world operating emissions. To satisfy these requirements, the mobile laboratory can also be deployed in a “chase” mode to specifically sample selected individual vehicles and vehicle classes under a full range of on road operating parameters, from idle to high load acceleration or uphill cruise. Methods to quantify both fine particle and gaseous emissions from plume penetration pollutant/carbon dioxide ratio measurements for targeted on-road motor vehicles are now well established (16, 17, 23, 24). We have previously presented results on both particulate (17) and gaseous pollutants (16) from New York City transit buses.

The basic logic for this type of measurement is illustrated in Figure 10, where above ambient CO₂ measurements are used to identify exhaust plume intercept periods and normalize exhaust pollutant measurements. Note that, as indicated in Figure 10, procedures have to be developed to subtract ambient (on-road) background levels for both CO₂ and the traces exhaust pollutants of interest. This is similar to the procedure presented above for nontargeted fleet aggregate exhaust plume emission ratio measurements.

Figure 11, reprinted from ref 17, shows averaged particle size distributions measured with our AMS chasing standard NYC diesel transit buses on their normal routes. Both the organic and sulfate components show a primary particle size distribution peaking at a vacuum aerodynamic diameter of ~90 nm which is present in all the measured size distributions. A larger particle mode also with both organic and sulfate nonrefractory components peaks near a 600 nm but is present in a much smaller number of individual plume samples. It is likely that these larger particles represent organic and sulfate coated primary soot particle agglomerates that have

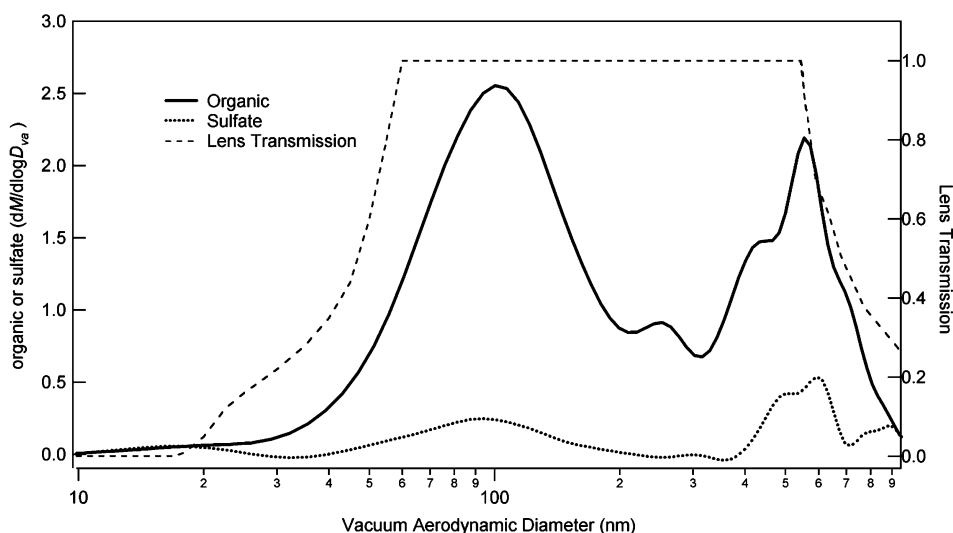


FIGURE 11. Average organic and sulfate “exhaust only” size distributions for diesel vehicle chase events. The “exhaust only” size distributions for each diesel chase event were calculated by taking the difference between the in-plume and background size distributions measured for each species during a chase event. The dashed line shows the calculated transmission efficiency curve for the aerodynamic lens used in this study. (Reprinted with permission from Canagaratna, M. R.; Jayne, J. T.; Ghertnerk, D. A.; Herndon, S.; Shi, Q.; Jimenez, J. L.; Silva, P. J.; Williams P.; Lanni, T.; Drewnick, F.; Demerjian, K. L.; Kolb, C. E.; Worsnop, D. R. Chase Studies of Particulate Emissions from in-use New York City Vehicles. *Aerosol Sci. Technol.* 2004, 38, 555–573. Copyright 2004 American Association for Aerosol Research.)

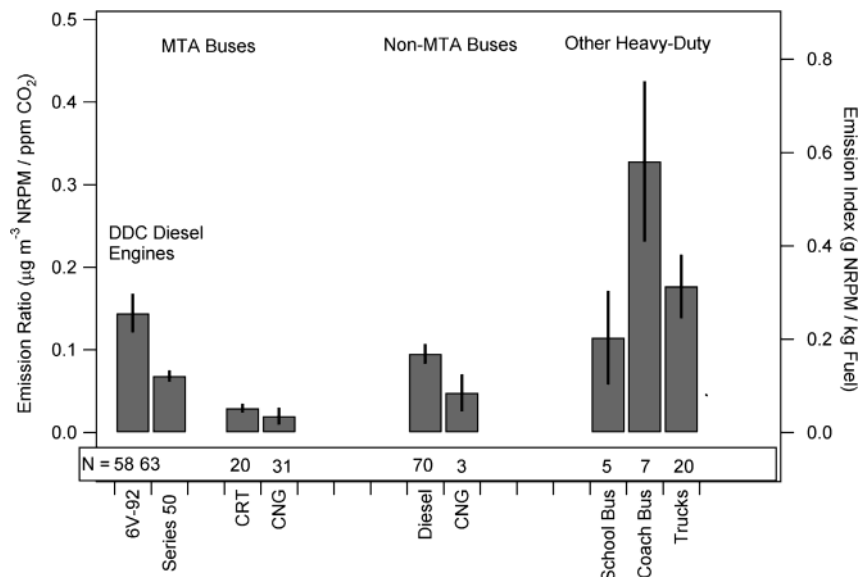


FIGURE 12. Classification of average New York City heavy duty vehicle nonrefractory fine PM emissions by vehicle type. The height of each bar reflects the average emission ratio calculated over all the relevant chase events that represent the particular vehicle class. The error bar represents ± 1 standard error of the mean. (Reprinted with permission from Canagaratna, M. R.; Jayne, J. T.; Ghertnerk, D. A.; Herndon, S.; Shi, Q.; Jiminez, J. L.; Silva, P. J.; Williams P.; Lanni, T.; Drewnick, F.; Demerjian, K. L.; Kolb, C. E.; Worsnop, D. R. Chase Studies of Particulate Emissions from in-use New York City Vehicles. *Aerosol Sci. Technol.* 2004, 38, 555–574. Copyright 2004 American Association for Aerosol Research.)

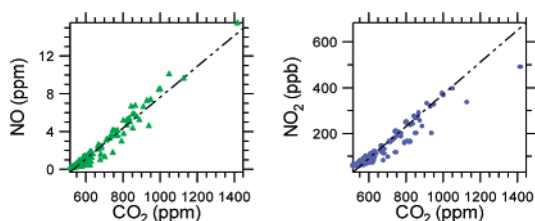


FIGURE 13. NO and NO₂ correlation with CO₂ in the exhaust of an in-use NYC diesel bus.

formed on the walls of the exhaust system and then sloughed off back into the exhaust flow. As discussed in ref 17 the organic fraction mass spectrum is indicative of unoxidized hydrocarbons and bears a strong resemblance to the mass spectrum for unburned motor oil.

Figure 12, also reprinted from ref 17, shows the mean and standard deviations of nonrefractory (primarily organic + sulfate) fine particle mass from a range of NYC heavy duty vehicles, including several bus technology variations used by New York's Metropolitan Transit Authority (MTA). Both MTA and non-MTA compressed natural gas (CNG) powered buses show considerably lower exhaust nonrefractory fine particle mass loadings than normal diesel (6V-92 and Series 50) buses. MTA diesel buses equipped with continuously regenerating trap (CRT) technology designed to trap and oxidize soot particles also show significantly lower non-refractory mass emissions. Intercity diesel coach buses and heavy duty diesel trucks have significantly higher non-refractory mass loadings than both MTA and non-MTA city transit buses.

Figure 13 shows chase mode correlation measurements between bus plume intercept NO and NO₂ measurements and plume CO₂ levels for a diesel transit bus, demonstrating that real-time plume intercept gaseous pollutant measurements can be expected to yield useful emission ratios for various target vehicle operating modes. Figure 14 shows a summary of NO_x emission data for a range of NYC buses. The lowest NO_x emission ratios for buses were from MTA hybrid diesel electrics and school buses, although the sample sizes were small. The high NO₂ levels for diesel buses

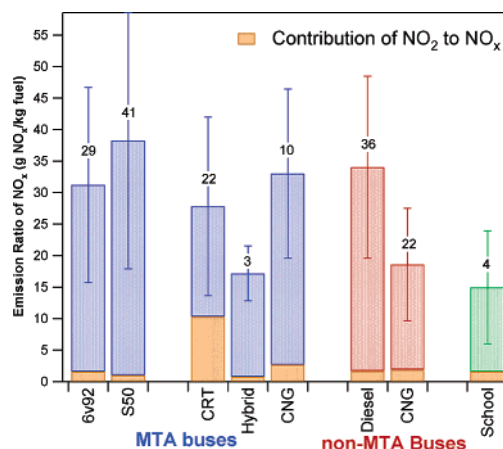


FIGURE 14. NO_x emissions from NYC buses.

equipped with CRT fine particle oxidation traps are illustrative of the fact that efforts to control one criteria pollutant (fine particles) can lead to increases of another (NO₂).

Mobile source exhaust emissions of toxic compounds is an issue of growing air quality concern (34), with recent attention focused on a short list of priority gaseous aromatics (benzene, toluene), aldehydes (formaldehyde, acetaldehyde, acrolein), 1,3-butadiene, and diesel particulates. The ability of mobile laboratory chase experiments to characterize diesel particulate material has been illustrated above and presented elsewhere by our group (17) and others (23, 24). The ability to monitor and quantify multiple on-road gaseous air toxic emissions in chase experiments is illustrated in Figure 15 where the correlation of formaldehyde, acetaldehyde, benzene, and toluene exhaust emissions with plume CO₂ from a colectivo (public transit minibus) in Mexico City is presented. Formaldehyde measurements were made with an ARI TILDAS instrument, while acetaldehyde, benzene, and toluene measurements were made using a PTR-MS unit deployed by B. Knighton of Montana State University on our mobile laboratory. We are currently investigating the mid-IR TILDAS detection of acrolein and 1,3-butadiene in the laboratory and expect to be able to measure mobile emissions

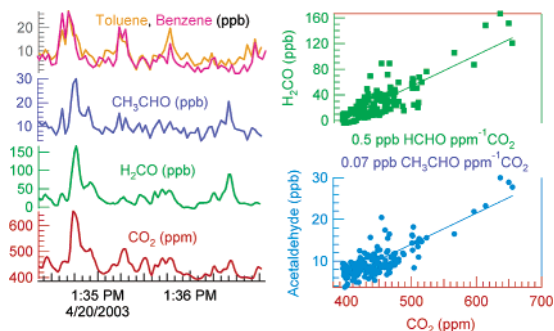


FIGURE 15. Air toxics emission correlated with excess exhaust plume CO₂ from an on-road Mexico City colectivo.

of these species in future chase experiments. Several groups have recently demonstrated the ability of properly calibrated PTR-MS instruments to rapidly and accurately measure selected VOCs in urban air (35–37). However, while airborne PTR-MS studies are common, we believe that Knighton's successful reconfiguration of a commercial PTR-MS instrument for deployment under the higher impact conditions found in an on-road mobile laboratory operating on some very rough roadways is noteworthy.

Mobile Laboratory Measurement Challenges

While the examples presented above show that on-road measurements using fast response instruments in a mobile laboratory can produce valuable and, in some cases, unique data on ambient pollutant distributions and both fixed and mobile emission fluxes, there are significant challenges that must be overcome for successful operation.

One major challenge is obvious, most fast response pollutant instruments rely on spectroscopic or mass spectrometric detection, and the sharp jolts encountered in operating at higher speeds on poorly surfaced or unpaved roadways can easily misalign optical systems, break vacuum connections, and disconnect or damage vital electrical components. They can also threaten disk drives and other components in instrument control and data logging computers. Shock mounting of almost all instruments is required, and instruments with few or no moving parts fare better than mechanically complex instruments. It is inadvisable to assume that instruments that function well in fixed laboratories or even in aircraft will operate on-road without refitting.

A second major challenge is thermal management. The instrument load illustrated in Figure 1, the associated pumps, and the on-board generator produce many kilowatts of waste heat that must be removed in order to prevent instrument, computer, and operator overheating. This can be a nontrivial challenge, particularly on hot days with full sunlight adding to the thermal burden. Sufficient on-board air conditioning is a must, but the generator must be large enough to support both air conditioning and instrument/pump requirements. Conversely, starting-up instrumentation in a cold mobile laboratory equilibrated with well below freezing ambient conditions can also be a challenge if sufficient heating capacity is not available.

In general, stationary operation with the on-board generator is problematic since its exhaust cloud will often contaminate ambient samples, even if the sample inlets are positioned on the opposite end of the vehicle from the generator exhaust port. Even in mobile operation it is important to establish that there is sufficient headwind to carry the rear facing generator and vehicle exhausts away from the sample inlets. We utilize a forward facing sonic anemometer positioned just above the main sample inlet to archive times when net wind flow is from the rear of the

vehicle and data quality may be questionable. Hydrogen powered fuel cells for both instrument power generation and vehicle propulsion would alleviate this issue but are prohibitively expensive and/or impractical at this time.

Data management and archiving can also be a challenge, since multiple real-time instruments produce a lot of data in a hurry. On a recent 5-week field campaign the instrument suite and associated equipment illustrated in Figure 1 produced over 100 gigabytes of archived data. While the availability of cheap, fast hard drives makes data acquisition and storage of this magnitude manageable, reducing, quality ensuring, and finally analyzing data sets of this magnitude remain challenging. Automated data analysis routines for the highest data rate instruments, like the ARIAMS, are under continuous development.

Careful control of sampling flows is required to ensure that air samples are delivered to each instrument at known and acceptable pressures, that particles or "sticky" gases such as NH₃ or HNO₃ are not lost on sampling line walls before they reach the relevant instruments or that inlet calibrations quantify such losses, and that variations in flow times to various instruments are stable and known, so that pollutant correlations can be made at subsecond accuracy using data from the full range of pollutant instruments. These sample timing issues are obviously much more stringent in mobile operation when plume penetrations may last only a few seconds than they are for fixed site instruments which normally do not have to correlate data on such short time scales. In practice, the sampling system needs to be calibrated periodically to ensure that sample losses are minimal and subsequent data correlations are valid.

As with any instrument suite, some mobile laboratory instruments need individual periodic calibration for accurate operation. These requirements vary with instrument type. For instance, TILDAS based instruments using sweep integration rely on fitting spectral features with well-known absorption strengths and pressure broadening coefficients and require infrequent calibration as long as the recorded spectra match expectations and any inlet/sampling line losses are accounted for. On the other hand, mass spectrometric instruments like the AMS and PTR-MS require periodic calibration with either test particles of known size and composition (AMS) or selected VOC calibration gas standards (PTR-MS). Commercial fine particle and trace gas detectors generally must be calibrated at specified intervals, just as they are in fixed site deployments.

Some of the measurement challenges listed above are common to both fixed site and mobile laboratories. However, it is clear that mobile instruments are subject to additional abuse so that more frequent maintenance and calibration requirements should be expected.

While measurements using state-of-the-art mobile laboratories are challenging, the use of innovative methods to characterize intertwined urban air quality issues, including photochemical smog, fine particulate loadings, airborne toxics, and greenhouse gas sources will be required. Utilization of mobile platforms equipped with fast response instruments may be particularly important in developing megacities that are very sparsely equipped with traditional fixed site air quality monitoring instruments and have poor emissions inventories.

Acknowledgments

We thank B. K. Lamb, E. Allwine, S. M. O'Neill, and H. Westberg of Washington State University, B. Knighton of Montana State University, E. Scheuer and R. W. Talbot of the University of New Hampshire, R. C. Harriss currently of the National Center for Atmospheric Research, K. L. Demerjian of the State University of New York at Albany, T. R. Lanni of the New York Department of Environmental Conservation,

G. J. McRae, L. T. Molina, and M. J. Molina of the Massachusetts Institute of Technology, and R. Ramos Villegas of the Gobierno de Distrito Federal, Mexico City for their contributions to the conception and execution of mobile laboratory measurements. Financial support for mobile laboratory measurements from the National Aeronautics and Space Administration, the Environmental Protection Agency through SUNY Albany, and the Comisión Ambiental Metropolitana (of Mexico City) through MIT and for fast response instrument development from the National Science Foundation, the Environmental Protection Agency, the National Aeronautics and Space Administration, the Department of Energy, and the Office of Naval Research is gratefully acknowledged.

Literature Cited

- (1) Anderson, J. G.; Brune, W. H.; Proffitt, M. H. *J. Geophys. Res.* **1989**, *94*, 11,465–11,479.
- (2) Trainer, M.; Ridley, B. A.; Buhr, M. P.; Kok, G.; Walega, J.; Hübler, G.; Parrish, D. D.; Fehsenfeld, F. C. *J. Geophys. Res.* **1995**, *100*, 18,823–18,834.
- (3) Nunnermacker, L. J.; Imre, D.; Daum, P. H.; Kleinman, L.; Lee, Y.-N.; Lee, J. H.; Springston, S. R.; Newman, L.; Weinstein-Lloyd, J.; Luke, W. T.; Banta, R.; Alvarez, R.; Senff, C.; Sillman, S.; Holdren, M.; Keigley, G. W.; Zhou, X. *J. Geophys. Res.* **1998**, *103*, 28,129–28,148.
- (4) Klemm, O.; Ziomas, I. C. *J. Air Waste Manage. Assoc.* **1998**, *48*, 16–25.
- (5) Marenco, A.; Thouret, V.; Nédélec, P.; Smit, H.; Helten, M.; Kley, D.; Karcher, F.; Simon, P.; Law, K.; Pyle, J.; Poschmann, G.; Van Wrede, R.; Hume, C.; Cook, T. *J. Geophys. Res.* **1998**, *103*, 25, 631–25, 642.
- (6) Thouret, V.; Cho, J. Y. N.; Newell, R.; Marenco, A.; Smit, H. G. *J. J. Geophys. Res.* **2000**, *105*, 17,379–17,392.
- (7) Blaha, D.; Mosher, B.; Harriss, R. C.; Kolb, C. E.; McManus, J. B.; Shorter, J. H.; Lamb, B. *Geo. Info. Systems* **1994**, *4*, 34–38.
- (8) Lamb, B.; McManus, J. B.; Shorter, J. H.; Kolb, C. E.; Mosher, B.; Harriss, R. C.; Allwine, E.; Blaha, D.; Howard, T.; Guenther, A.; Lott, R. A.; Siverson, R.; Westberg, H.; Zimmerman, P. *Environ. Sci. Technol.* **1995**, *29*, 1468–1479.
- (9) Shorter, J. H.; McManus, J. B.; Kolb, C. E.; Allwine, E. J.; Lamb, B. K.; Mosher, B. W.; Harriss, R. C. Partchatka, V.; Fisher, H.; Harris, G. W.; Crutzen, P. J.; Karbach, H. *J. Atmos. Chem.* **1996**, *24*, 121–140.
- (10) Czepiel, P. M.; Mosher, B.; Shorter, J. H.; McManus, J. B.; Kolb, C. E.; Allwine, E.; Lamb, B. K.; Harriss, R. C. *J. Geophys. Res.* **1996**, *101*, 16,711–16,719.
- (11) Shorter, J. H.; McManus, J. B.; Kolb, C. E.; Allwine, E. J.; Siverson, R.; Lamb, B. K.; Mosher, B. W.; Harriss, R. C.; Howard, T.; Lott, R. A. *Environ. Sci. Technol.* **1997**, *31*, 2012–2019.
- (12) Mosher, B. W.; Czepiel, P. N.; Harriss, R. C.; Shorter, J. H.; Kolb, C. E.; McManus, J. B.; Allwine, E.; Lamb, B. K. *Environ. Sci. Technol.* **1999**, *33*, 2088–2094.
- (13) Jiménez, J. L.; McManus, J. B.; Shorter, J. H.; Nelson, D. D.; Zahniser, M. S.; Koplow, M.; McRae, G. J.; Kolb, C. E. *Chemosphere: Global Change Sci.* **2000**, *2*, 397–412.
- (14) Shorter, J. H.; McManus, J. B.; Kolb, C. E.; Allwine, E. J.; O'Neill, S. M.; Lamb, B. K.; Scheuer, E.; Crill, P. M.; Talbot, R. W.; Ferreira, J., Jr.; McRae, G. J. Recent Measurements of Urban Metabolism and Trace Gas Respiration, *American Meteorological Society Proceedings, Second Urban Environment Symposium*, Albuquerque, NM, 1998, pp 49–52.
- (15) Shorter, J. H.; McManus, J. B.; Kolb, C. E.; Lamb, B. K.; O'Neill, S. M.; Allwine, E. J.; Talbot, R. W.; Scheuer, E.; Crill, P. M.; Ferreira, J., Jr.; McRae, G. J. Understanding the Influence of Local and Regional Sources on the Temporal and Spatial Variability of Pollutants in Urban Environments, *American Meteorological Society Proceedings, Third Symposium on the Urban Environment*, 2000, pp 90–91.
- (16) Shorter, J. H.; Herndon, S. C.; Zahniser, M. S.; Nelson, D. D.; Jayne, J. J.; Kolb, C. E. Characterization of heavy-duty vehicle exhaust in dense urban environments, *Proceedings of the 10th International Symposium Transport and Air Pollution*, Boulder, Colorado, 2001, pp 33–40.
- (17) Canagaratna, M. R.; Jayne, J. T.; Ghertner, A.; Herndon, S.; Shi, Q.; Jiménez, J. L.; Silva, P.; Williams, P.; Lanni, T.; Drewnick, F.; Demerjian, K. L.; Kolb, C. E.; Worsnop, D. R. *Aerosol Sci. Technol.* **2004**, *38*, 555–573.
- (18) Whitby, K. T.; Clark, W. E.; Marple, V. A.; Sverdrup, G. M.; Sem, G. J.; Willeke, K.; Liu, B. Y. H.; Pui, D. Y. H. *Atmos. Environ.* **1975**, *9*, 463–482.
- (19) Mathai, C. V.; Harrison, A. W. *Can. J. Chem.* **1982**, *60*, 1001–1007.
- (20) Vogt, R.; Kirchner, U.; Scheer, V.; Hinz, K. P.; Trimborn, A.; Spengler, B. *J. Aerosol Sci.* **2003**, *34*, 319–337.
- (21) Bukowicki, N.; Dommen, J.; Prévôt, A. S. H.; Richter, R.; Weingartner, E.; Baltensperger, U. *Atmos. Environ.* **2002**, *36*, 5569–5579.
- (22) Seakins, P. W.; Lansley, D. L.; Hodgson, A.; Huntley, N.; Pope, F. *Atmos. Environ.* **2002**, *36*, 1247–1248.
- (23) Vogt, R.; Scheer, V.; Casati, R.; Benter, T.; *Environ. Sci. Technol.* **2003**, 4070–4076.
- (24) Kittelson, D.; Johnson, J.; Watts, W.; Wei, Q.; Drayton, M.; Paulsen, D. Diesel Aerosol Sampling in the Atmosphere. *SAE Technical Paper Series*, 2000-01-2212; 2000.
- (25) Zahniser, M. S.; Nelson, D. D.; McManus, J. B.; Keabian, P. L. *Philos. Trans. R. Soc. London A* **1995**, *351*, 371–382.
- (26) Nelson, D. D.; Shorter, J. H.; McManus, J. B.; Zahniser, M. S. *Appl. Phys. B* **2002**, *75*, 343–350.
- (27) McManus, J. B.; Nelson, D. D.; Shorter, J. H.; Zahniser, M. S. Quantum Cascade Lasers for Open- and Closed-Path Measurement of Atmospheric Trace Gases. In *Diode Lasers and Applications in Atmospheric Sensing, SPIE Proceedings*; 2002; Vol. 4817, pp 22–33.
- (28) Jayne, J. T.; Leard, D. C.; Zhang, X.; Davidovits, P.; Smith, K. A.; Kolb, C. E.; Worsnop, D. R. *Aerosol Sci. Technol.* **2000**, *33*, 49–70.
- (29) Jiménez, J. L.; Jayne, J. T.; Shi, Q.; Kolb, C. E.; Worsnop, D. R.; Yourshaw, I.; Seinfeld, J. H.; Flagan, R. C.; Zhang, X.; Smith, K. A.; Morris, J.; Davidovits, P. *J. Geophys. Res.* **2003**, *108* (D7), 8425, doi: 10.2912/2001JD00123.
- (30) Allan, J. D.; Coe, H.; Bower, K. N.; Williams, P. I.; Gallagher, M. W.; Alfarra, M. R.; Jiménez, J. L.; Worsnop, D. R.; Jayne, J. T.; Canagaratna, M. R.; Nemitz, E.; McDonald, A. G. *J. Geophys. Res.* **2003**, *108*, 4090, doi: 10.1029/2002JD002358.
- (31) McManus, J. B.; Shorter, J. H.; Zahniser, M. S.; Kolb, C. E.; O'Neill, S. M.; Stock, D.; Napelno, S.; Allwine, E. J.; Lamb, B. K.; Scheuer, E.; Talbot, R. W.; San Martini, F.; Adamkiewicz, G.; Pun, B. K.-L.; Wang, C.; McRae, G. J.; Cao, L.; Ismail, A. A.; Kawabata, M.; Yeang, C.-H.; Narasimhan, G.; Humbad, S.; Zhang, M.; Ferreira, J., Jr. *Measurements and Analysis of Urban Metabolism and Trace Gas Respiration*; Report No. ARI-RR-1330; Aerodyne Research, Inc.: Billerica, MA, 2002.
- (32) Kirchstetter, T. W.; Harley, R. A.; Kreisberg, N. M.; Stolzenberg, M. R.; Hering, S. *Atmos. Environ.* **1999**, *33*, 2955–2968.
- (33) Bishop, G. A.; Stedman, D. H.; Asbaugh, L. *J. Air Waste Manage. Assoc.* **1996**, *46*, 667–675.
- (34) The National-Scale Air Toxics Assessment, <http://www.epa.gov/ttn/atw/nata/>.
- (35) Haywood, S.; Hewitt, C. N.; Sartin, J. H.; Owen, S. M. *Environ. Sci. Technol.* **2002**, 1554–1560.
- (36) Karl, T.; Jobson, T.; Kuster, W. C.; Williams, E.; Stutz, J.; Shetter, R.; Hall, S. R.; Goldan, P.; Fehsenfeld, F.; Lindinger, W. *J. Geophys. Res.* **2003**, *108*, D16, doi 10.1029/2002JD003333.
- (37) Warneke, C.; De Gouw, J. A.; Kuster, W. C.; Goldan, P.; Fall, R. *Environ. Sci. Technol.* **2003**, 2494–2501.

Received for review December 8, 2003. Revised manuscript received May 20, 2004. Accepted June 1, 2004.

ES030718P