West Oakland Monitoring Study

DRAFT REPORT

APPENDICES

Sampling and Analytical Methods

Prepared for:
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September 9, 2010

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A. Appendix A. Sampling and Analytical Methods

1. PASSIVE SAMPLING METHODS

Passive sampling methods are viable alternatives to continuous instruments or active sampling methods and are especially applicable for saturation monitoring and assessment of personal exposures. The ability of passive methods to collect samples over long exposure times allows for monitoring of ambient concentrations with comparable or better limits of detection and precision than active sampling methods. Passive monitors have no pumps or other moving parts and are very compact and portable. No special training is required for their deployment and operation. The low associated labor means that passive monitoring is often cost-effective over other methods of measurement.

The basic principle employed in passive sampling is given by Fick's Law of Diffusion. Fick's first law, Equation 1, describes the rate of diffusion, J, of a solute across a surface area, A, and following a path length, l (J= m/At). D is the diffusion coefficient (length^2 time^{-1}) and C is concentration (mass length^{-3}).

$$J = -D\frac{\partial C}{\partial l} \qquad (1)$$

The continual adsorption of the pollutant from the air maintains a concentration gradient near the surface that allows uptake of the pollutant to occur without any forced air movement (i.e., no pump or fan is required). After sampling, the collected pollutant is desorbed from the sampling media by thermal or chemical means and analyzed quantitatively. The average concentration of the pollutant in the air to which the sampler was exposed can be calculated from the following relationship:

$$Concentration = \frac{AnalyteMass}{SamplingRate \times Time}$$

The sampling rate can be determined theoretically or experimentally and is regulated by Fick's first law, which can be alternately expressed as follows.

$$\frac{dm}{dt} = DA\frac{dC}{dl} \qquad (2)$$

$$\frac{m}{t} = D\frac{A}{l}(C - C_o) \qquad (3)$$

Assuming the blank value of the media is zero, the concentration C is that of the ambient compound of interest and approximation of equation 3 gives the sampling rate, Q (l/min) (equation 4). D is the coefficient of diffusion and is dependent on the affinity of the adsorbing material for the analyte. Theoretical calculation of the coefficient of diffusion is possible, but the real world dependencies regulating its value are extensive and ambient tests are required for validation. Therefore, experimental determination of sampling rates in chambers and controlled field studies is usually preferred (Sunesson, 2007). The concentration, C, is determined from the mass of analyte, m, and time of exposure, t (Equation 5)

$$\frac{m}{tC} = D\frac{A}{l} = Q \qquad (4)$$

$$C = \frac{m}{tQ} \qquad (5)$$

Several different geometries of passive samplers have been developed to control the diffusion rates according to Fick's first law. Thus sampling rates can be varied depending on the desired exposure time and expected ambient concentrations of the compounds of interest. Since the coefficient of diffusion, D and the concentration, C, are known, the sampling rate is proportional to the diffusive path area, A, and inversely proportional to the path length, L. To improve analytical sensitivity, m should be increased by increasing Q. Since D is constant, Q is proportional to A/l. Figure 1-1 shows three different geometries of passive monitors. The tube geometry is best for low sampling rates, while the shield (e.g., Ogawa) and radial geometry (e.g., Radiello) were developed for applications where higher diffusion rates are desired.

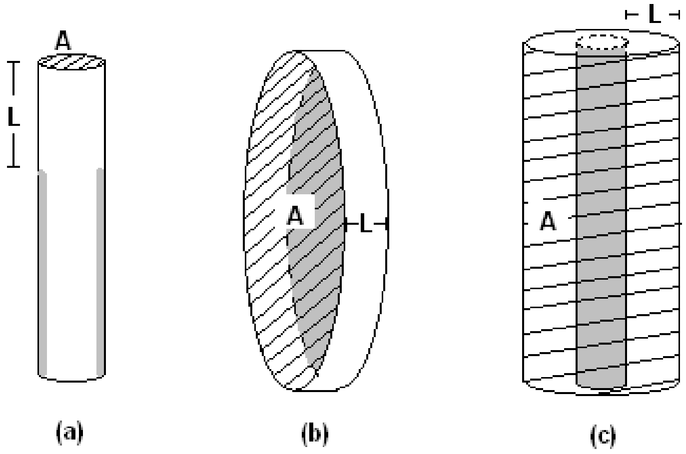

Figure 1-1. Schematics of (a) tube, (b) shield, and (c) radial geometry passive samplers with path length, L; Dashed area represents diffusive path area, A; Grey area represents adsorbent surface.

The WOMS used five different types of passive sampler, each with a unique combination of adsorbent and method of analysis (Table 1-1). The sampling rate for every analyte is calculated experimentally since pumps are not used in passive collection. Radiello[1] and Ogawa and Company[2] supply these sampling rates for a number of commonly collected compounds. These sampling rates were recently validated at DRI as part of the Harbor Communities Monitoring Study sponsored by the California Air Resources Board and the South Coast Air Quality Management District. Evaluations included chamber experiments for NO_x, formaldehyde, acrolein, BTEX, and SO_2 (Mason et al., 2010; Fujita et al. 2009). Because 1,3-butadiene is more volatile than the other the BTEX compounds, it is more prone to back diffusion (desorption). The results for 1,3-butadiene from passive samplers with Carbograph 4 were not quantitative due to back diffusion and were not reported in the HCMS. Radiello recently introduced samplers with Carbopack X, which has been shown to eliminate the desorption of 1,3-butadiene. However, the Carbopack X samplers were not available for use in WOMS.

Table 1-1. Diffusive samplers and analytical methods with manufacturer supplied minimum detection limits for 7-day exposures.

Pollutant	**Diffusive Body**	**Adsorbent**	**Analytical Method**	**MDL (168 hours exposure)**
NO_2	Ogawa 3300 Sampler	Triethanolamine	Colorimetry for nitrite	0.32 ppb
NOx	Ogawa 3300 Sampler	Triethanolamine + PTIO	Colorimetry for nitrite	0.32 ppb
SO_2	Ogawa 3300 Sampler	Triethanolamine	Ion Chromatography for sulfate	0.54 ppb
VOC	Radiello 120-2, polycarbonate and yellow microporous polyethylene cylindrical diffusive body	Radiello 145, ss net cylindrical cartridge, o.d. 4.8 mm packed with 350 mg of 35-50 mesh graphitic charcoal (Carbograph 4)	Thermal Desorption GC/MS	benzene 0.05 etbenzene 0.02 toluene 0.02 xylenes 0.02 (ug/m^3)
Carbonyl Compounds	Radiello 120-1, polycarbonate and blue microporous polyethylene cylindrical diffusive body	Radiello 165, ss net cylindrical cartridge, o.d. 5.9 mm with 900 mg of 35-50 mesh DNPH coated florisil	HPLC-UV	formaldehyde 0.1 acetaldehyde 0.1 acrolein 0.3 (ug/m^3)

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[1] Information about Radiello passive samplers can be found at http://www.radiello.com.

[2] Information about Ogawa passive samplers can be found at http://www.ogawausa.com/.

1.1 Ogawa Passive Samplers for NOx, NO_2 and SO_2

Ogawa Passive Sampling Systems (Rupprecht and Patashnick Co., Inc.) were used for monitoring NOx, NO_2, and SO_2. NOx, and SO_2 were collected over weeklong periods using pre-coated 14.5 mm sampling pads, deployed in personal sampling bodies. NO concentrations were calculated by subtracting NO_2 from NOx concentrations. Sampling and analysis were performed according to manufacturer protocols (Ogawa & Co., USA, Inc., http://www.rpco.com/assets/lit/lit03/amb3300_00312_protocolno.pdf). For the Ogawa samplers the sampling rate conversion factor α (ppb-min/ng) is given by the equations:

$$\alpha_{NOx} = \frac{10000}{(-0.78 \cdot P \cdot RH) + 220} \qquad \alpha_{NO2} = \frac{10000}{(0.677 \cdot P \cdot RH) + (2.009 \cdot T) + 89.8}$$

$$\text{where } P = \left(\frac{2P_N}{P_T + P_N} \right)^{2/3}$$

and RH is the relative humidity in percent, T is the air temperature in ^{o}C, and P_N and P_T are the vapor pressure of water in mmHg at 20 ^{o}C and ambient temperature, respectively. α_{SO2} was determined from tables provided by the manufacturer, and varies from 44 - 35 ppb-min/ng for the temperature range 0 – 40 ^{o}C. The Ogawa NO_2 and NO_x pads were extracted and mixed with a solution of sulfanilamide and N-(1-Naphthyl)-ethylenediamine dihydrochoride to produce a colored nitrite solution which was analyzed on a Technicon (Tarrytown, NY) TRAACS 800 Automated Colorimetric System (AC). The Ogawa SO_2 pads were extracted in 8 ml of deionized-distilled water (DDW), 1.75% hydrogen peroxide is added and sulfate was measured with a Dionex 2020i (Sunnyvale, CA) ion chromatograph (IC). These analyses were performed by the Environmental Analysis Facility (EAF) of DRI.

1.2 Radiello Diffusive Samplers for VOCs

Unlike other samplers that use axial diffusion from one surface to another, Radiello samplers use radial diffusion over a microporous cylinder into an absorbing inner cylinder, which gives about a 100 times higher uptake rate. Radiello diffusive samplers (adsorbing cartridge code 145) were used for passive sampling of benzene, toluene, ethylbenzene, and xylenes (BTEX). VOC samples were collected over weeklong periods using stainless steel net cylinders (3x8 um mesh, 4.8 mm diameter x 60 mm length) packed with Carbograph 4 (350 mg) and deployed in the diffusive sampling bodies, according to the manufacturer's procedures (http://www.radiello.com). The Radiello samplers are insensitive to humidity within the range 10-90% RH and wind speed between 0.1 and 10 m/s. Sampling rates were calculated based on ambient temperature during sampling using the following equation:

$$Q_T = Q_{298}(T/298)^{1.5}$$

where Q_T is the sampling rate at ambient temperature T in ^oK and Q_{298} is the reference value at 25 ^oC. This produces a variation of ± 5% for ± 10 ^oC variation from 25 ^oC.

All VOC passive samples were analyzed by the thermal desorption-cryogenic pre-concentration method, followed by high-resolution gas chromatographic separation and mass spectrometric detection (GC/MS) of individual compounds. A Gerstel ThermoDesorption System (TDS) unit, equipped with 20–position autosampler, attached to the Varian Saturn 2000 GC/MS system, was used for sample desorption and cryogenic preconcentration. A 60 m (0.32 mm i.d., 0.25 mm film thickness) DB-1 capillary column (J&W Scientific, Inc.) was used to achieve separation of the target species. For calibration of the GC/MS, a set of standard Carbograph 4 cartridges were prepared by spiking the cartridges with a known amount of gaseous calibration mixture of benzene, toluene, ethylbenzene, o-, m- and p- xylene (BTEX) and 1, 3–butadiane, purchased from Scott Specialty Gases. Three different concentrations (plus one blank) were used to construct calibration curves.

1.3 Radiello Diffusive Samplers for Carbonyl Compounds

Radiello diffusive samplers consisting of a stainless steel net cartridge filled with 2,4-dinitrophenylhydrazine (2,4-DNPH) coated florisil (Code 165) were used to passively collect carbonyl compounds. Sampling rates vary from the value at 25 ^oC according to the following equation:

$$Q_T = Q_{298}(T/298)^{0.35}$$

This produces a variation of ± 1% for ± 10 ^oC variation from 25 ^oC. Carbonyl compounds react with 2,4-DNPH forming corresponding 2,3-dinitrophenylhydrazones. The hydrazones were extracted and analyzed with a Waters 2690 Alliance System HPLC with 996 Photodiode Array UV Detector. The VOC and carbonyl compound analyses were performed by the Organic Analytical Laboratory (OAL) of DRI.

Despite the widespread use of the DNPH methods, interferences and sampling artifacts have been associated with the methods. The analytical method is well established, and questions regarding the accuracy of the DNPH method are mainly concerned with sampling. The major concerns are: 1) incomplete collection of carbonyls, 2) loss of carbonyl compounds by physical processes such as adsorption or chemical reaction with co-pollutants such as ozone, and 3) conversion of the hydrazone during sampling and subsequent storage. Radiello acknowledges the potential for ozonolysis of dinitrophenylhydrazones on active supporting materials such as silica gel, but claim that ozonolysis is less important on the code 165 cartridge, packed with coated florisil. Apart from acetaldehyde, the ozone effect becomes relevant only at levels higher than 100 ppb as an average over the entire exposure period. Sampling rates for acetaldehyde are lower by about 10 and 25 percent at ozone levels of 50 and 100 ppb, respectively. A recent study found that although active sampling on commercial DNPH cartridges was adequate for the measurement of formaldehyde, low recovery (< 60%) was observed for acetaldehyde for a sampling duration greater than 8 hours. The recovery decreased with increasing sampling time (Herrington et al., 2007). Thus, even the traditional method for measuring acetaldehyde is not particularly quantitative.

Acrolein is known to rearrange on DNPH cartridges to an unknown degradation product (acrolein-X) (Tejada, 1986). Disappearance of the acrolein hydrazone in the analytical sample matrix correlates quantitatively almost on a mole for mole basis with the growth of acrolein-X, and the sum of acrolein and acrolein-X appears to be invariant with time (Tejada, 1986). This process of rearrangement is sufficiently rapid that most of the acrolein may convert to acrolein-X, unless the sample is analyzed within a few hours. The problem is compounded by the fact that acrolein-X co-elutes in our HPLC analysis with another common carbonyl compound, butyraldehyde. The UV spectra from the photodiode array detector show that there is substantial overlap in the chromatographic retention time of acrolein-X with butyraldehyde. Thus, the sum of acrolein and butyraldehyde represents an upper-bound estimate of acrolein that was originally present in the sample.

DRI's Organic Analytical Laboratory recently performed experiments to determine if a more accurate measurement of acrolein could be obtained by post-analysis reprocessing of the HPLC spectra. This work was done for the Health Effects Institute for samples collected in the Los Angeles area for another project during summer and fall/winter 2004 (Fujita et al., 2008). An acrolein-X standard was generated by collecting a known concentration of acrolein onto a DNPH cartridge and letting it remain in the sample matrix long enough for part of the acrolein to convert to acrolein-X. The concentration of acrolein-X was calculated as the difference between the known amount of acrolein deposited on the DNPH cartridge and concentration determined from HPLC analysis. The apparent concentration of acrolein-X (from the peak identified as butyraldehyde) detected in the analysis is equivalent to the concentration of acrolein collected on the DNPH cartridge. A 'standard' for acrolein-X was generated in this manner. Several mixtures containing varying relative amounts of acrolein-X and butyraldehyde were analyzed to obtain spectra for which the correct proportions were known. Then, using an iterative solution process, peaks from the spectra of the two pure compounds were added together to obtain the closest match to the spectrum of each mixture, as shown in Figure 1-2. The scaling factors applied to the spectra from the acrolein-X and butyraldehyde spectra to obtain the best fit indicated the estimated amounts of each compound in the mixture.

Results from this experiment were quite good, yielding agreement to within 20% of the actual concentrations for all mixtures except those where the concentration of butyraldehyde was much higher (e.g. 10x) than acrolein. We applied the same technique to the previously analyzed HPLC data from samples collected in the Los Angeles area for a previous study (Fujita et al., 2008) in order to estimate the concentrations of acrolein and butyraldehyde in each sample. Comparing the sum of the two separated compounds to the original concentration of unresolved acrolein-X + butyraldehyde for each sample showed very strong correlations and good agreement, but there is some indication of bias due to variations in the instrument response over time. Although chemical standards are analyzed during each analysis run in order to compensate for variations in detector response, no standard for acrolein-X is available for routine use so there is some uncertainty connected with the reprocessing of the spectra using standards analyzed at a later time. However, Figure 1-3 indicates that the effect is relatively small even over a period of many months.

Figure 1-2. Sample of results of curve fitting program to reconstruct acrolein data from original spectrum. Absorbance is in units of cm^{-1}.

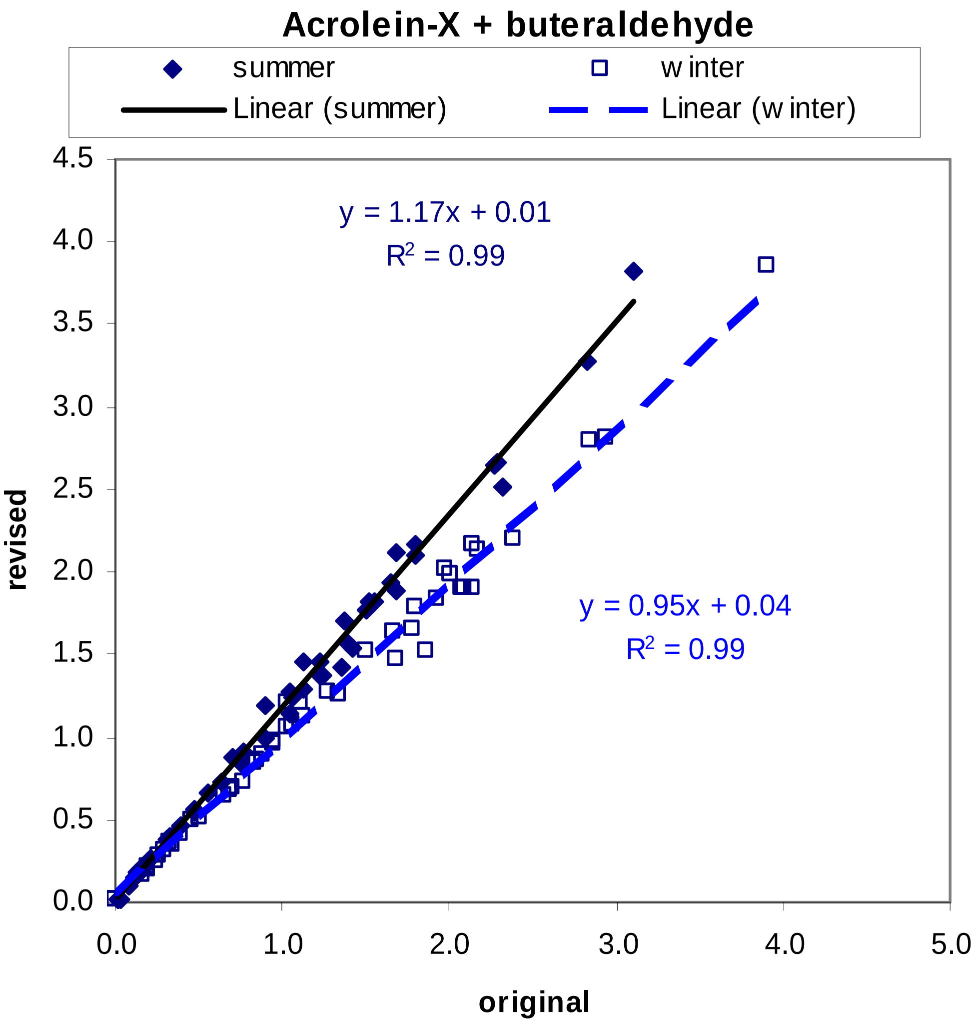

Figure 1-3. Regression plot comparing reconstructed sum of acrolein-X and butyraldehyde to original, unresolved total (DNPH adduct in µg/sample). Data from the two field sampling periods are grouped separately due to differences in instrument calibration.

1.4 Accuracy and Precision of Passive Measurements.

The Ogawa and Radiello passive sampling methods were recently evaluated for the California Air Resources Board as part of the Harbor Communities Monitoring Study (HCMS) (Fujita et al., 2009). Precision, accuracy, and sampling rates of the passive sampling methods were evaluated under both laboratory and field conditions prior to the monitoring program. They were first evaluated in the laboratory using a flow-through chamber with known pollutant concentrations. Then a pilot study was conducted at the SCAQMD monitoring station in North Long Beach to determine the replicate precision of passive measurements for NO_2, NOx, SO_2, H_2S, benzene, toluene, ethylbenzene, xylenes, 1,3-butadiene, formaldehyde, acetaldehyde, and acrolein under field conditions. The passive measurements were compared with the SCAQMD continuous NOx, NO_2 and SO_2 data and time-integrated samples collected and analyzed by DRI for organic air toxics using active sampling methods (i.e., canisters and chemically-impregnated cartridges). Concentrations of $PM_{2.5}$ mass, OC and EC measured on the 7-day integrated aerosol samples were also compared to the corresponding averages of daily 24-hour samples. One of the core HCMS sampling sites was collocated at a SCAQMD monitoring site during the main field study for quality assurance purposes. Passive samples were collected in triplicate at this site (LHUD) during the winter and summer seasons to determine measurement precision and were compared to the District's continuous monitors and parallel samples collected by DRI with active sampling methods.

Passive sampling methods for NOx, NO_2, SO_2, H_2S, BTEX and formaldehyde are viable alternatives to continuous instruments or active sampling methods and are especially applicable for saturation monitoring and assessment of personal exposures. The ability of passive methods to collect samples over long exposure times allows for monitoring of ambient concentrations with comparable or better limits of detection and precision than active sampling methods. Passive monitors have no pumps or other moving parts and are very compact and portable. No special training is required for their deployment and operation. The low associated labor means that passive monitoring is often cost-effective over other methods of measurement. Laboratory analysis costs are the main expense for this type of monitoring.

The detection limits and precision specified by the manufacturer for compounds quantified in the HCMS are compared in Table 1-2 to the mean values measured at the HCMS quality assurance site. Mean ambient concentrations were well above the detection limits during the study for all compounds with the exception of SO_2, H_2S, and acrolein. The replicate precisions for the HCMS were better than 10 percent for compounds with ambient concentrations greater than five times the limit of detection. The results for 1,3-butadiene from passive samplers with Carbograph 4 were not quantitative due to back diffusion and were not reported in the HCMS. Radiello plans to sell samplers with Carbopack X, which has shown to reduce the desorption of 1,3-butadiene. The Perkin Elmer Thermal Diffusion Tubes with Carbopack X is an alternative. DRI evaluated these samplers but did not obtain satisfactory results.

The accuracy of the passive measurements were evaluated in the laboratory using a flow-through chamber with known pollutant concentrations, and in the field during a pilot study and the summer and winter seasons of the main study. The field evaluations compared the 7-day integrated passive measurements with corresponding time averages of continuous NOx and SO_2 measurements or averages of seven consecutive 24-hour canisters and DNPH cartridge samples. The results summarized in Table 1-3 show that most passive measurements were in reasonable agreement with the measurements methods that are commonly used in state and local monitoring air programs. The accuracy of passive measurements of acrolein and H_2S could not be evaluated during this study as their ambient concentrations were often below the limits of detection.

Table 1-2. Seven-day average mixing ratios (ppbv) of passive measurements at the Hudson monitoring station during the HCMS and measurement precision based on replicate samples.

	DQO [1]		**HCMS Winter**			**HCMS Summer**		
	MDL	Precision	Mean	Precision [2]		Mean	Precision [2]	
	ppbv	%	ppbv	ppbv	%	ppbv	ppbv	%
Nitrogen Oxides (NOx)	0.32		73.0	2.03	2.8%	29.4	0.65	2.2%
Nitorgen Dioxide (NO_2)	0.32		28.5	1.50	5.3%	19.5	0.96	4.9%
Sulfur Dioxide (SO_2)	0.54		1.1	0.107	9.8%	1.0	0.196	19.8%
Hydrogen Sulfide (H_2S)	0.20	8.7%	0.8	0.036	4.8%	0.9	0.117	12.5%
Benzene	0.015	8.3%	0.6	0.014	2.3%	0.3	0.026	7.5%
Toluene	0.002	8.3%	1.7	0.039	2.3%	1.0	0.044	4.2%
Ethylbenzene	0.002	9.1%	0.3	0.008	2.4%	0.2	0.014	6.7%
Xylenes	0.002	11.3%	1.4	0.031	2.2%	0.7	0.063	9.2%
Formaldehyde	0.07	13.8%	2.7	0.06	2.2%	1.8	0.12	6.7%
Acetaldehyde	0.05	15.9%	1.9	0.05	2.8%	0.7	0.03	4.7%
Acrolein	0.120	16.5%	0.028	0.015	52.0%	0.010	0.005	47.4%

[1] Data quality objectives (DQO) are based upon manufacturers' specifications for 7-day exposure period and one standard deviation precision.

[2] Mean of the absolute differences between average of triplicates and individual sample (12 values per season).

Note: Shaded values denote mean ambient values that are less than five times the minimum detection limit (MDL).

Passive measurements of NOx were in good agreement (± 6%) with time-averaged continuous NO data during the laboratory evaluations. Passive NOx measurements were consistently lower than SCAQMD's NOx analyzer by about 15 to 20% during the pilot study, but these differences may be related to occasional concentration gradients from vehicles passing by the monitoring station because the inlet for District continuous monitors was located at the front of building and passive samplers were at the back. Passive SO_2 measurements were within 20% of the District continuous monitor, which is comparable to its precision during the summer HCMS. Passive measurements of NOx were generally in good agreement with SCAQMD's NOx analyzer during the main study when ambient levels were above the detection limit of the continuous analyzers.

Table 1-3. Assessments of accuracy of passive measurements using standards and comparisons with reference methods and commonly used active sampling methods.

Compounds	Lab Evaluation		Pilot Study		HCMS Winter	
	Reference Value (ppbv)	Passive-Ref % Δ	Reference Value (ppbv)	Passive-Ref % Δ	Reference Value (ppbv)	Passive-Ref % Δ
Nitrogen Oxides (NOx)	17.20	6.2%	10.8	-24.6%	80.1	-8.9%
Nitorgen Dioxide (NO_2)	21.80	-1.4%	17.2	-17.9%	42.2	-24.5%
Sulfur Dioxide (SO_2)			1.7	18.2%		
Hydrogen Sulfide (H_2S)	2.10	-5.2%				
Benzene	2.57	-18.3%	0.37	-21.6%	0.70	-13.8%
Toluene	2.37	-5.5%	1.09	20.2%	1.93	-11.1%
Ethylbenzene	1.28	41% or (-6%)[1]	0.13	31% or (-8%)[1]	0.37	0.1%
m,p-Xylenes	1.02	-12.7%	0.45	2.2%	1.26	-11.7%
o-Xylene	0.43	-12.2%	0.18	0.0%	0.51	-7.5%
Formaldehyde	5.20	-2.3%	1.10	11.8%	4.97	-38.9%
Acetaldehyde			1.04	-43.3%	1.91	31.0%
Acrolein			0.24	-79.2%		

[1] Using our experimentally determined sampling rate of 37.4 ml/min rather than 25.7 ml/min published by Radiello reduced values by factor of 0.69.

Verifying the sampling rates of the passive samplers was a major objective of the laboratory evaluations. The experimentally determined sampling rates for benzene, toluene xylenes were within 20% of those published by Radiello. A significantly higher sampling rate than that reported by Radiello was measured for ethylbenzene. The experimentally determined sampling rate for ethylbenzene was 37.4 ml/min versus 25.7 ml/min published by Radiello. The experimentally determine sampling rate was used to determine ethylbenzene concentrations for the main HCMS, which results in concentrations that are a factor of 0.69 lower than using the rate published by Radiello. The passive samples for all BTEX compounds were stable for storage times of up to 14 days at -18º C. Passive measurements of BTEX species were generally within ± 15% of corresponding samples collected by active sampling methods that are commonly used in state and local monitoring programs.

Passive measurements of formaldehyde and acetaldehyde were in good agreement with diluted standards for the laboratory evaluations. Passive sampler values were slightly higher during pilot study for formaldehyde compare to time-averaged DNPH samples. However, one out of the seven 24-hour DNPH samples was invalid. Acetaldehyde measured by the passive sampler was 43% lower than values obtained by active sampling on DNPH cartridges. Acetaldehyde had poor accuracy probably due to effects from ozonolysis and from low collection efficiencies, which may also apply to “reference” samples collected actively on DNPH cartridges.

2. TIME-INTEGRATED AEROSOL SAMPLES

2.1 Sampling Methods

Mini-Volume Particle Samples

MiniVol portable $PM_{2.5}$ air samplers from AirMetrics Corporation were used for particle sampling for seven continuous days coincident with the passive samples. The sampler is equipped with an inlet containing an impactor unit with 2.5-µm particle cut point and a flow control system capable of maintaining a constant flow rate within the design specifications of the inlet. The impactor is designed for a 50% collection efficiency for particles of aerodynamic diameter of 2.5 µm at a flow rate of 5 L/minute. The following substrates were used in the HCMS:

- Gelman (Ann Arbor, MI) polymethylpentane ringed, 2.0 mm pore size, 47 mm diameter PTFE Teflon-membrane Teflo filters (#RPJ047) for particle gravimetric mass and elements.

- Pallflex (Putnam, CT) 47 mm diameter pre-fired quartz-fiber filters (#2500 QAT-UP) for organic and elemental carbon measurements

The portable aerosol samplers were specially equipped to operate from either AC or DC power sources. In the DC mode, the sampler is attached to a charged battery pack prior to field sampling, making the sampler siting independent of external power. During a previous study (Fujita et al, 2009) we experienced a number of equipment failures with the Aerometrics Mini-Vol filter samplers, even though they had been individually tested before deployment. In subsequent testing at DRI, we determined that the problems were primarily related to failure of the internal battery and/or charging system over the course of the week-long sampling period. The rechargeable lead-acid batteries provided by the manufacturer are not well-suited to (or intended for) long-term continuous use. To rectify the problem, a direct power system, using a switch-mode 110VAC to 12VDC power supply in place of the battery system, was tested and proved reliable over period of 5 weeks of continuous operation. These power systems were used in WOMS. The new systems are also lighter in weight and require only about 300 mA of 110V line power to operate (less than a 40W light bulb).

DRI Medium-Volume Sequential Filter Sampler

The DRI sequential filter sampler (SFS) was used to collect daily 24hr Teflon and quartz filters for $PM_{2.5}$ mass, ions, elements and organic and elemental carbon. The SFS consists of an aluminum plenum to which a $PM_{2.5}$ inlet is attached. Up to 12 sampling ports within the plenum are controlled by solenoid valves which divert flow from one channel to the next by means of a programmable timer. These ports accept filters which have been pre-loaded into open-faced 47mm Nuclepore® filter holders. The holders are plugged into quick disconnect fittings on the SFS. The sample flow can be divided for simultaneous collection on two or more filter media. The differential pressure volumetric flow controller splits the flow between filters and maintains a constant flow rate despite filter loading.

The flow rate is controlled by maintaining a constant pressure across a valve with a differential pressure regulator. Flow rates of 20 to 55 lpm can be drawn through each of the two filter packs simultaneously; flow rates of 110 lpm can be drawn through a single filter pack. The remaining flow rate needed by the inlet is drawn through a makeup air port. The $PM_{2.5}$ size fraction is transmitted through a Bendix/Sensidyne 240 cyclone and into a plenum. Nuclepore 47mm diameter polycarbonate filter holders are used for the SFS filter packs. This configuration has two channels:

- Channel 1 consists of a Teflon-membrane filter, which is analyzed for mass and elemental analyses.
- Channel 2 of the $PM_{2.5}$ SFS consists of a quartz-fiber filter, which is submitted to carbon analyses.

For the WOMS, flow rates were set to approximately 50 lpm for each channel, with no flow through the makeup air port. A transfer flow standard (rotameter) was used to validate the flow rate before and after each sampling period.

DRI SVOC Sampler

The DRI semi-volatile organic compound (SVOC) sampler was used to collect daily 24hr samples on 100mm diameter Teflon-impregnated quartz fiber filters with backup XAD adsorbant cartridges to capture material volatilized from the filters. These are programmable 2-channel sequential samplers with a $PM_{2.5}$ cylcone inlet equivalent to the one used in the SFS. Flow rates are set and maintained at approximately 113 lpm by needle valves downstream from the filters. A transfer flow standard (rotameter) was used to validate the inlet flow rate before and after each sampling period.

2.2 Laboratory Analysis of Time-integrated PM Samples for PM Mass, Ions and Carbon

Samples collected during the field study were retrieved each week from the sampling sites and returned the same day to climate-controlled storage at DRI until analyzed by the Environmental Analysis Facility or Organic Analysis Laboratory.

Gravimetric Mass

Unexposed and exposed Teflon-membrane filters were equilibrated at a temperature of 20 °C and a relative humidity of 30 % for a minimum of 24 hours prior to weighing. Weighing was performed on a Cahn 31 electro microbalance with ± 0.001 mg sensitivity. The charge on each filter is neutralized by exposure to a polonium source for 30 seconds prior to the filter being placed on the balance pan. The balance is calibrated with a 20 mg Class M weight and the tare is set prior to weighing each batch of filters. After every 10 filters are weighed, the calibration and tare are re-checked. If the results of these performance tests deviate from specifications by more than ± 5 µg, the balance is re-calibrated. If the difference exceeds ± 15 µg, the balance is recalibrated and the previous 10 samples are re-weighed. At least 30% of the weights are checked by an independent technician and samples are re-weighed if these check-weights do not agree with the original weights within ± 15 µg.

Elemental and Organic Carbon

Elemental carbon (EC) and organic carbon (OC) were measured by thermal optical reflectance (TOR) method using the IMPROVE (Interagency Monitoring of Protected Visual Environments) temperature/oxygen cycle (IMPROVE TOR). A section of the quartz filter is placed in the carbon analyzer oven such that the optical reflectance or transmittance of He-Ne laser light (632.8 nm) can be monitored during the analysis process. The filter is first heated under oxygen-free helium purge gas. The volatilized or pyrolyzed carbonaceous gases are carried by the purge gas to the oxidizer catalyst where all carbon compounds are converted to carbon dioxide. The CO_2 is then reduced to methane, which is quantified by a flame ionization detector (FID). The carbon evolved during the oxygen-free heating stage is defined as "organic carbon". The sample is then heated in the presence of helium gas containing 2 percent of oxygen and the carbon evolved during this stage is defined as "elemental carbon". Some organic compounds pyrolyze when heated during the oxygen-free stage of the analysis and produce additional EC, which is defined as pyrolyzed carbon (PC). The formation of PC is monitored during the analysis by the sample reflectance or transmittance. EC and OC are thus distinguished based upon the refractory properties of EC using a thermal evolution carbon analyzer with optical (reflectance or transmittance) correction to compensate for the pyrolysis (charring) of OC. Carbon fractions in the IMPROVE method correspond to temperature steps of 120°C (OC1), 250°C (OC2), 450°C (OC3), and 550°C (OC4) in a non-oxidizing helium atmosphere, and at 550°C (EC1), 700°C (EC2), and 850°C (EC3) in an oxidizing atmosphere.

The system is calibrated by analyzing samples of known amounts of methane, carbon dioxide, and potassium hydrogen phthalate (KHP). The FID response is ratioed to a reference level of methane injected at the end of each sample analysis. Performance tests of the instrument calibration are conducted at the beginning and end of each day's operation. Intervening samples are re-analyzed when calibration changes of more than ±10% are found. Known amounts of reagent grade crystal sucrose and KHP (certified by the American Chemical Society) are committed to TOR as a verification of the organic carbon fractions. Fifteen different standards are used for each calibration. Widely accepted primary standards for elemental and/or organic carbon are still lacking. Results of the TOR analysis of each filter are entered into the DRI data base.

Laboratory Analysis of Time-integrated PM Samples for Particulate PAHs

Samples are extracted by the accelerated solvent extraction (ASE) method, using Dionex ASE 300. Prior to extraction, the following deuterated internal standards are added to each sample: naphthalene-d8, biphenyl-d10, acenaphthene-d8, phenanthrene-d10, anthracene-d10, pyrene-d12, benz[a]anthracene-d12, chrysene-d12, benzo[a]pyrene-d12, benzo[e]pyrene-d12, benzo[k]fluoranthene-d-12, benzo[g,h,i]perylene-d12, coronene-d12, cholesterol-2,2,3,4,4,6-d6, levoglucosan-u-13C6, hexanoic-d11 acid, benzoic-d3 acid, decanoic-d19 acid, palmitic-d31 acid, heptadecanoic-d33 acid, myristic-d27 acid, succinic-d4 acid, phthalic 3,4,5,6-d4 acid, cholestane- d6, dodecane-d26, hexadecane-d34, eicosane-d42, octacosane-d58, tetracosane-d50, and hexatriacontane-d74. Filters are extracted with dichloromethane followed by acetone. The extracts are combined and concentrated by rotary evaporation at 20 °C under gentle vacuum to ~1 ml, and filtered through 0.45 mm Acrodiscs (Gelman Scientific). Approximately 200 µl of acetonitrile is added to the sample and the solvent evaporated under a gentle stream of nitrogen.

The sample was then split into two fractions: the first fraction is analyzed without further alteration for non-polar compounds (i.e. PAH, hopanes/steranes, alkanes), and the second fraction is derivatized to convert polar compounds to their trimethylsilyl derivatives for GC/MS analysis.

Complex samples for non-polar analysis (first fraction) that contain analytical interferences are precleaned prior to GC/MS analysis, using silica gel semi-prep Solid Phase Extraction (SPE 6-mL 0.5-g LC-SI, Supelco Silica), as described previously (Zielinska et al., 2004; Fujita et al., 2007)). A mixture of bis(trimethylsilyl)trifluoroacetamide and pyridine is used to convert the polar compounds in the second fraction into their trimethylsilyl derivatives for the analysis of organic acids, cholesterol, sitosterol, and levoglucosan (Fujita et al, 2007, Mazzoleni et al, 2007). Both fractions are analyzed by EI (electron impact) GC/MS technique using Varian CP 3800 GC equipped with an 8200CX Automatic Sampler and interfaced to a Varian Saturn 2000 or Varian 4000 Ion Trap, as described before (Fujita et al., 2007, Zielinska et al., 2004, Mazzoleni et al., 2007).

Calibration curves for GC/MS quantification are made for the molecular ion peaks of compounds of interest using the corresponding deuterated species (or the deuterated species most closely matched in volatility and retention characteristics) as internal standards. Individual neat standards will be used to make calibration solutions. A four to six level calibration will be performed for each compound of interest and the calibration check (using a median calibration solution of standards) is run every ten samples to check for accuracy of the analyses. If the relative accuracy of measurement (defined as a percentage difference from the standard value) is less than 20%, the instrument is recalibrated and samples are reanalyzed.

3. CONTINUOUS MONITORING METHODS

This section describes the continuous monitors that were used in WOMS to conduct the spatial survey of pollutant concentrations. The instrumented BAAQMD monitoring van was used to determine spatial variations in pollutant concentrations at the Port of Oakland and within the West Oakland area adjacent to and within the port. The instrument platform is a 2008 Ford E-350 cargo van modified by E-N-G Mobile Systems, Inc. to include an instrument rack, desk/workbench, calibration gas cylinder rack, and 100VAC and 12VDC power system that can be operated off of on-board batteries or line power. Data from all instruments were recorded at 10 second intervals along with gps coordinates.

3.1 Continuous Methods for Criteria and Other Gaseous Pollutants

Ozone

An O_3 monitor from 2B Technologies (Model 202) with a limit of detection of 1 ppb based on absorption of ultraviolet light at 254 nm was used. The monitor has low power consumption (~ 5 watts), response time of 10 seconds, sensitivity <5 ppb, and has been certified by the EPA as a Federal Equivalent Method (FEM): EQOA-0410-190.

NO/NOx or NO2

Nitric oxide (NO) is typically measured continuously by the chemiluminescence nitric oxide-ozone method. Standard sensitivity instruments have detection limits of about 0.5 to 3 ppb (60 sec averaging times) and are suitable for air quality monitoring in urban and suburban areas, however they are rather large and heavy for mobile monitoring and require substantial power. Thermo Environmental Instruments, Inc. (TEI) Model 42C and Monitor Labs 8440 and 8840 are examples of this type of instrument. For WOMS a compact 12V NO monitor sold by 2B Technologies (Model 400) was used instead. This instrument uses UV absorption technology to determine the depletion of ozone by NO and calculates the NO concentration by assuming a 1:1 stoichiometric ratio for the NO/O_3 reaction cycle. It has dynamic range of 2000 ppb and resolution as low as 2 ppb at the mimimum averaging time of 10 seconds. Since this instrument measures NO by difference between ambient and ozone-titrated concentrations, measurement precision decreases at very low concentrations. For mobile monitoring this typically results in an uncertainty of ±20 ppb when ambient concentrations are below 30 ppb. At higher concentrations accuracy and is comparable to the chemiluminescence method.

Carbon Monoxide

CO was monitored continuously by a TEI model 48 gas-filter correlation CO monitor. This reck-mounted EPA reference method instrument has a resolution of 0.1 ppm and continuous analog data output which was recorded by the 2Btech 202 ozone monitors A/D converter.

Volatile Organic Compounds.

A RAE Systems ppbRAE 300 portable PID monitor was used to continuously monitor ambient VOC levels. The monitor is equipped with a 10.6 eV photoionization (PID) detector and responds to certain organic and inorganic gases that have an ionization potential of less than 10.6 eV, which includes aromatic hydrocarbons, olefins, and higher molecular weight alkanes. It does not respond to light hydrocarbons such as methane, ethane, and propane or to acetylene, formaldehyde or methanol. The monitor has < 5-second response and lower detection limit of ~20 ppb. Because the total response of the PID depends upon the specific mix of VOC's, the response must be calibrated to the expected mix of VOC. For the rapidly varying mixtures of VOC that are encountered during mobile monitoring this measurement can only be considered semi-quantitative so the standard calibration was used. Instruments utilizing flame ionization detection (FID) are sensitive to a broader range of hydrocarbons, but do not provide the sensitivity and rapid response time required for ambient exposure monitoring.

3.2 Continuous PM Mass, Black Carbon and Size Distributions

PM2.5 Mass

The TSI DustTrak (model 8530) is a portable, battery-operated, laser-photometer that measures 90° light scattering (different from the total light scattering measured by an integrating nephelometer) and reports it as PM mass concentration. Because it is sensitive, requires low flow rates, offers good time resolutions, and is portable and relatively inexpensive, the TSI DustTrak nephelometer is well suited for the continuous onboard PM measurements made in this study. It can be fitted with inlet of varying size-cuts. We equipped the monitor for this project with a $PM_{2.5}$ inlet.

The reported PM mass concentration is factory-calibrated using the respirable fraction of an Arizona Road Dust standard (ISO 12103-1, A1), which consists of primarily silica particles (70%) that are provided with some particle size specifications. The mass scattering efficiency depends on particle shapes, size distribution, and composition (index of refraction). By volume, the standard consists of 1–3% particles with diameter less than 1000 nm (1 µm), 36–44% with diameter less than 4000 nm (4 µm), 83–88% with diameter less than 7000 nm (7 µm), and 97–100% with diameter less than 10,000 nm (10 µm). This standard contains a larger quantity of coarse 2500 nm (>2.5 µm) particles than are usually found in ambient aerosol. $PM_{2.5}$ has a higher mass scattering efficiency, so the DustTrak overestimates $PM_{2.5}$ for smaller, chain aggregate soot particles. The laser diode used by the DustTrak has a wavelength of 780 nm, which limits the smallest detectable particle to about 100 nm. Combustion aerosols typically have a mass median diameter between 100 nm and 300 nm. Although direct optical light scattering of particles in this size range is limited, it has been shown to correlate reasonably well with gravimetric mass from vehicle exhaust samples. In the recent Gasoline/Diesel PM Split Study, the DustTrak was found to exceed gravimetric mass concentrations of the motor vehicle-dominated ambient samples by a factor of 2.24 with an R^2 of 0.75 (Fujita et al., 2005b).

Black Carbon (soot)

The photoacoustic instrument has been developed at DRI and has been described in several publications (Arnott, Moosmüller et al. 1999; Arnott, Moosmüller et al. 2000). Briefly, light from a 1047 nm laser is power-modulated at the operating frequency of an acoustical resonator. Sample air is continuously drawn through the resonator at a flow rate of 1 – 3 lpm. Light absorbing aerosol (black carbon) will absorb some of the laser power, slightly heating the aerosol (typically much less than 1 C). The heat transfers very rapidly from the aerosol to the surrounding air, and the local pressure increases, contributing to the standing acoustic wave in the resonator. The acoustic wave is measured with a microphone as a measure of the light absorption. For the operating conditions of the resonator, and the laser wavelength used, the light absorption measurement is linearly proportional to the mass concentration of the black carbon aerosol in the sample air. The constant of proportionality has been inferred from correlations of black carbon measurements with elemental carbon as determined by the TOR method, and an efficiency factor of 5 square meters per gram is used to go from aerosol light absorption to estimated black carbon mass concentration. No filters are needed for the photoacoustic measurement, and the flow rate is not used in the calculation of aerosol mass concentration. The flow rate must only be sufficient to adequately sample the air with minimal particle loss in the instrument and sample lines. The resolution of the instrument for a 3 second averaging time is usually 2.5 Mm^{-1} for light absorption, corresponding to 0.5 microgram per cubic meter for black carbon mass concentration. The resolution scales as the square root of sampling time, so for example, a resolution of 0.25 micrograms per cubic meter can be obtained for a 9 second averaging time. The photoacoustic measurement does not receive interference from exhaust gases, in our experience so far, and it is a zero-based measurement when no light absorbing aerosols are present. DRI has successfully used this technology for on-road monitoring of black carbon in several projects, including the HEI Exposure to Air Toxics in Mobile Source Dominated Microenvironments Study and the DOE Gasoline/Diesel PM Split Study.

For the WOMS a compact, low-power, portable version of the photoacoustic instrument was used. This "mini-PA" was designed for the just-completed API Exposure Classification Project and is still in development. Although it exhibited performance in stationary tests similar to that described above, increased baseline drift and background noise reduced the precision during mobile sampling to ±1-2 $\mu g/m^3$. Due to the generally low concentrations of BC observed during WOMS (< 5 $\mu g/m^3$) this significantly compromised the accuracy of the measurements. Numerous modifications were made to try and reduce this problem. Modifications include:

- Switched from automatic zero adjustments to manual zeroing during stops to reduce drift.
- Installed a pulse damper in the inlet line to reduce noise from the van's inlet manifold duct fan.
- Removed the laser TTL drive buffer and replaced it with a non-inverting operational amplifier buffer. This resulted in elimination of electronic background signal at our operating frequency.
- Removed the acoustical resonator and replaced it with one having a larger diameter. This was done to reduce the sensitivity of the instrument to laser beam drift.
- Replaced the Brewster windows on the resonator with new ones, and with our new custom window holder that has an aperture built in for reducing stray light.
- Installed a mirror on the outlet of the instrument to direct the laser beam to the laser power meter. The laser power meter had to be placed farther from the resonator to reduce the effects of stray light from getting back into the resonator.
- Recalibrated the resonance frequency and quality factor of the instrument.
- Installed new software to calculate the resonance frequency and quality factor for the acoustical resonator as a function of the ambient pressure, temperature, and relative humidity so that the instrument will be more accurate under wider ranging operating

parameters.

- Recalibrated the instrument for light absorption and black carbon mass concentration. Calculation of black carbon from aerosol light absorption was corrected by a factor of 1.59.

Particle Size Distribution

Optical particle counters (OPC) can determine the number of particles in various size ranges or bins by measuring the angle at which laser light is scattered by individual particles as they pass thru a sensing chamber. By assuming a fixed particle mass density and spherical shape the particle counts can be converted into an estimate of particle mass as a function of diameter. This information may be useful for evaluating the age, source, and respirable fraction of ambient aerosols. A wide variety of OPCs are available, many of which are portable. Most can detect particles larger than 0.3 μm in aerodynamic diameter. An Aerocet handheld OPC was initially installed in the van and tested, but due to its minimum averaging time of 2 minutes it was deemed to be inappropriate for mobile monitoring and it was replaced with a DustTrak.

For detecting particles smaller than 0.3 μm in aerodynamic diameter a condensation particle counter (CPC) is required. These instruments pass aerosol thru a humidification chamber, typically containing an alcohol or ethylene glycol bath, which causes the particles to grow in size due to condensation so that they can be counted by an OPC or other optical method. Although these instruments can detect ultra-fine particles as small as 10 nm in diameter, they cannot distinguish between particle sizes. A CPC combined with scanning a Scanning Mobility Particle Sizer (SMPS) will also give size distribution information but such instruments are not suited for mobile sampling applications. A TSI model 3007 was used for WOMS. This portable model operates with non-toxic isopropyl alcohol and is less sensitive to movement than laboratory models so that it can be operated in a vehicle.

A.3 Meteorological Parameters

A Davis Instruments meteorology package was used to measure wind speed and wind direction The wireless sensor package was deployed at several locations during each mobile sampling period while the van was parked for 10 minutes or more.

West Oakland Monitoring Study

FINAL REPORT

APPENDIX B

Spatial Survey Plots of Mobile Monitoring Data

Prepared for:
Bay Area Air Quality Management District
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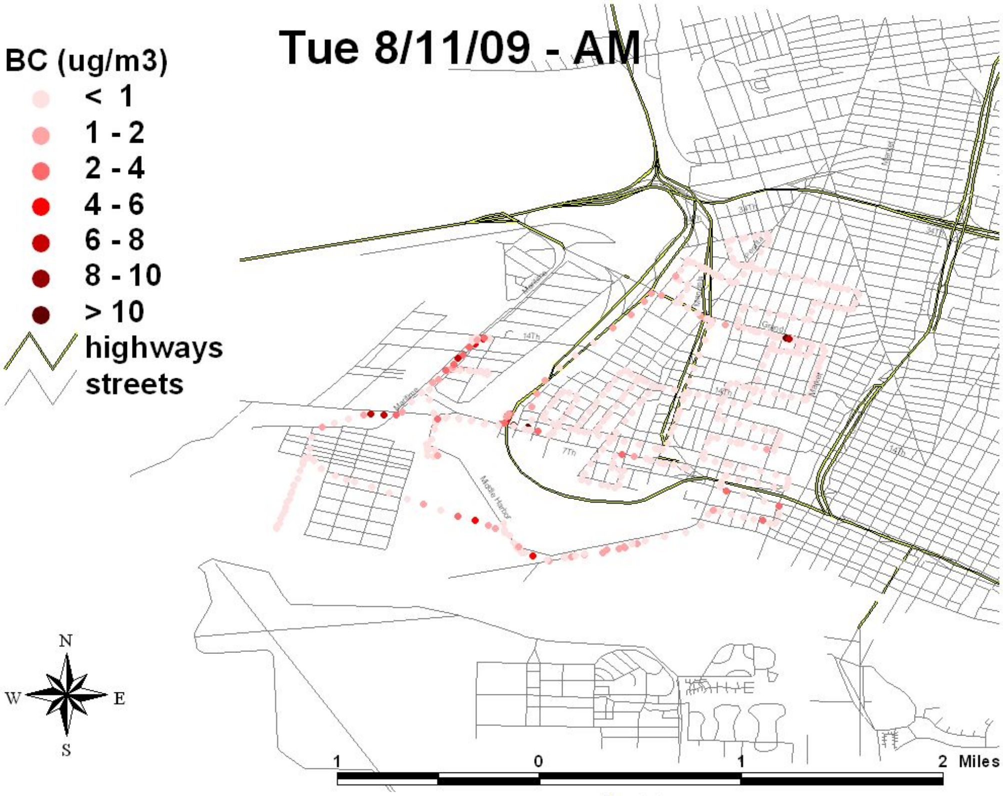
September 9, 2010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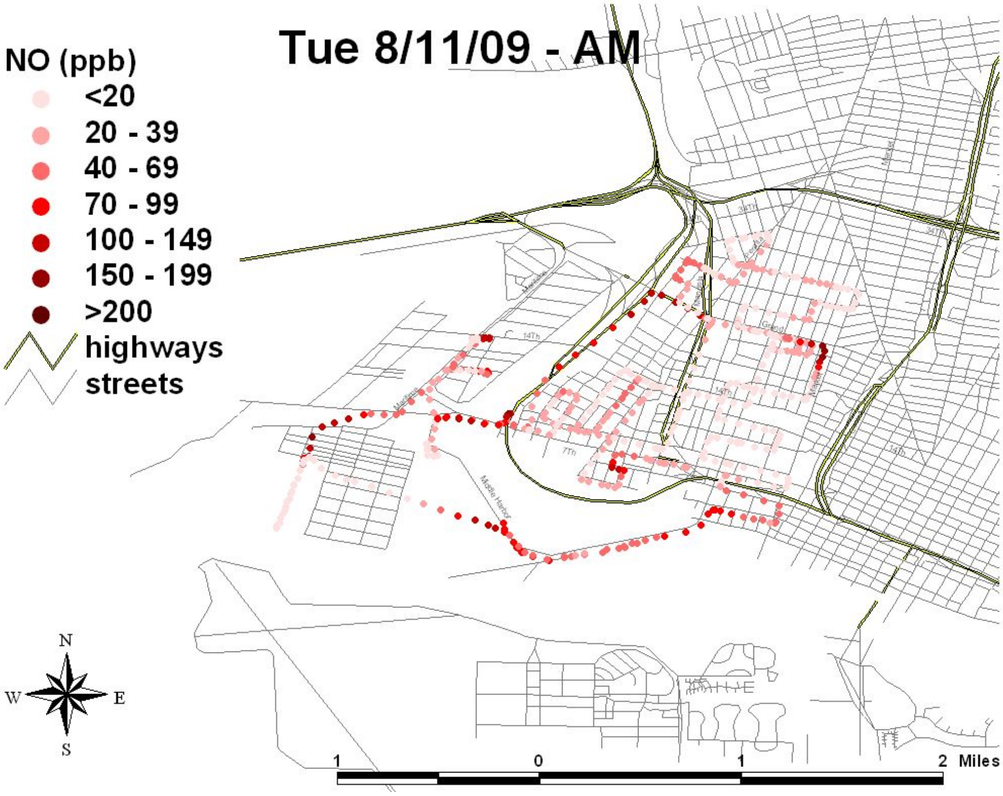
BC (ug/m3)
< 1
1 - 2
2 - 4
4 - 6
6 - 8
8 - 10
> 10
highways
streets
N
W
E
S
1
0
1
2 Miles
34Th
14Th
7Th
Grand
Market
Maritime
Middle Harbor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20 - 39
40 - 69
70 - 99
100 - 149
150 - 199
>200
highways
streets
N
W
E
S
1
0
1
2 Miles
34Th
14Th
7Th
Grand
Market
Maritime
Middle Harbor

Figure 3-13a. Spatial variations in BC and NO concentration (10 second averages) during morning of August 11, 2009.

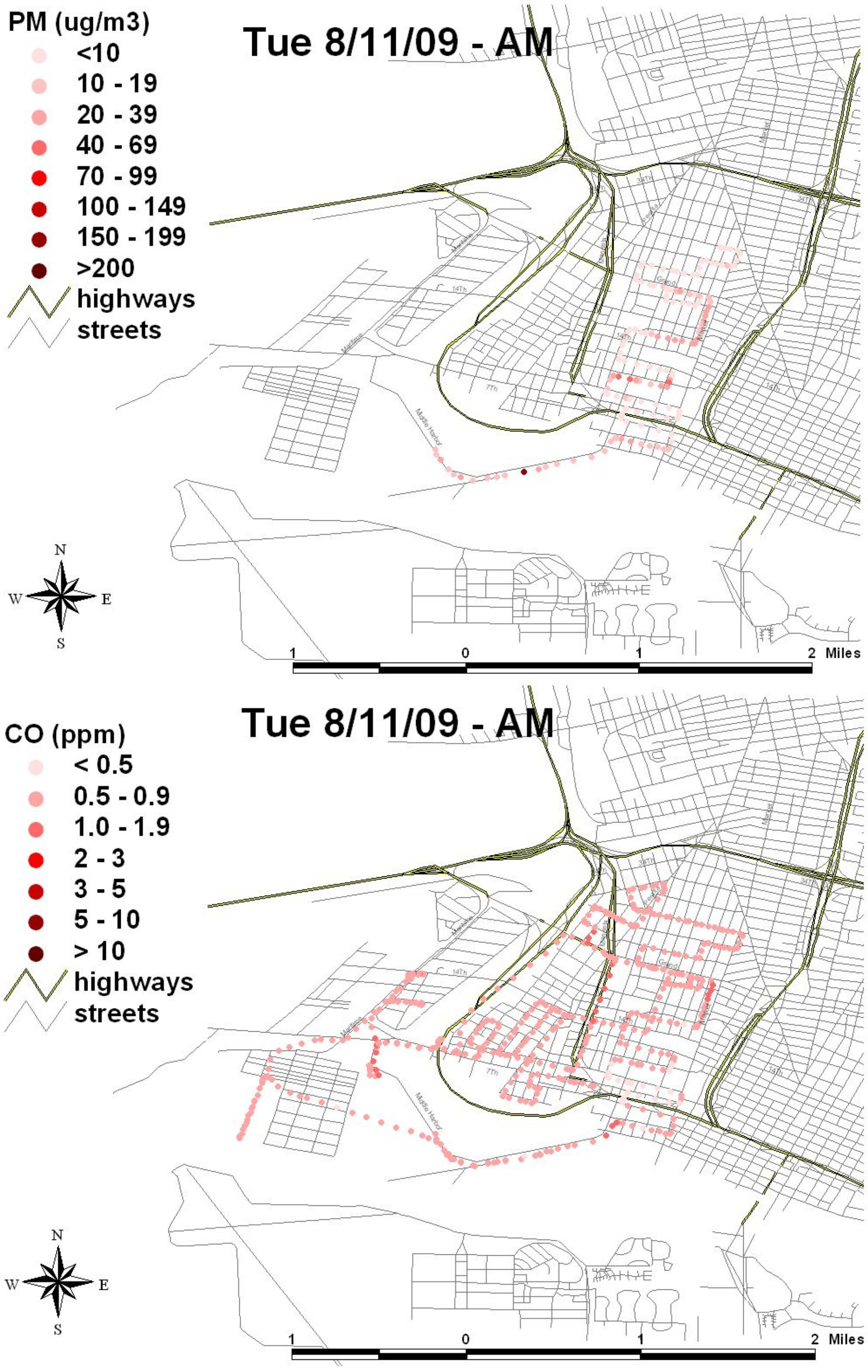

Figure 3-12b. Spatial variations in $PM_{2.5}$ and CO concentration (10 second averages) during morning of August 11, 2009.

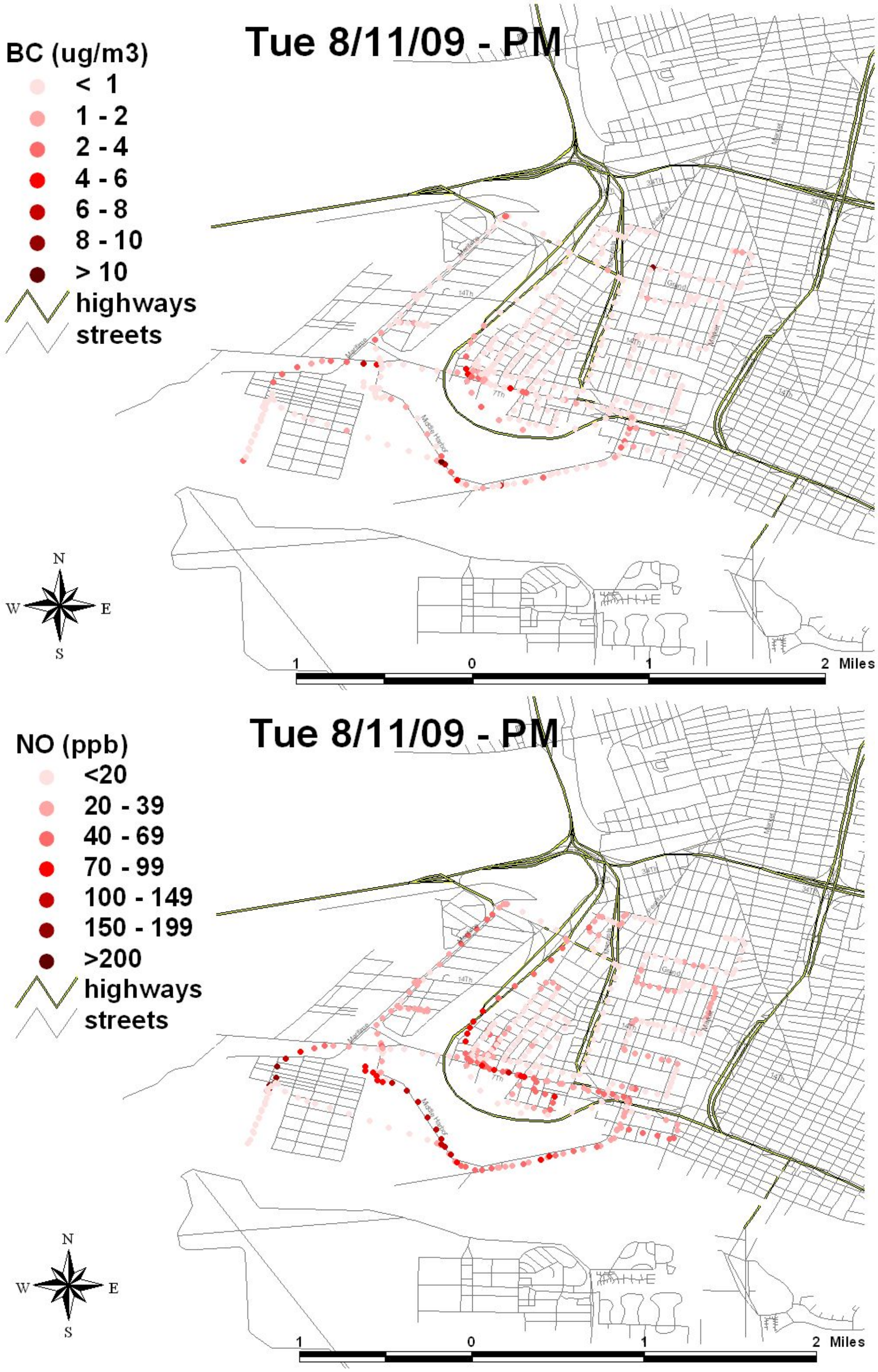

Figure 3-13a. Spatial variations in BC and NO concentration (10 second averages) during afternoon of August 11, 2009.

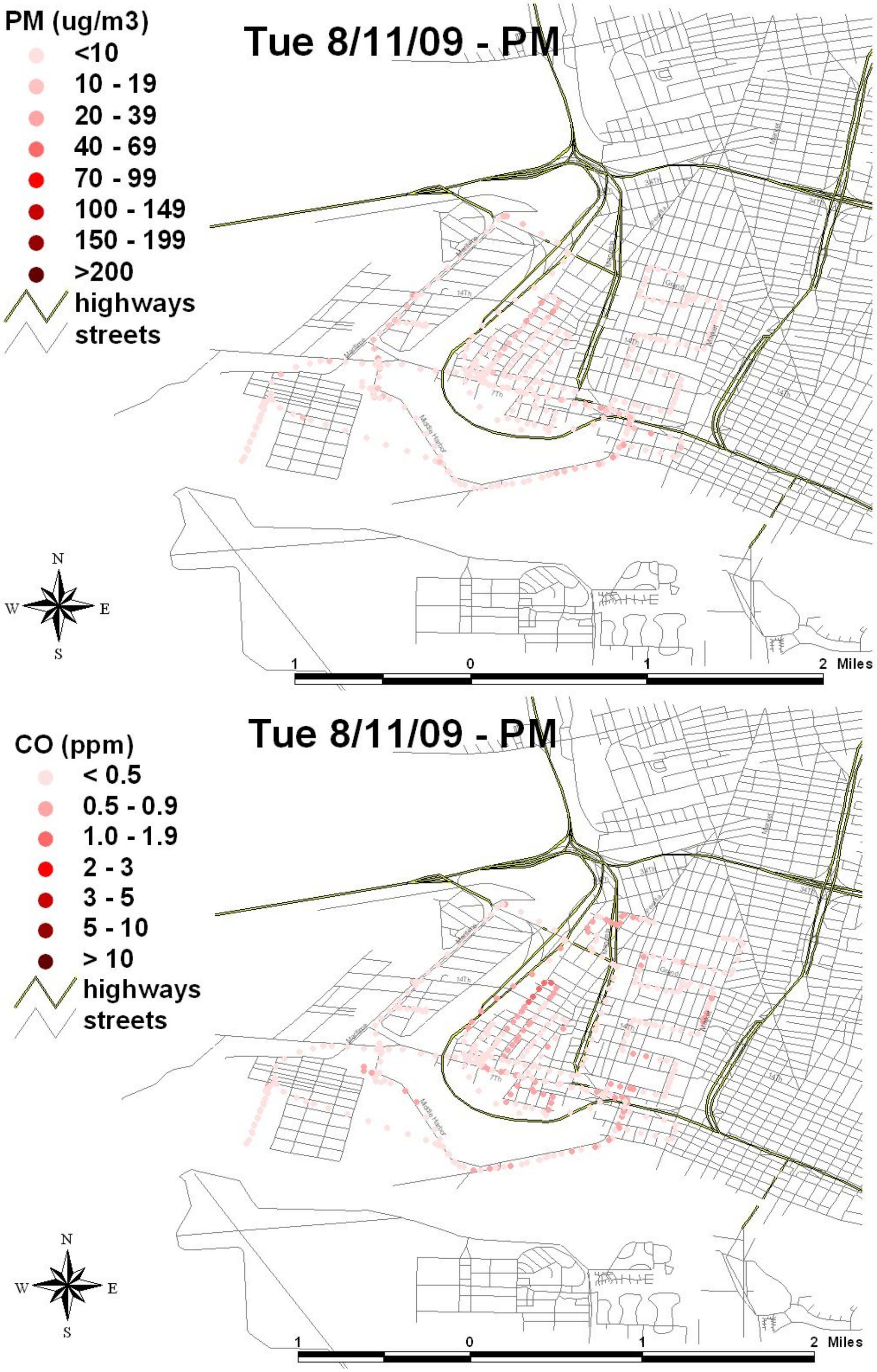

Figure 3-13b. Spatial variations in $PM_{2.5}$ and CO concentration (10 second averages) during afternoon of August 11, 2009.

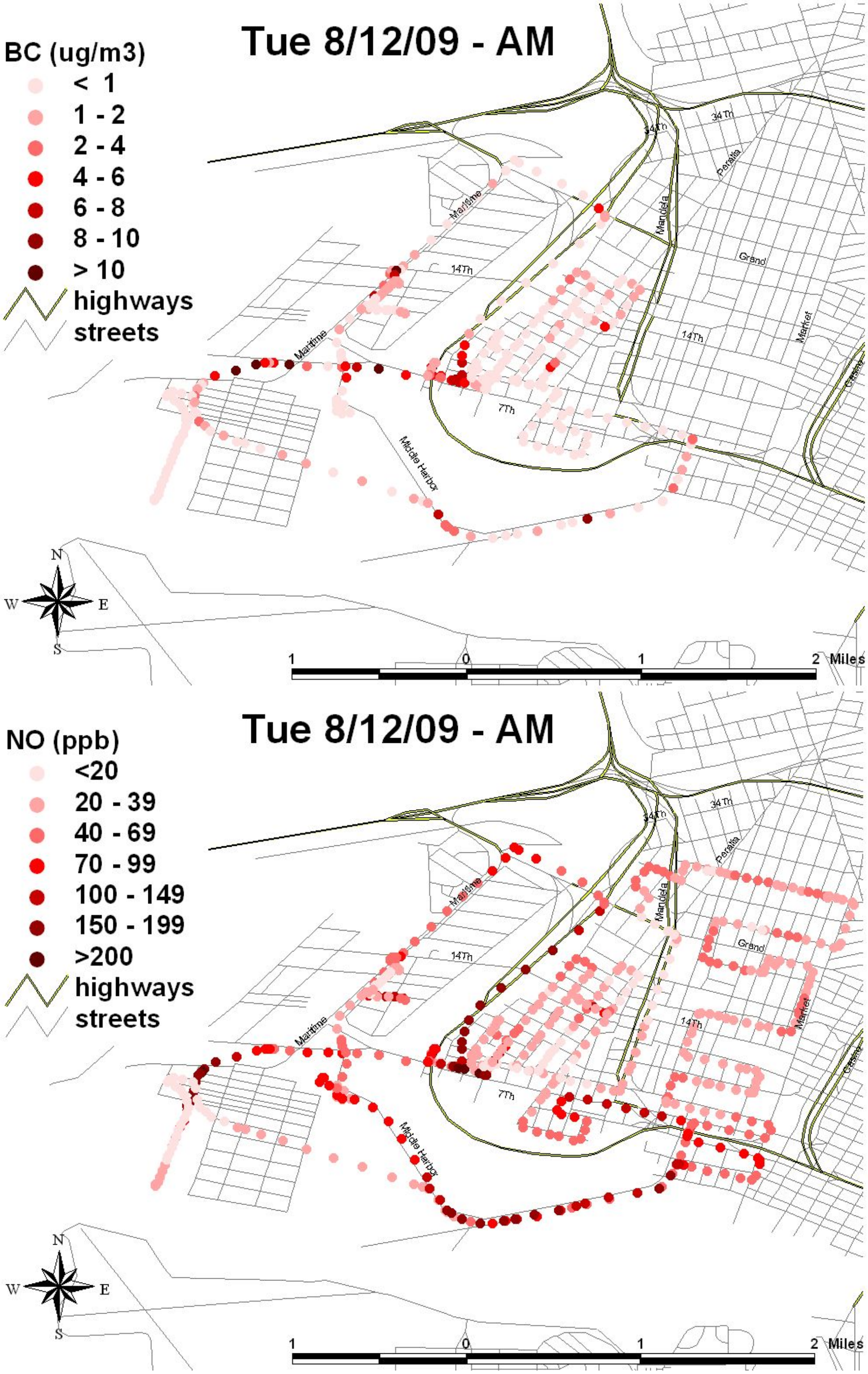

Figure 3-14a. Spatial variations in BC and NO concentration (10 second averages) during morning of August 12, 2009.

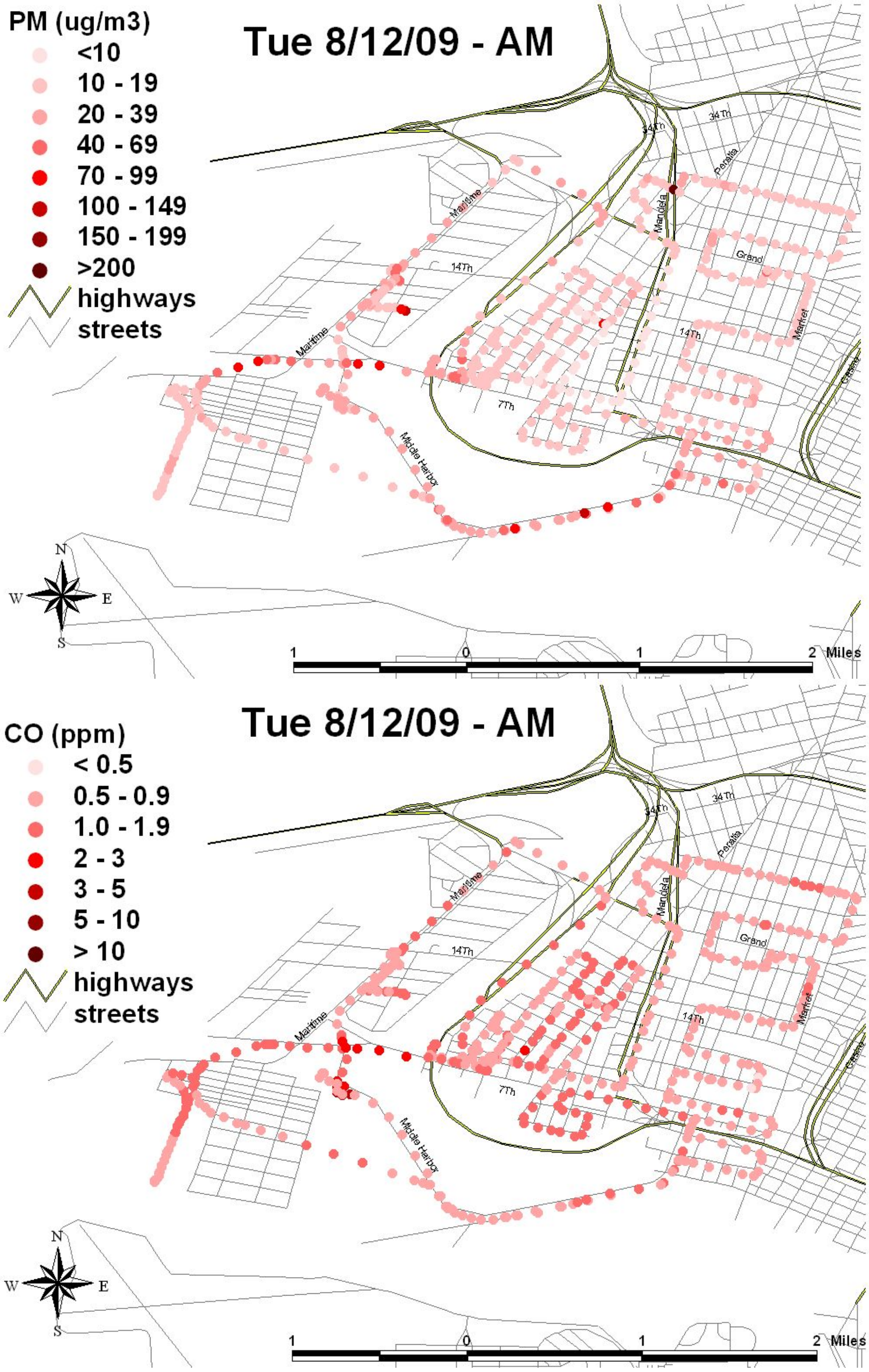

Figure 3-14b. Spatial variations in $PM_{2.5}$ and CO concentration (10 second averages) during morning of August 12, 2009.

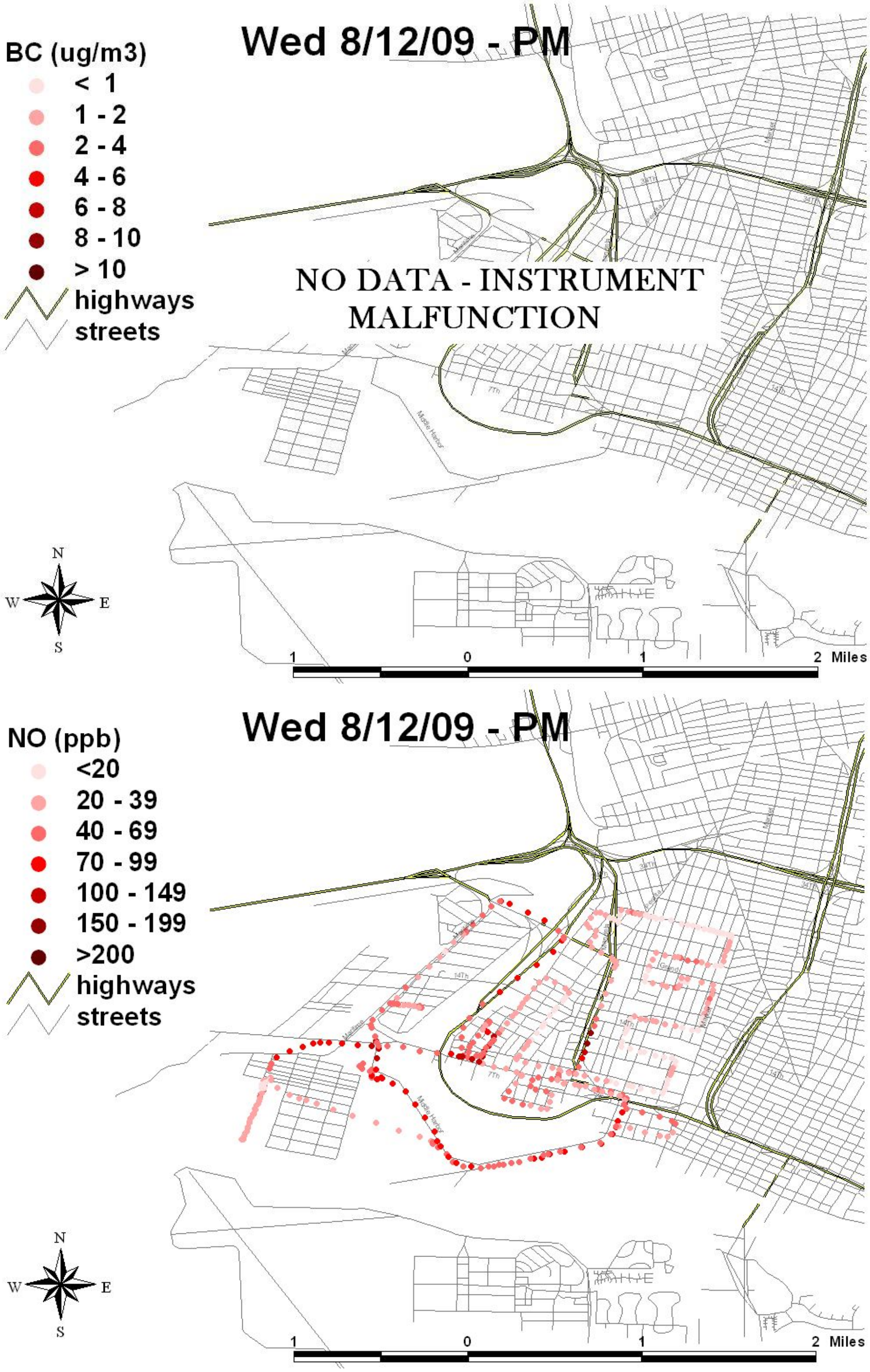

Figure 3-15a. Spatial variations in BC and NO concentration (10 second averages) during afternoon of August 12, 2009.

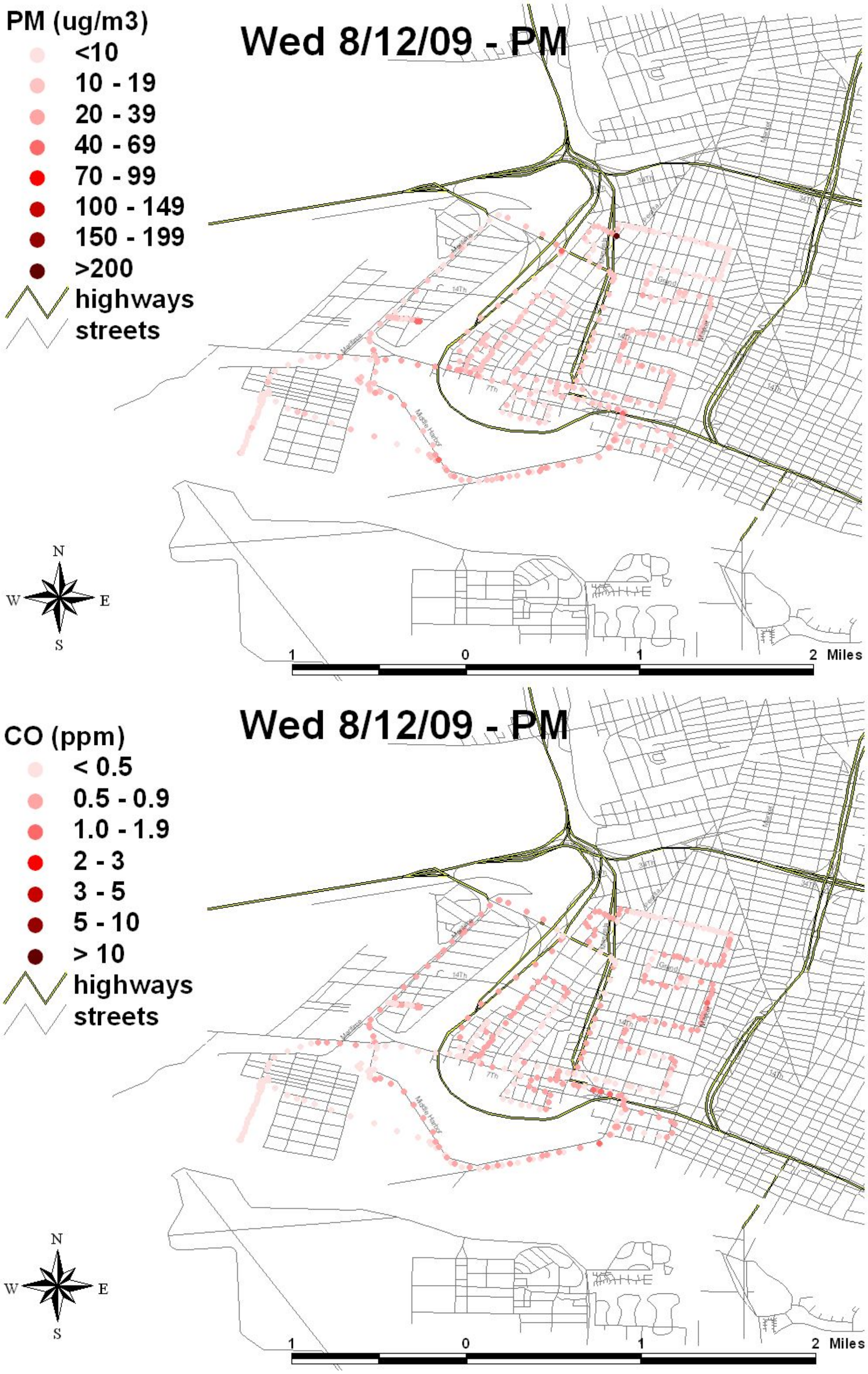

Figure 3-15b. Spatial variations in $PM_{2.5}$ and CO concentration (10 second averages) during afternoon of August 12, 2009.

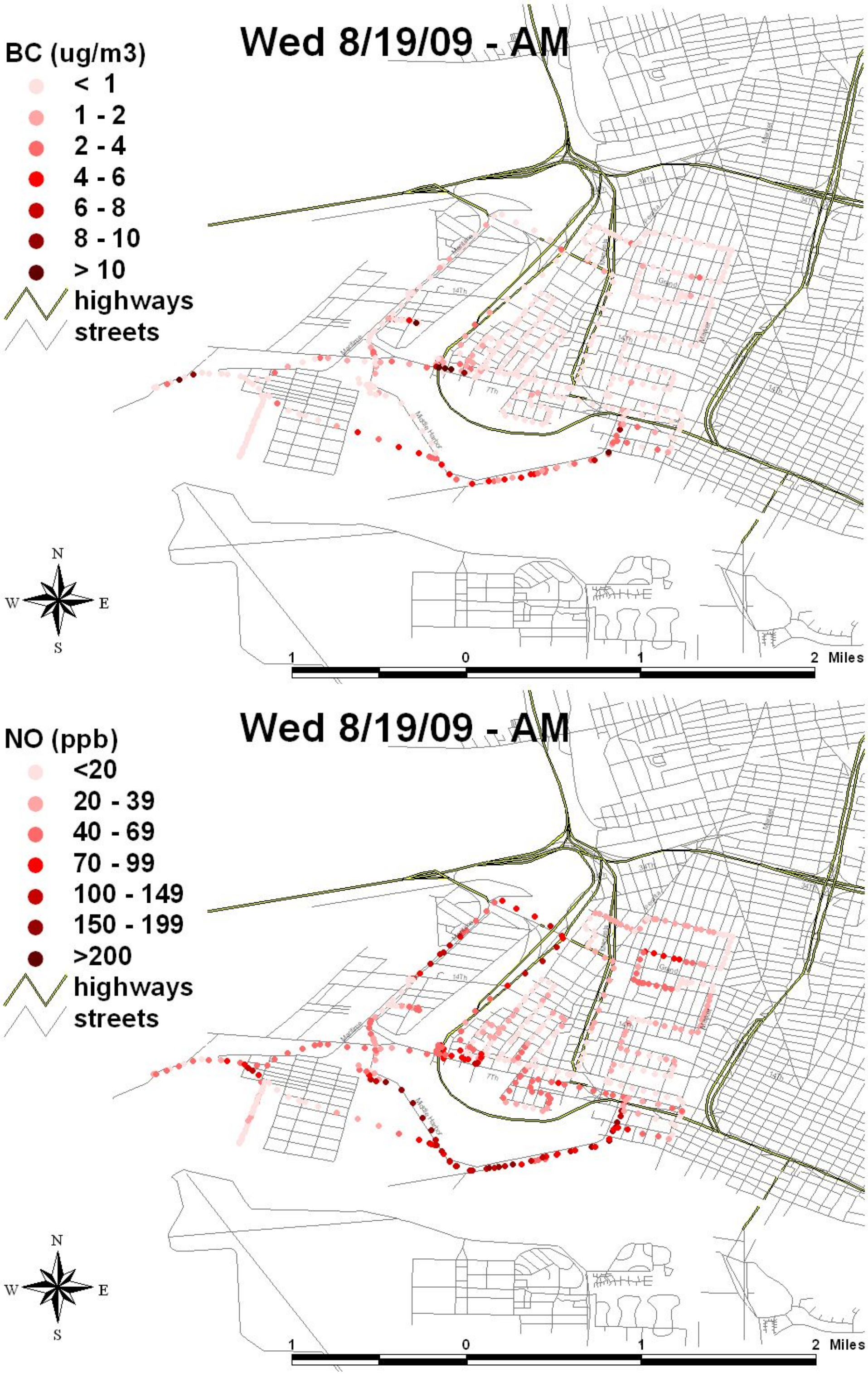

Figure 3-16a. Spatial variations in BC and NO concentration (10 second averages) during morning of August 19, 2009

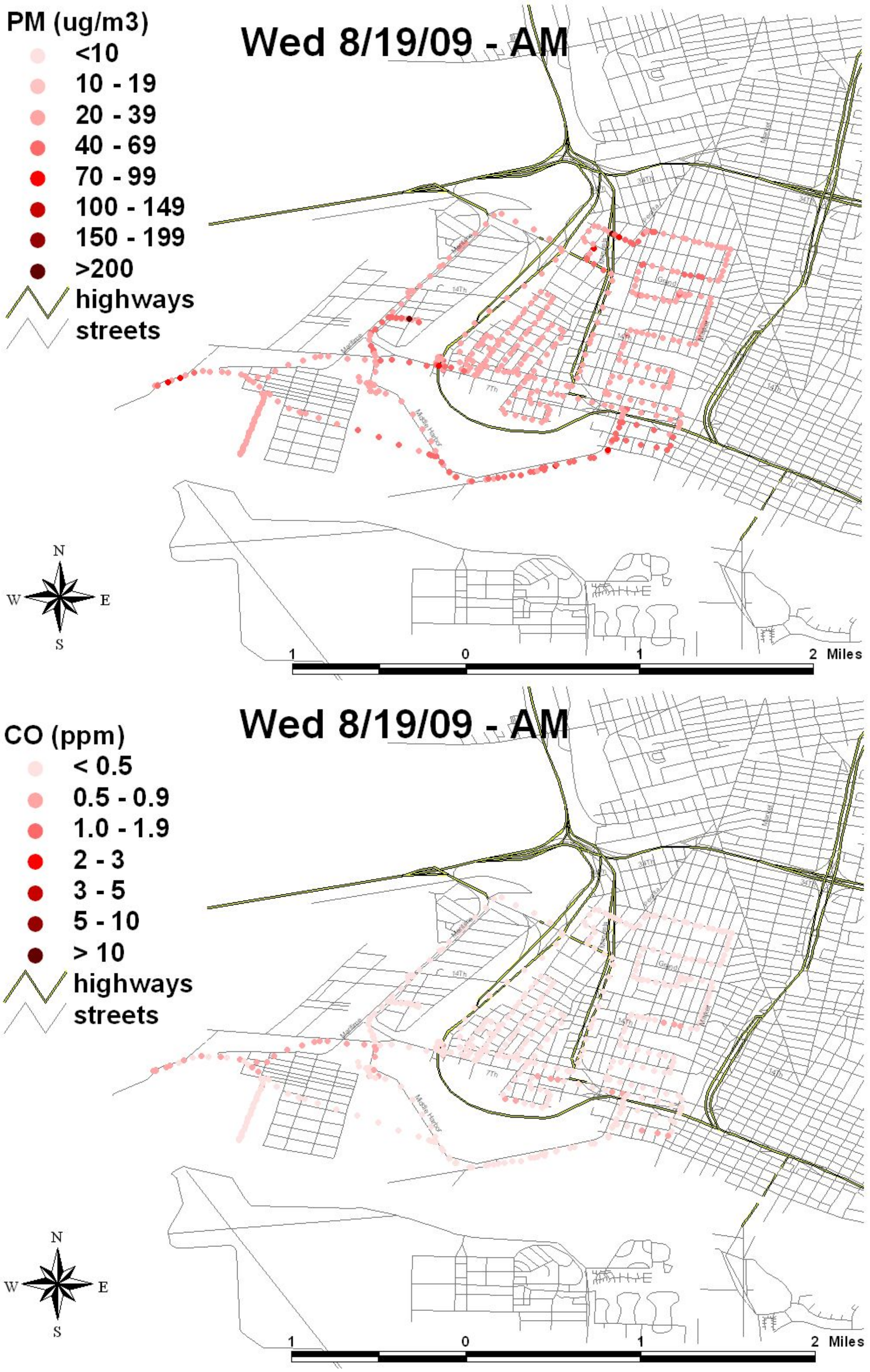

Figure 3-16b. Spatial variations in $PM_{2.5}$ and CO concentration (10 second averages) during morning of August 19, 2009.

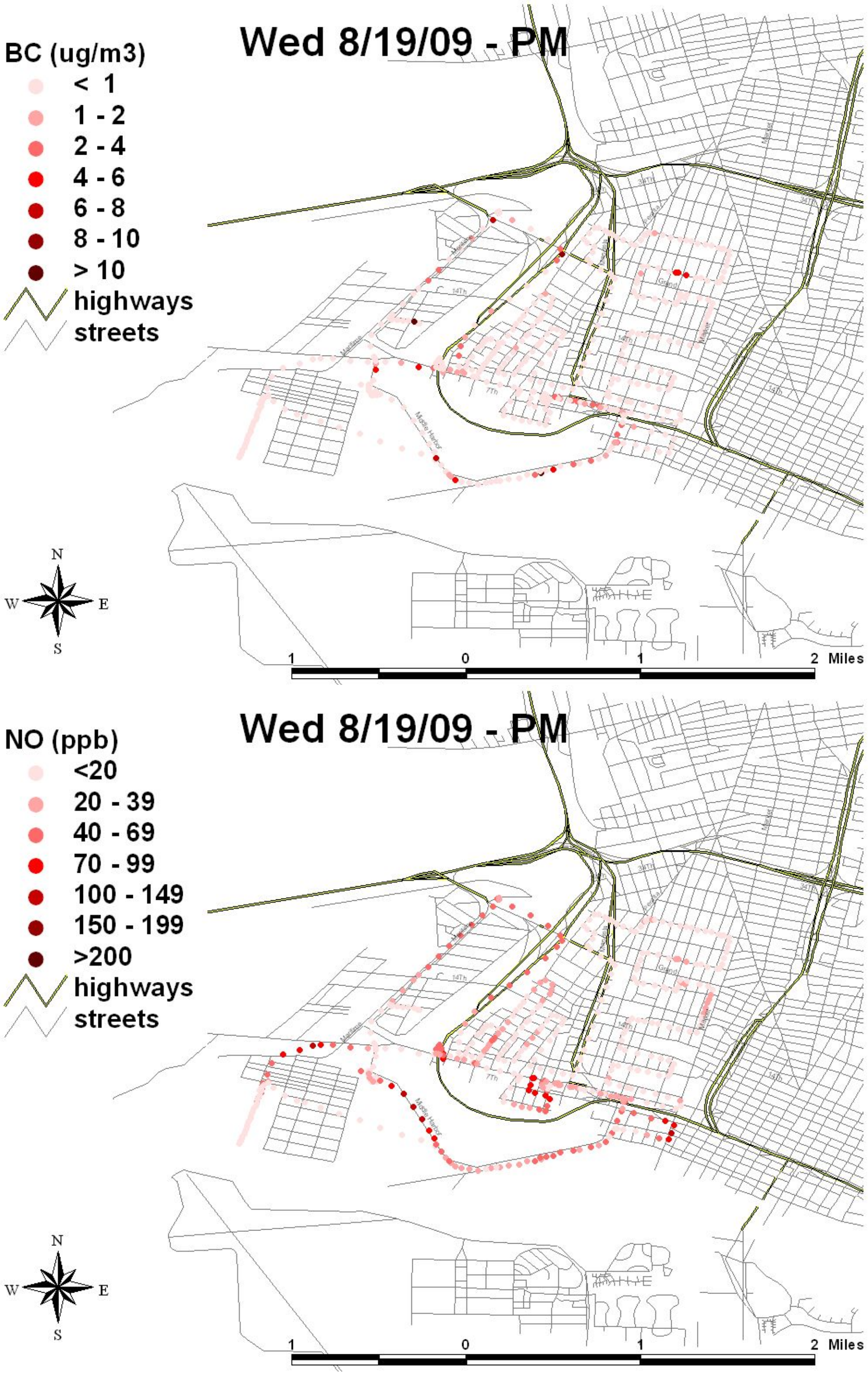

Figure 3-17a. Spatial variations in BC and NO concentration (10 second averages) during afternoon of August 19, 2009.

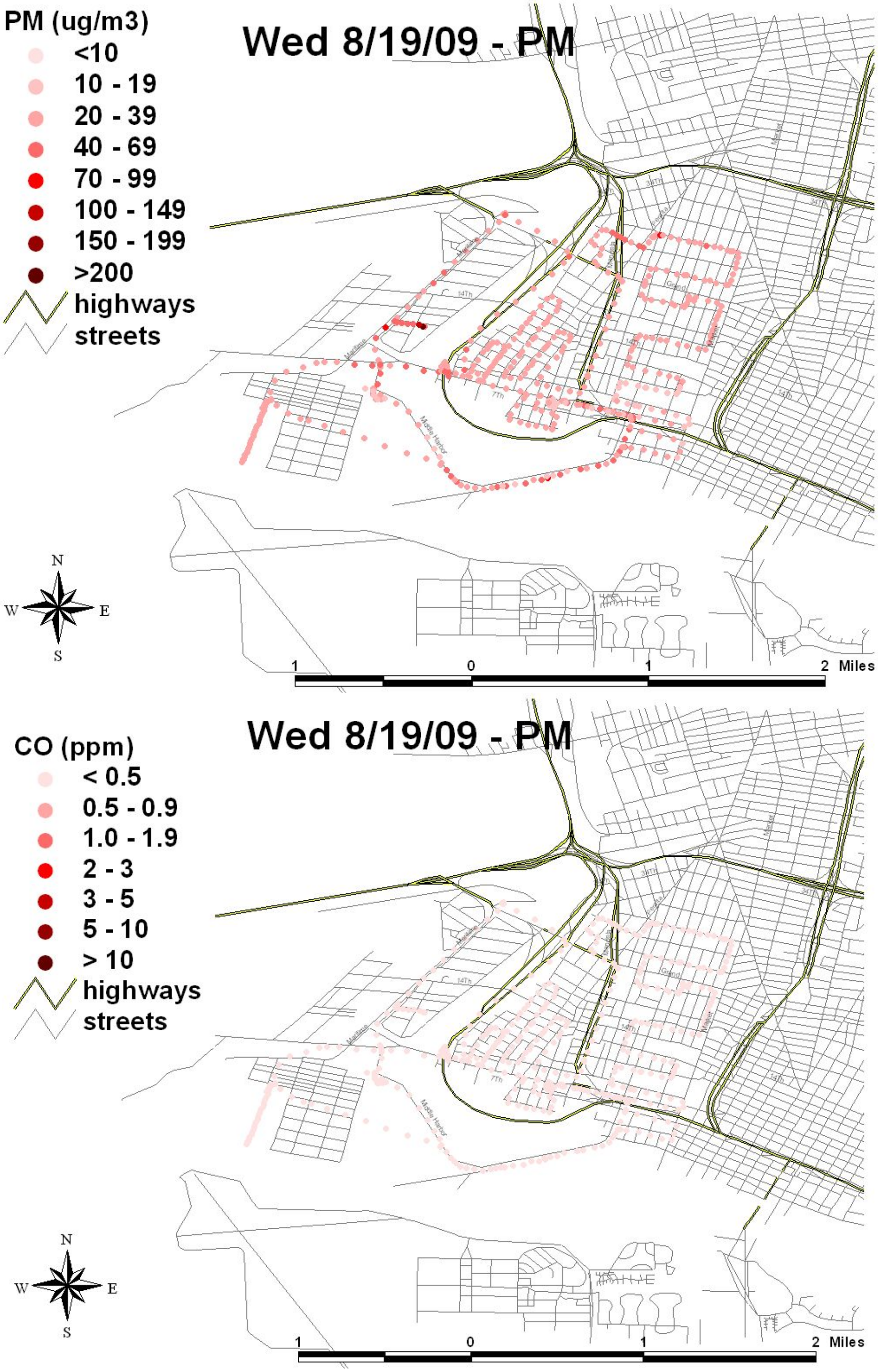

Figure 3-17b. Spatial variations in $PM_{2.5}$ and CO concentration (10 second averages) during afternoon of August 19, 2009.

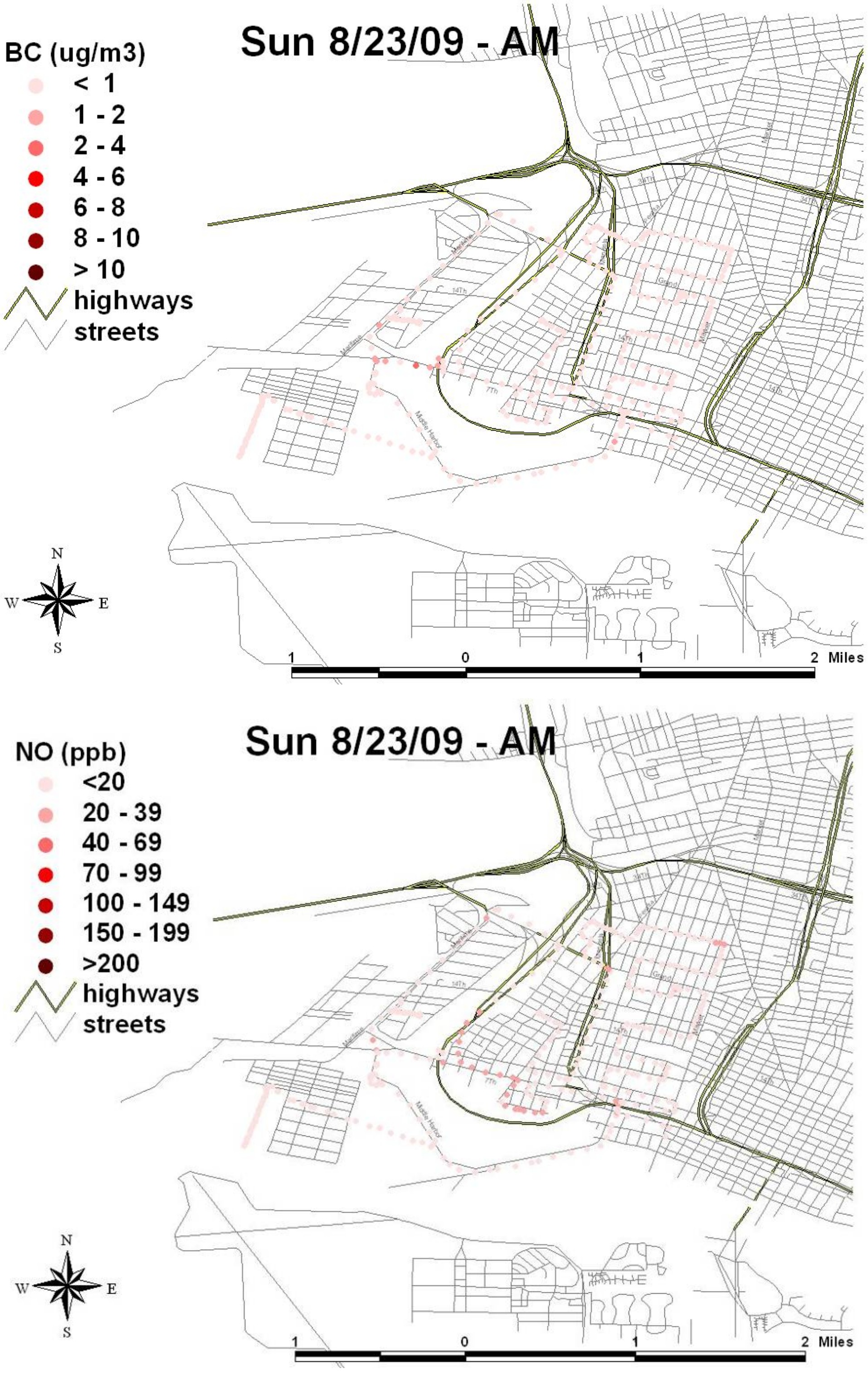

Figure 3-18a. Spatial variations in BC and NO concentration (10 second averages) during morning of August 23, 2009.

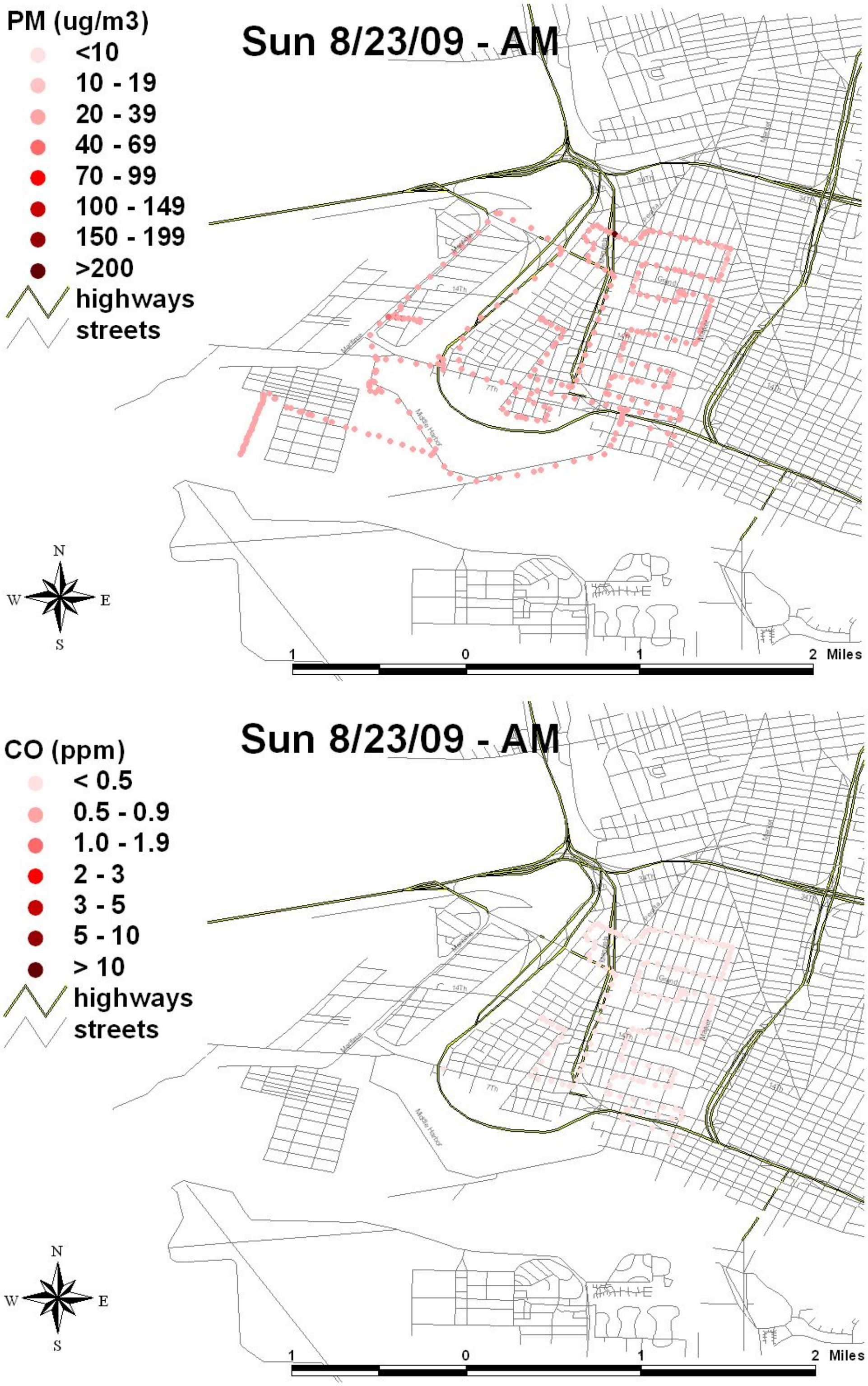

Figure 3-18b. Spatial variations in $PM_{2.5}$ and CO concentration (10 second averages) during morning of August 23, 2009.

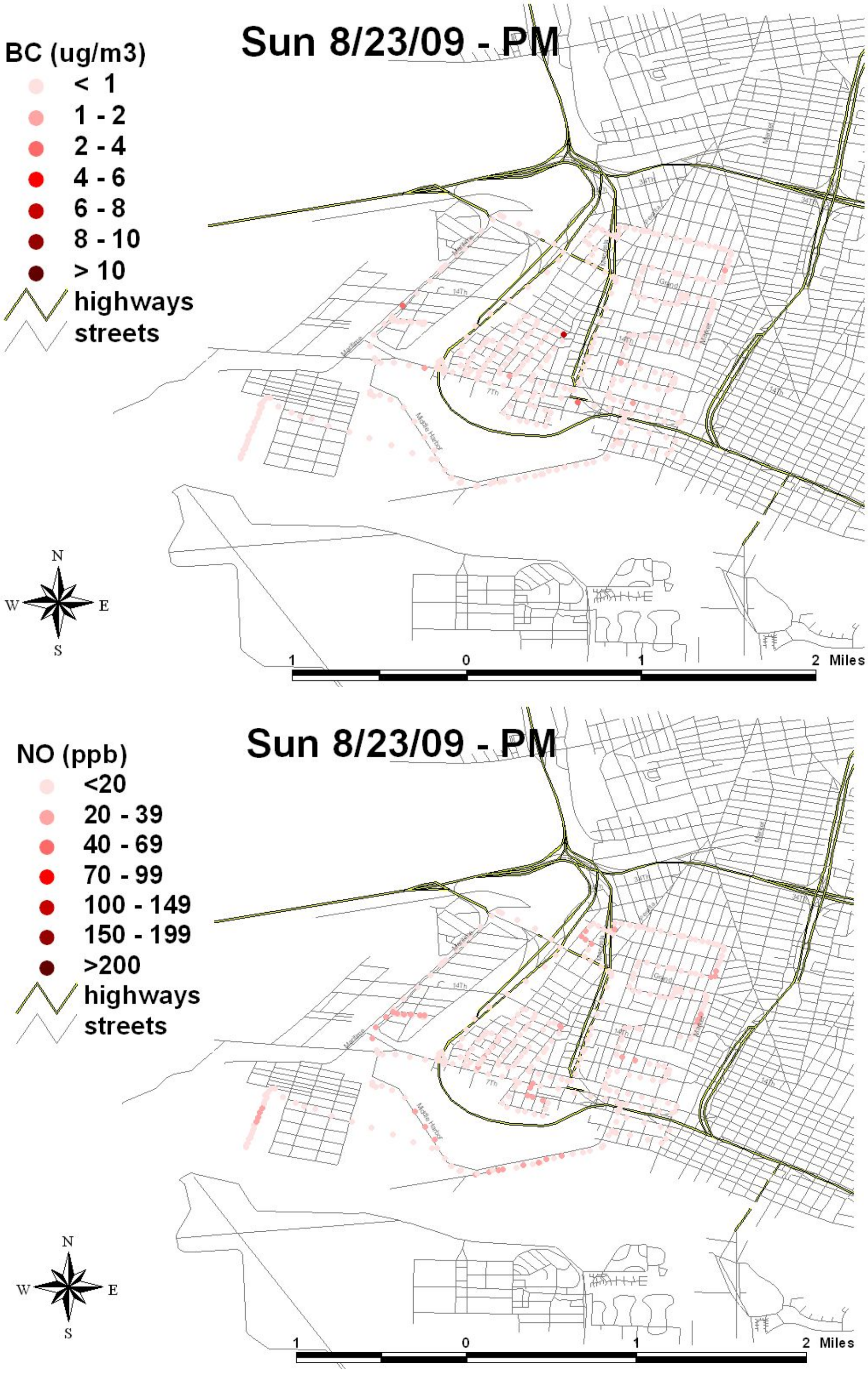

Figure 3-19a. Spatial variations in BC and NO concentration (10 second averages) during afternoon of August 23, 2009.

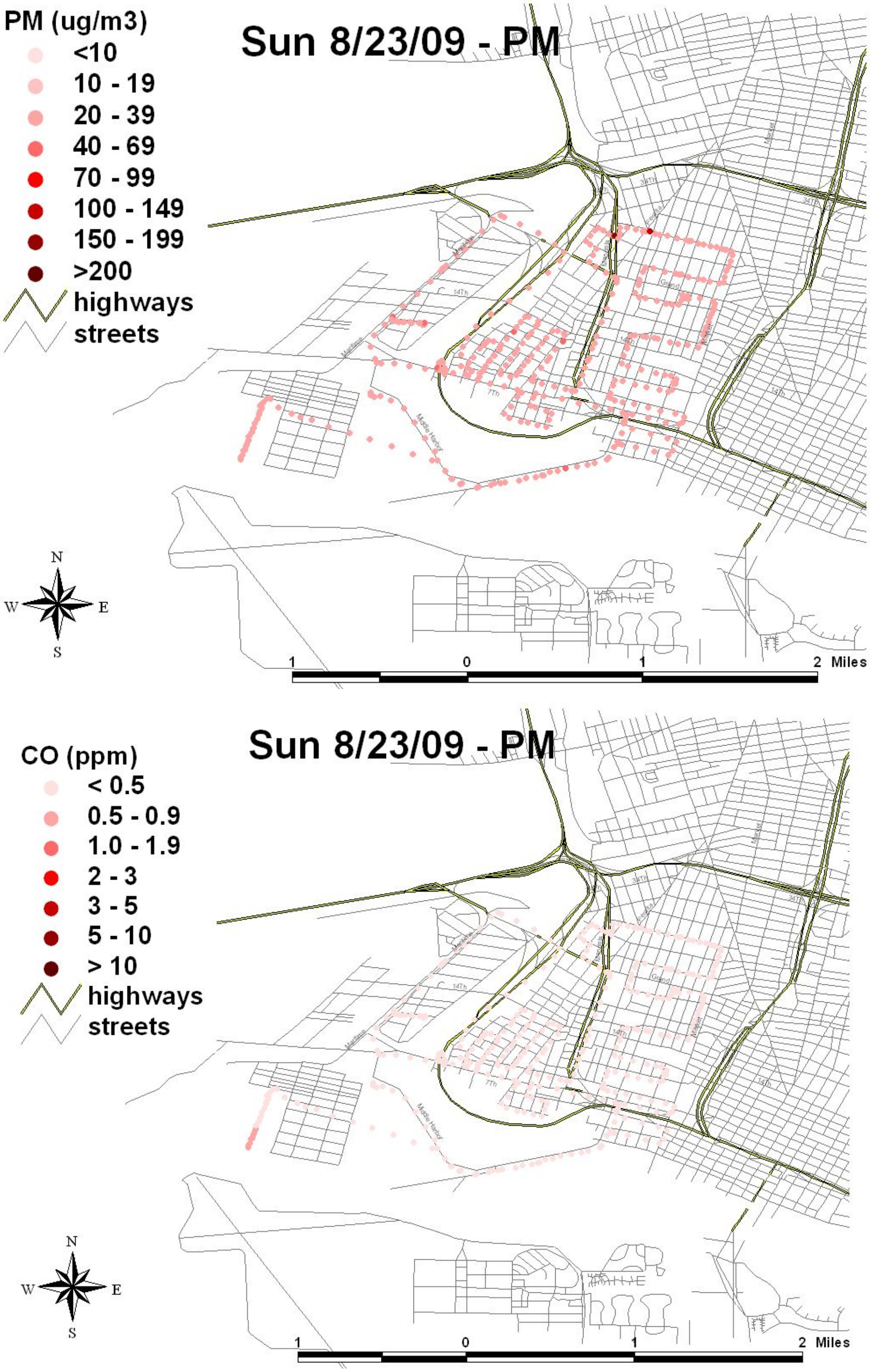

Figure 3-19b. Spatial variations in $PM_{2.5}$ and CO concentration (10 second averages) during afternoon of August 23, 2009.

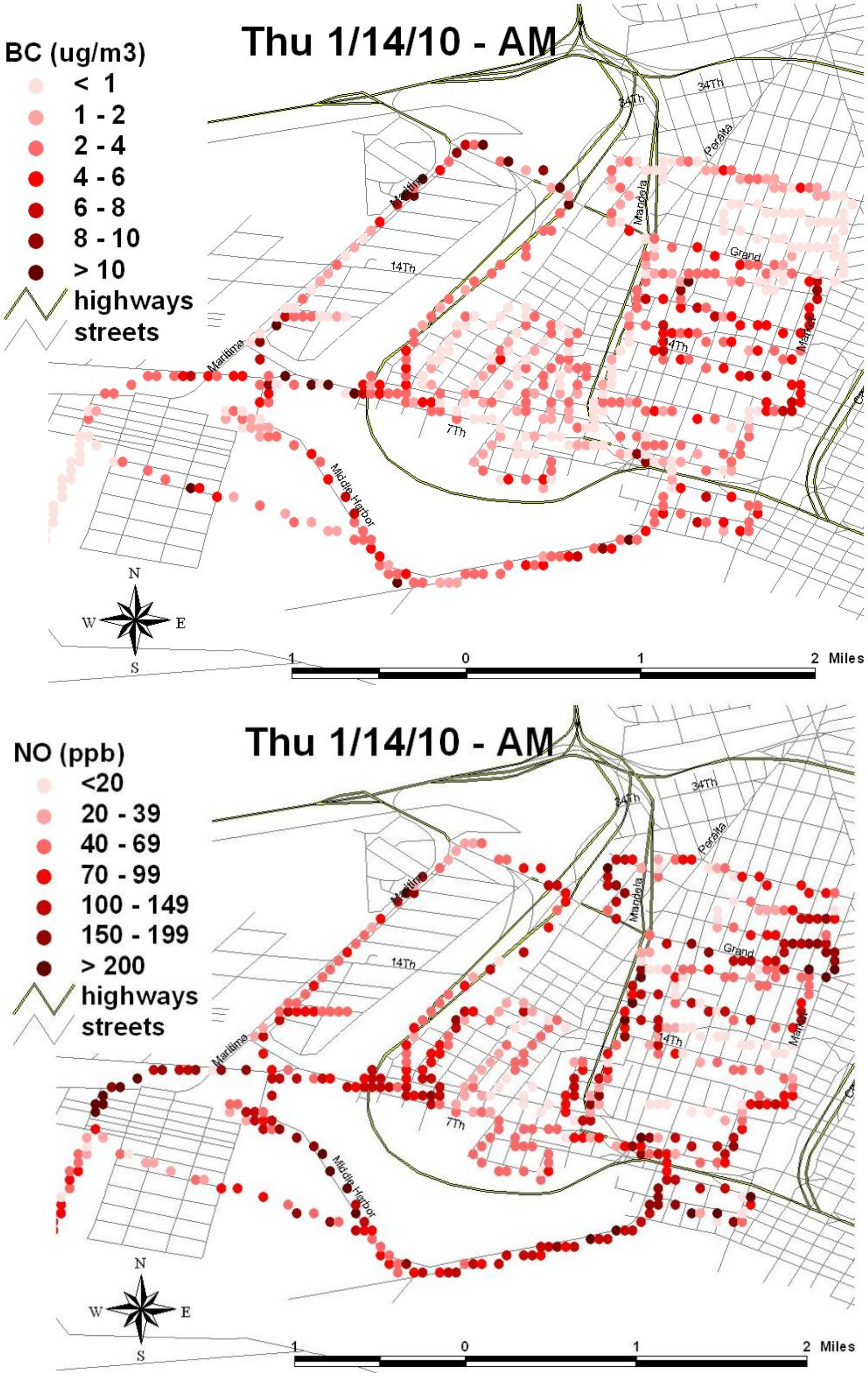

Figure 3-20a. Spatial variations in BC and NO concentration (10 second averages) during morning of January 14, 2010.

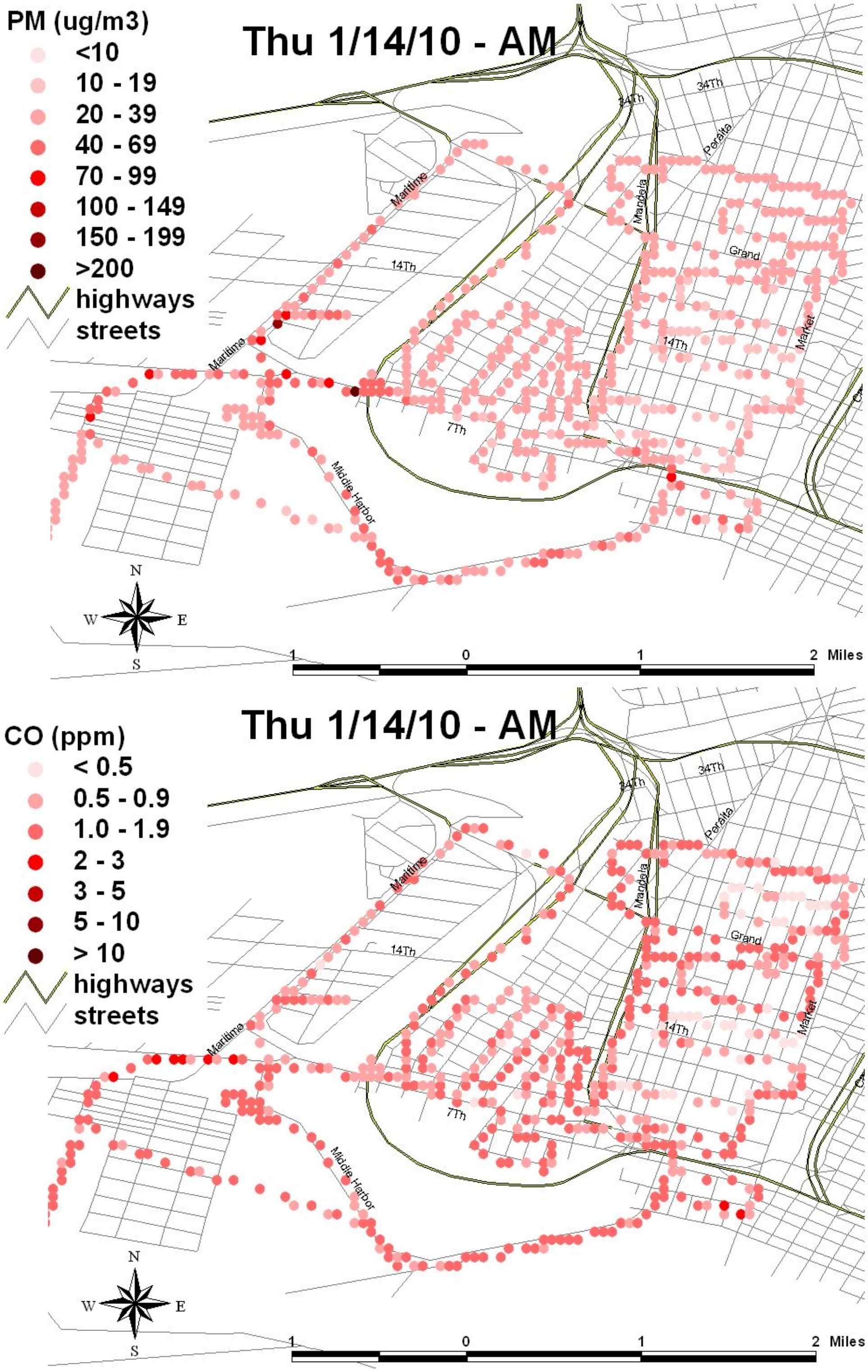

Figure 3-20b. Spatial variations in $PM_{2.5}$ and CO concentration (10 second averages) during morning of January 14, 2010.

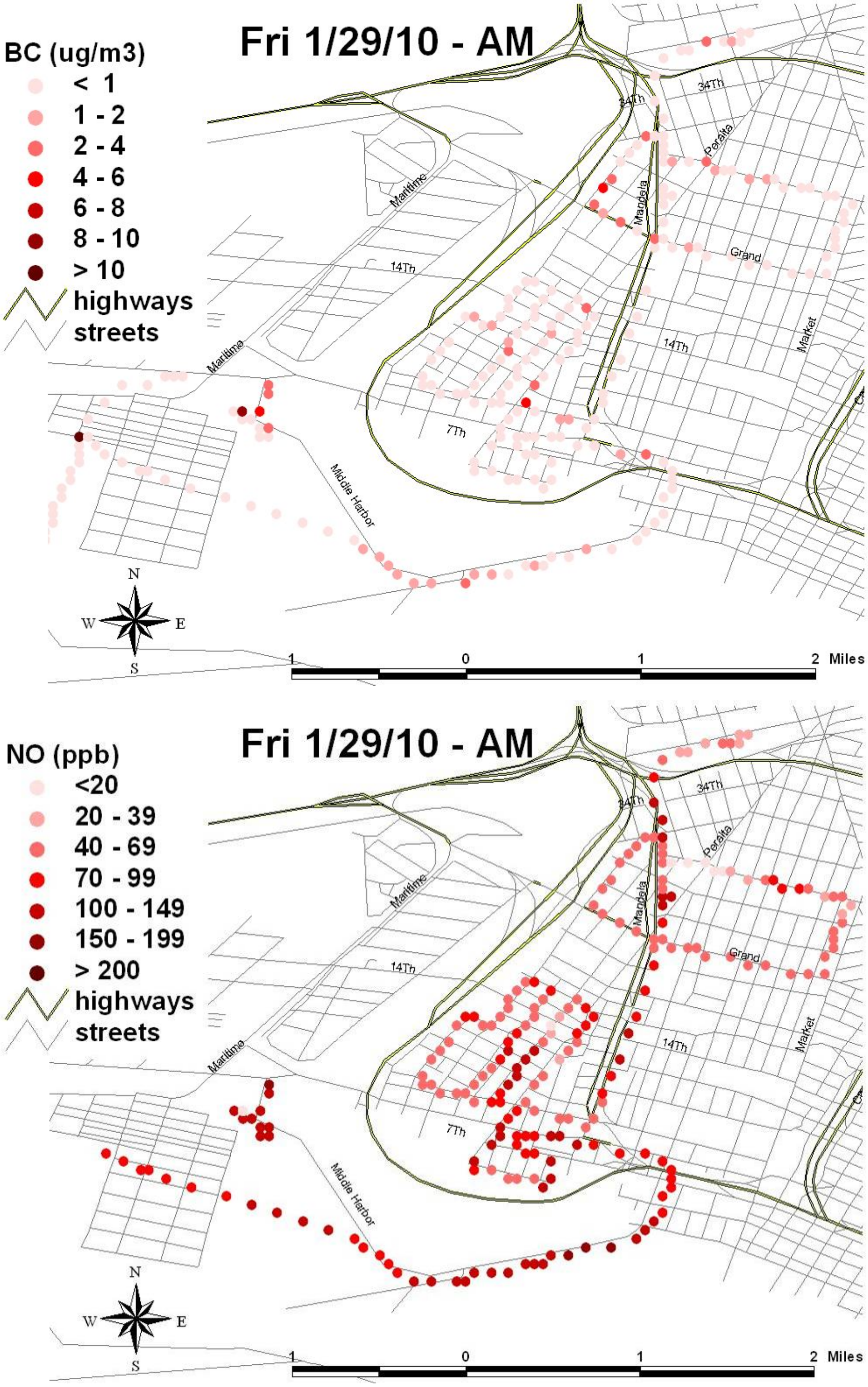

Figure 3-21a. Spatial variations in BC and NO concentration (10 second averages) during morning of January 29, 2010.

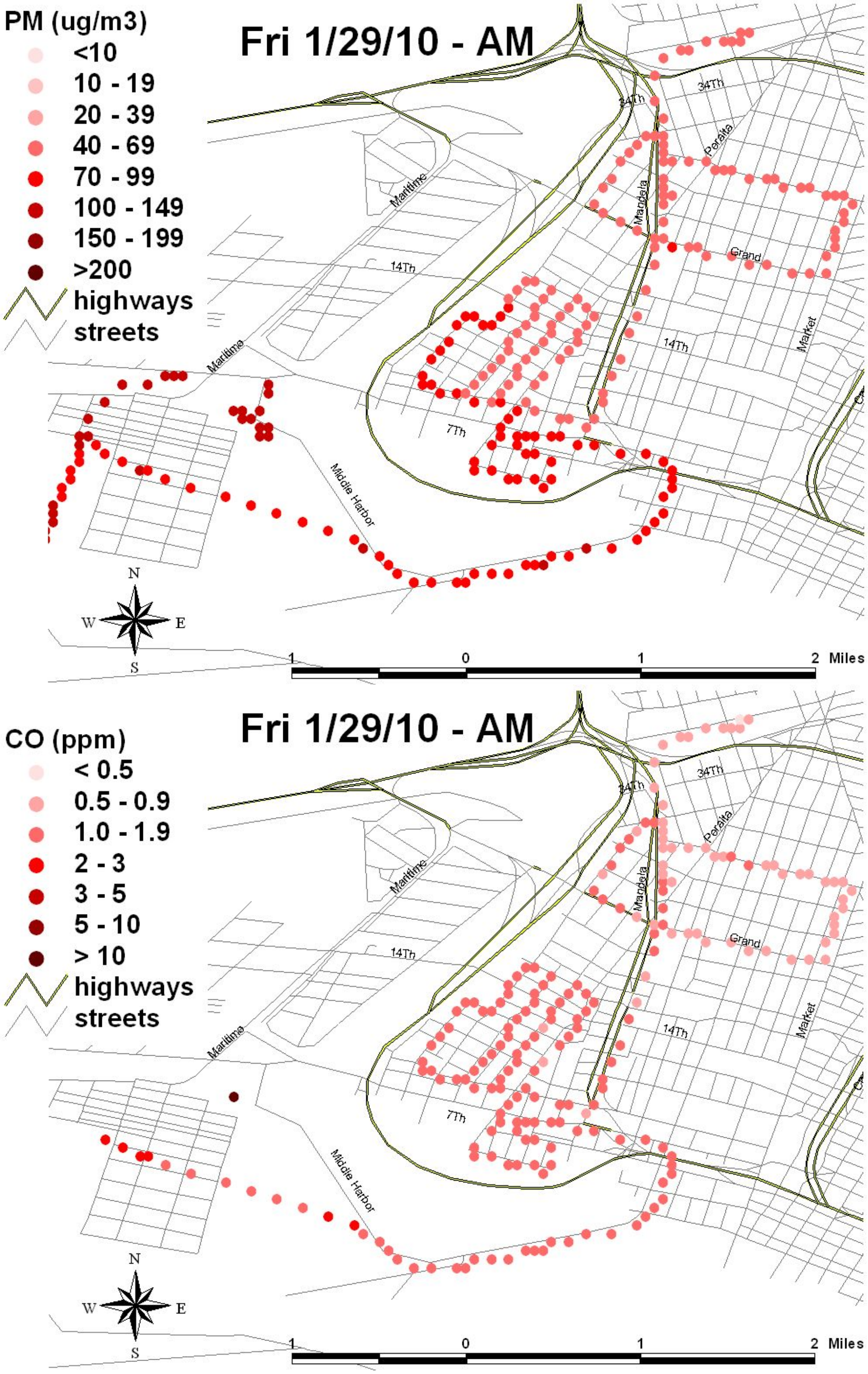

Figure 3-21b. Spatial variations in $PM_{2.5}$ and CO concentration (10 second averages) during morning of January 14, 2010.

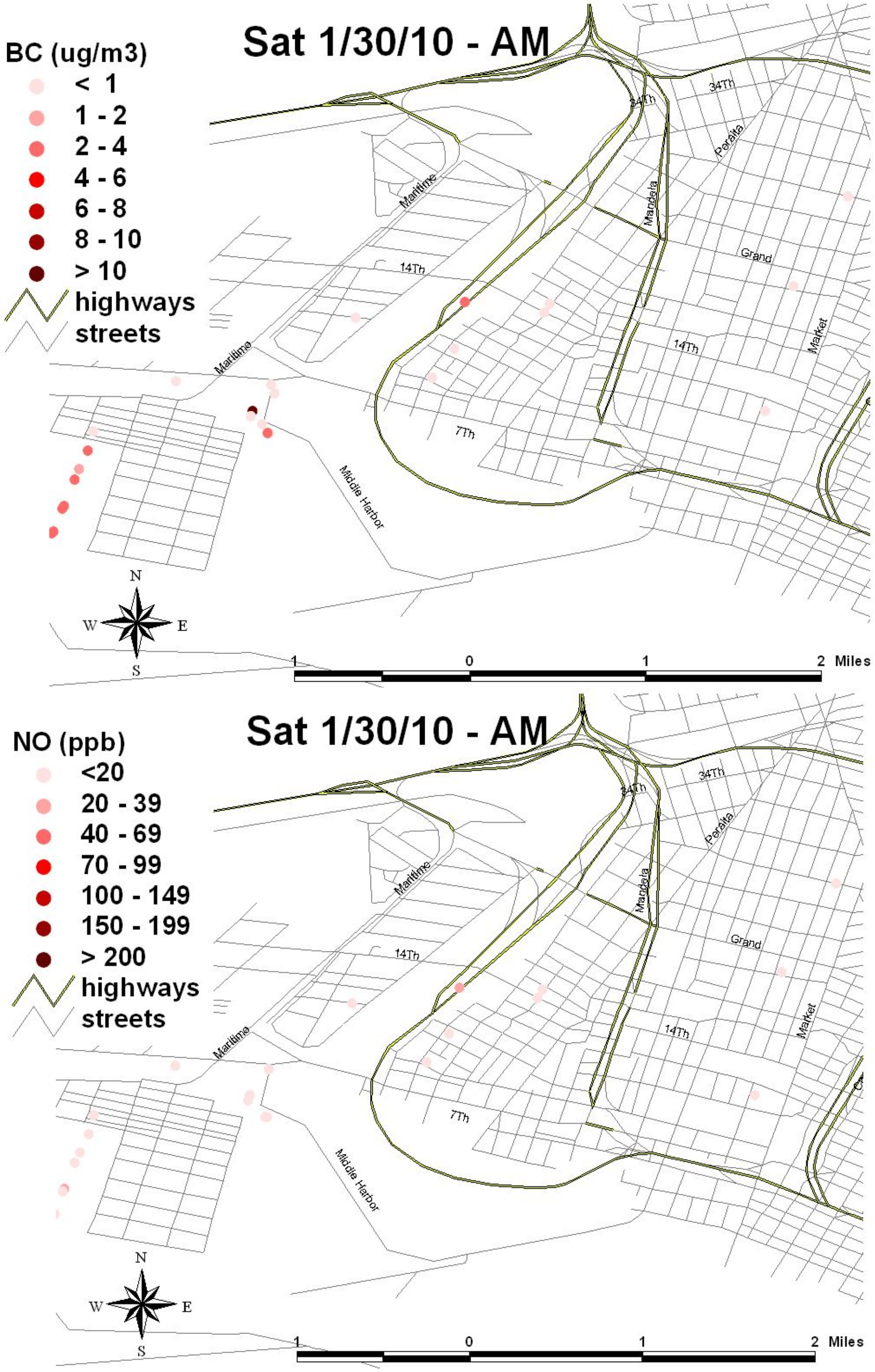

Figure 3-22a. Spatial variations in BC and NO concentration (10 second averages) during afternoon of January 30, 2010.

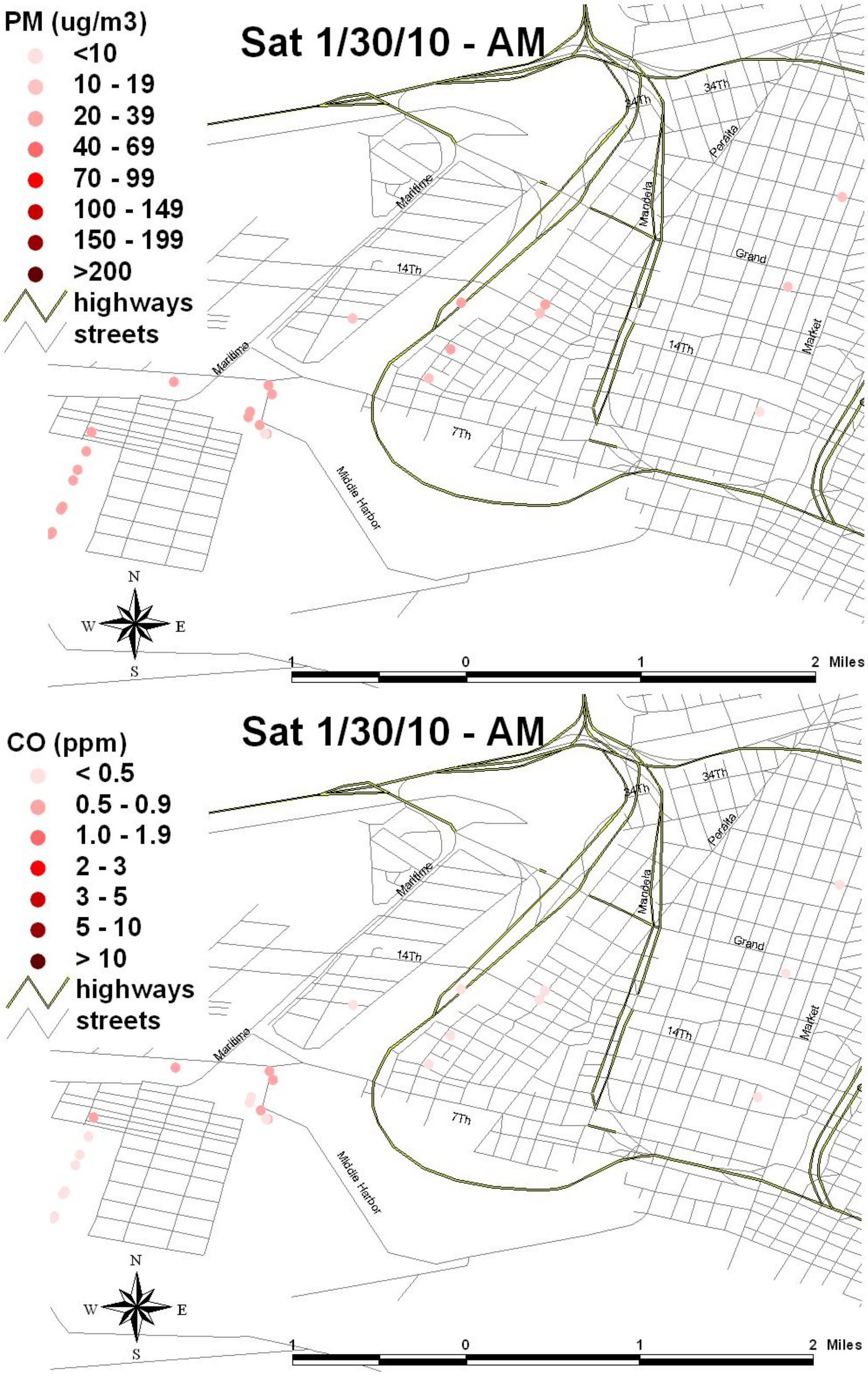

Figure 3-22b. Spatial variations in $PM_{2.5}$ and CO concentration (10 second averages) during morning of January 29, 2010.

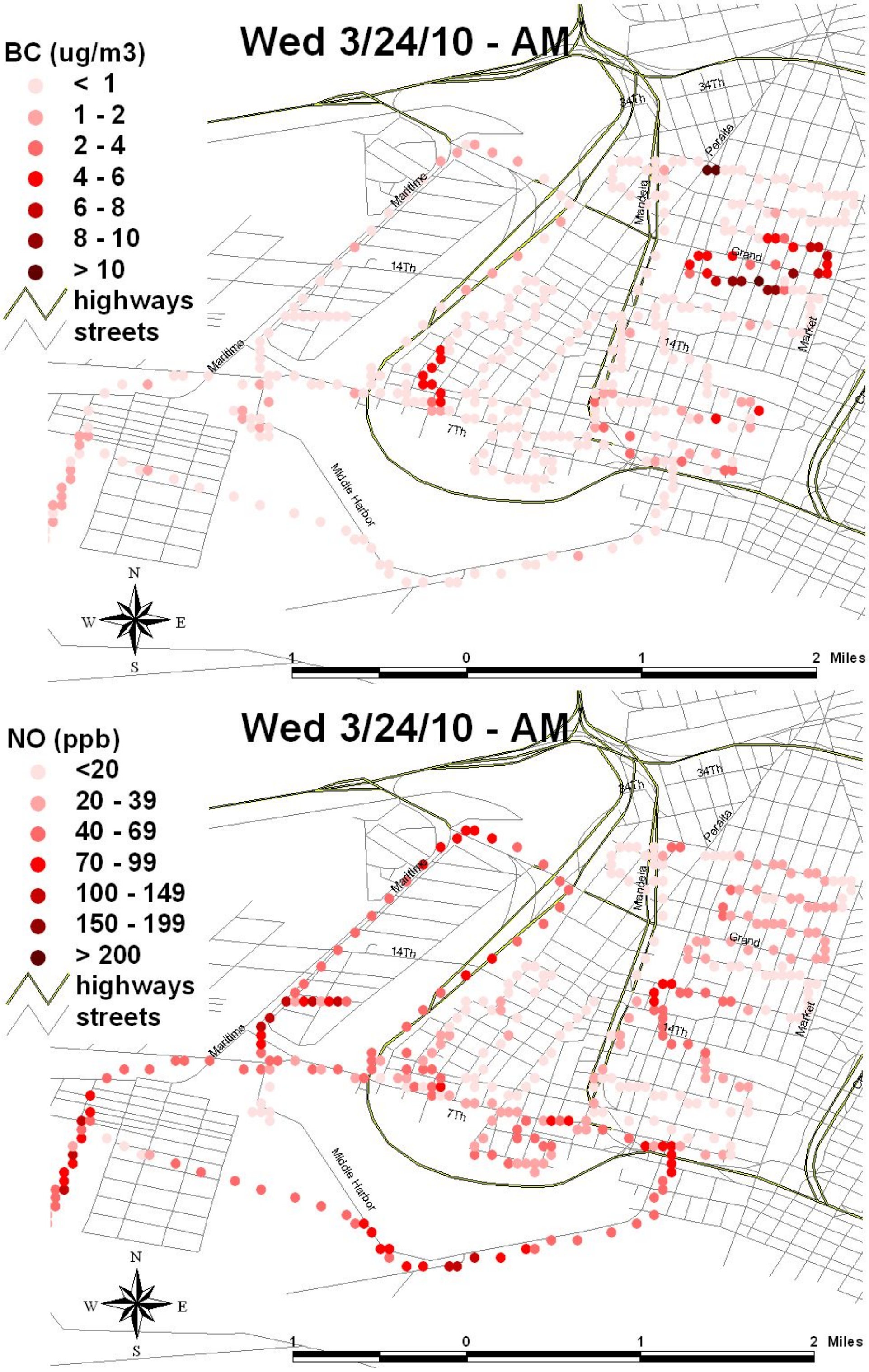

Figure 3-23a. Spatial variations in BC and NO concentration (10 second averages) during afternoon of March 24, 2010.

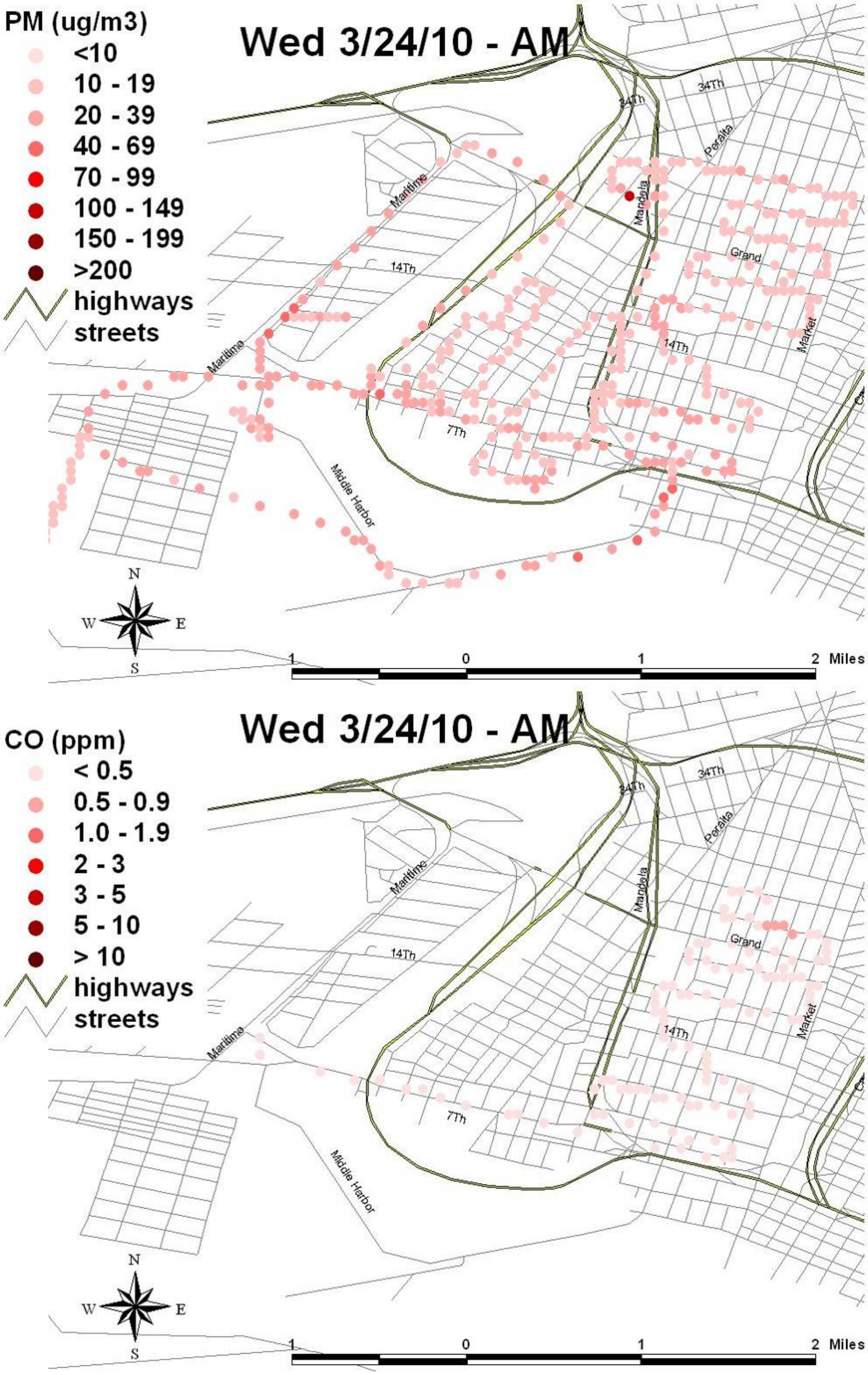

Figure 3-23b. Spatial variations in $PM_{2.5}$ and CO concentration (10 second averages) during morning of March 24, 2010.

West Oakland Monitoring Study

FINAL REPORT

APPENDIX C

Operating procedures for BAAQMD mobile monitoring system

Prepared for:
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2215 Raggio Parkway

September 9, 2010

This document describes basic setup and operating procedures for the mobile air quality monitoring system used in the West Oakland Monitoring Study (WOMS) in 2009-2010. The instrument platform is a 2008 Ford E-350 cargo van with raised roof and rear air conditioning modified by E-N-G Mobile Systems, Inc. to include an instrument rack, desk/workbench, calibration gas cylinder rack, and 100VAC and 12VDC power system that can operate off of on-board batteries or line power. The following instruments/measurements were included during the WOMS:

Instrument	**Parameters measured**
2Btech model 400	NO
2Btech model 202	O3
TEI model 48	CO
DRI mini-photoacoustic	BC
TSI model 3007 CPC	Ultrafine particle conc.
ppbRAE 3000	VOC
TSI DustTrak II model 8530	PM
Garmin GPS-16	Lat, long, elevation, speed, direction
Davis Weather Envoy	T, RH, wind speed, direction

All instruments listed are capable of making real-time measurements of the listed parameters with averaging times as low as 10 seconds, which was the time-scale used during mobile monitoring during the WOMS.

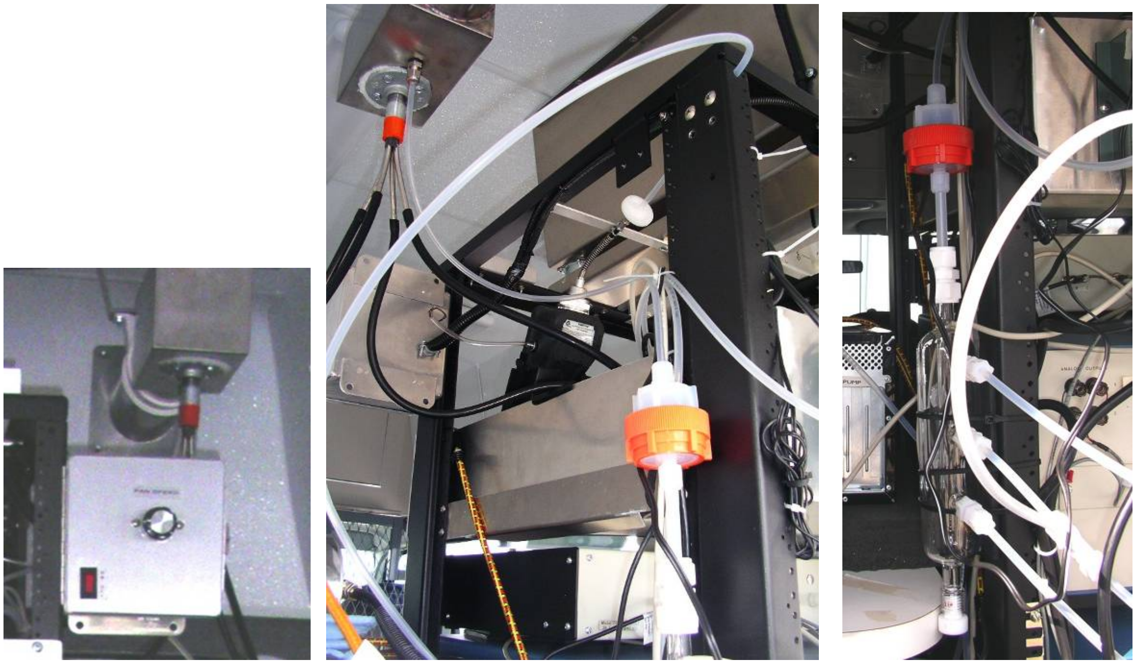
Ambient air is drawn into the van via an electric fan-driven roof duct into glass and stainless-steel plenums for connecting gas and particle sampling instruments, respectively. The air velocity in the duct can be adjusted via the fan control to minimize anisokinetic sampling effects when making aerosol pollutant measurements while the van is in motion, or if there is a significant cross-wind at a stationary sampling location.

A gas-diluter and ozone generator is also included to allow frequent checks of the accuracy of the gaseous pollutant monitors if zero air and the appropriate certified gas standards are available.

Air inlet manifold

There are four ¼” stainless-steel tubes exiting the inlet duct that can be connected to particle sampling instruments via flexible conductive tubing. The connection tubes are curved to avoid impaction losses, and sharp bends in the conductive tubing should be avoided. A ¼” Teflon hose also exits the fan duct and connects to a particle filter cartridge that is followed by a glass plenum with up to 4 connection ports for gaseous pollutant sampling. The output of the gas calibrator should also be attached to this plenum. If additional connections are required it is permissible to install “T” connectors in the lines downstream of the plenum for gas sampling.

Before the start of monitoring each day, check that there are no open ports on either the glass or stainless steel inlet manifolds. Turn on the fan in the inlet duct and adjust to an appropriate setting. The fan speed should be set to produce air velocity at the intake on the roof that is near the median value of the anticipated ambient wind speed and/or van travel speed. An assistant with a handheld anemometer is recommended for making this adjustment.



Photos of the inlet duct and fan control, stainless steel plenum exiting duct, and glass plenum with particle filter (replaceable paper disk filter is in the orange cartridge).

On-board power system

The on-board power systems are operated from the control panel located on the wall behind the driver's seat:

Turn on inverter by pressing the On/Off button in the Inverter section.

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The LED indicator should change from Standby to Invert. If not, see the Prosine manual for diagnostic procedures.

Flip on AC Circuit switches for inverter, instrument rack, and utility outlets.

INSTRUMENTS

2Btech model 400 Nitric Oxide monitor

Connections:
12VDC power supply must be connected to jack on rear panel of instrument and plugged into 110V power strip on rack.
9-pin RS232 serial cable connected from instrument rear panel to Com port on rear of photoacoustic instrument. Serial data stream is logged along with the black carbon data by the photoacoustic instrument computer.
¼” Teflon tubing from inlet on rear panel to glass manifold.

Startup:
Press power switch on front panel.
Wait 20 minutes for warm-up cycle to complete, after which display will show NO concentration alternating with flow and ozone supply readings. Internal datalogging must <u>not</u> be enabled to allow logging to photoacoustic computer. Averaging time should be set to 10 seconds (default). If the photoacoustic instrument will not be used, see manual for datalogging and communication instructions.

2Btech model 202 Ozone monitor

Connections:
12VDC power supply must be connected to jack on rear panel of instrument and plugged into 110V power strip on rack.
9-pin RS232 serial cable connected from rear panel to USB port on rear of photoacoustic.via serial-USB adapter.
¼” Teflon tubing from inlet on rear panel to glass manifold.

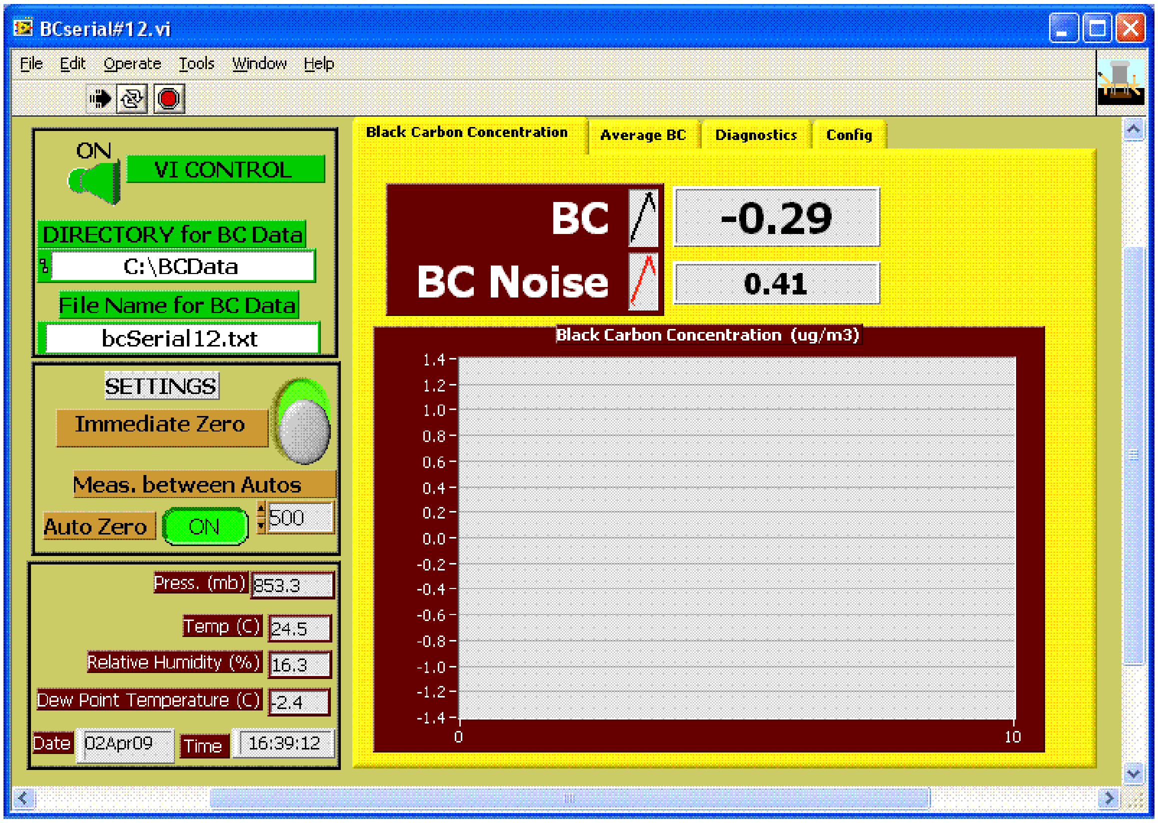
Startup:
Press power switch on front panel.
Internal datalogging must <u>not</u> be enabled to allow logging to photoacoustic computer. Averaging time should be set to 10 seconds (default). If the photoacoustic instrument will not be used, see manual for datalogging and communication instructions.

DRI mini-photoacoustic (PA)

Connections:
Universal power cord to 110V outlet.
Conductive tubing (black plastic) from inlet on rear panel to one of the stainless steel manifold tubes exiting from the duct on ceiling.
Flexible mesh-wall tubing from outlet (rear panel) to vacuum pump inlet using quick disconnects.
USB hub connected to front panel USB port.
USB cable to keyboard/touchpad combo or mouse.

Wireless monitor transmitter connected to USB hub. Wireless monitor must be connected to 12VDC power outlet and to receiver via serial cable. Receiver power supply plugged into 110V outlet.

Startup:
Power switch on rear of case On.
Turn computer on by pressing button on front panel (right of monitor). Blue LED will light.
Switch on vacuum pump.
Monitors have power button below screen (should be left on).
LabView application should start up automatically. If not, see PA documentation.
Allow to warm up for at least 30 minutes. Check laser power graph on Diagnostic tab to verify stability before starting data collection.
Once all instruments have completed warmup cycles, go to the “O3 and NO tab” and enable data logging for these instruments. Current values should appear within 10 seconds. Warning: enabling serial data logging when no data is being transmitted by the instruments may cause the program to freeze up.



ON VI CONTROL

DIRECTORY for BC Data: C:\BCData

File Name for BC Data: bcSerial12.txt

SETTINGS

Immediate Zero

Meas. between Autos: 500

Auto Zero: ON

Press. (mb): 853.3

Temp (C): 24.5

Relative Humidity (%): 16.3

Dew Point Temperature (C): -2.4

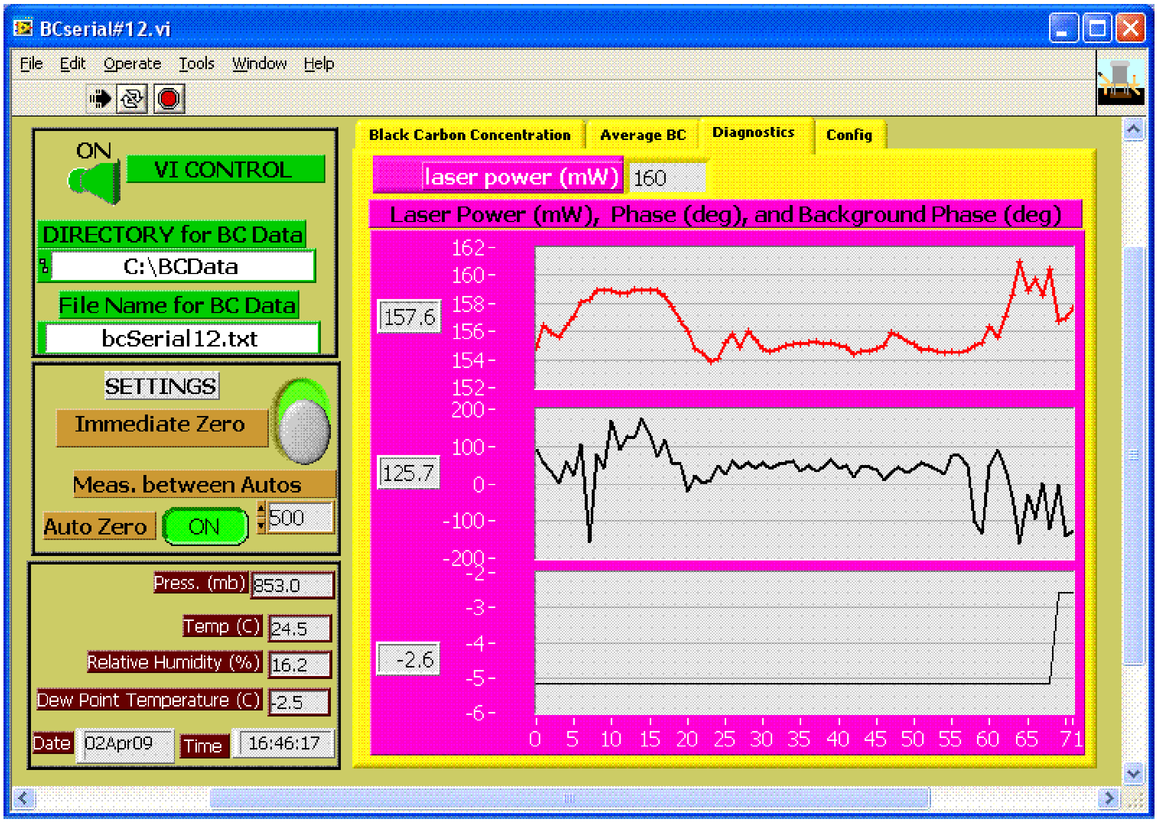
Date: 02Apr09

Time: 16:39:12

BC: -0.29

BC Noise: 0.41

Initial screen view of photoacoustic instrument LabView program



DIRECTORY for BC Data: C:\BCData

File Name for BC Data: bcSerial12.txt

laser power (mW) 160

Meas. between Autos 500

Auto Zero ON

Press. (mb) 853.0

Temp (C) 24.5

Relative Humidity (%) 16.2

Dew Point Temperature (C) -2.5

Date 02Apr09

Time 16:46:17

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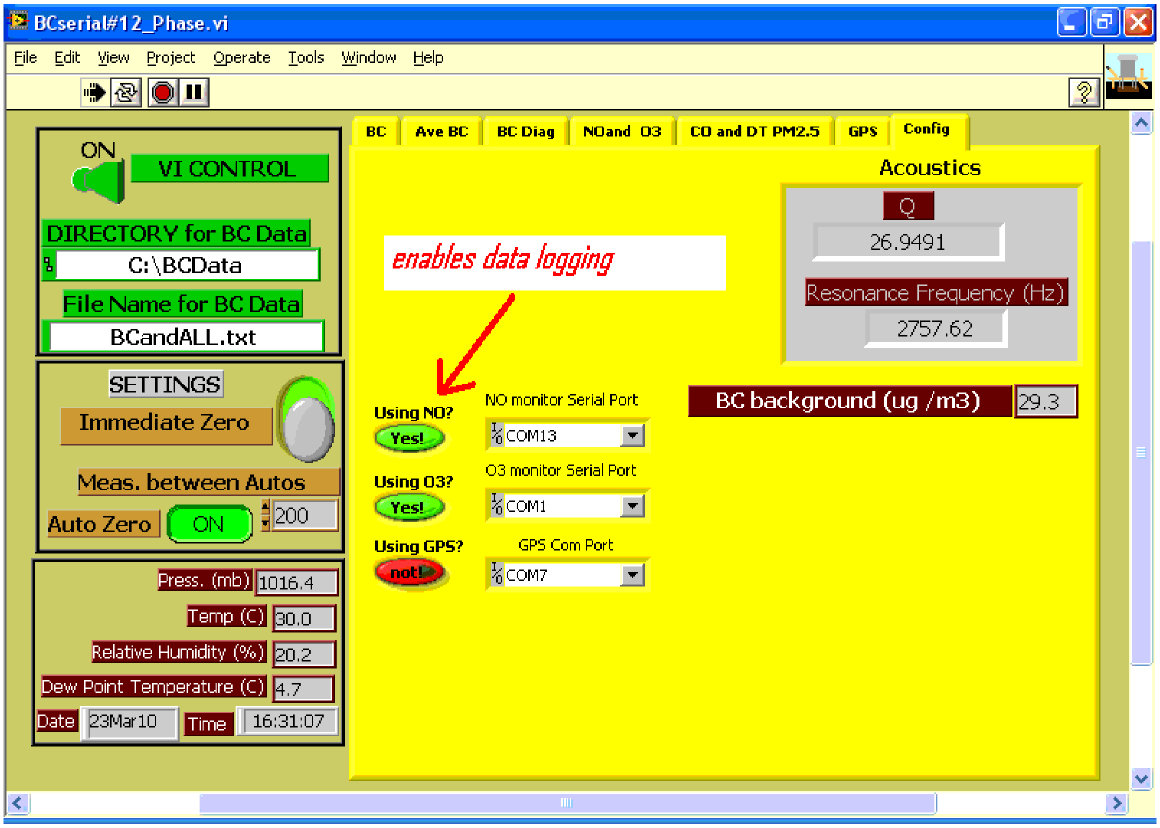
Diagnostics tab of photoacoustic instrument LabView program. Top graph shows laser power during warmup (not stabilized yet).

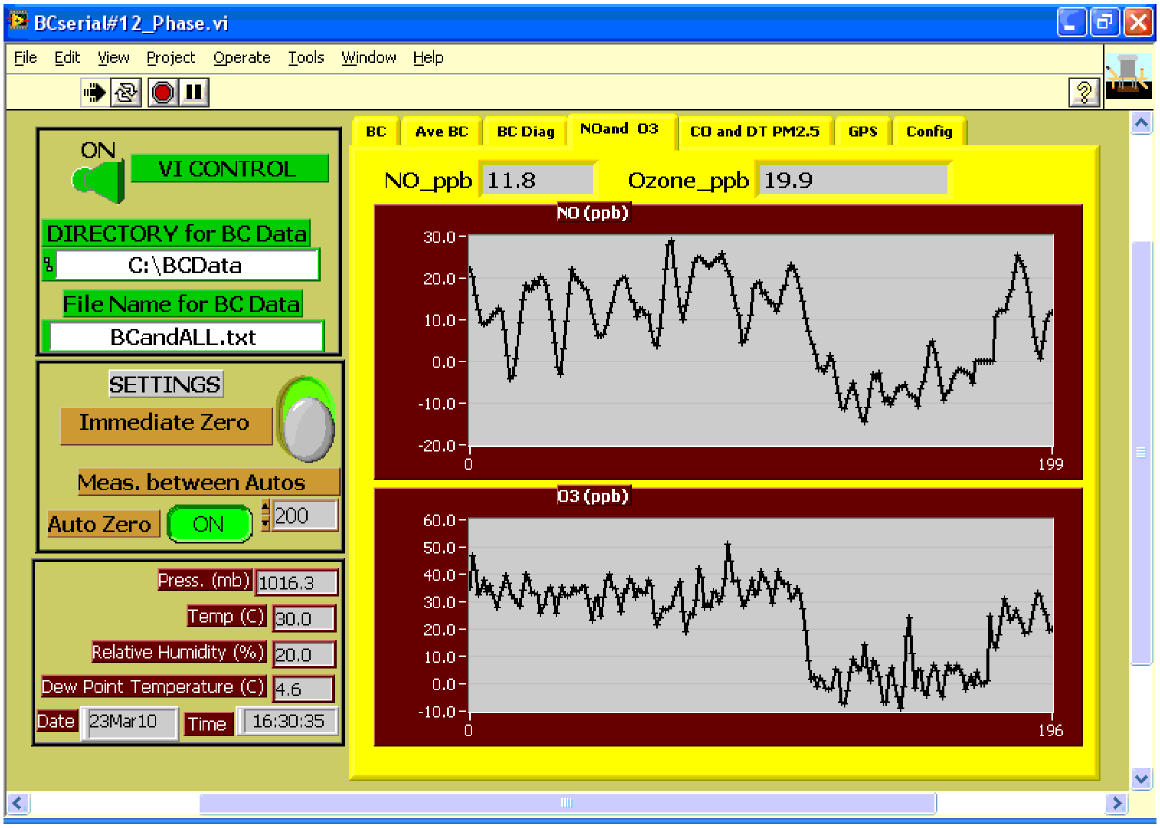


enables data logging

DIRECTORY for BC Data: C:\BCData
File Name for BC Data: BCandALL.txt
Meas. between Autos: 200
Auto Zero: ON
Press. (mb): 1016.4
Temp (C): 30.0
Relative Humidity (%): 20.2
Dew Point Temperature (C): 4.7
Date: 23Mar10
Time: 16:31:07
Using NO?: Yes!
NO monitor Serial Port: COM13
Using O3?: Yes!
O3 monitor Serial Port: COM1
Using GPS?: not!
GPS Com Port: COM7
Q: 26.9491
Resonance Frequency (Hz): 2757.62
BC background (ug /m3): 29.3

Config tab where datalogging for NO and O3 are enabled by clicking on the oval buttons. CO data logging is enabled along with O3, since the voltage output from the CO monitor is processed using the analog input function of the ozone monitor*N*

Note: if communication error occurs when datalogging is started, disable and check for data streams from the other instruments using Hyperterm (shortcuts on PA computer desktop). If Com port assignments have changed, you will need to reset them in the pull-down lists to the right of each button. This is more likely to occur for devices connected via USB.



NO_ppb 11.8

Ozone_ppb 19.9

DIRECTORY for BC Data C:\BCData

File Name for BC Data BCandALL.txt

Meas. between Autos 200

Auto Zero ON

Press. (mb) 1016.3

Temp (C) 30.0

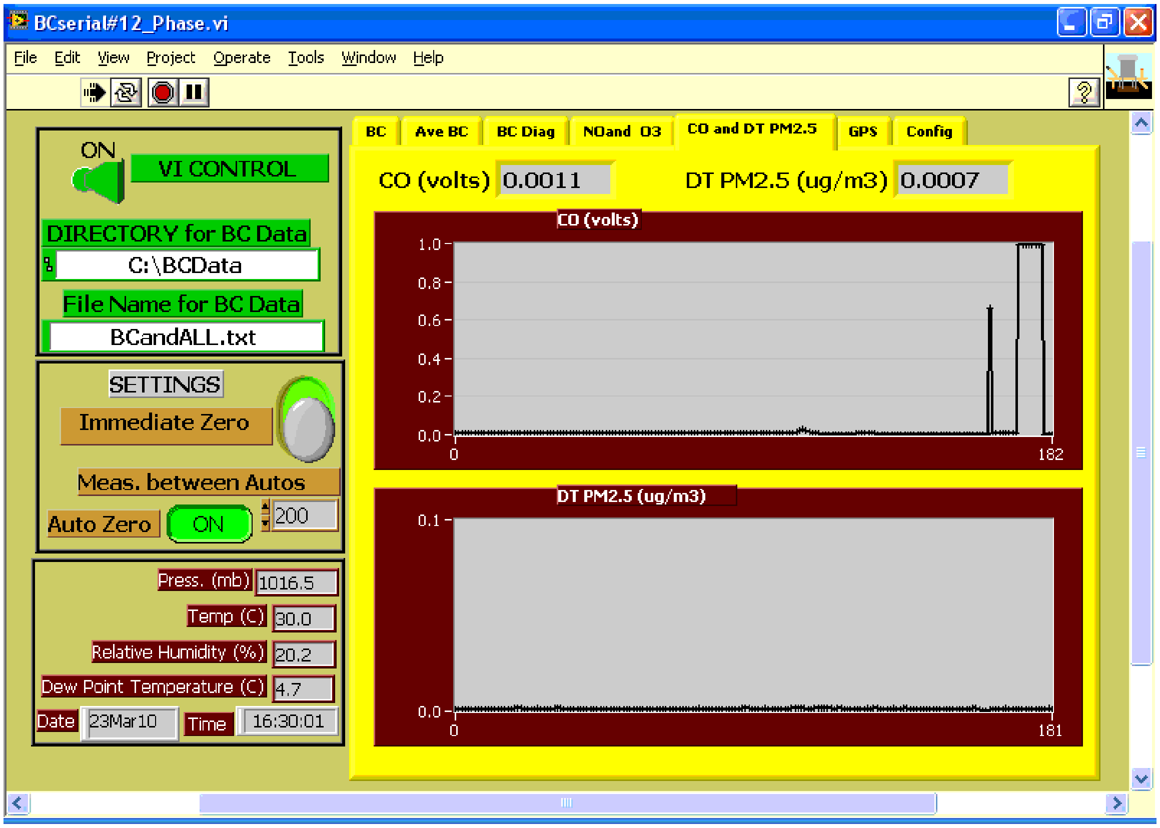
Relative Humidity (%) 20.0

Dew Point Temperature (C) 4.6

Date 23Mar10

Time 16:30:35

NO and O3 tab showing data traces. Values above charts should update to match instrument front panel displays every 10 seconds.



DIRECTORY for BC Data: C:\BCData
File Name for BC Data: BCandALL.txt
Meas. between Autos: 200
Auto Zero: ON
Press. (mb): 1016.5
Temp (C): 30.0
Relative Humidity (%): 20.2
Dew Point Temperature (C): 4.7
Date: 23Mar10
Time: 16:30:01
CO (volts): 0.0011
DT PM2.5 (ug/m3): 0.0007

CO and PM tab. Top chart displays the actual voltage output of the analog signal from the TEI CO monitor. The factor for conversion to ppm (approx. 40x) should be verified during daily span checks. The lower chart is intended to show PM2.5 signal from the DustTrak II aerosol monitor, but is not used *(the continuous data output features of that instrument are not available due to a design flaw).*

ppbRAE 3000 VOC monitor

connections:
¼” Teflon tubing from inlet probe to glass manifold
For run times greater than 8 hrs, connect 12VDC battery charger to the instrument cradle and plug into 110V outlet. Otherwise, charge the instrument overnight.
USB device cable from jack on left side to USB port on laptop (for downloading stored data).

startup:
press center yellow button and hold until beep. Verify that data is logging (floppy disc icon at bottom of display. Allow 1 minute for warm-up.

DustTrak II aerosol monitor

connections:

Conductive tubing (black plastic) from inlet on rear panel to one of the stainless steel manifold tubes exiting from the duct on ceiling.
For run times greater than 12 hrs, connect 12VDC battery charger to the instrument cradle and plug into 110V outlet. Otherwise, charge the instrument overnight.
(IMPORTANT: the battery only charges while unit is turned <u>on</u>).
USB device cable from jack on left side to USB port on laptop (for downloading stored data).

startup:
press On button above display.
When ready, touch Start on screen. Should start logging data within 1 minute. No warmup needed.

TSI 3007 CPC

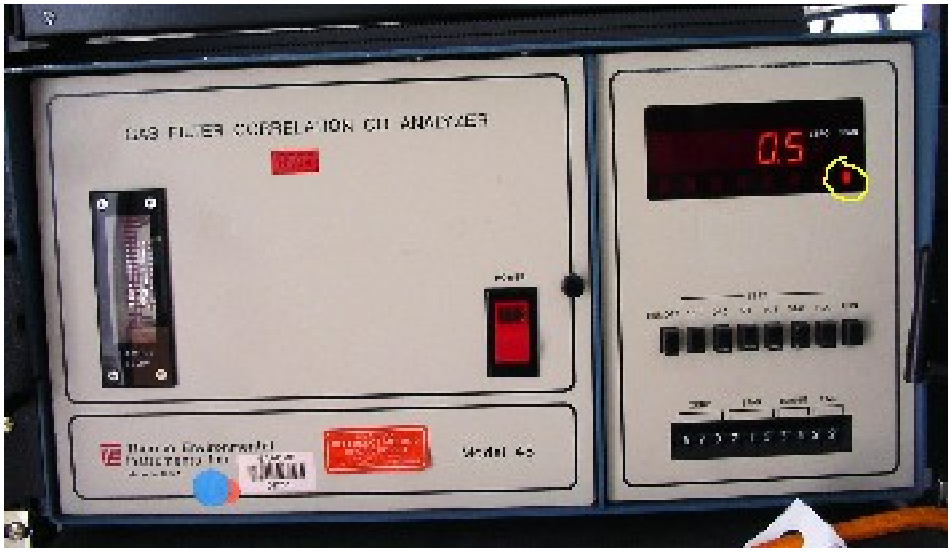
connections:
¼” Teflon tubing from inlet to glass manifold.
6VDC power supply, coaxial jack next to inlet.
USB serial cable to laptop for data acquisition.

startup:
Replace the alcohol cartridge with a freshly charged one, if necessary. Cartridges must be refreshed after 5-6 hours of operation.
Press black button to start 10 minute warmup cycle. Warmup can be skipped by pressing the enter key.
Start TSI Aerosol Instrument manager software on laptop. Open new file of type for 3007. When instrument is recognized, press Start to begin data logging.
The logging interval can be adjusted via the Log Mode 1 tab of the dialog box accessed from the Run/Properties menu item. *Make sure the number of samples is set to a large enough value to accommodate the logging interval and run time you wish to use.* Com port assignment and the Instrument Clock can also be changed via the Properties menu.

TEI CO monitor

Connections:
Universal power cable to 110V power strip on back of rack.
Analog output cable to analog input A (stereo mini-plug jack) on back of 2Btech 202 (data is logged along with ozone data).
¼” Teflon tubing from inlet probe to glass manifold.

Startup:
Press start button on front panel.
Allow to warm up for about 30 minutes prior to data collection. Check rotameter on front panel for stable flow rate (about 0.7 lpm).
If necessary, press Run button until indicator lights under Zero and Span on display are <u>off</u>.



TEI CO analyzer front panel with light indicating instrument is in Span mode circled – this indicator should be off when collecting data.

GPS

Check that GPS USB cable is attached to laptop Start 'Spanner' program. It should indicate that a Garmin GPS-18 is recognized. If not, try reconnecting USB cable, and/or rebooting. Once Spanner is running, start Hyperterm from the shortcut named 'Garmin GPS.ht' on desktop. Once connected, data should begin streaming. If connection fails, try changing Com port. When data is streaming, start Capture Text (under Transfer menu) to store data to a text file. *Other, more sophisticated software packages for logging the GPS data have been tested but caused frequent system crashes due to the rapidly streaming data produced. Also, since Hyperterm writes continuously to a text file no data is lost if the system goes down.*

Meteorology Package

If met data is desired during operation, the wireless sensor package should be deployed to a suitable location. Plug in the power supply for the met station console/receiver. Confirm communication with the sensor package by moving the wind vane and observing the wind rose on the display. The sensor package should then be mounted on the tripod with the arm of the anemometer pointing due North. Data from the station can be downloaded and/or viewed in real time by connecting the console to a USB port on the laptop and running the WeatherLink software.


Wireless met station console.

Synchronizing clocks:

Should be done before the start of data collection each day if 10 second average data is being collected. For longer averages, weekly synchronization may be adequate.

Adjust Windows system time on laptop to match GPS (in data stream starting with $GPRMC, the first number is hhmmss in GMT).
Adjust Windows system time on PA computer to match laptop (you can do this while the LabView program is running, but it may result in duplicate time signatures in the data logs if you adjust to an earlier time). This will sync all data being logged together (BC, NO, O3, and CO).
For DustTrak, set time via the Setup menu, which is only accessible when sampling is stopped.
For CPC, sync internal clock to laptop when starting AIM software
For ppbRAE, press N/- twice to see system time and date. If needed, sync internal clock by accessing the instrument configuration using ProRAE Suite software on the laptop (see data retrieval instructions).

Data Retrieval

The ppbRAE 3000 does not allow real-time data acquisition, so data from the internal logs must be downloaded. To download:

1. start the ProRAE Suite software on the laptop
2. press the N/- button on the instrument repeatedly until the “Enter PC comm” message appears, then press Y/+
3. select “Receive Data” from software menu and follow prompts
4. to backup data files to laptop, select on screen and use the “Options/export”??? menu item.

DustTrak internal data logs can be retrieved using TSI TrakPro software on the laptop. Stop the instrument (but don't turn off), then start the program. The software should detect the instrument if it is connected to a USB port. Click the ?? button on the software menu and follow instructions to download. Data can be backed up to Excel-readable files via the File/export menu item?.

PA data files can be copied from the C:\BCdata directory on the PA computer. This can be done while the LabView program is running or stopped. Two text files in a date-named folder are created each day. One contains complete 'raw' data (recorded about every 2 seconds) with lots of diagnostics, and the other contains 1 minute averages of BC, NO, O3, CO and selected BC diagnostics.

Shut down

At the end of data collection:

Switch off the pump for the PA. Stop the PA LabView program by clicking on the green On/Off switch on the left side of the application window. The program should stop after a few seconds. The computer can be shut down via the normal Windows method after data is copied.

Stop the GPS text capture via the Transfer menu in the Hyperterm window on the laptop.

Click the stop button of the AIM application on the laptop to cease acquiring CPC data. After downloading data, press and hold the center yellow button on the ppbRAE for 5 extremely loud beeps until shutdown occurs.

Press the Stop button on the DustTrak screen. Power off by pressing the button above the screen (*this will prevent battery charging and data retrieval*).

Press the black power button on the CPC to shut down. If the instrument will not be used again that day, remove the alcohol cartridge and place it in a recharging tube. Plug the instrument chamber with the cap from the tube.

The 2Btech instruments and TEI CO can be switched off at any time, but if a span check or calibration is planned it may be advisable to leave them running to avoid additional warm-up time.

After backing up all data, close all applications on the laptop and shut down.

Turn all AC and DC circuits off via switches on left side of control panel.

If system will be used again soon: Connect van to shore power, if available. Switch the inverter to Standby using the On/Off switch and, if check that the green Charge LED is lit in the Charger section of the control panel.

If system will not be used for an extended period: Switch off inverter on control panel. Check battery voltage on display. If fully charged (>13V), turn off charger with On/Off switch in Charger section of control panel. Otherwise, allow to charge (deep-cycle batteries may be damaged is left in a discharged state for extended periods).

Calibration checks

Periodic zero and span checks are required to ensure the accuracy of the measurements. If time permits, checks should be done prior to and immediately after each period of data collection.

NO and CO can be checked using compressed zero air and a certified gas standard. A gas dilution system like the TEI Model 146 will produce known concentrations of the target gases at concentrations ranging from zero to the upper limit of the range of anticipated ambient concentrations (i.e., the span value). See the manufacturer's instructions for the required line pressures and calculation of dilution settings.
With all instruments fully warmed up, zero air should be introduced to the glass inlet manifold at a flow rate in excess of the total intake flows of all instruments connected to the manifold. Wait until readings appear to be stable[1] and record the average value over a period of 5 minutes. If the average reading differs significantly from zero, adjust the offset value via the instrument's setup menu (see manual). Once the zero has been checked and adjusted, introduce gas at the span value concentration and record the average[2]. If desired, the displayed span readings may be adjusted, however significant variations generally indicate some sort of malfunction.

The zero value of the ppbRAE 3000 VOC monitor may also be checked and adjusted during this process. An automated zero adjustment is done via the setup menu (hold down ??. For maximum low end senstitivity, zeroing with an activated carbon filter tube on the inlet is recommended (see manual for instructions). Span adjustment is also possible, but is of limited value since the response of the PID varies substantially with organic pollutant composition.

The zero reading of the aerosol monitors (BC, PM, CPC) should be checked by attaching a particle filter to the inlet, recording the low reading, then running the automated zeroing cycle (touch ?? on screen). The photoacoustic instrument automatically adjusts the zero value at regular intervals during data collection, but an occasional check with a particle filter on the inlet is still recommended. Generation of known concentrations of aerosol particles is beyond the scope of field operations, so no span checks are possible.

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[1] *Since the NO monitor measures the difference in ozone concentration before and after titration by ambient NO, the readings at concentrations below 20 ppb are subject to a relatively large amount of electronic noise making them very unstable.*

[2] Application of extremely low humidity (compressed) air to the 2BTech NO monitor will result in erroneous readings. Span gas should be humidified using a 24" length of Naphion tubing attached to the inlet during calibration checks.

Maintenance

Inlet filters are used on all gas monitors to remove moisture and particles from the incoming air. This is particularly important for the NO monitor. The line filter installed between the ceiling duct and the glass manifold should be inspected periodically and the replaced if dirty or clogged. The frequency will depend on the concentration and nature of aerosols as well as ambient humidity. Operating in extremely dusty conditions such as on unpaved roads or in areas with high concentrations of combustion aerosols will require more frequent filter changes.

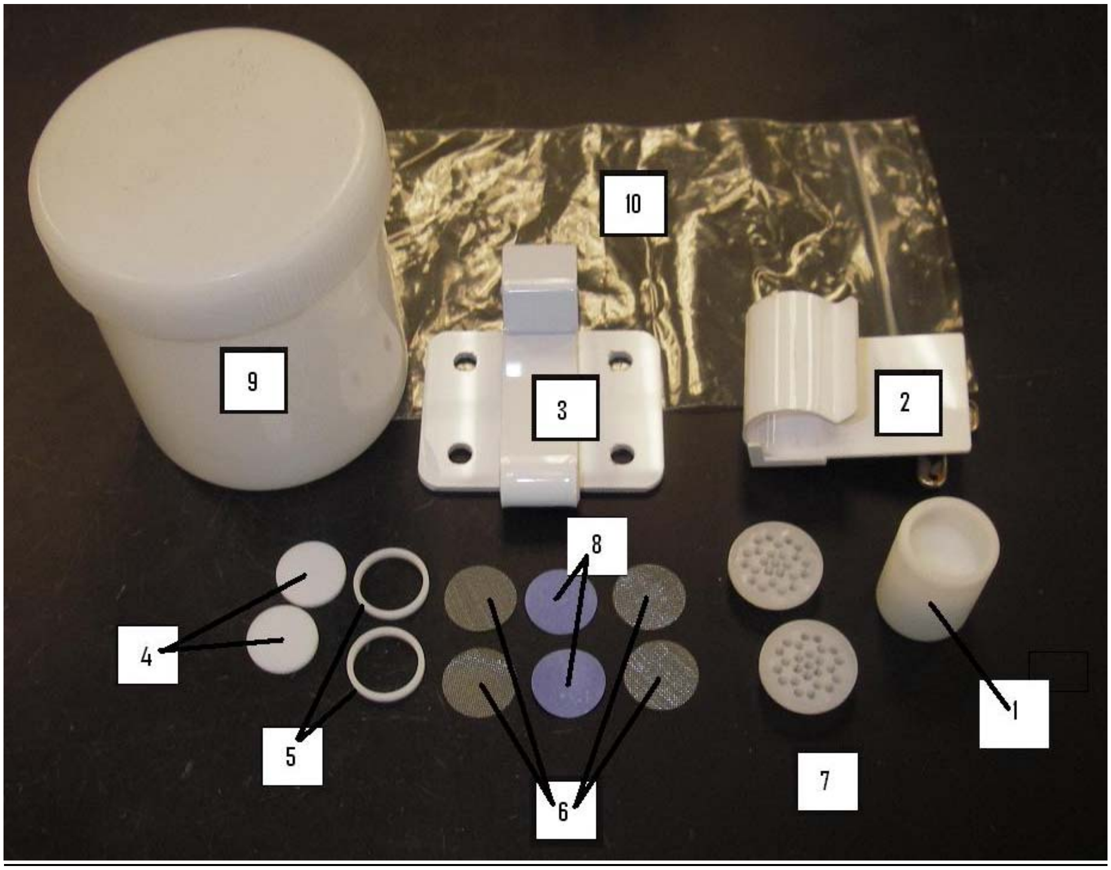
The ppbRAE and DustTrak have internal filters that should be checked and replaced periodically. See the manuals for details.

Although the concentrations reported by the continuous monitoring instruments are not a function of the air flow rate, the inlet flows should be checked periodically with a reference meter to assure that they are within the specified range. Significant variations in flow rate are usually symptomatic of internal leaks or pump failure. The entire inlet system should also be checked for leaks by comparing the total flow at the inlet manifold to the sum of the individual instrument flows.

Although all instruments can be operated on line power, it may be desirable at times to reduce power use by running on internal batteries. The batteries also provide backup in the event of a power outage. The DustTrak and ppbRAE have rechargeable internal batteries, but the CPC and weather station use replaceable alkaline or NIMH AA batteries.

Appendix D

Standard Operating Procedure for Ogawa Passive Monitors



Equipment List - Ogawa Passive Sampler

ID #	Description	Quantity
1	Sampler Housing	1
2	Sampler Holder	1
3	Mounting Bracket	1
4	Solid Pad	2
5	Pad Retaining Ring	2
6	Stainless Screen	4
7	Diffuser End Cap	2
8	Pre-Coated Collection Pad	2
9	Shelter/Vial	1
10	Sample Bag	1

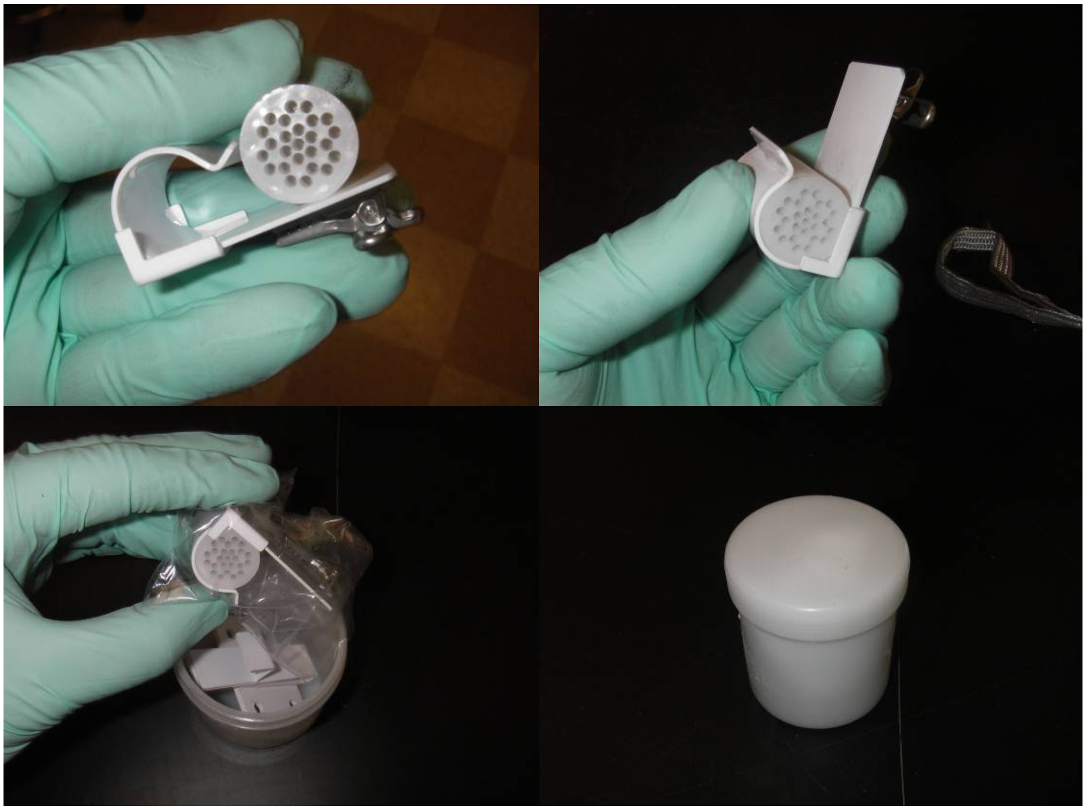
The Ogawa *Pre-Coated Collection Pads* come in a few varieties depending on the application. Specific information on the correct parts for each monitoring application can be found at the company website (www.ogawausa.com).

Assembly of the Ogawa Passive Sampler should be completed in a clean, indoor environment devoid of dust and then transported to the sampling site. Dirt and oils from your skin can affect the Ogawa Sampler if contact is made with the *collection pads* so gloves and/or a sterile pair of tweezers should be used for assembly.

To assemble, remove the Ogawa *Sampler Housing* from the *Sampler Holder* and the *Opaque Vial*. Remove the *Diffuser End Cap* from one side of the *Sampler Housing* and remove the two stainless screens behind the *Diffuser End Cap*. The *Solid Pad* and *Pad Retaining Ring* should be visible inside of the sampler and should not be removed. If they come loose, just insert the *Solid Pad* into the *Sampler Housing* first and then slide the *Pad Retaining Ring* above it to hold it in place.

The *Pre-Coated Collection Pads* will come sealed in a vial and a resealable aluminum envelope. Remove one *Collection Pad* from the vial with the tweezers and place it in between the two *Stainless Screens*. Insert this assembly into the S*sampler Housing* taking care that it sits level on top of the *Retaining Ring*. The fit should be loose. If it feels snug, then remove and try again. Then, snap the *Diffusion End Cap* into place. Repeat this process on the other end of the *Sampler Housing* if two measurements are being conducted. See below.

After assembling the *Sampler Housing*, insert it into the *Sampler Holder* as shown below. The assembled sampler should now be sealed into the *Sample Bag*, removing as much as air as possible to prevent contamination. Place the bag inside the *Opaque Vial* with the *Mounting Bracket*, screw on the lid, and transport to the sampling site. See Below.



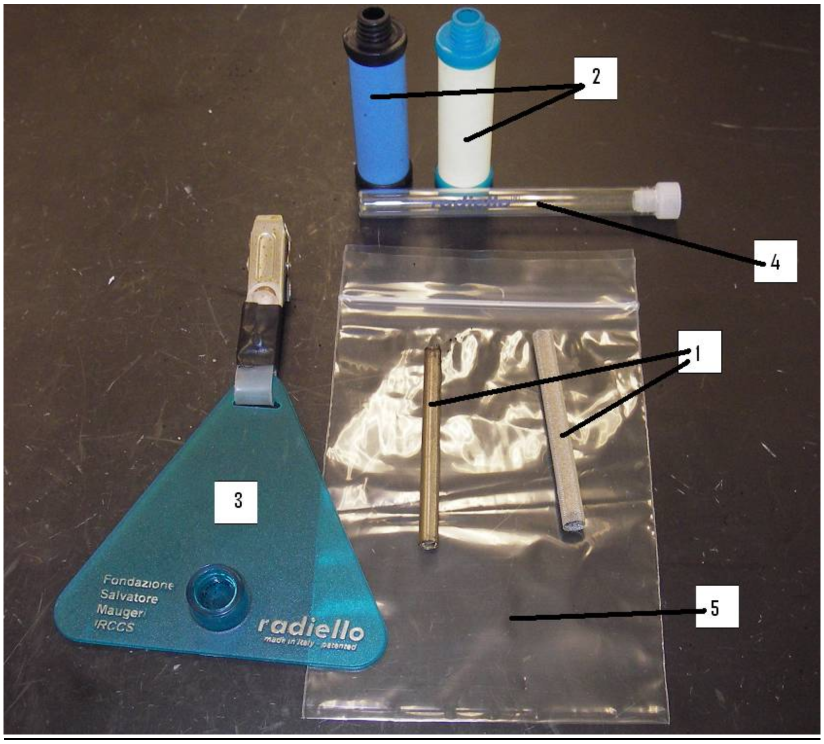
At the sampling site, remove the Ogawa Sampler from the *Opaque Vial* and *Sample Bag*. Attach the sampler to clothing for personal exposure or to the *Mounting Bracket* for ambient monitoring as shown below.

The *Mounting Bracket* can be easily attached to objects such as fences and poles with zip ties. If sampling outdoors, the *Opaque Vial* should be used as a shelter. It can easily be slipped over the *Mounting Bracket* and sampler as shown below. Keep the *Opaque Vial* lid and sealed *Sample Bag* for later. Note time and date when sampling begins.

Make sure to note the time and date when sampling ends. After sampling, remove the *Opaque Vial* and sampler from the *Mounting Bracket*. Seal the Ogawa Sampler inside the *Sample Bag* removing as much air as possible and store the *Sample Bag* inside the capped *Opaque Vial*. The Exposed Sampler inside the *Opaque Vial* should be stored in a freezer or in a cooler on blue ice for transportation to a laboratory for analysis.

Appendix E

Standard Operating Procedure for Radiello Passive Monitors



Equipment List - Radiello Passive Sampler

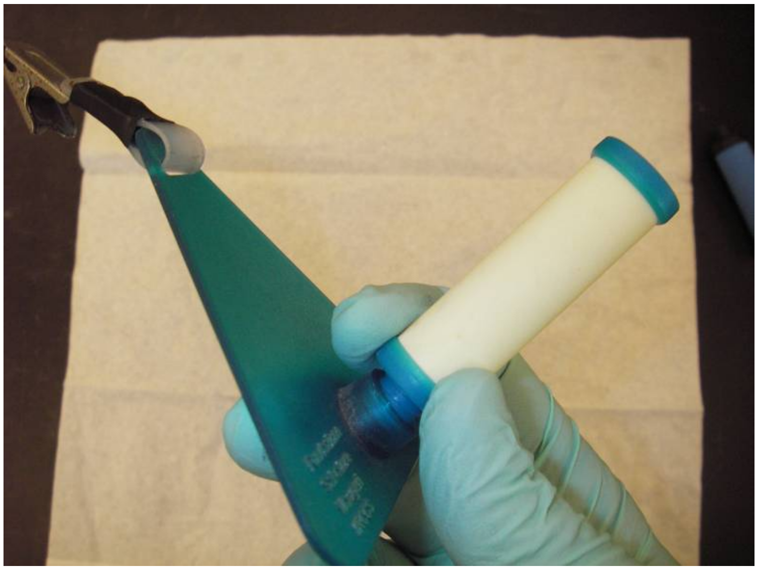
ID #	Description	Quantity
1	Radiello Adsorbing Cartridge	1
2	Diffusive Body	1
3	Supporting Plate	1
4	Glass Vial	1
5	Sample Bag	1

The *Radiello Adsorbing Cartridges* and *Diffusive Bodies* come in a few varieties depending on the application. Specific information on the correct parts for each monitoring application can be found at the company website (www.radiello.com).

Assembly of the Radiello Passive Sampler is simple and should be completed at the location where sampling will take place. Dirt and oils from your skin can affect the Radiello Sampler if contact is made with the porous midsections of the *Diffusive Body* or with the *Adsorbing Cartridge* so gloves should be worn during assembly.

The *Adsorbing Cartridge* will arrive sealed in the *Glass Vial* and may be wrapped in plastic in addition. Remove the plastic wrapper, if necessary, and the cap from the *Glass Vial*. Slide the *Adsorbing Cartridge* into the *Diffusive Body* as shown below. Try to handle the *Diffusive Body* from the hard plastic ends. If the opening of the *Glass Vial* is mated with the opening on the *Diffusive Body*, transfer can be made without touching the *Adsorbing Cartridge*. The *Glass Vial* will be used later to store the exposed cartridge so re-cap it to prevent contamination.

Next, screw the *Diffusive Body* into the *Supporting Plate* as shown below. Be careful, to ensure the threads are aligned properly before tightening. The fit should be snug, but do not over-tighten as this can result in breaking the *Supporting Plate* or the *Diffusive body*. Screw the assembly together upside-down to ensure that the *Adsorbing Cartridge* is not protruding from the end of the *Diffusive Body* during tightening.



Assembly of the Radiello Passive Sampler is now complete. Use the metal clip to attach the sampler to clothing for personal exposure monitoring or to another object for ambient monitoring. If monitoring is being done outside where the sampler may be exposed to rain, care must be taken to attach the sampler under an overhanging feature. Plastic shelters can be fashioned easily from disposable cups or other containers but make sure not to inhibit airflow from reaching the sampler. Note start time and date. See below.

After exposure, note end time and date. Sampler should be taken down by unscrewing the D*iffusive Body* from the *Supporting Plate*. Slide exposed *Adsorbing Cartridge* back into *Glass Vial* by mating the two openings. Recap the *Glass Vial* containing the *Adsorbing Cartridge* and seal it into the *Sample Bag*. Remove as much air as possible from the *Sample Bag* to prevent contamination. Place the *Sample Bag* into a freezer or cooler containing blue ice for transportation to a laboratory for analysis.