**SUPPORTING INFORMATION**


**APPROACH TO ESTIMATING PARTICIPANT POLLUTANT EXPOSURES IN THE MULTI-ETHNIC STUDY OF ATHEROSCLEROSIS AND AIR POLLUTION (MESA AIR)**

Martin A. Cohen[1*], Sara D. Adar[1], Ryan W. Allen[1,2], Edward Avol[3], Cynthia L. Curl[1], Timothy Gould[4], David Hardie[1], Anne Ho,[1] Patrick Kinney[5], Timothy V. Larson[4], Paul Sampson[6], Lianne Sheppard[7], Karen D. Stukovsky[7], Susan S. Swan[1,8], L-J Sally Liu[1,9], Joel D. Kaufman[1]

11 pages
2 tables
2 figures

## Measurement Methods
### $PM_{2.5}$ mass

       $PM_{2.5}$ mass concentrations were measured using single-stage Harvard Personal Environmental Monitor (HPEM) impactors (Thermo-Fisher, Waltham, MA) with 37-mm Teflon filters (PTFE Teflo Membrane model R2PJ037, Pall Corporation, East Hills, NY) and silicon vacuum grease on the impaction plates.  SidePak 530 (TSI, St. Paul, MN) pumps were selected for $PM_{2.5}$ sampling based on the presence of an internal flow meter with data logging capability and the ability to perform intermittent sampling.  These pumps were operated at 1.8 L/min on a 50% (5 minutes on and 5 minutes off) duty cycle to prevent overloading of the filters during a two-week period.  For home and fixed site sampling, these pumps were run on AC power for the 2-week duration while personal samples utilized a rechargeable battery pack so as to not interfere with the participant's regular daily activities.  These battery packs and the associated Teflon filters were changed every two or three days by the field technicians, resulting in approximately 6 sequential integrated filter samples per 2 week personal monitoring period.  This is in contrast to a single filter per two-week period for all other monitoring.  Common to all monitoring, flow rates were confirmed before and after all sampling events using an external rotameter (model EW-03267-20, Cole-Parmer, Chicago, IL) that was calibrated at least annually at the University of Washington (UW).

       The Teflon filters used to determine $PM_{2.5}$ mass concentration were pre- and post-weighed at the UW using a UMT-2 microbalance (Mettler-Toledo, Columbus, OH) in a temperature and humidity controlled environment [27] using standard filter weighing procedures [28].  Filters were shipped to field centers for HPEM assembly and field deployment.

### Light Absorbing Carbon (LAC)

The Teflon filters used for the gravimetric analyses were also used to determine the amount of LAC, a surrogate for EC, using a Smokestain Reflectometer (Model 43D EEL, Diffusion Systems Ltd., London, UK). The pre-sample filter reflectance was measured prior to the pre-sample weighing session, and the post-sample reflectance was measured after post-sample weighing. The absorption coefficient, $b_{ap}$ ($m^{-1}$), of each sample was determined from its pre- and post-exposure reflectance readings and adjusted by a city-specific average field blank value. The relationship between light absorption and EC concentration is developed empirically in each area based on comparison with direct measurements of EC.

### PM$_{2.5}$ Elemental Composition

Filter samples from the homes selected for paired indoor-outdoor or personal monitoring were analyzed for elemental composition. Following post-sample gravimetric analysis and reflectometry, the filters were analyzed for 48 elements by x-ray fluorescence (XRF) (Cooper Environmental Services; Portland, OR). Method sensitivity was defined by a set of acceptable detection levels for a subset of 21 key elements from the Method IO-3.3 analyte list. An uncertainty value was reported by element for each sample.

### Measurement of Elemental and Organic Carbon

The EC and OC portions of PM$_{2.5}$ were determined using pre-fired quartz fiber filters collected with the previously described field methodology for Teflon filters. These samples were analyzed by Sunset Laboratory Inc. (Tigard, OR) using a method (IMPROVE-A) designed to be comparable with the Interagency Monitoring of Protected

Visual Environments (IMPROVE) method recently adopted by the EPA for analysis of its chemical speciation network (CSN) monitoring site samples.

### *Gaseous Co-Pollutants*

Ogawa passive samplers (Ogawa & Co, Pompano Beach, FL) were used to measure $NO_2$, $NO_x$, $SO_2$, and $O_3$. Pre-coated pads were loaded and unloaded into the samplers at the UW. All Ogawas were disassembled using standard methods and pads placed into sealed vials within 14 days of sampling.

Ion chromatography (IC) was used to analyze the sample extracts for nitrite, nitrate, and sulfate for the quantification of $NO_2$, $O_3$, and $SO_2$, respectively. The IC system used was a Dionex ICS1000 with an AS40 autosampler and conductivity detector, all controlled by Chromeleon ver. 6.60 software (Dionex, Sunnyvale, CA). A Dionex IonPac AS9-HC analytical column and AG9-HC guard column were used along with an ASRS-ULTRA-II suppressor run in recycle mode at a current of between 37 and 45mA. A 25μL sample loop was used with a 9mM sodium carbonate eluent, set to a flow rate of between 0.75 and 1.00 ml/min.

The IC system was calibrated during each analysis session by using standards ranging from 0.032 to 12 ppm. The purity of the standards was checked periodically by comparing against a 7-Anion Standard mixture (Dionex), which is a NIST-traceable mixture of known concentrations of seven anions, including nitrite, nitrate, and sulfate.

For analysis of $NO_x$ we used a Molecular Devices Spectromax 190 absorbance microplate reader (Molecular Devices Corp., Sunnyvale, CA). Nitrite ions were detected colorimetrically at a wavelength of 545 nm. Similar to the IC process, the UV Spectrometer was calibrated during each analysis session using nitrite ion standards of

varying concentrations (0.032 to 10 ppm).  The mass of $NO_2$ was subtracted from the

mass of $NO_x$ to estimate the net mass of NO.  Ambient concentrations of NO, $NO_x$, $O_3$,

and $SO_2$ were then calculated using the equations and tables provided by Ogawa &

Co.[29]

## *Quality Assurance/Quality Control/Chain of Custody*

Quality Assurance (QA) Processes

All field staff underwent extensive training including performance-based

evaluation and certification.  Consistency between field centers was maintained using

standard operating procedures and weekly teleconferences.

Both field blanks and co-located duplicate samples were deployed at a rate of

10% of samples at the fixed and homes sites for all sampling media.  Blanks and

duplicate samples were deployed during community saturation sampling at rates of 10%

and 15%, respectively.  Due to the additional burden of carrying sampling equipment, no

duplicate $PM_{2.5}$ samples were collected during personal monitoring.  Duplicate Ogawa

samples were collected in personal sampling at a rate of 15%.  As a result of artifact

issues associated with quartz filter sampling [30], we used both standard blanks (10% of

samples) and dynamic blanks (20% of samples); the latter are back up filters placed

downstream of the sample filter to collect any off-gassed organic carbon compounds.

Quality Control (QC) Processes

All field data were reviewed for completeness and checked for errors.  This QC

was performed under the guidance and supervision of a QA committee and compiled for

periodic reports.  The analytic and method limits of detection (LODs) and method

precision are shown in Table S1.

We organized and participated in two "round robin" laboratory comparison studies, one for gravimetric analysis and the other for LAC. The gravimetric comparison included a total of 6 independent laboratories, while the LAC comparison included 4 independent laboratories. Filters were initially weighed and reflected at the UW and then sent sequentially to the other laboratories. When the filters were returned to the UW, their identities were blinded from the analyst and then weighed and reflected again. Results show that the UW measurements were well within 10% of the overall mean of the filter weights and LAC reported by all laboratories.

## Quality Control Outcomes
### *Design goals*

Table S2 provides a summary of the number of sampling locations by area. Overall, we were generally successful in meeting our design goals for siting of our samples. For example, approximately 21 and 26% of the homes sampled were near (<50 m) and far (>300) from major roadways, respectively. By design our community saturation samples were more focused on near roadway effects and had nearly 30% of the locations sited within 50 meters of a major roadway. These community saturation samples also captured differing levels of population density with 47%, 22%, and 31% of the samples collected in low, medium, and high population density areas. They also captured regions of residential (66%) and non-residential (34%) land-use. Fixed sites were also successfully situated such that at least one site per area was located within 100 meters of an interstate or state highway with the one exception of Rockland County, NY.

## *Data Quality*

An estimate of the precision of the measurements is shown in Figure S1, which is a plot of the relative percent difference (RPD) of the duplicate samples divided by the square-root of 2. All of the mean RPDs are less than 10%, which is the Data Quality Objective (DQO) for precision of these measurements. Data less than the limit of detection were not included in this chart for $O_3$ and $SO_2$ because inclusion of those samples would have falsely inflated the results because of the relatively low levels measured compared to the limit of detection. Method accuracy was investigated by plotting the 2-week average MESA Air results against calculated 2-week average concentrations for the measurements taken at the co-located AQS site between July 1, 2005 and August 31, 2008. These plots are shown in Figures S2a-d. For $PM_{2.5}$ and LAC, data were only used if there were 5 or more daily measurements made to calculate the 2-week averages. Because there is relatively large between-area variability in concentrations, the results appear clustered by area.

**Table S1**  Limits of detection and analytic precision.

| Parameter | Analytic LOD[a] | Method LOD[b] | Analytic Precision[c] |
|---|---|---|---|
| $PM_{2.5}$ (µg/m3) | 0.28 | 4.4 | 1.45 µg |
| LAC ($m^{-1}$) | $0.03 \times 10^{-5}$ | $0.16 \times 10^{-5}$ | 0.13 RU |
| $NO_2$ (ppb) | 1.3 | 3.6 | 4.3% |
| $NO_X$ (ppb) | 1.6 | 6.6 | 4.5% |
| $O_3$ (ppb) | 0.92 | 2.0 | 5.0% |
| $SO_2$ (ppb) | 0.20 | 0.86 | 2.8% |

[a]Defined as 3 times the standard deviation of the mean laboratory blank concentration for $NO_2$, $O_3$, and $SO_2$, by analysis batch.  As $NO_X$ is a derived value, the LOD for $NO_X$ is calculated as the root sum square of the IC-$NO_2$ and the UV-Nitrate LODs.  For $PM_{2.5}$ and light absorbing carbon, the analytic LOD is defined as the minimum acceptable difference to be detected, divided by the nominal sampling volume.  The analytic LOD listed is for all two-week samples.

[b]Defined as 3 times the standard deviation of the field blanks, averaged across cities. Because $NO_X$ blank levels are significantly influenced by differences in batches of samplers sent by the manufacturers, the LOD was determined by taking the median of the standard deviations of the field blanks in two month intervals, as a surrogate for batch-correction.

[c]For $NO_2$, $O_3$ and $SO_2$ our data quality objectives (DQOs) require that the RPD/$\sqrt{2}$ (%) between duplicate IC runs be less than 10%.  For $NO_X$, our DQOs require that the CV of triplicate UV measurements be less than 10%.  For $PM_{2.5}$ and LAC, analytic precision is defined as the mean difference between repeated measurements, which were required by our DQOs to be within 5 µg and 1.0 Reflectance Units (RU), respectively.

**Table S2.** Unique Monitoring Locations by MESA Air Area and Sampling Campaign

| MESA Air Area | Fixed Sites[a] | Outdoor Home Samples | Indoor Home Samples | Personal Samples | Saturation Samples |
|---|---|---|---|---|---|
| Baltimore, MD | 4 | 88 | 60 | 14 | 103 |
| Chicago, IL | 5 | 98 | 57 | 12 | 111 |
| Los Angeles, CA[b] | 5 | 84 | 79 | 12 | 167 |
| Riverside, CA | 2 | 36 | 34 | 4 | 57 |
| New York City, NY | 2 | 95 | 65 | 16 | 110 |
| Rockland, NY | 1 | 25 | 25 | 5 | 45 |
| St Paul, MN | 4 | 102 | 57 | 13 | 97 |
| Winston-Salem, NC | 4 | 92 | 66 | 12 | 103 |
| **Total** | **27** | **620** | **443** | **88** | **793** |
| **% with repeat sampling** | **100** | **80** | **89** | **94** | **97** |

[a]There were between 71 and 83 2-week sampling rounds at these fixed sites.
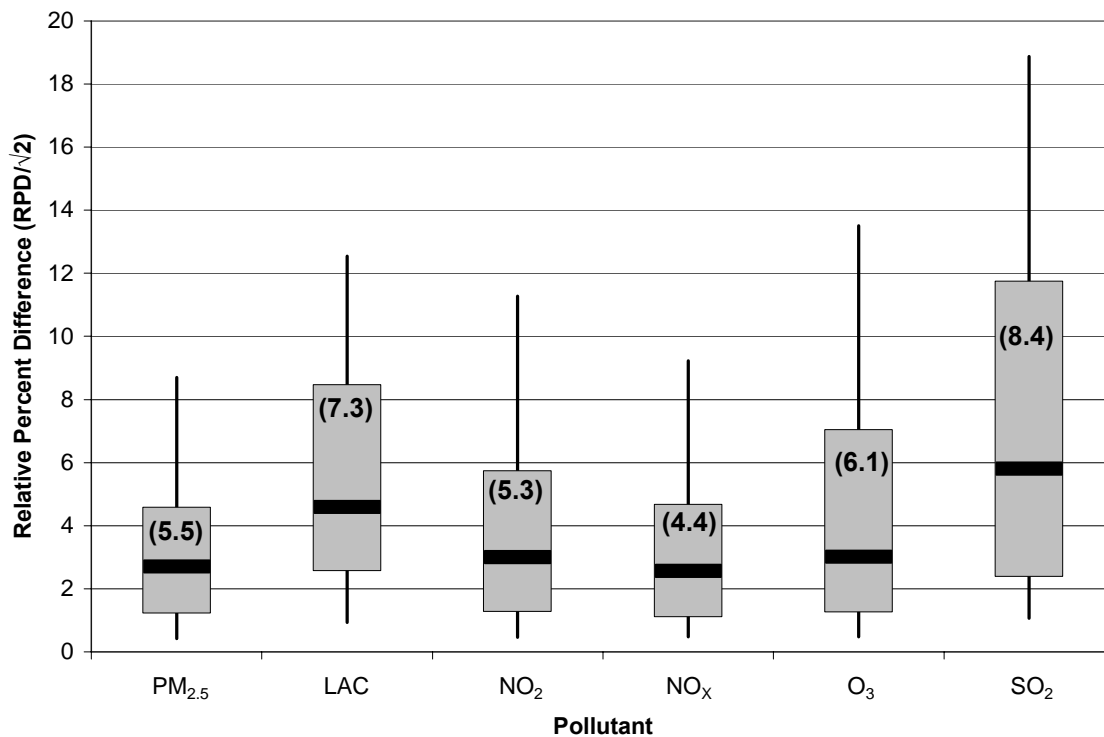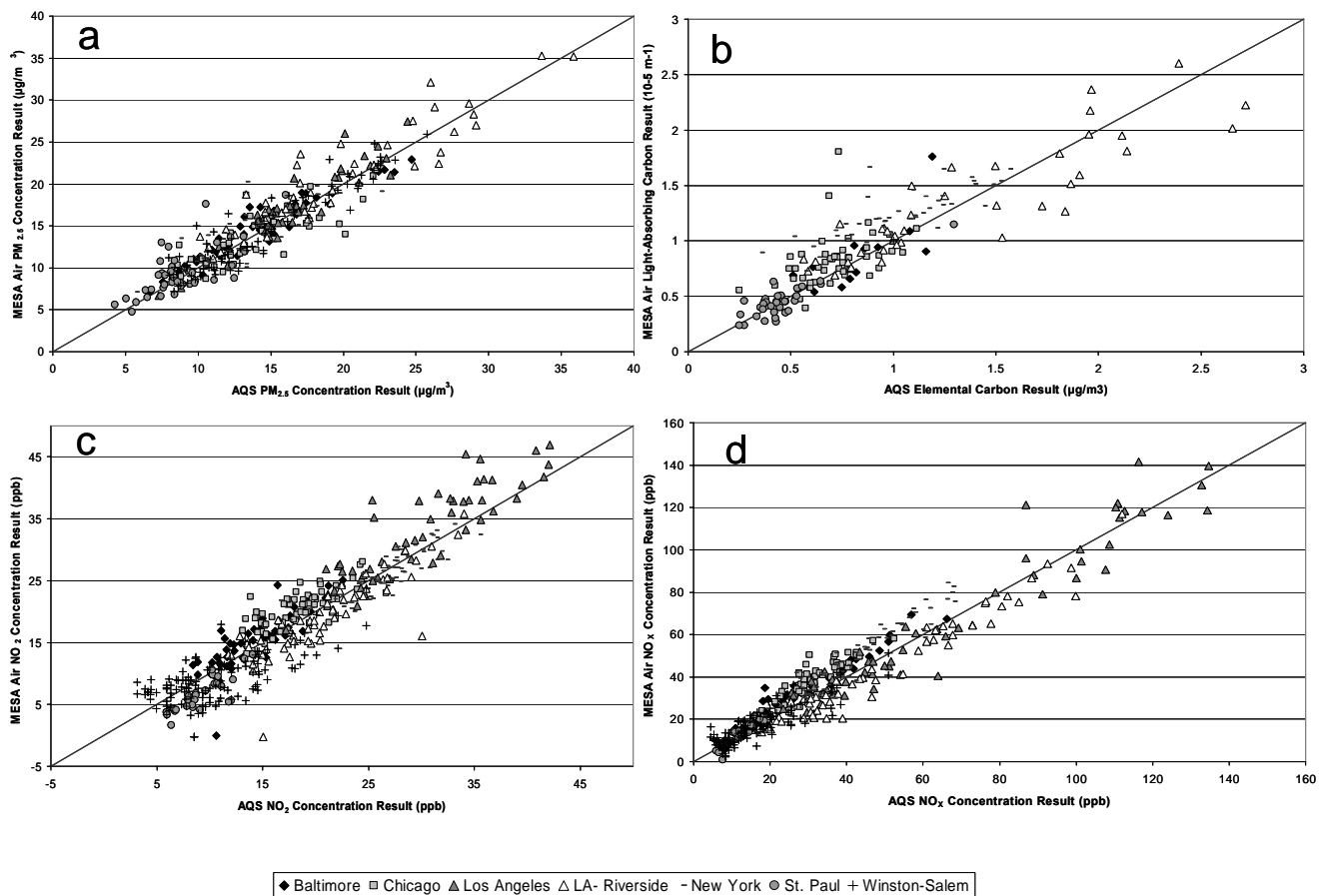[b]This includes coastal Los Angeles sites.

Figure S1. Relative percent difference between co-located duplicate samples, by sample type. Bar is median value, box indicates 25-75 percentiles, and whiskers are 10th and 90th percentiles. Number in parenthesis is the mean.

Figures S2a-d. MESA Air measurements versus AQS measurements for PM$_{2.5}$ (a), LAC (b), NO$_2$ (c), and NO$_X$ (d). Respective R$^2$'s are 0.91, 0.56, 0.69, and 0.93. For PM2.5 and LAC, AQS measurements were only included if there were 5 or more daily measurements collected at the co-located sampling site during that time period.