Community Assessment

Spokane Air Toxic Study 2005
Final Data Summary

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Abstract

An EPA program was conducted in 2005 that provided airborne toxic measurements at four different locations in Spokane, WA. The hope was that air toxic data obtained in this community assessment program could be used to characterize exposure levels, better understand temporal and spatial trends, as well as, provide measurement data for air quality model evaluation. Samples were collected over the course of the year on a one-in-six day schedule. The targeted airborne toxic compounds include VOCs, carbonyls and metals contained in PM_{10} particulate matter. Ambient concentration levels have been tabulated and evaluated for 15 of EPA's "core" urban air toxics. Spatial and temporal patterns of the air toxics are described in this report along with annual average concentrations. In addition, an examination of source-receptor relationships, modeled concentrations for some air toxics are compared to measured levels, and an exposure assessment using EPA's HAPEM model are included in this document.

Acknowledgements

The Washington State University group wishes to thank John Williamson for technical assistance and the Washington Department of Ecology for financial support of this work. In addition, we greatly appreciate the sampling help provided by Ron Edgar and his colleagues at the Spokane County Air Pollution Control Authority.

Executive Summary

An ambient air sampling study designed to assess airborne toxics was conducted in Spokane, WA during the 2005 calendar year. The goal of this community assessment program was to provide data that could be used to characterize human exposure levels to air toxics, better understand temporal and spatial trends of the air toxics, as well as, provide measurement data for air quality model evaluation. Samples were collected over the course of the year at four sites on a one-in-six day schedule. The targeted airborne toxic compounds include VOCs, carbonyls and metals contained in PM_{10}. Ambient concentration levels have been tabulated and evaluated for EPA's fifteen "core" urban air toxics.

The highest annual average ambient concentrations of most air toxics were observed at the Crown Zellerbach (CZ) site. CZ is centrally located in a commercial/industrial zone. The exception was acetaldehyde and formaldehyde, which exhibited their maximum annual averages at the most northeasterly School District (SD) and Orchard School (OC) sites. Lowest annual average air toxic levels were recorded at the most westerly Health District (HD) site. On a temporal basis, many air toxics exhibited elevated levels in the wintertime and lower ambient concentrations during the summer months. Summertime concentrations were larger for the carbonyls due to more favorable secondary formation during this period of the year. Tetrachloroethylene exhibited sporadic peaks throughout the year while the other chlorinated species (CCl_4, $CHCl_3$, and TCE) remained low in all seasons. Annual average concentrations for Spokane "core" air toxics in 2005 were as follows: benzene 0.24 ppbv; 1,3-butadiene 0.05 ppbv: carbontetrachloride 0.11 ppbv; chloroform 0.01 ppbv; tetrachloroethylene 0.04 ppbv; trichloroethylene 0.02 ppbv; acetaldehyde 1.4 ppbv; formaldehyde 2.0 ppbv; arsenic 0.9 ng/m^3; beryllium 0.02 ng/m^3;

cadmium 0.2 ng/m^3; chromium 4.8 ng/m^3; lead 4.9 ng/m^3; manganese 19 ng/m^3; nickel 5.6 ng/m^3; and, PM_{10} 24.5 ug/m^3. These levels are similar to those reported in other U.S. cities.

We examined source-receptor relationships for the air toxics using several different techniques. Strong correlations, suggesting a common source, existed between benzene and 1,3-butadiene at all four sites. The same was true for acetaldehyde and formaldehyde. With the trace metals, significant correlations between arsenic, cadmium and lead inferred a common source. There was a very high correlation between chromium and nickel in PM_{10} collected at the CZ site indicating a nearby source of these trace metals.

An analysis of lead isotopes (^{206}Pb, ^{207}Pb, ^{208}Pb) measured in PM_{10} provided information about lead sources in Spokane. The lead isotope ratios varied depending on season and meteorology. On warm, windy summer days, isotope measurements showed most of the lead in PM_{10} to originate from crustal sources, while during low ventilation periods in the winter, combustion processes contributed most of the airborne lead. On an annual average basis, the lead isotope ratios measured at the CZ site implied about a 50:50 mix of crustal and combustion sources for lead in Spokane's particulate matter.

Positive matrix factorization (PMF) on the combined Spokane data set yielded five factors. There are two factors that have high aluminum and/or iron content that relate to crustal sources. Two other factors lack the crustal tracers and are rich in combustion related species (benzene, arsenic, cadmium and lead). The fifth factor contains chromium and nickel nearly exclusively and represents industrial emissions near the CZ site. The PMF analysis indicated roughly a 50:50 split annually in the crustal and combustion sources of PM_{10} in Spokane.

In order to pinpoint specific VOC sources in the neighborhoods surrounding each of the four Spokane urban sites, we outfitted a mobile van with real-time sensors that allowed emission plumes to be easily identified. A Proton Reaction Transfer Mass Spectrometer (PTR-MS) was used to locate emission sources of benzene, acetaldehyde, several low molecular weight oxygenated solvents and certain BTEX (toluene, xylenes, etc) species. For example, plumes emanating from auto repair shops included high concentrations of acetone and xylenes. A large source of styrene was recorded in the vicinity of Spokane's Industrial Park east of the city. Particle bound polycyclic aromatic hydrocarbon (PPAH) concentrations and surface areas were measured along Spokane's roadways using sensors in the mobile van. Background PPAH levels in Spokane were on the order of 7 ng/m^3 compared to an average concentration of 81 ng/m^3 measured on streets in Spokane. Chase experiments with the mobile unit clearly showed diesel vehicles to be a large source of PPAH. There was good agreement between PPAH concentration vs. surface area relationships for Spokane diesel vehicles and controlled diesel-chamber experiments. Fixed location sampling with the mobile van at the SD site during a 24-hr sampling day provided a temporal record of air toxic concentrations that can be used to better understand diurnal pollutant behavior.

Air quality in Spokane is predicted daily by Washington State University using the AIRPACT-3 model system. This model estimates benzene, 1,3-butadiene, acetaldehyde, formaldehyde and PM_{10} hourly concentrations in Spokane. The air quality model has 12 km resolution, which provided one cell that encompassed all four sites. Modeled concentrations for the air toxics listed above were compared with measured levels recorded on five sampling days in December 2005. This was a useful exercise in that it provided some insight into model shortcomings. For example, the model over predicts benzene and an evaluation of the reason for the difference indicated a problem with the model's benzene emission inventory. In a similar vein, the model greatly under predicted the carbonyl concentrations. The reason for this is most likely unrealistically low boundary/initial conditions employed for acetaldehyde and formaldehyde in the model.

A final task in this community assessment program was to evaluate citizen exposure levels to air toxics in neighborhoods surrounding the four sampling sites. This was accomplished in two ways. First we conducted a simple screening test to see which of the air toxics exceeded a screening value based on cancer and/or non-cancer risk factors. This showed that of the 15 "core" air toxics all but chloroform, beryllium and lead exceeded the chronic screening value (CSV). In order to establish more quantitative exposure levels, we ran EPA's Hazardous Air Pollutant Exposure Model (HAPEM5) using air quality data gather at each of the four sites. Modeled exposures for cadmium and nickel were below the CSV except for nickel in the neighborhood surrounding the CZ site. Thus, benzene, 1,3-butadiene, carbon tetrachloride, tetrachloroethylene, trichloroethylene, acetaldehyde, formaldehyde, arsenic, chromium, and manganese exceeded the health screening value in Spokane neighborhoods.

In summary, a very successful community assessment study was conducted in Spokane that has provided a wealth of information about air toxic levels, sources and exposures in the region.

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1.0 Introduction

Hazardous air pollutants (HAPs) that are deemed to adversely affect human health and welfare are regulated under the Clean Air Act. Currently, there are 188 HAPs that are designated for control. However, relatively little is known about human exposure to these toxic materials in the ambient environment. As a result, the U.S. EPA has developed a national air toxics program with the objective being to characterize the impacts of HAPs on public health and the environment. Ambient measurement data are needed to estimate human and environmental exposures to toxics. Several cities/regions across the U.S. are currently determining or soon will be measuring the levels of toxic materials in their environs.

At present, it is not feasible to measure all 188 of the HAPs that require control by the CAA. Consequently, EPA has identified a subset comprised of 33 HAPs that should receive the greatest attention. The 33 compounds fall into four chemical categories: volatile organic compounds (VOCs); carbonyl compounds (aldehydes); semi-volatile organic compounds (SVOCs); and metals. Collection and analytical methodologies are constantly evolving for these urban HAPs. At present, several of the HAPs lack approved ambient collection/analytical techniques. The SVOCs are troublesome because they can exist both as gases and as aerosols in the troposphere. Some of the less stable urban HAPs such as acrolein and ethylene oxide are easily lost during collection and storage prior to analysis. This has lead to an even shorter list of toxic compounds that can be reliably measured in the urban environment. EPA has categorized these as urban air toxic (UAT)”core” species. There are nine VOCs, two carbonyls, and seven metals listed as “core” toxics (Table 1).

In this manuscript, we report ambient concentration data for the VOC, carbonyl and metal compounds listed in Table 1. In addition, some other related VOCs (e.g., BTEX compounds) were measured and are reported herein. UAT sampling was initiated in January of 2005 at four new sites in Spokane. The sampling sites were in three residential neighborhoods and one commercial-industrial area. Sampling continued on an every sixth day basis for the remainder of 2005. This data set is being used to assess baseline air toxic concentrations in Spokane, source-receptor relationships, air quality model evaluations and citizen exposure levels. Each of these assessments is addressed in this report.

Table 1. **Urban air toxic "core" species.**

VOCs	Carbonyls	Metals
Benzene	Acetaldehyde	Arsenic
1,3-Butadiene	Formaldehyde	Beryllium
Carbon tetrachloride		Cadmium
Chloroform		Chromium
Dichloromethane		Lead
1,2-Dichloropropane		Manganese
Tetrachloroethylene		Nickel
Trichloroethylene		
Vinyl chloride		

2.0 Experimental

2.1 Analytical Methods Summary

Twenty-four hour integrated ambient air samples were collected at a frequency of every six days at all air toxics monitoring sites. Ambient air samples collected at each of the sites in stainless steel canisters were analyzed for VOCs using Compendium Method TO-14A (GC-FID/ECD). Ambient air samples collected on DNPH-coated silica cartridges at each site were analyzed for carbonyl compounds using Compendium Method TO-11A (HPLC). The VOC and carbonyl analyses were performed by Washington State University (Laboratory for Atmospheric Research). Commercial ZonTech instruments were employed for VOC and carbonyl field sample collections at all of the sites. The UAT "core" metals data were obtained from quartz fiber PM_{10} filters and analyzed by RJ Lee Group, Inc. in Pasco, WA using ICP-MS (Compendium Method IO-3.5). A more detailed description of the analytical procedures follows.

2.2 Sampling Sites

Sampling locations employed in this study were selected to reflect potential "community-oriented" population exposure. Samplers represented average concentrations within a 0.5 to 4.0km^2 area, which is termed "neighborhood-scale". Neighborhood-scale measurements provide population exposures that can be used to estimate potential long-term risk since they are thought to reflect units of typical urban population exposures. All sampling stations met U.S. EPA's guidelines for set back distances, inlet heights, and other siting considerations. This population-oriented approach is analogous to the core network for $PM_{2.5}$ and the National Air Monitoring Station (NAMS) trend network for the criteria pollutants. The four air toxics monitoring stations were sited to provide air quality information relative to mobile, industrial, wood smoke, and other area sources. Stations were located in distinctly different sub-regions within the urban area, so that spatial variability of air toxics concentrations could be characterized. The four sites (see Figure 1) were located as follows:

- The **Health District (HD)** site was located on the roof of the Spokane County Health District office building on College Avenue. Immediately to the south is the Spokane River and beyond the river Spokane's main urban core. There are residential neighborhoods to the west and north. The area to the east of the HD site is occupied by commercial businesses.
- **Crown Zellerbach (CZ)** is best classified as a commercial-industrial site. Air toxic sampling instrumentation was housed on the roof of a multi-story building. This site is part of EPA's $PM_{2.5}$ speciation network. The site is on Ferry Avenue and is highly impacted by mobile sources, rail transportation and industrial emissions.
- The **School District (SD)** sampling site was located in the Hillyard district of northeast Spokane. Samples were collected on the roof of a School District #81 warehouse building just off of Garland Avenue. The vicinity around this site consisted of commercial activities interspersed in residential neighborhoods.
- The most easterly sampling site was located at the **Orchards School (OC)** on Buckeye Avenue. This was primarily a residential neighborhood not far from the Felts Field airport.

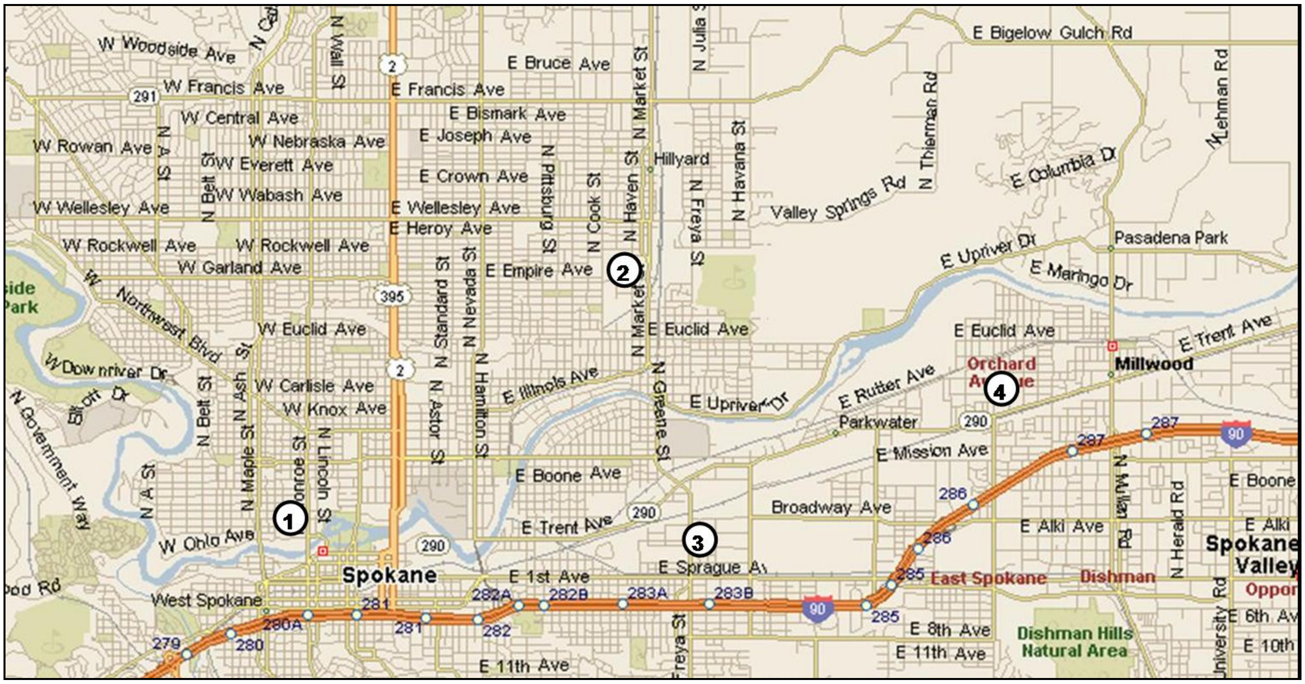


Figure 1. **Map showing Spokane sites (1=HD, 2=SD, 3=CZ, 4=OC)**

2.3 VOC Sampling

The XonTech 910A samplers were programmed to fill a 6-liter passivated, stainless steel canister to about 1.5 atm. (~ 10 L) over the collection period. At the end of the 24-hour collection period, sample canisters were removed from the collection system and shipped to Pullman WA for VOC analysis

2.4 Carbonyl Sampling

XonTech 925PC carbonyl samplers were employed for determination of formaldehyde and acetaldehyde. A measured amount of air was passed through a silica gel cartridge impregnated with 2, 4-dinitrophenyl hydrazine (DNPH). The cartridges were sealed and shipped to Pullman for analysis. An ozone scrubber was attached to the inlet line.

2.5 Particulate Sampling

Twenty-four hour integrated ambient air samples were collected at a frequency of every six days at each of the four Spokane sites. Fifty-eight to 60 ambient air samples were obtained at each site between January and December 2005. Airborne PM_{10} samples were collected using high volume samplers. Quartz filters were provided by the Spokane County Air Pollution Control group. They did the filter conditioning and determined the particulate mass gravimetrically.

2.6 VOC Analysis

Hewlett Packard 5890 and 6890 gas chromatographs were used for VOC analyses. DB-1 fused silica capillary columns (J & W Scientific) were employed to resolve VOCs in the C_3-C_{12} molecular weight range. The HP 5890 was equipped with a flame ionization detector for determination of the true hydrocarbons. Halocarbons were analyzed using the HP 6890 GC with electron capture detector. In both systems, the normal carrier gas flow system was modified to include a freeze-out trap for concentrating organics in the ambient air sample. Nitrogen at 1 $cm^3\ min^{-1}$ was used as the carrier gas with the DB-1 fused silica capillary columns. Optimum results were obtained by temperature programming the column ovens from -50 to 150 °C at 4 °C min^{-1}.

Air from the sample canister was drawn through the cryogenic trap into an evacuated cylinder. The sample volume was determined by measuring the pressure change in the cylinder. Normally, 500 ml of air was passed through the freeze-out trap, which was maintained at -186 °C (liquid oxygen). The trap itself consisted of a 3.18 mm x 15.24 cm stainless steel tube containing 60-80 mesh glass beads. This trap was attached to the gas chromatograph via a mini-volume gas-sampling valve (Valco Inst.).

Peak identities for the pure hydrocarbons (e.g. benzene, 1,3-butadiene, etc) were based on comparison of retention times and mass spectra with known standards. The concentration of the hydrocarbons was determined by comparing the instrument response for each peak to that recorded for a known concentration of 2,2-dimethylbutane. The concentration of the 2,2-dimethylbutane standard was assigned through comparison with a NIST purchased propane SRM. Quantitation of the halogenated hydrocarbons was based on a comparison of peak area responses to a certified TO-14 standard purchased from a commercial supplier. Each chromatogram was visually examined to ensure data quality.

2.7 Carbonyl Analysis

Exposed DNPH cartridges were eluted with acetonitrile (ACN), the elutant volume was measured, and the hydrazones in the eluted samples were quantified by a Hewlett Packard 1090 series II High Performance Liquid Chromatograph with a diode array detector (DAD) operated at 360 nm. Peak separation was accomplished with a 10 cm OD-MPS reverse phase column (Supelco) with a gradient elution ranging from 50:50 to 30:70 H_2O:ACN over the period from 5 to 17minutes. A 20 μL sample loop was employed and the total solvent flow rate was 0.8 mL min^{-1}. Qualitative identification of the hydrazones was performed by matching the retention times with those of known standards. For quantitation, pure carbonyl hydrazone derivatives were prepared or purchased. High concentration master standards were prepared for each carbonyl of interest and these were then used to prepare a set of working standards ranging from 0.2 to 5 mg mL^{-1}. A running calibration for relating peak areas to hydrazone concentrations was formed by taking the running mean of the standard analyses (area counts for each analyte) over the time period the analyses were conducted. Ambient carbonyl concentrations were calculated from the recorded peak area, eluant mass, and air volume sampled.

2.8 PM Chemical Analysis

The EPA's Urban Air Toxics "core" metals were determined using Compendium Method IO-3.5. The "core" metals include arsenic, beryllium, cadmium, chromium, lead, manganese and nickel. Iron and aluminum are not classified as air toxics but were measured to help with source apportionment of the PM_{10} . Iron and aluminum are not classed as air toxics but were measured to help with source apportionment of the PM_{10}. Microwave extraction was utilized to get the metals off the filter particulate and into solution for analysis. The CEM Corporation MARS 5 microwave oven employed in this study was equipped with both temperature and pressure regulating features. The digestion vessels containing the samples were heated to 160°C over 10 minutes followed by a 15-minute hold at that temperature. After cooling, 10 mL of reagent water was added to the digestion vessel and the sample was vortexed for 30-45 seconds. The entire contents of the vessel were then transferred to a 50 mL tube, centrifuged, and filtered prior to ICP-MS analysis.

A Perkin-Elmer SCIEX ELAN 6100 ICP-MS was used for the analysis of filter extracts**.** Table 2 shows the isotopes monitored and equations that were used to calculate metals concentrations. Method detection limits (MDLs) for the determination of metals in ambient particulate matter were determined using filter blank solutions run through the entire analytical method and analyzed using ICP-MS in accordance with 40 CFR Part 136 Appendix B. Ten replicates were spiked, subjected to the entire analytical method and analyzed. The MDLs were calculated using the following equation:

MDL=(t)*(S)

Where: t = Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom (t = 2.764 for eleven replicates).

S = standard deviation (n-1 degrees of freedom) of the replicate analyses.

Table 2. Isotopes Monitored and Equations Used for Isotope Correction.

Analyte	Isotopes Monitored	Correction Equations
Beryllium	9	
Chromium	52, 54	
Manganese	55	
Nickel	60	
Arsenic	75	As 75=As 75-3.127*[ArCl 77-(0.815*Se 82)]
Cadmium	111	Cd 111=Cd 111-1.073*[MoO 108-(0.712*Pd 106)]
	114	Cd 114=Cd 114-0.026826*Sn 118
Lead	208	Pb 208=Pb 208+1*Pb 206+1*Pb 207
Iron	57	
Aluminum	27	

3.0 Baseline Air Toxic Concentrations in Spokane

Sample recoveries were good at all four of the Spokane area sampling sites resulting in 57 to 60 samples each and approximately 240 samples in which to examine temporal and spatial air toxic behavior in Spokane. Of the UAT "core" VOCs, all but 1,2-dichloropropane and vinyl chloride consistently exhibited measurable concentrations. Chromatographic separation of dichloromethane proved to be difficult and as a result it won't be reported at this time.

This section contains statistical summaries of air toxics data collected in Spokane. When reporting statistics in this manuscript, we have chosen to treat concentrations below the MDL (Table 3) as valid, rather than assigning a value such as one-half the MDL. Using the measured value vs. one-half the MDL has little effect on the statistics reported.

Table 3. Minimum Detection Levels for Air Toxics in the Spokane Study

	ppbv		ng/m^3
Benzene	0.01	Arsenic	0.008
1,3-Butadiene	0.02	Beryllium	0.002
CCl_4	0.01	Cadmium	0.001
$CHCl_3$	0.02	Chromium	0.139
PCE	0.01	Lead	0.069
TCE	0.01	Manganese	0.091
Acetaldehyde	0.01	Nickel	0.084
Formaldehyde	0.02		

In succeeding sections (3.1 through 3.16) data for each "core" air toxic and PM_{10} mass is presented in a series of tables and figures. These provide statistical, spatial, and temporal summaries.

3.1 Benzene

Benzene is used as an industrial solvent as well as being a component of gasoline and auto exhaust. In Spokane, mobile emissions are expected to be the primary source of benzene. The benzene annual mean for all samples collected in Spokane was 0.24 ppbv. The maximum 24-hr average concentration recorded was 1.94 ppbv (Table 4). The max value was recorded at the industrial CZ site and it had the highest annual mean (0.30 ppbv). Benzene concentrations were relatively high and quite variable during the colder months (Figure 3 and Figure 4). Ambient benzene levels were generally lowest during the summer months when meteorological mixing was strongest.

Table 4. Benzene statistics determined at Spokane area sites in 2005.

Site	Mean (ppbv)	95% CI	Median (ppbv)	Min (ppbv)	Max (ppbv)	n
HD	0.17	0.04	0.10	0.03	0.93	61
CZ	0.30	0.09	0.14	0.04	1.94	61
SD	0.24	0.07	0.16	0.04	0.99	57
OC	0.23	0.06	0.14	0.04	1.14	60

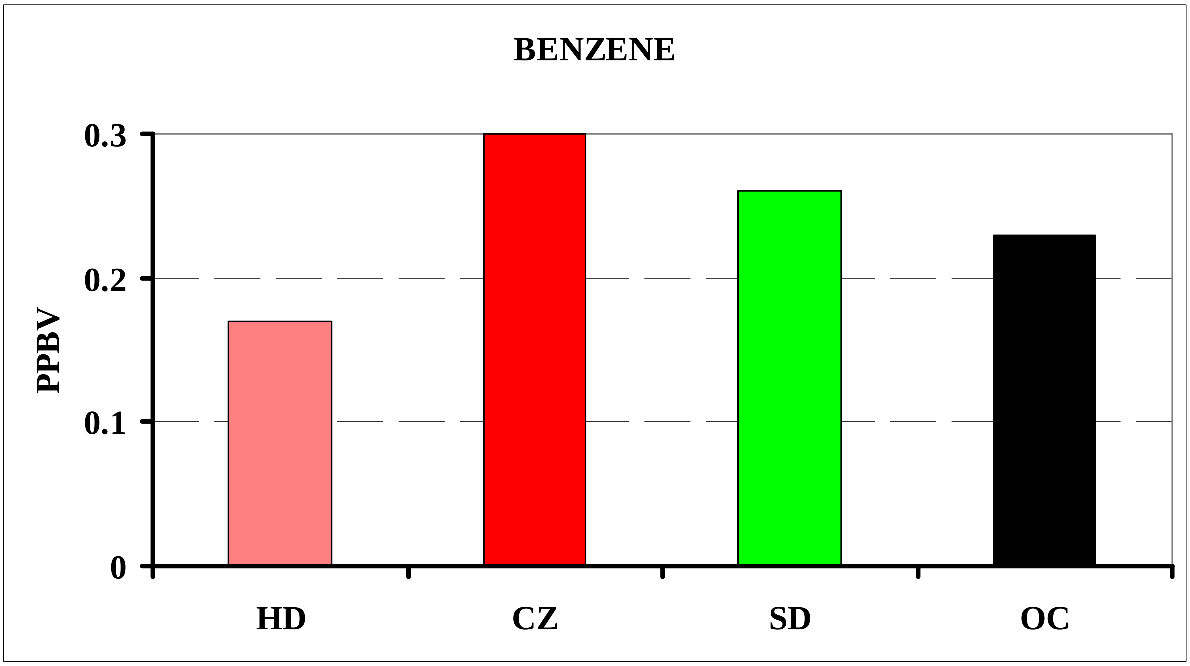


Figure 2. Annual average benzene concentrations at the four Spokane sites in 2005.

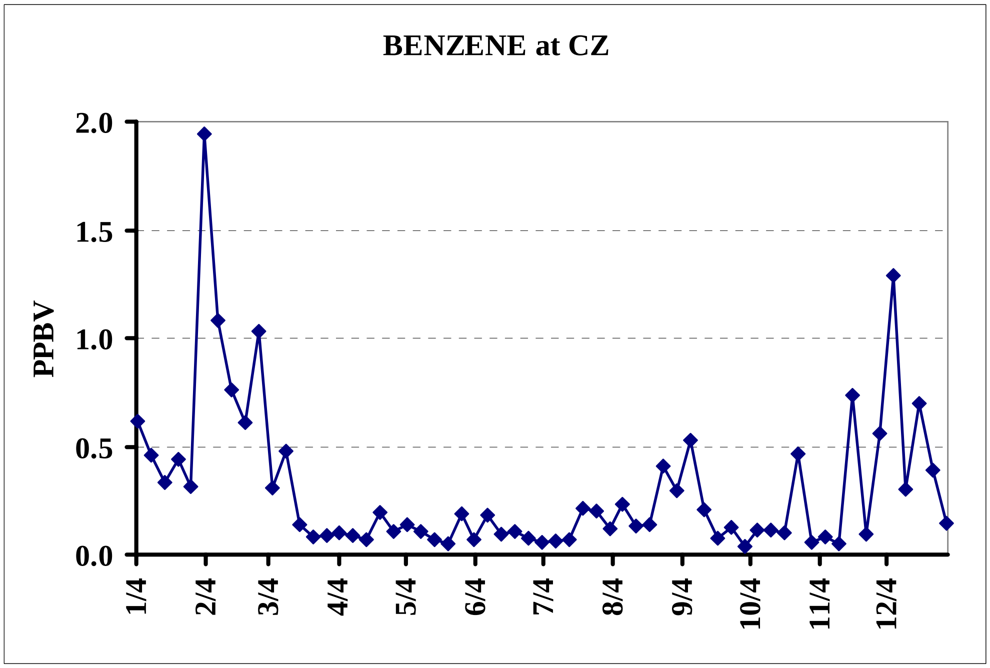


Figure 3. Benzene temporal behavior at the Crown Zellerbach site

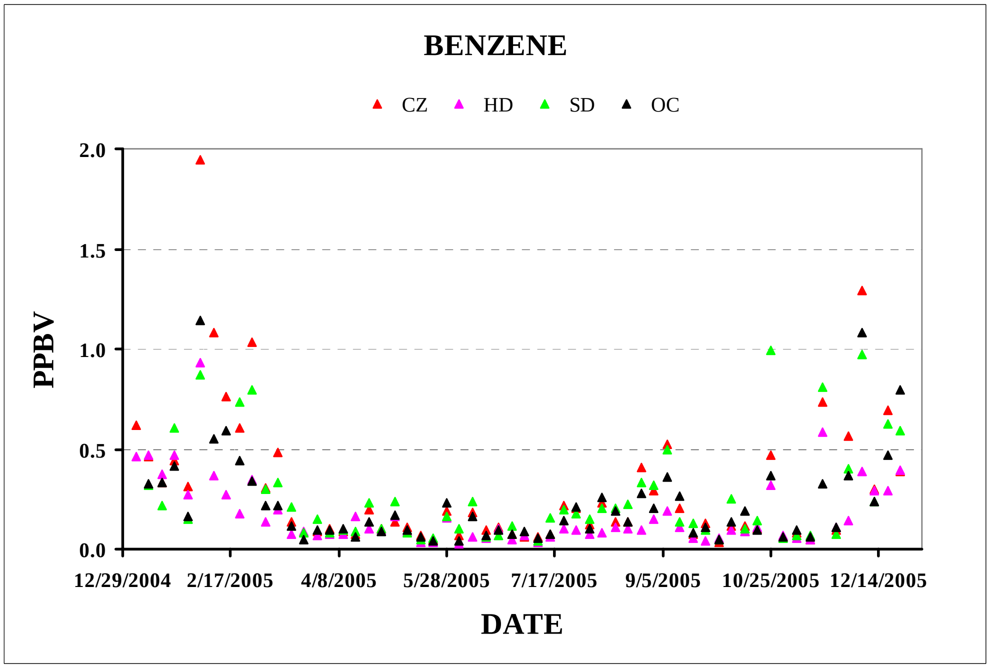


Figure 4. Benzene temporal behavior at the four Spokane area sites in 2005

3.2 1,3-Butadiene

1,3-Butadiene is used in rubber manufacturing processes and is emitted from combustion sources. The main source of 1,3-butadiene in Spokane is expected to be mobile source emissions. This is reflected by a fairly uniform annual mean of 0.05 ppbv throughout the Spokane area. As with benzene, the highest annual mean was recorded at the CZ site (Table 5). The 1,3-butadiene temporal pattern (Figure 6) is very similar to benzene with highest levels during the winter months and lower levels in the summer.

Table 5. 1,3-Butadiene statistics determined at Spokane area sites in 2005.

Site	Mean (ppbv)	95% CI	Median (ppbv)	Min (ppbv)	Max (ppbv)	n
HD	0.03	0.01	0.02	0.01	0.12	61
CZ	0.06	0.02	0.03	0.01	0.39	61
SD	0.05	0.01	0.03	0.01	0.20	57
OC	0.04	0.01	0.02	0.01	0.22	60

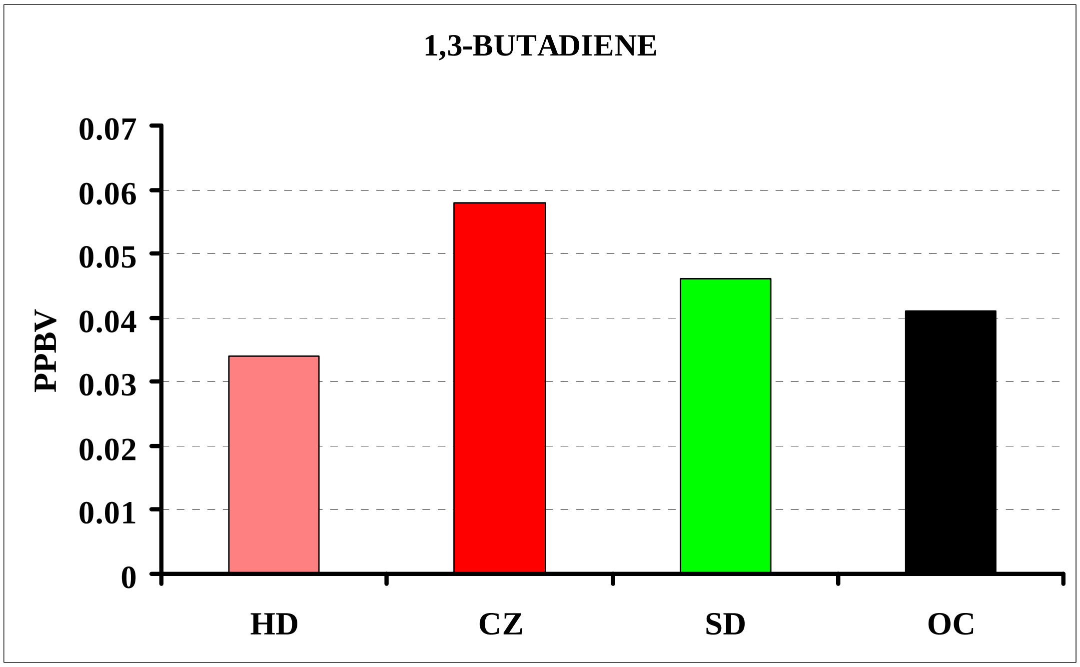


Figure 5. Annual average 1,3-butadiene concentrations at the four Spokane sites in 2005.

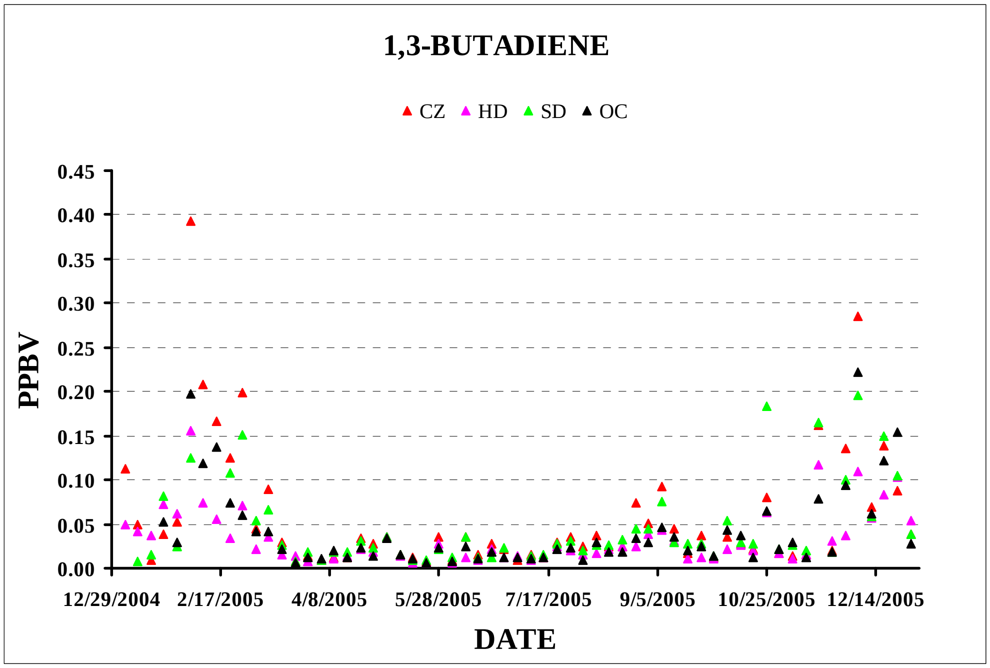


Figure 6. 1,3-Butadiene temporal behavior at the four Spokane area sites

3.3 Carbontetrachloride

Carbontetrachloride, because of its long lifetime in the troposphere, is a serious threat to stratospheric ozone depletion. Consequently, its use has been completely curtailed. Over the past several years, global ambient concentrations have stabilized at about 0.10 ppbv. Carbontetrachloride concentrations recorded during the 2005 study in Spokane were temporally and spatially constant at this global background concentration.

3.4 Chloroform

Annual average chloroform concentrations were very similar at the four Spokane area sites with means of about 0.01 ppbv (Table 6). This is very near the continental background level, which implies that chloroform sources in Spokane are minimal. An exception can be seen in the OC temporal behavior (Figure 8) where a late summer enhancement in ambient chloroform levels is evident.

Table 6. Chloroform statistics determined at Spokane area sites in 2005.

Site	Mean (ppbv)	95% CI	Median (ppbv)	Min (ppbv)	Max (ppbv)	n
HD	0.01	0.001	0.01	0.01	0.03	61
CZ	0.01	0.002	0.01	0.01	0.07	61
SD	0.01	0.001	0.01	0.01	0.02	57
OC	0.01	0.001	0.01	0.01	0.04	60

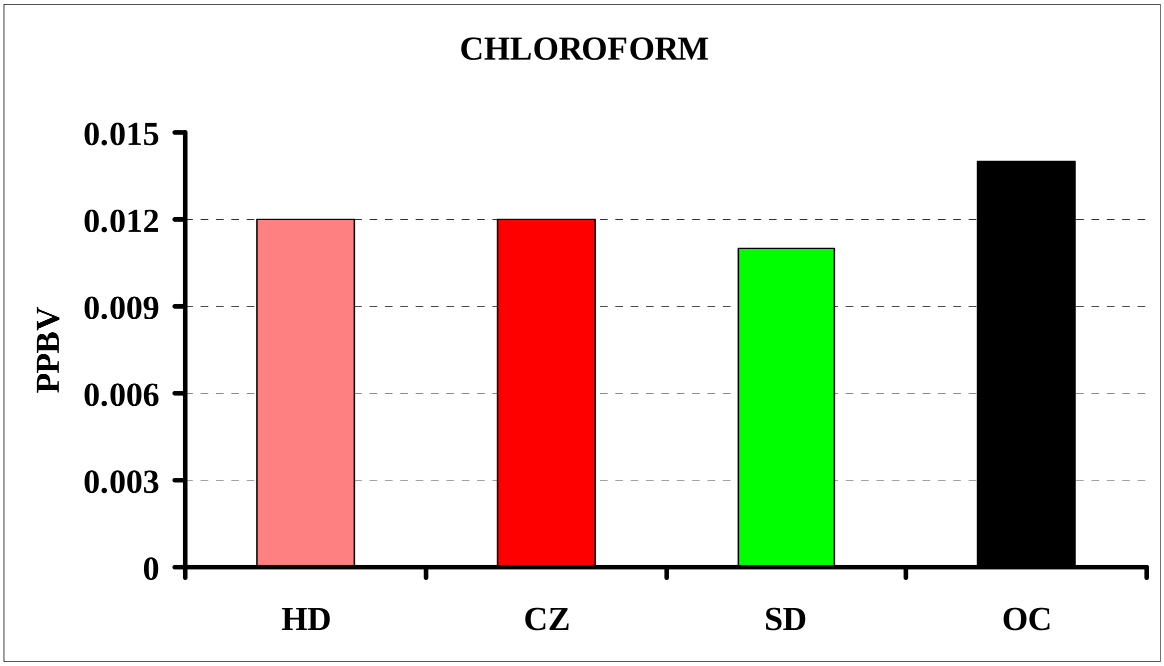


Figure 7. Annual average chloroform concentrations at the four Spokane sites in 2005.

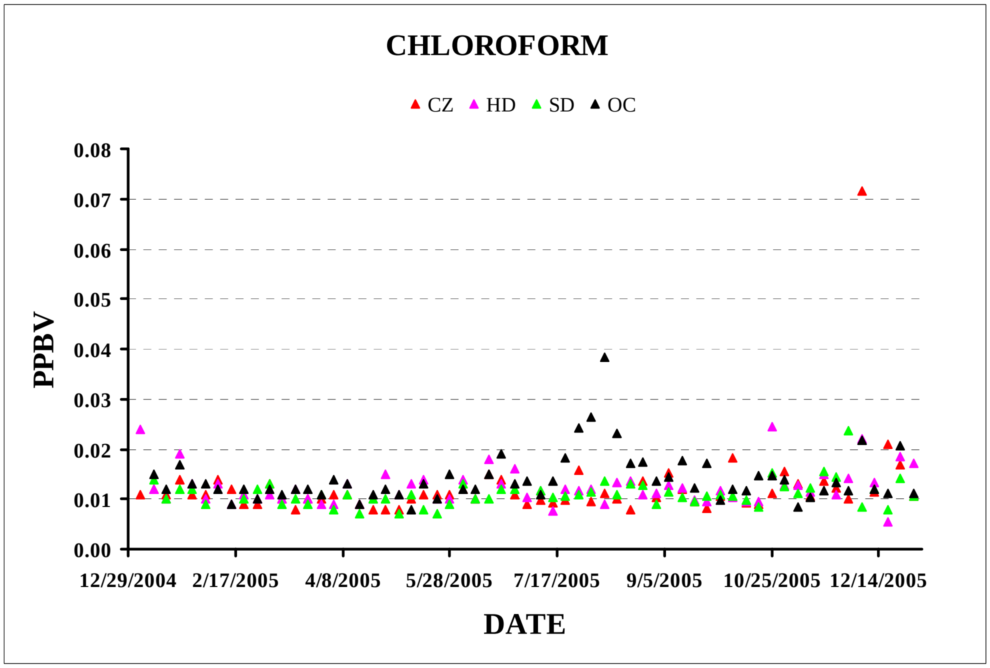


Figure 8. Chloroform temporal behavior at the four Spokane area sites

3.5 Tetrachloroethylene

Tetrachloroethylene is employed as an industrial solvent. It is used in cleansing processes such as degreasing of metals and dry cleaning. The two most commercialized sites, SD and CZ, had the highest annual means (0.05 ppbv) for tetrachloroethylene (Table 7).

Table 7. Tetrachloroethylene statistics determined at Spokane area sites in 2005.

Site	Mean (ppbv)	95% CI	Median (ppbv)	Min (ppbv)	Max (ppbv)	n
HD	0.03	0.01	0.03	0.01	0.21	61
CZ	0.05	0.02	0.03	0.01	0.045	61
SD	0.05	0.01	0.03	0.01	0.24	57
OC	0.03	0.01	0.02	0.01	0.42	60

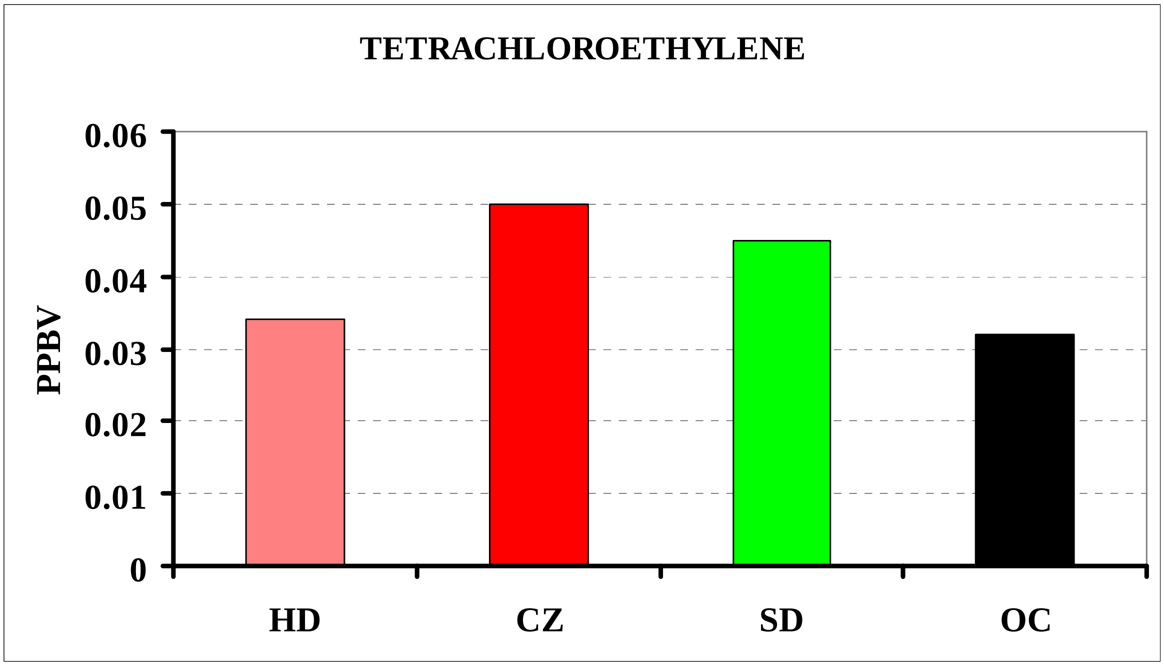


Figure 9. Annual average tetrachloroethylene concentrations at the four Spokane sites in 2005.

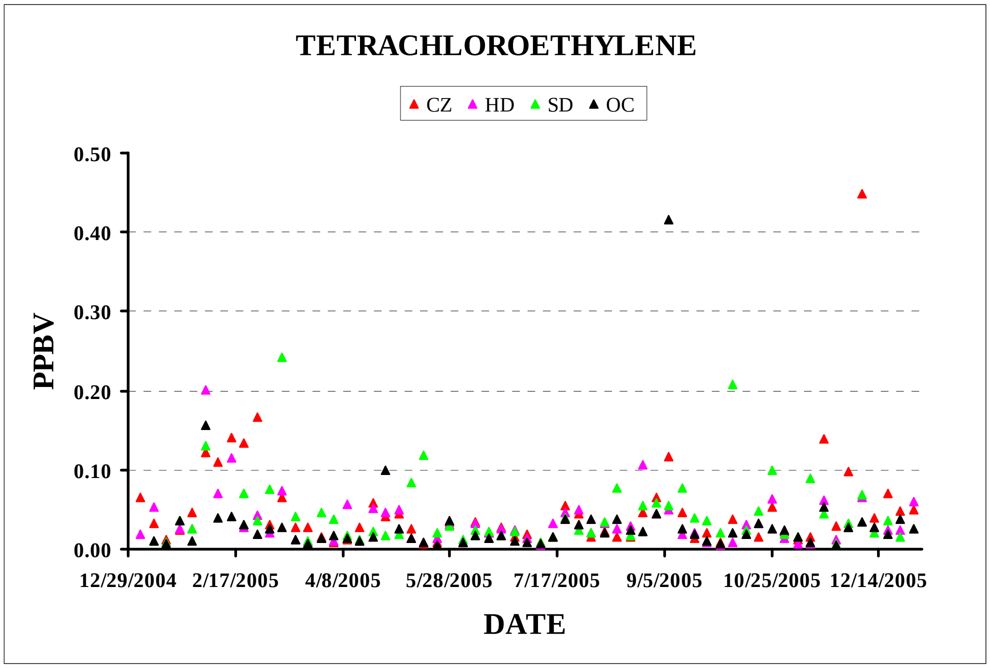


Figure 10. Tetrachloroethylene temporal behavior at the four Spokane area sites

3.6 Trichloroethylene

As with tetrachloroeyhylene, trichloroethylene (TCE) is primarily used as an industrial solvent. The annual means for TCE were low throughout Spokane averaging about 0.02 ppbv (Table 8).

Table 8. Trichloroethylene statistics determined at Spokane area sites in 2005.

Site	Mean (ppbv)	95% CI	Median (ppbv)	Min (ppbv)	Max (ppbv)	n
HD	0.02	0.002	0.02	0.002	0.04	61
CZ	0.02	0.01	0.01	0.001	0.12	61
SD	0.02	0.003	0.02	0.001	0.05	57
OC	0.01	0.002	0.01	0.002	0.03	60

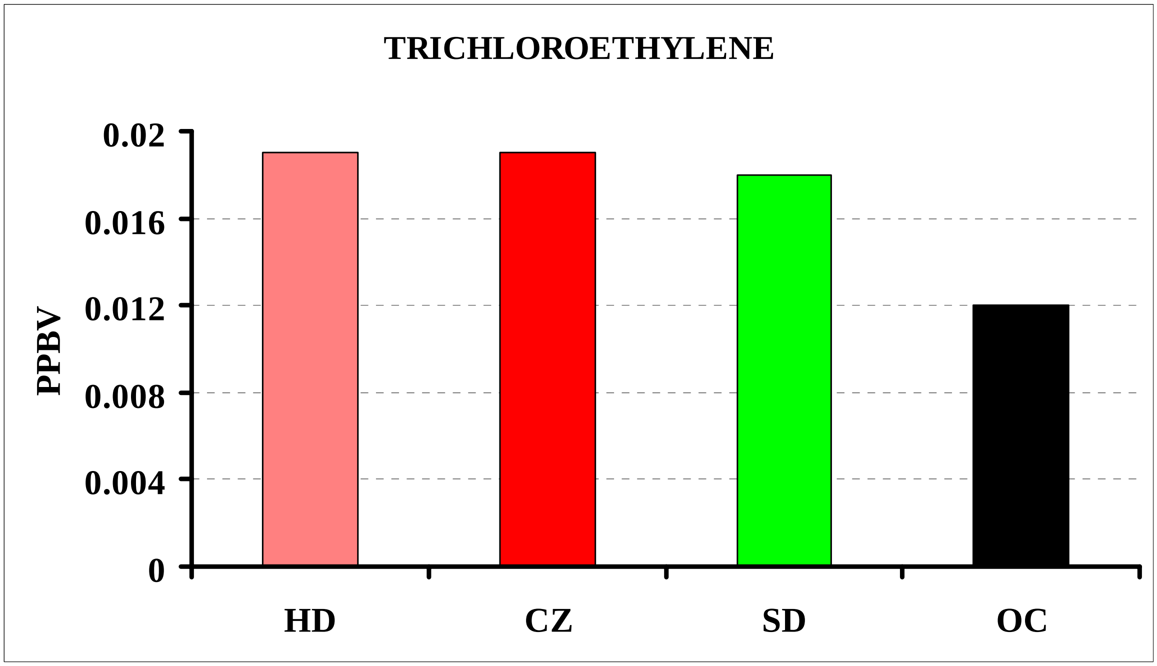


Figure 11. Annual average trichloroethylene concentrations at the four Spokane sites in 2005.

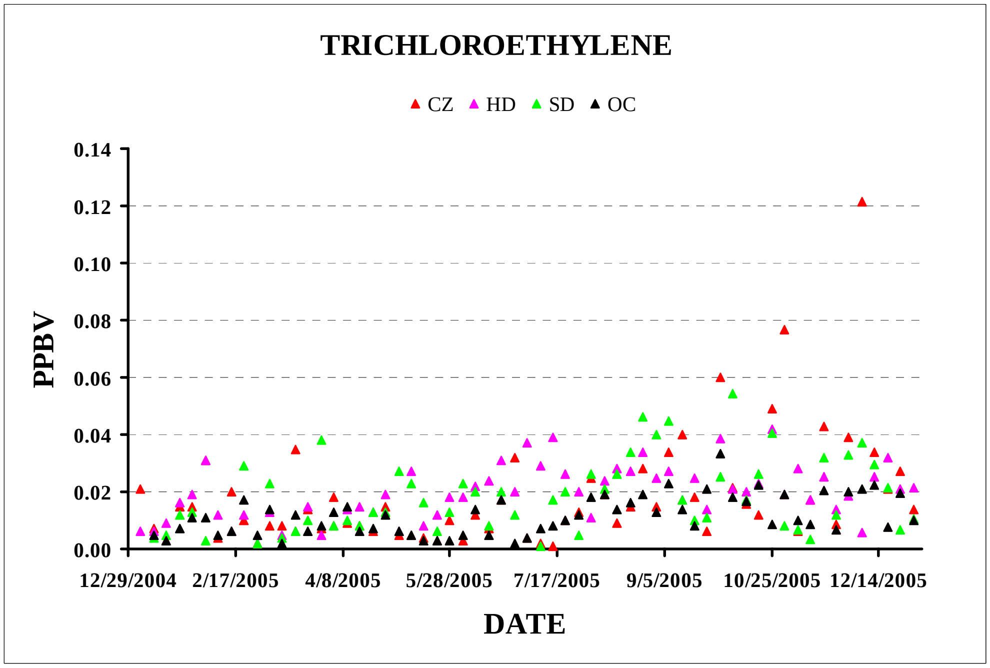


Figure 12. Trichloroethylene temporal behavior at the four Spokane area sites

3.7 Arsenic

Arsenic concentrations ranged from 0.04 to 5.92 ng/m^3 with a Spokane area mean of 0.90 ng/m^3. The 95% confidence interval around the mean was ± 0.13. As shown in Table 9, arsenic concentrations were lowest at the most westerly HD site and highest at the commercial-industrial CZ site. The temporal behavior (Figure 14 and Figure 15) shows maximum concentrations generally prevailing during the winter months.

Table 9. Arsenic statistics determined at Spokane area sites in 2005.

Site	Mean (ng/m^3)	95% CI	Median (ng/m^3)	Min (ng/m^3)	Max (ng/m^3)	n
HD	0.52	0.09	0.46	0.04	1.98	59
CZ	1.39	0.32	0.87	0.17	5.92	60
SD	0.91	0.27	0.54	0.08	5.62	58
OC	0.76	0.13	0.61	0.09	2.19	59

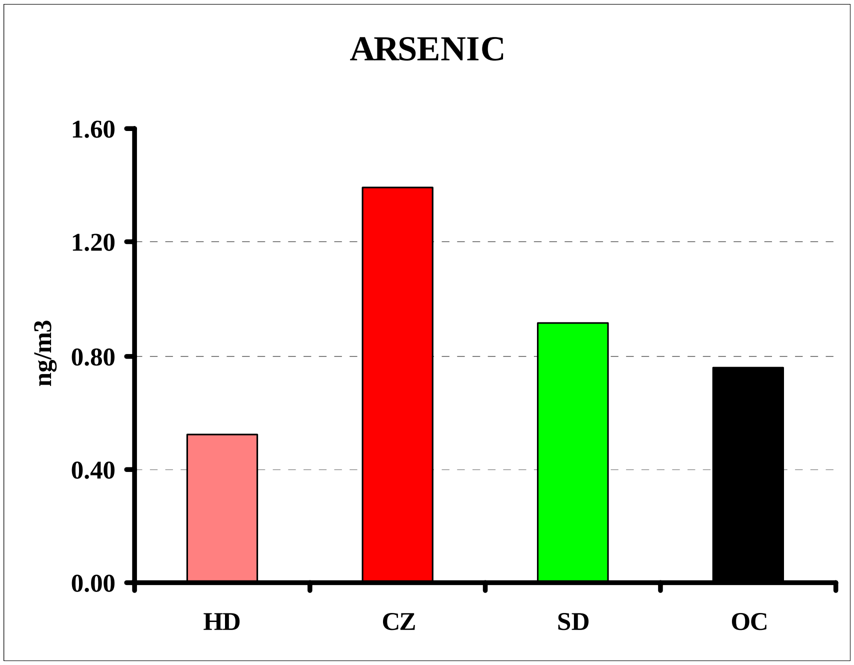


Figure 13. Annual average arsenic concentrations at the four Spokane sites in 2005

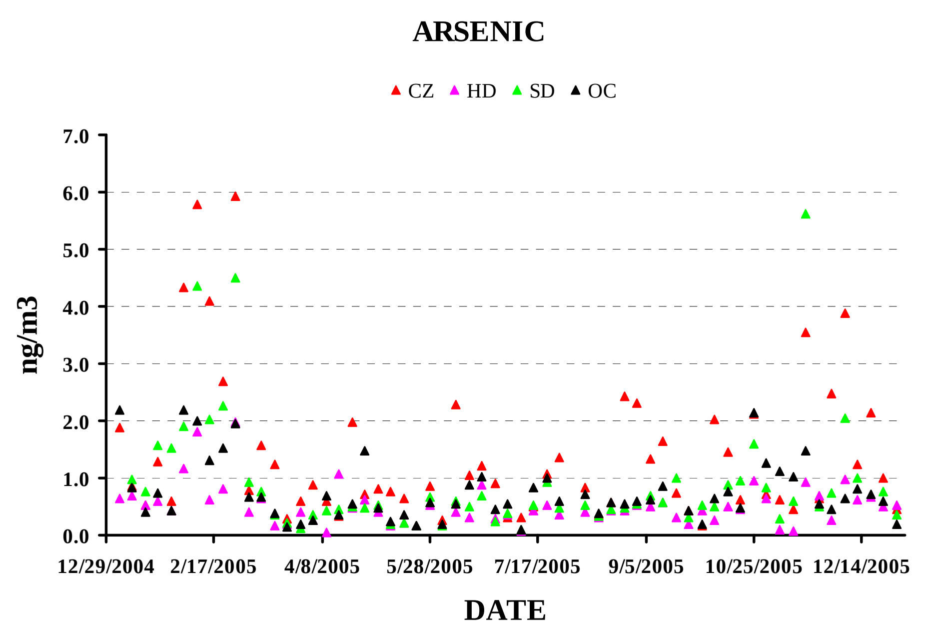


Figure 14. Arsenic temporal behavior at the four Spokane area sites

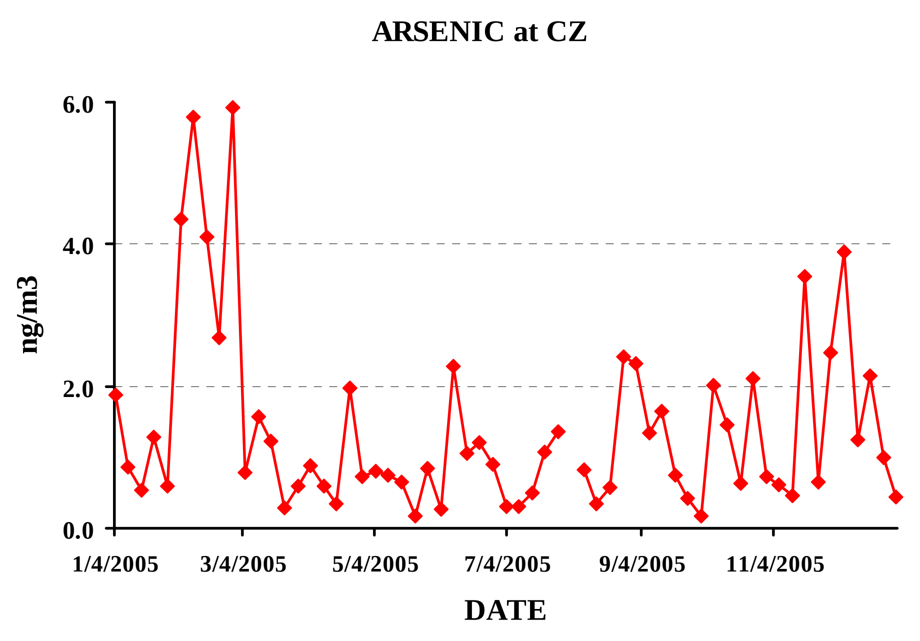


Figure 15. Arsenic temporal behavior at the CZ site.

3.8 Beryllium

Beryllium is a trace metal present in soil, as well as, dust and fumes from the burning of coal, oil and tabacco. It was the least abundant metal in Spokane PM_{10}. As shown in Table 10, annual mean concentrations at the four sites varied from 0.011 to 0.020 ng/m^3. From the temporal plot (Figure 17), it can be seen that all four sites exhibited elevated Be levels during a summer (June 21) dust event and the highest concentrations were recorded on two occasions at the OC site during the fall.

Table 10. Beryllium statistics determined at Spokane area sites in 2005.

Site	Mean (ng/m^3)	95% CI	Median (ng/m^3)	Min (ng/m^3)	Max (ng/m^3)	n
HD	0.011	0.004	0.006	non-detect	0.093	59
CZ	0.020	0.006	0.008	non-detect	0.125	60
SD	0.016	0.005	0.010	non-detect	0.087	58
OC	0.016	0.008	0.007	non-detect	0.174	59

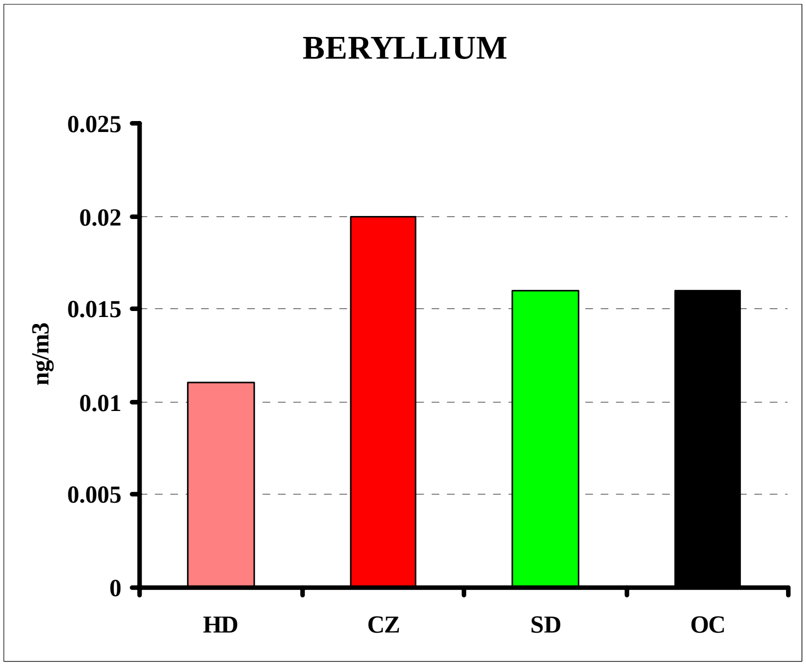


Figure 16. Annual average beryllium concentrations at the four Spokane sites in 2005

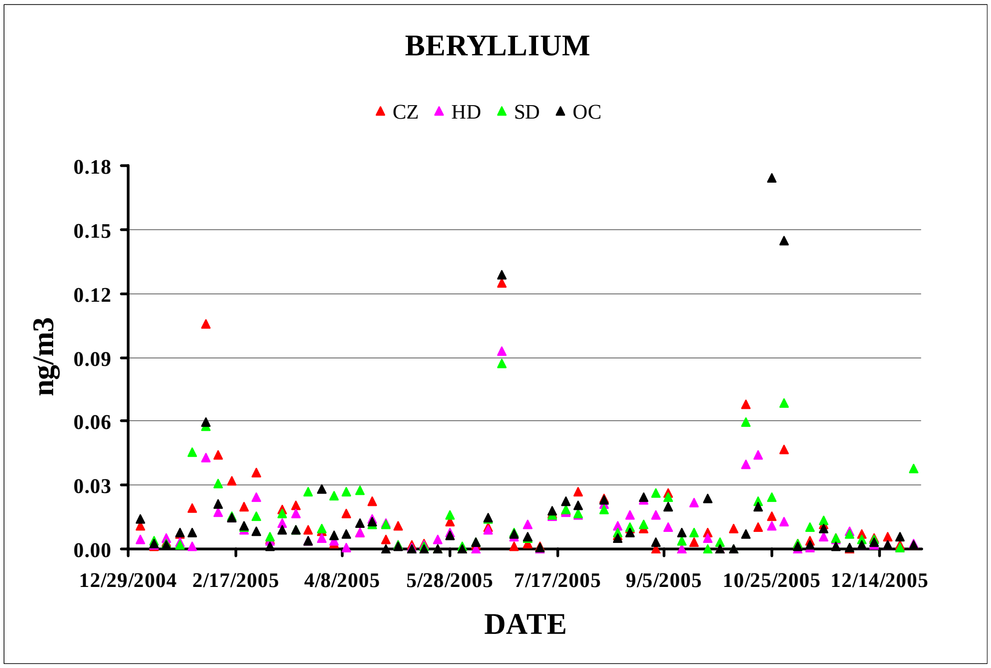


Figure 17. Beryllium temporal behavior at the four Spokane area sites

3.9 Cadmium

Like arsenic, the lowest annual mean (0.12 ng/m^3) and minimum (0.01 ng/m^3) cadmium levels were observed at the HD site (Table 11). The highest annual mean cadmium concentrations were measured at the CZ (0.20 ng/m^3) and OC (0.21 ng/m^3) sites. Cadmium concentrations during 2005 in Spokane ranged from 0.01 to 1.39 ng/m^3 with a city mean of 0.18 ng/m^3 and 95% confidence interval of ± 0.02. After beryllium, cadmium was the least abundant of the UAT metals measured in Spokane. The temporal pattern (Figure 19) shows highest concentrations to be present during the winter months.

Table 11. Cadmium statistics determined at Spokane area sites in 2005.

Site	Mean (ng/m^3)	95% CI	Median (ng/m^3)	Min (ng/m^3)	Max (ng/m^3)	n
HD	0.12	0.03	0.08	0.01	0.80	59
CZ	0.20	0.06	0.12	0.02	1.39	60
SD	0.17	0.05	0.11	0.02	1.05	58
OC	0.21	0.07	0.12	0.03	1.56	59

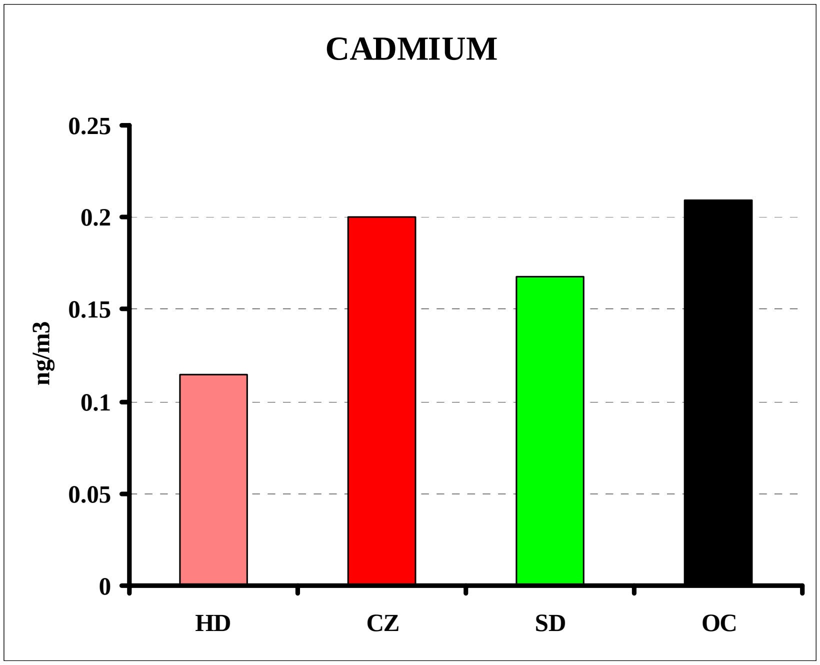


Figure 18. Annual average cadmium concentrations at the four Spokane sites in 2005

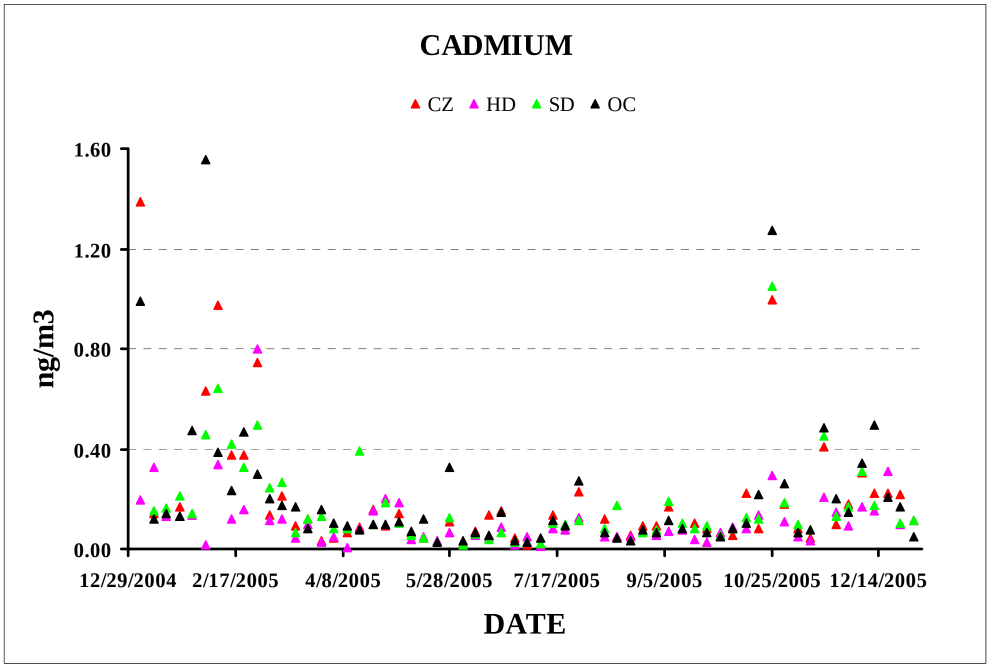


Figure 19. Cadmium temporal behavior at the four Spokane area sites

3.10 Chromium

Annual mean chromium concentrations in Spokane were very similar at the HD, SD and OC sampling sites. The mean for these three sites was 1.03 ng/m^3. However, as shown in Table 12 the mean concentration at the CZ site was 15 times larger (15.9 ng/m^3). The highest concentration recorded at the CZ site was 187 ng/m^3. Elevated chromium levels were measured throughout the year (Figure 21) which implies a source close to the CZ sampling site.

Table 12. Chromium statistics determined at Spokane area sites in 2005.

Site	Mean (ng/m^3)	95% CI	Median (ng/m^3)	Min (ng/m^3)	Max (ng/m^3)	n
HD	1.04	0.29	0.64	non-detect	6.91	59
CZ	15.9	8.36	2.05	non-detect	187	60
SD	1.01	0.26	0.51	non-detect	4.90	58
OC	1.03	0.23	0.68	non-detect	4.18	59

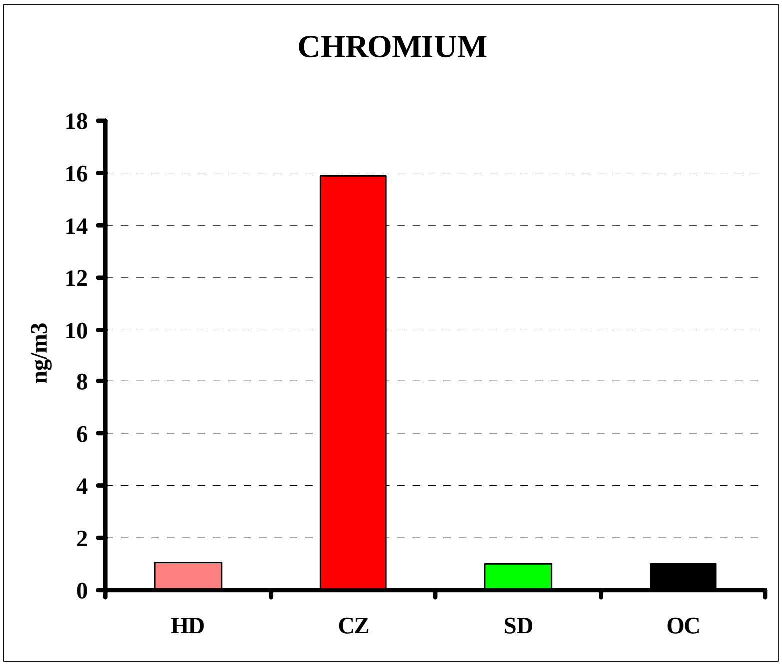


Figure 20. Annual average chromium concentrations at the four Spokane sites in 2005

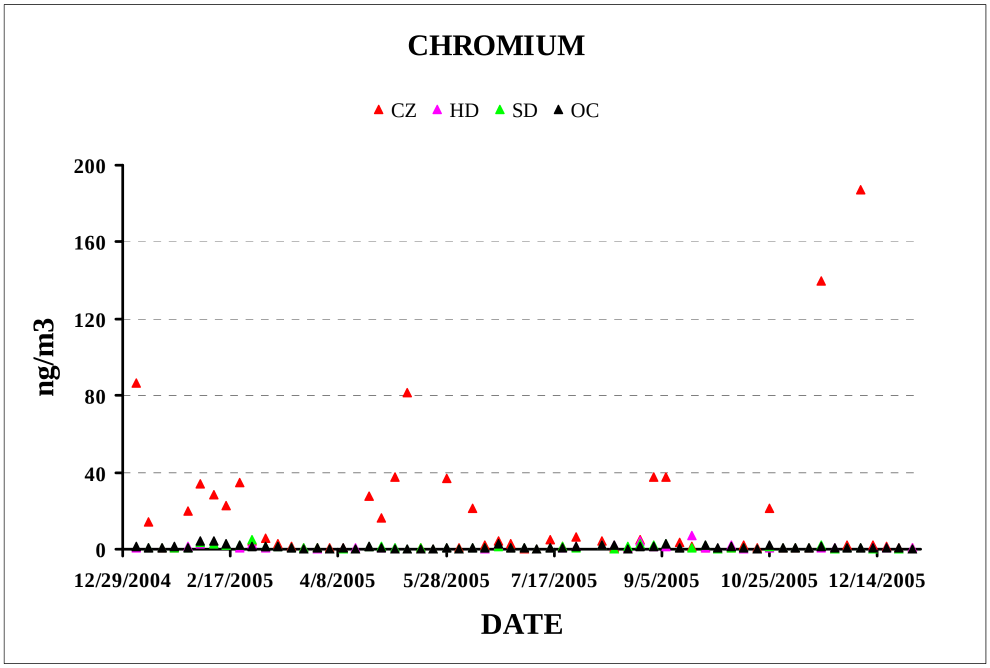


Figure 21. Chromium temporal behavior at the four Spokane area sites

3.11 Lead

Lead concentrations in the Spokane area ranged from less than 0.20 ng/m³ to 30.2 ng/m³ (Table 13). Crown Zellerbach had the highest mean (5.88 ng/m³) followed by OC (5.13 ng/m³). The HD site once again was the lowest at 3.70 ng/m³. The Spokane area mean with 95% confidence interval for lead was 4.90 ± 1.13 ng/m³. Like arsenic and cadmium, highest lead levels were recorded during the winter months (Figure 23).

Table 13. Lead statistics determined at Spokane area sites in 2005

Site	Mean (ng/m^3)	95% CI	Median (ng/m^3)	Min (ng/m^3)	Max (ng/m^3)	n
HD	3.70	0.67	3.10	0.20	13.0	59
CZ	5.88	1,45	4.17	0.66	30.2	60
SD	4.84	1.19	3.20	0.47	20.6	58
OC	5.13	1.19	3.18	non-detect	27.9	59

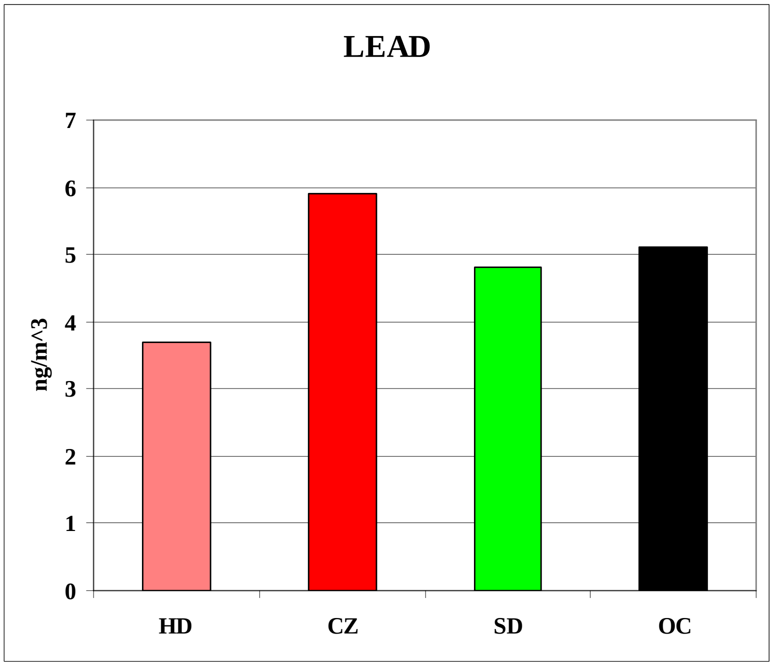


Figure 22. Annual average lead concentrations at the four Spokane sites in 2005

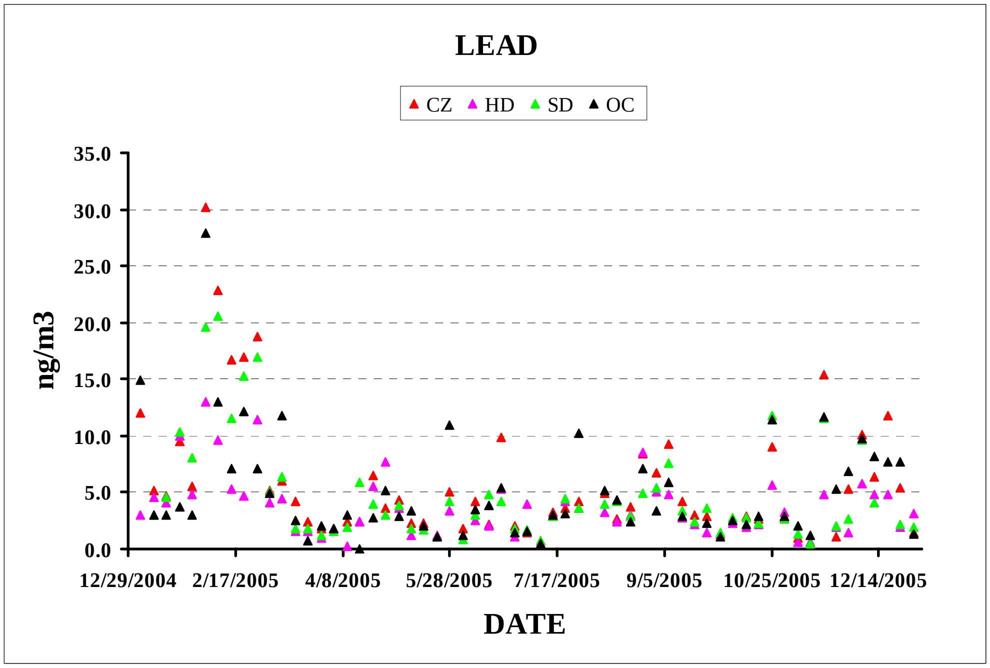


Figure 23. Lead temporal behavior at the four Spokane area sites

3.12 Manganese

Manganese was the most abundant of the metals measured in Spokane. It had a four-site mean of 18.7 ± 5.42 ng/m^3. The Spokane area maximum value of 125 ng/m^3 was recorded at the CZ site; however, the other three sites all had maximum values greater than 75.0 ng/m3 (Table 14). As shown in Figure 24, the annual mean of 31.0 ng/m3 at CZ was double that measured at the other three sites. The seasonal pattern of manganese concentrations (Figure 25) exhibited high and low values during all seasons.

Table 14. Manganese statistics determined at Spokane area sites in 2005

Site	Mean (ng/m^3)	95% CI	Median (ng/m^3)	Min (ng/m^3)	Max (ng/m^3)	n
HD	14.0	4.02	6.60	0.50	78.6	59
CZ	31.0	8.15	20.1	1.27	125	60
SD	15.6	5.03	6.31	0.65	89.2	58
OC	14.3	4.48	6.93	1.09	101	59

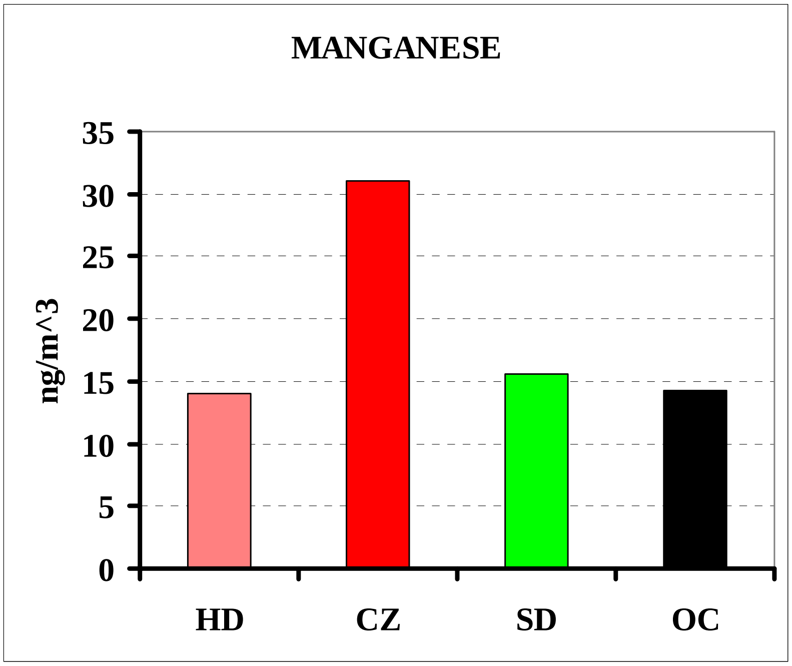


Figure 24. Annual average annual manganese concentrations at the four Spokane sites in 2005

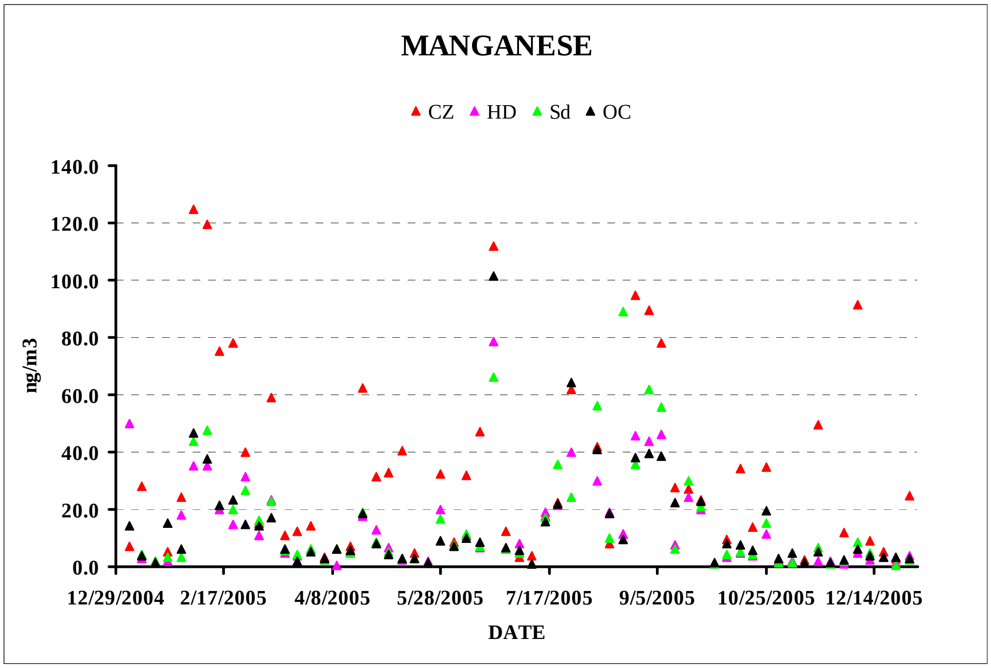


Figure 25. Manganese temporal behavior at the four Spokane area sites

3.13 Nickel

The mean nickel concentration at the HD, SD and OC sites varied between 1.80 and 2.38 ng/m³ (Table 15). As with chromium, the annual mean nickel concentration was an order of magnitude higher at the CZ site than the other three (Figure 26). There was a high correlation between chromium and nickel at the CZ site (compare Figure 21 and Figure 27). The range of nickel concentrations varied from below our detection level (0.08 ng/m³) at all four sites to 182 ng/m³ at Crown Zellerbach.

Table 15. Nickel statistics determined at Spokane area sites in 2005

Site	Mean (ng/m^3)	95% CI	Median (ng/m^3)	Min (ng/m^3)	Max (ng/m^3)	n
HD	2.17	4.16	0.75	non-detect	15.7	59
CZ	15.6	7.27	3.83	non-detect	182	60
SD	1.80	0.78	0.64	non-detect	15.0	58
OC	2.38	1.23	0.68	non-detect	32.1	59

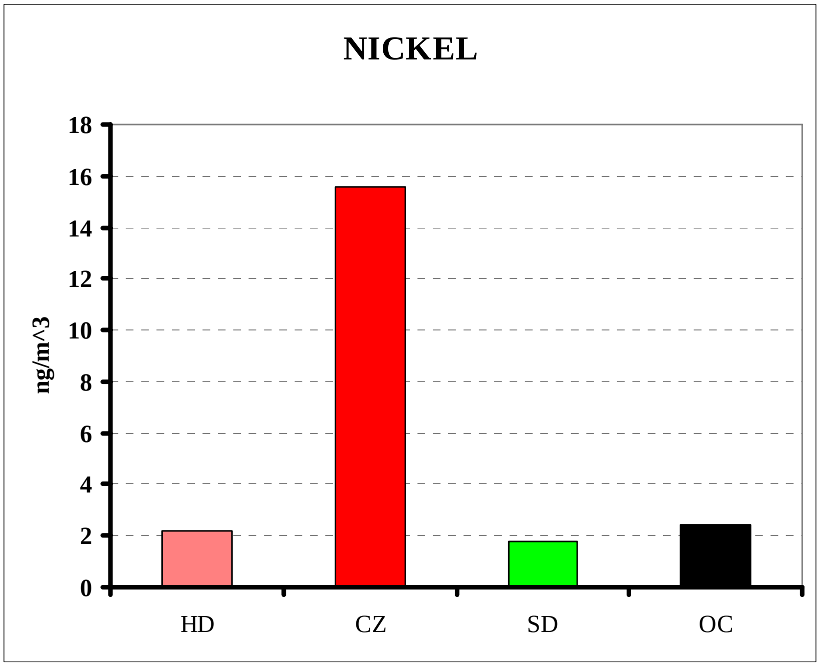


Figure 26. Annual average nickel concentrations at the four Spokane sites in 2005

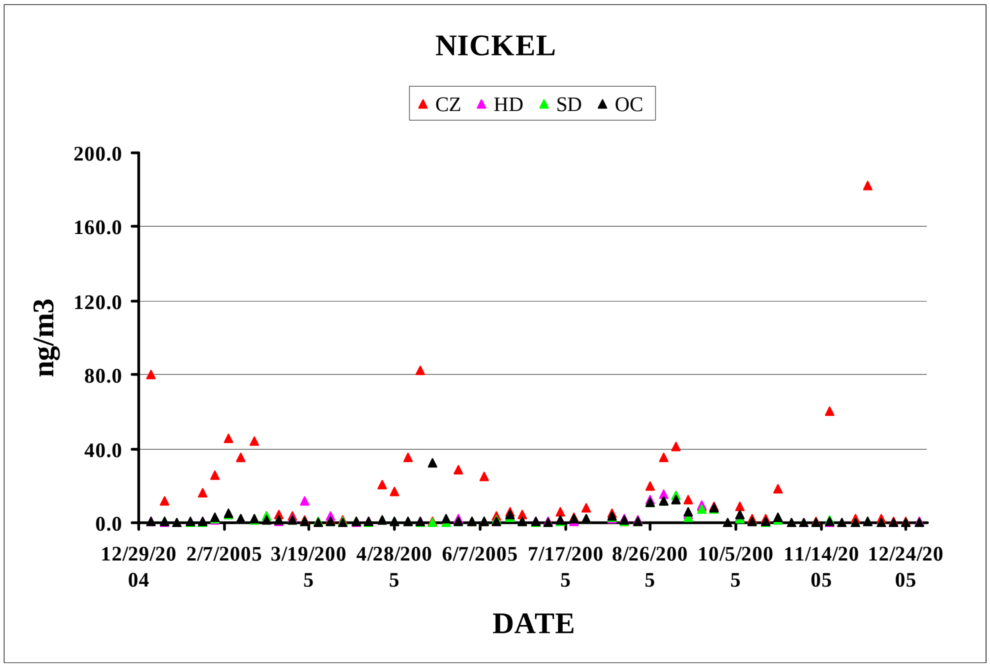


Figure 27. Nickel temporal behavior at the four Spokane area sites

3.14 Acetaldehyde

The two carbonyl compounds measured in this study have primary and secondary sources. Acetaldehyde is produced as an oxidation product in tropospheric photochemistry and is a common product of microbial degradation of organic materials. The annual mean for acetaldehyde (Table 16) was largest at the OC site (1.7 ppbv), intermediate at the CZ and SD sites (1.4 ppbv), and lowest at the most westerly HD site (1.2 ppbv). Contrary to the temporal patterns exhibited by benzene and 1,3-butadiene, which had wintertime maximums and low summertime values, acetaldehyde showed a summertime peak in concentrations. This is consistent with secondary production during the summer months.

Table 16. Acetaldehyde statistics determined at Spokane area sites in 2005

Site	Mean (ppbv)	95% CI	Median (ppbv)	Min (ppbv)	Max (ppbv)	n
HD	1.2	0.14	1.2	0.40	2.8	53
CZ	1.4	0.15	1.3	0.49	3.2	59
SD	1.4	0.14	1.3	0.46	2.8	58
OC	1.7	0.17	1.5	0.67	3.1	60

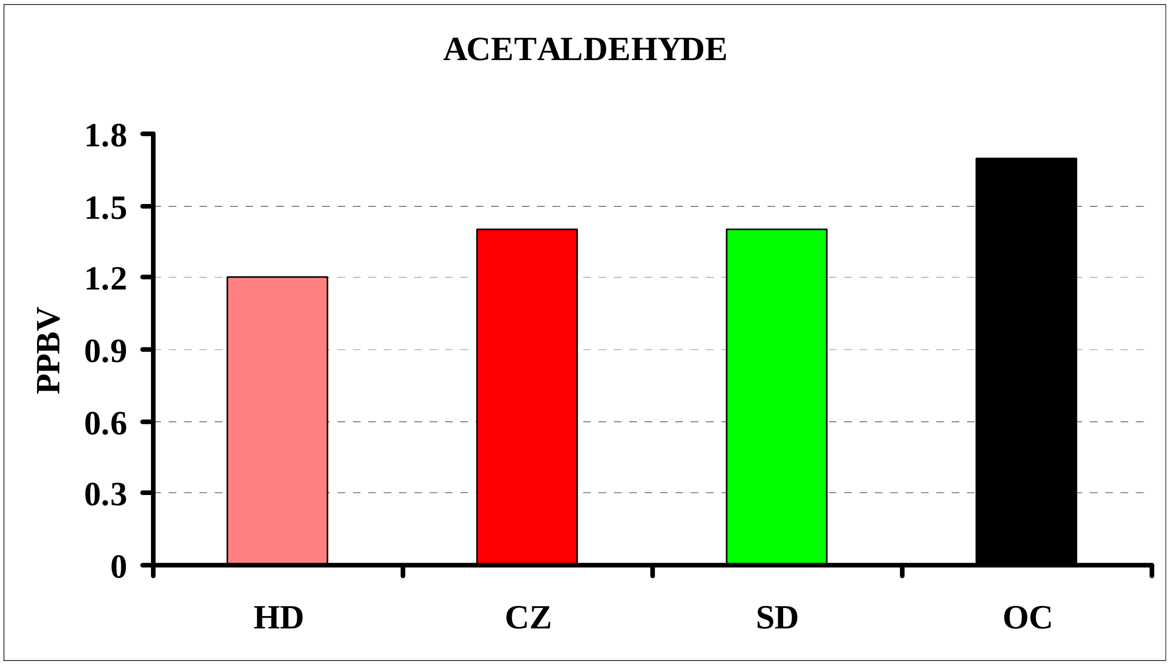


Figure 28. Annual average acetaldehyde concentrations at the four Spokane sites in 2005

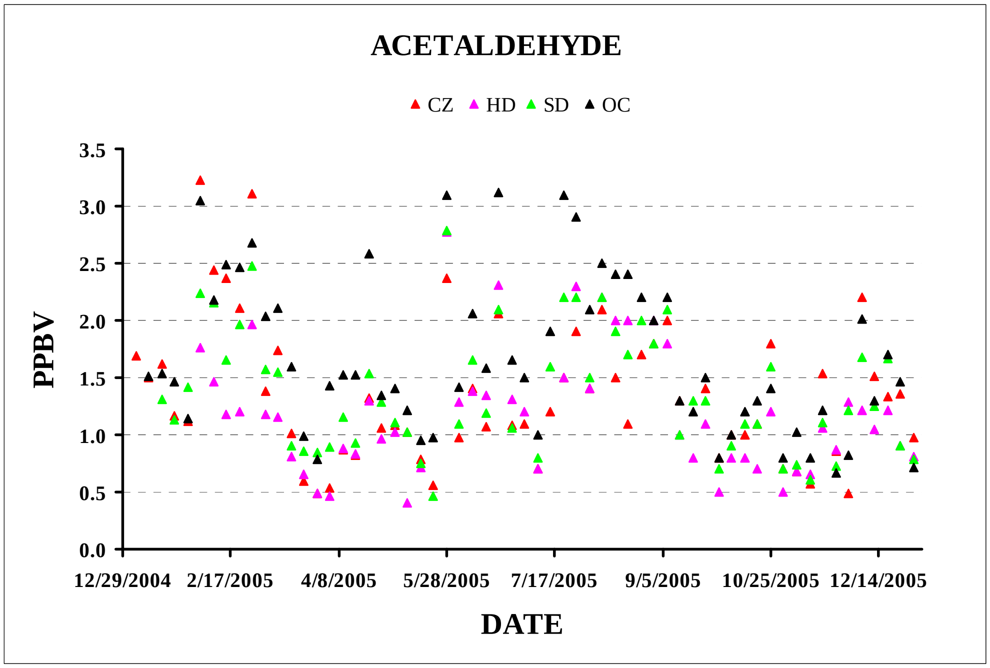


Figure 29. Acetaldehyde temporal behavior at the four Spokane area sites

3.15 Formaldehyde

Care must be exercised when sampling formaldehyde because of the ubiquitous nature of sources. Insulating foams, plywood resins, carpet materials all emit formaldehyde. Formaldehyde is produced photochemically via the same processes that generate ozone and other smog products. Highest annual average formaldehyde concentrations were recorded at the SD (2.5 ppbv) and OC (2.3 ppbv) sites (Table 17), which are to the north and east of the urban core. The secondary photochemical production of formaldehyde during the summer months is expected to impact these two sites more than the others.

Table 17. Formaldehyde statistics determined at Spokane area sites in 2005

Site	Mean (ppbv)	95% CI	Median (ppbv)	Min (ppbv)	Max (ppbv)	n
HD	1.5	0.20	1.3	0.37	3.4	53
CZ	1.8	0.25	1.6	0.45	4.8	59
SD	2.5	0.42	2.0	0.69	8.8	58
OC	2.3	0.22	2.1	0.71	4.2	60

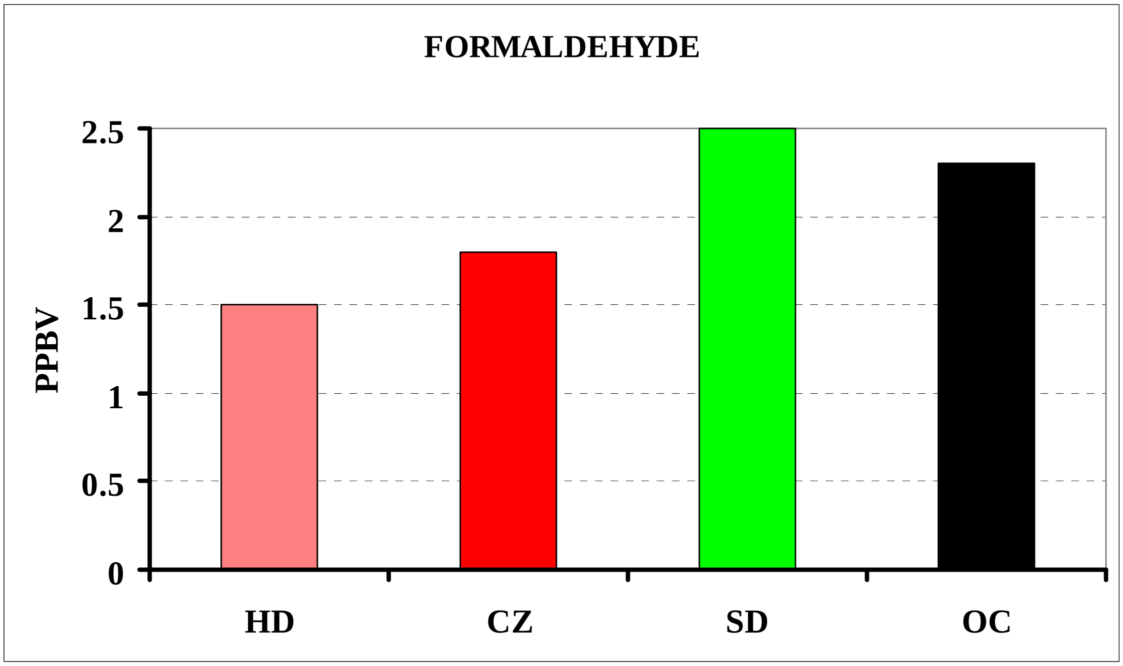


Figure 30. Annual average acetaldehyde concentrations at the four Spokane sites in 2005

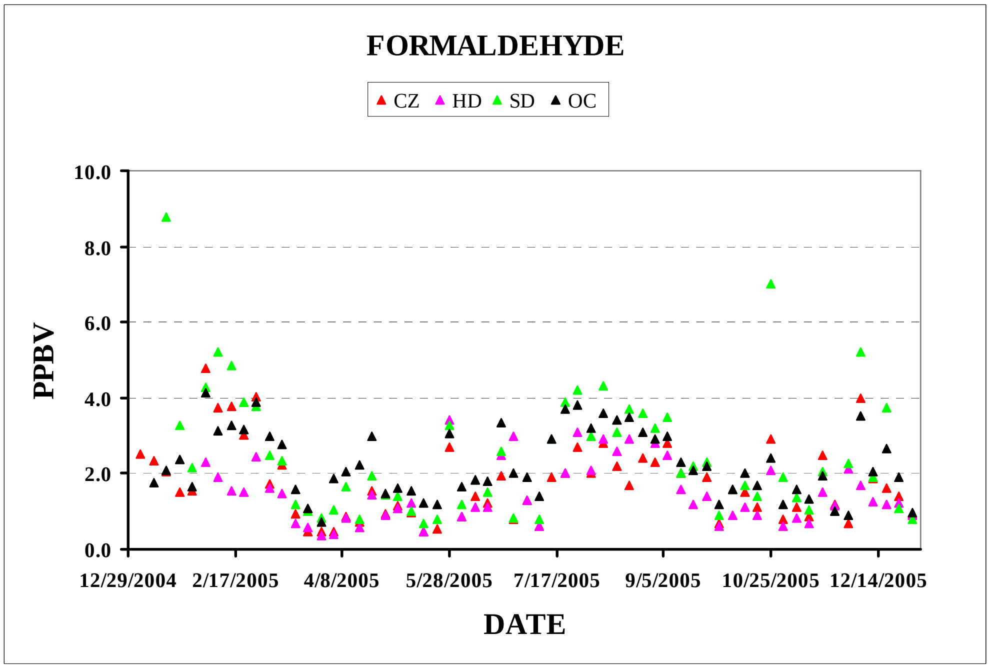


Figure 31. Formaldehyde temporal behavior at the four Spokane area sites

3.16 PM_{10}

PM_{10} annual mean concentrations varied from 21.6 to 29.4 ug/m^3 with the CZ site recording the highest mean value and HD the lowest (Table 18). Most of the high PM_{10} concentrations were recorded during February, the exception being June 21 when all four sites exhibited their maximum value for the year (Figure 33). June 21 was a very warm day (96 deg. F) with gusty winds as high as 40 mph. These meteorological conditions likely dictated a large crustal contribution to the PM_{10} loading on June 21.

Table 18. PM_{10} statistics determined at Spokane area sites in 2005

Site	Mean (μg/m^3)	95% CI	Median (μg/m^3)	Min (μg/m^3)	Max (μg/m^3)	n
HD	21.6	4.2	15.9	5.09	107	59
CZ	29.4	7.0	20.4	5.99	158	60
SD	22.6	4.5	15.6	4.32	5.38	58
OC	24.4	5.4	17.8	5.38	144	59

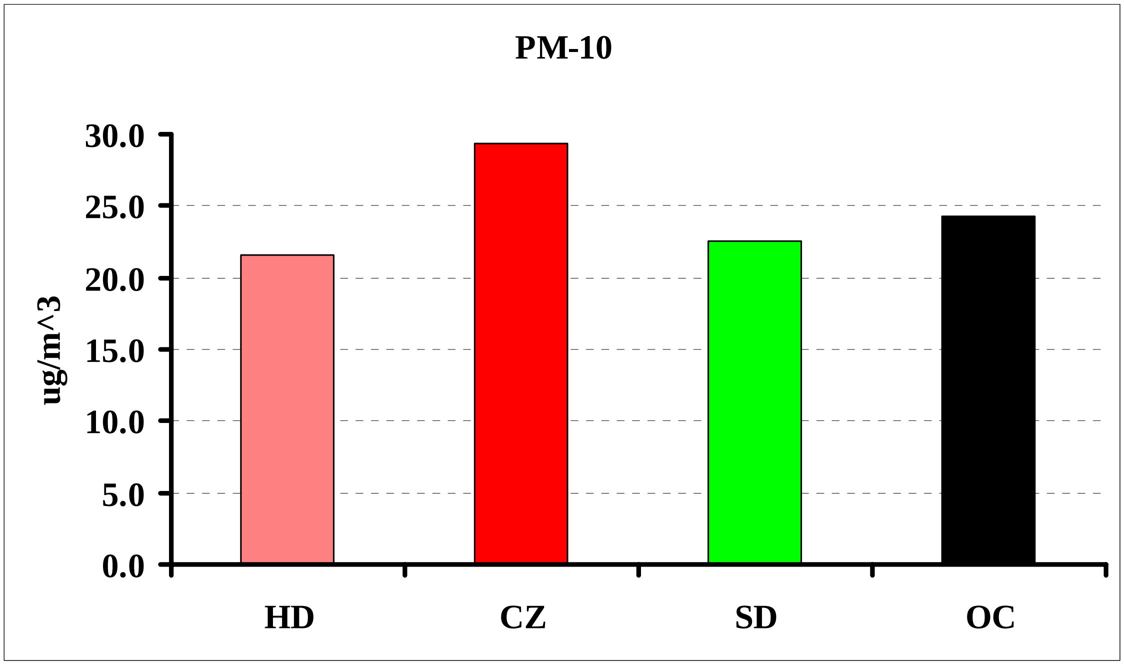


Figure 32. Annual average PM_{10} concentrations at the four Spokane sites in 2005

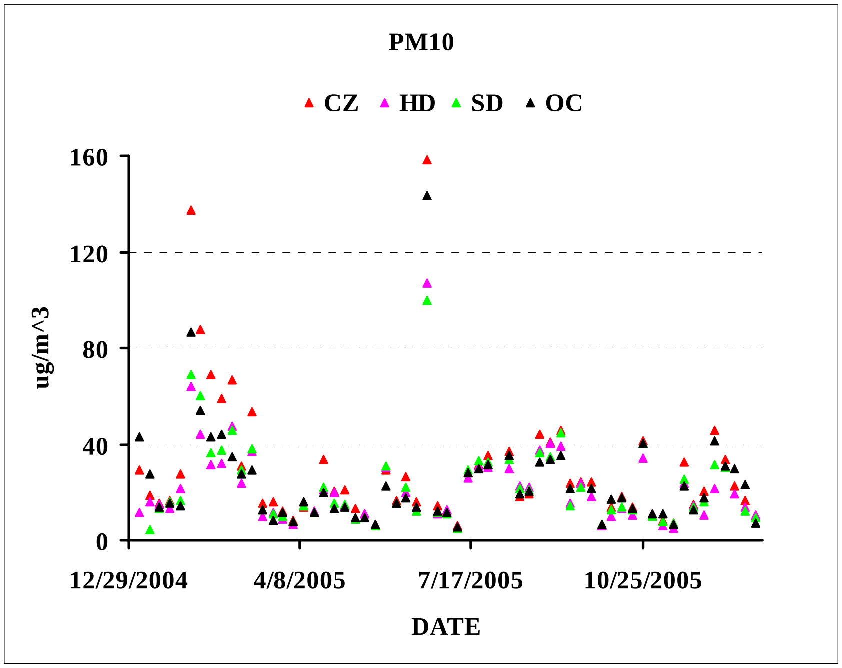


Figure 33. PM_{10} temporal behavior at the four Spokane area sites

3.17 Spokane Air Toxic Concentrations Compared to Other U.S. Cities

The question that will be asked is how Spokane's air toxic concentrations compare with other cities in the U.S. Sampling sites can play a large role in such comparisons. For example, the CZ site in Spokane has very high annual average chromium and nickel concentrations due to a local source. Thus, care must exercised when comparing ambient air toxic levels between urban regions because of siting differences. In spite of this uncertainty, it is of interest to compare annual average air toxic concentrations in Spokane with other cities. Table 19 and Table 20 provide such a comparison for the Seattle metropolitan area in 2005 and an average of ten large and small urban areas monitored in EPA's 2001 Pilot Cities Project. From the two tables, it appears that Spokane's air toxic levels are about the same as measured in Seattle and other U.S. cities.

Table 19. Air Toxic VOC comparison

(ppbv)	SPOKANE	SEATTLE	PILOT CITIES
BENZENE	0.24	0.18	0.53
1,3-BUTADIENE	0.05	0.03	0.05
CARBONTET	0.11	0.10	0.10
CHLOROFORM	0.01	0.05	0.04
PCE	0.04	0.03	0.04
TCE	0.02	0.03	0.06
FORMALD	2.0	1.1	3.3
ACETALD	1.4	0.8	1.1

Table 20. Air toxic metals comparison

(ng/m^3)	SPOKANE	SEATTLE	PILOT CITIES
ARSENIC	0.9	1.0	1.9
CADMIUM	0.2	0.2	0.2
CHROMIUM*	4.8 (1.0)	1.3	1.0
LEAD	4.9	4.4	10
MANGANESE	19	10	10
NICKEL*	5.6 (2.1)	3.1	4.0

**( ) Value including HD, SD and OC sites, excludes the CZ site.*

4.0 Source-Receptor Relationships

We have employed several different methods to better understand source-receptor relationships in the Spokane community. There are some strong correlations between air toxics that imply a common source. More quantitative methods including PMF modeling and the use of lead isotope ratios have been explored as a means of identifying sources and their impact on air quality in Spokane.

4.1 Correlation-Based Source Relationships

The most obvious case for a common source of two air toxics is chromium and nickel at the CZ site. Figure 34 shows a scatter plot of these trace metals at that site. The R^2 value is 0.89. Clearly, there is an industrial source of nickel and chromium close to the site. The high values were observed when winds were light from easterly quadrants.

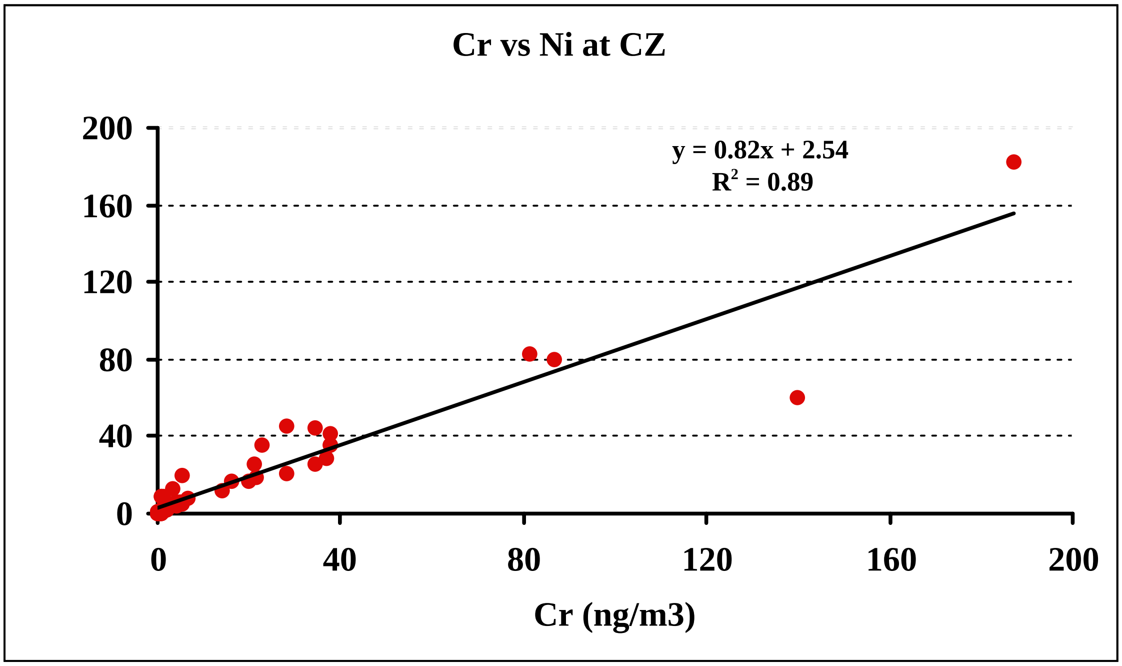


Figure 34. Nickel-chromium correlation at the CZ site.

Benzene and lead comprise another pair of air toxics that are highly correlated. This is especially true at the CZ site. The correlation coefficients between benzene and lead are 0.91. 0.84, 0.76, and 0.67 at the CZ, SD, OC and HD sites, respectively. Since benzene emissions are primarily associated with mobile sources, it is likely that most of the particulate lead at the CZ and SD sites is derived from mobile emissions.

Table 21 through Table 24 list correlations between the trace metals at each of the four sites. The highest correlations (r > 0.70) are highlighted in bold format. Arsenic, cadmium and lead in PM_{10} show a strong association, which suggests a common source for these metals. Combustion related processes likely emit these three metals. Of the remaining four metals, chromium, manganese and nickel exhibited weak to moderate correlations (r ~ 0.41-0.73) at some of the sites and, as described above, there is a strong correlation between chromium and nickel at the CZ site. Crustal and industrial sources likely provide the primary source of Cr, Mn and Ni in the Spokane airshed.

Table 21. Correlations (r) between trace metals at the HD site.

	Be	Cd	Cr	Pb	Mn	Ni
As	0.32	**0.75**	0.30	**0.75**	0.35	0.01
Be		0.05	0.39	0.34	0.64	0.21
Cd			0.16	0.56	0.12	-0.09
Cr				0.44	0.57	0.49
Pb					0.46	0.17
Mn						0.53

Table 22. Correlations (r) between trace metals at the CZ site.

	Be	Cd	Cr	Pb	Mn	Ni
As	0.38	0.64	0.43	**0.86**	0.66	0.46
Be		0.31	0.02	0.55	0.60	0.02
Cd			0.37	**0.70**	0.35	0.38
Cr				0.38	0.41	**0.94**
Pb					**0.70**	0.38
Mn						0.49

Table 23. Correlations (r) between trace metals at the SD site.

	Be	Cd	Cr	Pb	Mn	Ni
As	0.14	0.67	0.64	**0.81**	0.15	0.09
Be		0.20	0.26	0.25	0.34	0.09
Cd			0.48	**0.78**	0.11	0.05
Cr				**0.76**	0.68	0.59
Pb					0.35	0.24
Mn						0.60

Table 24. Correlations (r) between trace metals at the OC site.

	Be	Cd	Cr	Pb	Mn	Ni
As	0.44	**0.72**	0.62	0.69	0.30	-0.04
Be		0.47	0.41	0.25	0.44	0.03
Cd			0.52	**0.83**	0.20	-0.05
Cr				0.67	**0.73**	0.23
Pb					0.38	0.00
Mn						0.27

Table 25 lists the correlations of benzene and acetaldehyde with some of the other VOCs. Since benzene is a primary emission associated with mobile sources, VOCs that correlate highly with benzene should be mobile source related. As can be seen in Table 25, 1,3-butadiene shows a very high correlation (r> 0.90) at all four of the sites. The association between toluene and benzene is strong, as well. Formaldehyde and acetaldehyde correlate with benzene at the CZ site, but not at the other three sites. The aldehydes are emitted by mobile sources similar to benzene, but in addition are produced in the atmosphere by oxidation processes. The strong association between benzene and the aldehydes at the CZ site, implies fresh emissions measurement while more aged air masses that include secondary products are more common at the other three sites. There is a high correlation between acetaldehyde and formaldehyde concentrations at all four sites.

Table 25. VOC Correlations (r) at the four Spokane area sites.

	1,3-Butadiene	Toluene	Acetaldehyde	Formaldehyde
Benzene				
HD	**0.91**	**0.78**	0.20	0.24
CZ	**0.98**	**0.86**	**0.75**	**0.81**
SD	**0.95**	**0.80**	0.42	0.57
OC	**0.97**	**0.82**	0.37	0.49
Acetaldehyde				
HD				**0.78**
CZ				**0.86**
SD				**0.80**
OC				**0.82**

4.2 Lead Isotope Apportionments

Lead isotopes can be used to help identify sources of the trace metal in PM_{10}. Lead has four isotopes that can be measured using the ICP-MS technique. Lead 208, 207 and 206 are present in similar amounts while lead 204 normally exists at very low levels. Airborne particles of various origins (fossil fuel burning, wood burning, crustal re-suspension, etc.) are expected to have different isotope ratios.

We have carried out an isotope ratio analysis using lead isotope data measured in Spokane. The SCAPCA group provided us with an archived PM sample that had been collected upwind of Spokane during a major dust storm. We have assumed that the lead in this sample was associated with crustal materials. Unfortunately, we do not have a PM sample that we can say is representative of only mobile emissions nor do we have isotope ratios that can be assigned to wood smoke in the Spokane air shed. We have used lead isotope ratios measured in other locations as fingerprints for mobile and wood smoke emissions. Figure 35 shows a plot of the lead 208/207 vs. lead 207/206 ratios for several Spokane ambient lead PM_{10} isotope samples along with a literature related value for unleaded gasoline (Widory, et al., 2004). The point designated as Spokane crustal was determined from the windblown dust sample provide by SCAPCA. This and the unleaded gasoline mark the extreme ends of the range of ratios. Spokane 6/21/05 (Figure 35) is the average of the four sites on June 21, 2005. As indicated in an earlier section, the June 21 samples were collected during conditions (high temperatures and very gusty winds) conducive to windblown dust as the dominant PM_{10} source and the isotope analysis confirms a crustal origin. Meteorological conditions were much different during sample collection on February 21. The entire Pacific Northwest had been under stagnation conditions for several weeks in February. Wind speeds were low and the daytime mixing depth was shallow. Therefore, the PM_{10} collected at each station should reflect sources within a few kilometers. The point designated Spokane 2/21/05 is the average isotope ratios for the four sites on that date. The location of this point implies a predominantly anthropogenic source for the lead. The four additional points marked HD\CZ\SD and OC on the graph in Figure 35 show the isotope ratios measured at the four individual sites on 2/21/05. Location of the HD and CZ points imply a larger crustal contribution at those two sites compared to SD and OC. The OC ratio indicates that lead in the PM_{10} at this site came almost entirely from combustion sources. Finally, the point marked CZ annual average falls midway between the crustal and combustion derived ratios. Thus, implying that on average there is about equal contributions from the two source categories. On an annual basis, PM_{10} at the CZ site is composed of nearly equal amounts of soil and combustion related material.

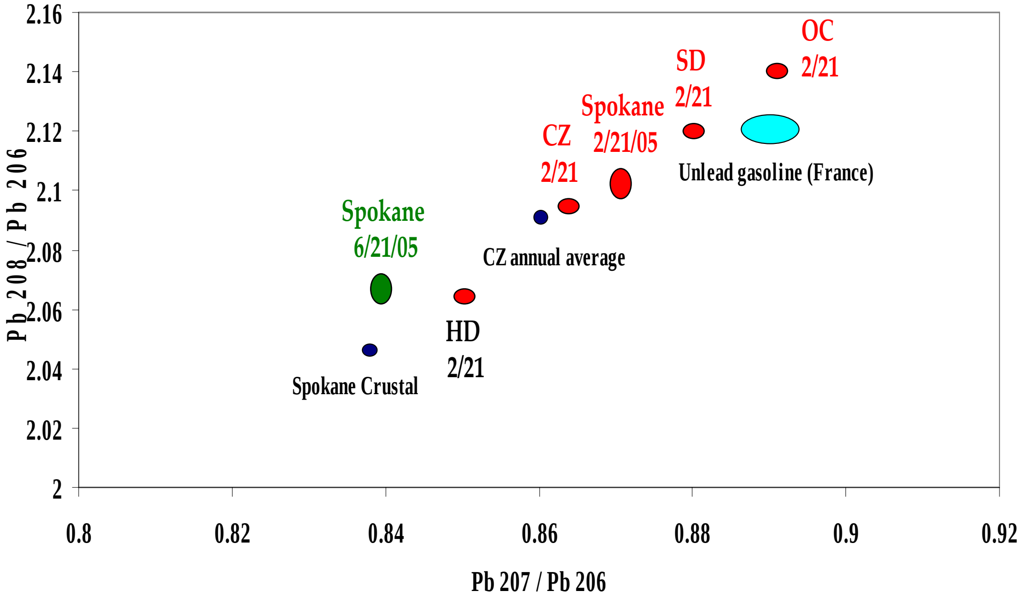


Figure 35. Lead isotope relationships measured in Spokane

4.3 Emission Tracking with a Mobile Laboratory

Ambient measurements close to various emission sources were made with a mobile lab fitted with several different sensors. Figure 36 shows the van used for mobile sampling in Spokane. Instrumentation included particle bound polycyclic aromatic hydrocarbon (PPAH) aerosol sensors, a proton transfer reaction mass spectrometer (PTR-MS), an Aerodynamic Particle Sizer (APS), a Global Positioning System (GPS) and a sonic anemometer. The PPAH instruments measure particle bound PAH concentration and active surface area. The PTR-MS measures VOCs that have a proton affinity greater than water. This includes most alkenes, aromatics and oxygenated hydrocarbons. The APS sensor is a particle spectrometer that provides the size distribution of particles from 0.5 to 20 µm. The GPS tracks the position of the van when in motion. The sonic anemometer provides wind data to identify plumes or remove periods with wind blowing from behind the van where a gasoline generator was placed to provide AC power for the instruments. All of these instruments have fast response capability (~ 1 Hz).

Mobile van sampling was conducted during a week in June and five days in December of 2005. During each of the two sampling periods, a day was spent in the vicinity of each of the four sampling sites. This consisted of circling the sites at distances varying from about one kilometer to four kilometers. In addition, time was spent traversing the major highways, around an industrial park in the Spokane valley and in the vicinity of other emission sources. Following the daytime sampling, the van was stationed at the SD site and measurements were made throughout the night at that site. During each of the summer and winter periods the van remained stationary at the SD site during the day when 24-h integrated sampling was conducted at the four fixed sites.

This allowed a comparison for certain VOC concentrations determined in the 24-h integrated canisters and those measured with the PTR-MS. Additionally, since the PTR-MS provided a continuous record, a temporal record of concentrations over the 24-h sampling period was obtained.

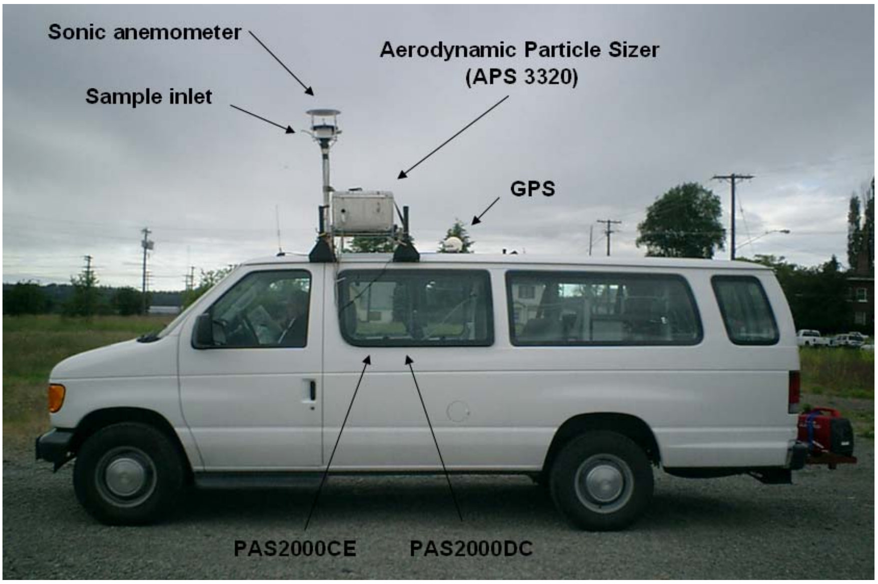


Figure 36. Picture of the mobile unit used during the Spokane 2005 field campaign.

4.4 PPAH Measurements

PAS-CE and PAS-DC sensors were used to determine PAH concentration and active surface area. The operational principle of the PAS-PC is described in detail by EcoChem Analytics (2000). Briefly, the PAS-PC employs pulsed UV light (207 nm) to ionize the PPAH, while gas molecules and other aerosols remain neutral. Following ionization, each photoelectron attaches to an oxygen molecule to form a negative ion in the carrier gas. The negative ion diffuses back to the particle if the particle is about 1 µm or larger in size (Siegmann *et al*., 1999). However, particles of smaller size remain positively charged, while the negative ions diffuse to the walls or are removed by an alternating electric field. The positively charged particles are collected on a filter element and the electric current generated is monitored by an electrometer. The electrometer provides an output signal that is proportional to the PAH mass adsorbed on particles with a diameter < 1 µm collected by the filter. Note that the PAS-PC instrument can measure only total PPAH and cannot provide PAH speciation, which requires techniques such as GC-MS or LC-MS.

To investigate the active surface area of the PPAH, particles must remain in the carrier gas. This can be achieved using a photoelectric aerosol sensor based on unipolar diffusion charging (PAS-DC), where ions are produced in the carrier gas by a corona discharge. The ions attach to the surface of the particles, which are collected in an electrically insulated particle filter. The electric charge is converted to a voltage signal.

The number of attached ions over a wide size range of particles depends linearly on the active surface, which can be interpreted as that fraction of the geometrical surface of the particles which is directly accessible from outside (Keller *et al.*, 2001).

The use of these two sensors in parallel allows evaluation of different physical and chemical characteristics of the particles, and qualitative identification of the major PPAH emission sources. For example, the ratio between the PPAH concentration and the total active surface area (PC/DC) has been described as a fingerprint for individual types of combustion particles (Bukowiecki *et al.*, 2002; Matter *et al.*, 1999; Siegmann *et al.*, 1999). A plot of the photoelectric charge versus the diffusion charge has been found to yield a linear relationship for any type of combustion. The amount of PAH from a combustion source varies widely depending on the fuel and the conditions of the combustion. Hence, ambient measurements can exhibit a characteristic PC/DC ratio according to the major emission source of each specific site with an associated variability due to the contribution of other sources. As an example, Figure 37 shows the PC signal plotted versus the DC signal for aerosols emitted by two diesel engines. The first engine was run under controlled conditions in an experimental chamber for health-exposure studies. The second engine corresponded to a charter bus running under real conditions on a roadway near to Spokane. Despite the differences in engines and weather conditions, both diesel engines showed similar slopes, demonstrating that the PC/DC ratio can be used as an indicator for the origin of the particles. In other studies, slopes between 1.18 and 1.83 ng mm^{-2} have been reported for diesel vehicles (Siegmann *et al.*, 1999; Velasco *et al.*, 2004).

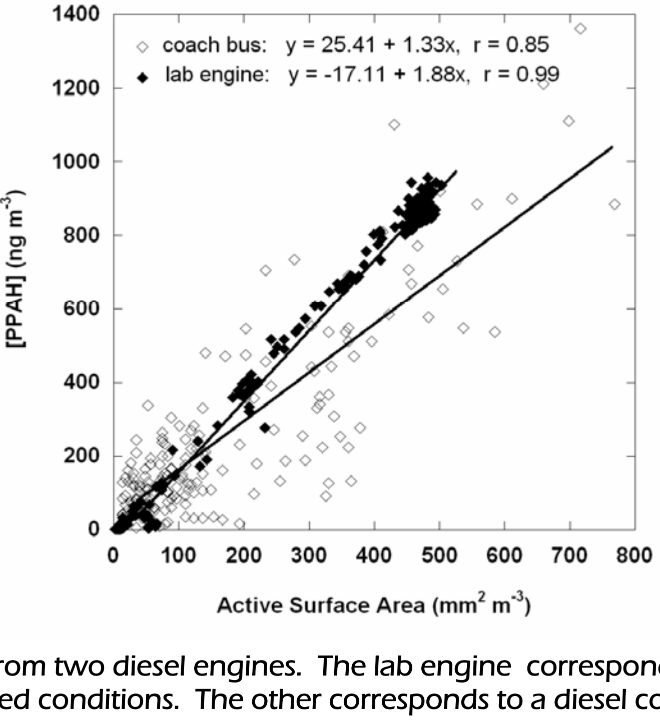


Figure 37. PC/DC ratios from two diesel engines. The lab engine corresponds to an engine run under controlled conditions. The other corresponds to a diesel coach bus.

Recall that the mobile lab study focused on roadways around the established monitoring sites: Chase measurements of some super-pollutant vehicles, such as dump trucks and charter buses, were conducted, as well.

PPAH measurements obtained along roadways and other locations are summarized in the following figures and tables. For example, Figure 38 shows the concentration profile for PPAH and total active surface area during a day of measurements. The top graphic shows high PPAH concentrations were measured during the daytime period when the lab was moving along roadways, and low concentrations during the nighttime hours when the van was stationary at the SD site. A baseline concentration of ~7 ngm^{-3} probably represents background concentrations in urban Spokane. Many of the sharp PPAH peaks above 300 ngm^{-3} were produced by diesel trucks. Both peaks in active surface area at 8:49 and 12:40 corresponded to emissions from urban buses. A traffic jam between 13:19 and 13:32 h yielded a visible decrease in the PPAH concentration compared to measurements in previous minutes (13:10 to 13:19 h), when traffic was heavy but moving. This illustrates that PPAH emissions are larger from accelerating vehicles than when in congested traffic at slow speed. Between 13:36 and 14:54 h the mobile lab was parked ~25 m from the I-90 freeway, and a median PPAH concentration of 50 ngm^{-3} and a median active surface area of 7.15 mm^{2}m^{-3} were measured. Most of the I-90 traffic during this sampling period consisted of gasoline powered automobiles. Both PPAH concentrations and active surface areas obtained when driving along I-90 were considerably higher than when measured at some distance from the freeway. Zhu et al. (2002) have reported that particle counts approach background levels in as little as 300 m downwind of freeways.

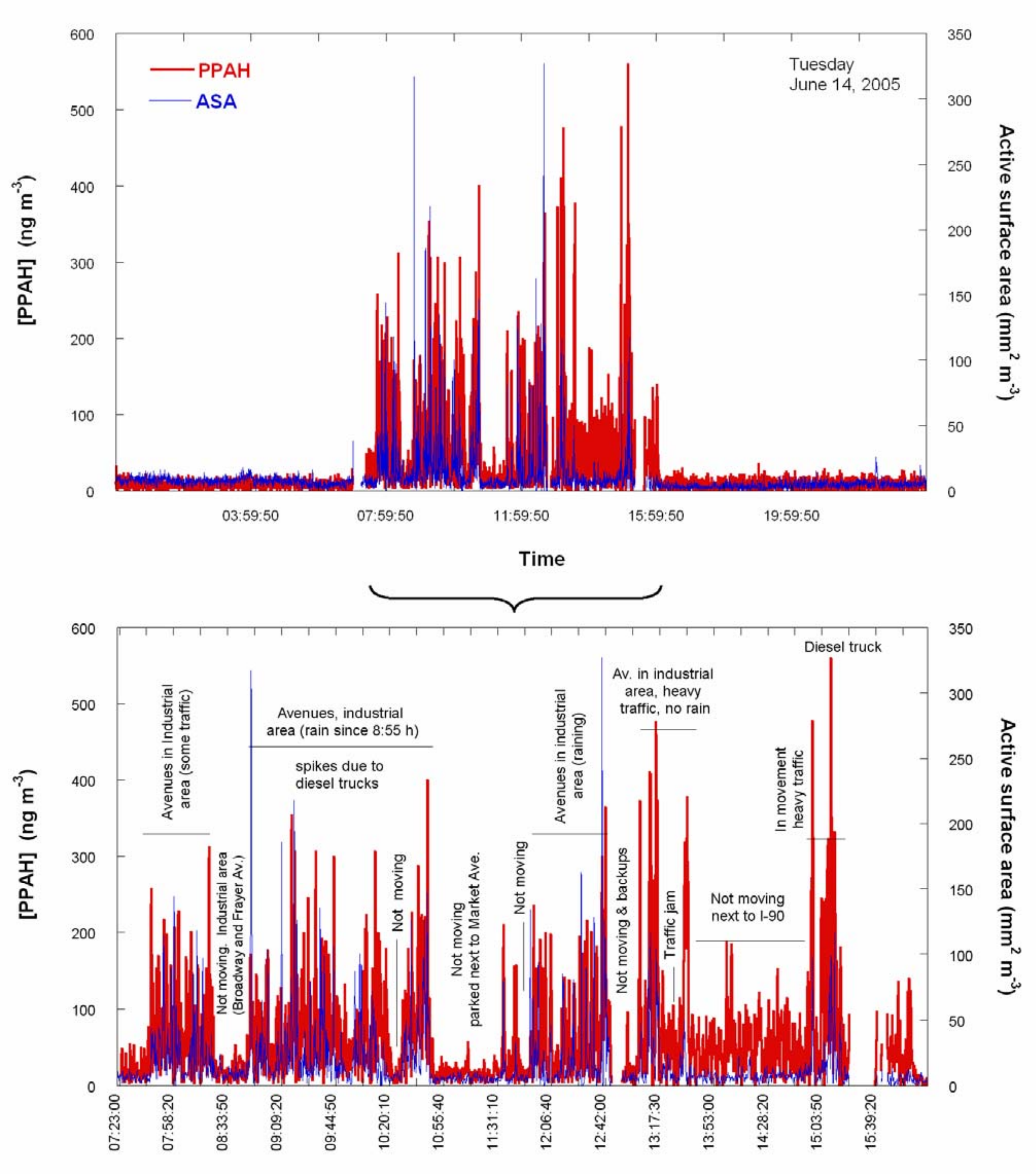


Figure 38. Time series of PPAH concentration and total active surface area measured on June 14. *The time resolution of measurements was 10 seconds. The top graphic shows the time series during the entire day, including measurements overnight and along roadways. The lower graph shows only measurements along roadways*

The GPS helps to reconstruct PPAH concentration data when the mobile unit is in motion. For example, Figure 39 shows the concentrations measured during the morning rush hour (8:00 to 9:00 h) along roadways near the SD site. The highest concentrations (darkest colors) are associated with diesel truck emissions. Along this route, five plumes with PPAH levels above 350 ngm^{-3} were registered. The median PPAH concentration was 86 ng m^{-3}, but concentrations lower than 50 ng m^{-3} and concentrations above 100 ngm^{-3} were measured throughout major portions of the track. As shown in Figure 40, PPAH profiles recorded along roadways can be superimposed on a map of the region to identify sectors of the city with high PPAH exposure.

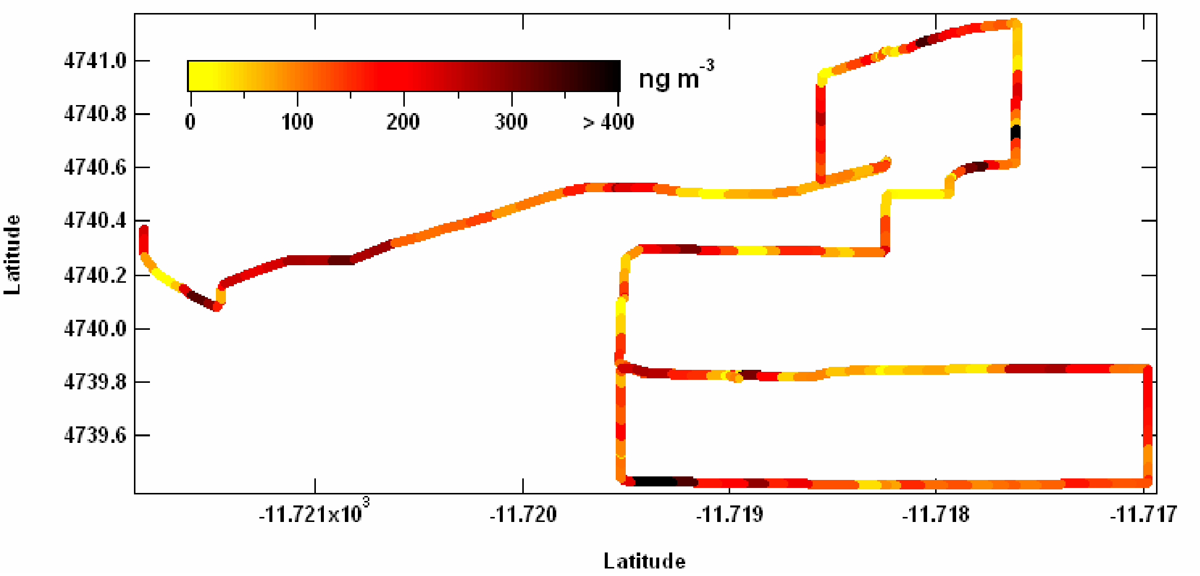


Figure 39. PPAH concentrations measured throughout different roadways around the SD-81 site on June 16 between 8:00 and 9:00 h.

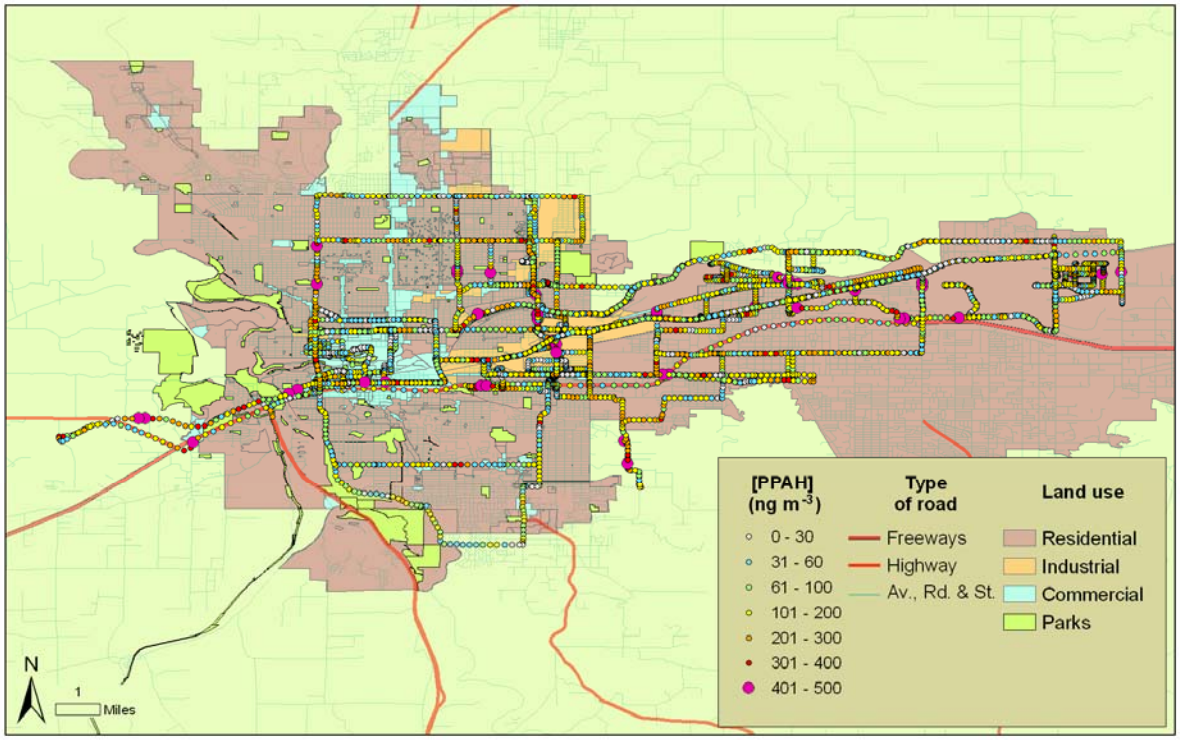


Figure 40. GIS map of all Spokane PPAH data

Figure 41 shows percentile plots of PPAH concentration and active surface area for the different kinds of measurements performed in this study. The median PPAH concentration observed in all urban avenues was 81 ng m^{-3}, which is much higher than the baseline concentration of 7 ng m^{-3} measured near the SD site,. However, sites located next to avenues can be heavily impacted by traffic, such as the one next to Sullivan Avenue (50 ng m^{-3}) listed in Figure 41.

To put some perspective on these data, the median PPAH concentration measured in this study on Spokane's avenues (81 ng m^{-3}) was higher than that reported in other US cities. Concentrations of 17 and 24 ng m^{-3} have been reported for New York and Boston, respectively (Zhiqiang *et al.*, 2000). In general, US cities have much lower PPAH concentrations than cities in Europe, Latin America and Asia. Siegmann *et al*. (1999) measured average concentrations above 650 ng m^{-3} in Paris and above 920 ng m^{-3} in Tokyo. In a similar monitoring study in Mexico City, we measured an average concentration of 173 ng m^{-3} (Velasco *et al*., 2004). There are not as many diesel cars in the US as in Europe (40% of passenger cars in Paris are diesel) or Tokyo. In Mexico City, although there are no diesel passenger cars, the PPAH concentrations are higher than in the US because of an older fleet and because not all cars are equipped with catalysts. Chase measurements of diesel trucks and buses in Spokane clearly indicated that these vehicles are the main source of PPAH in the city.

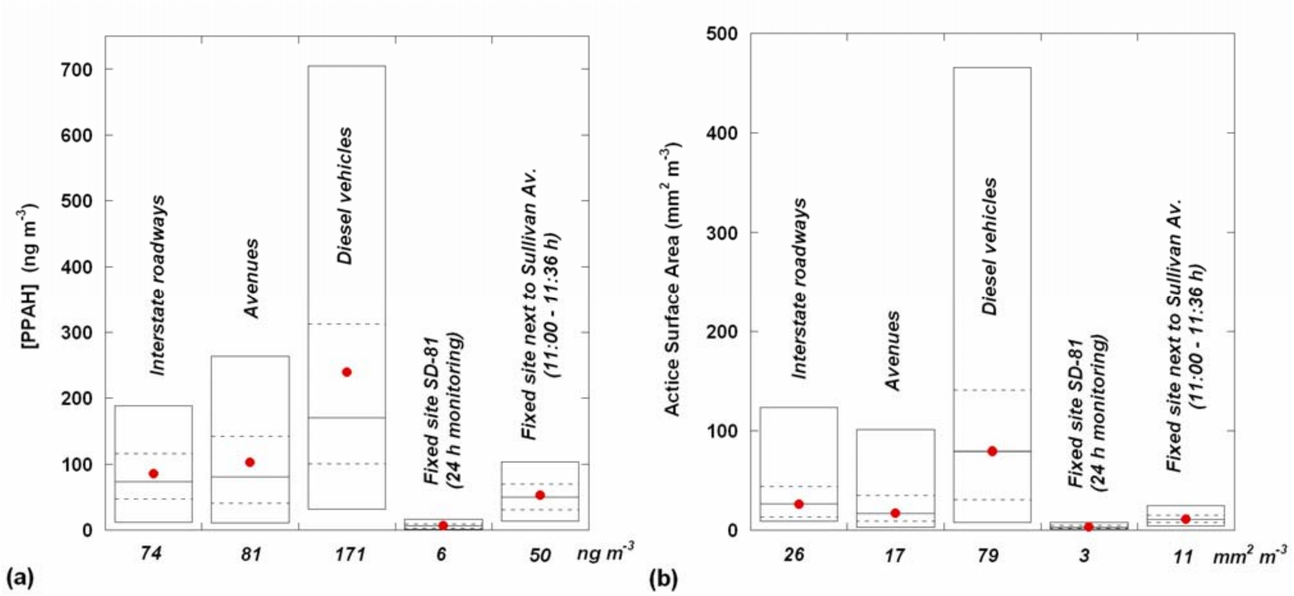


Figure 41. Percentile plots of PPAH concentrations (a) and active surface area (b) for different kind of measurements. Each box encloses 90% of the data.

The bottom and top of each box represent 5% and 95% of the data. Three lines are drawn inside each box. The middle line represents the median value as well as the number written below each column, while the lower and upper dashed lines represent 25% and 75% of the data, respectively. The red dots indicate the mean values

A complete summary of the PPAH data obtained during the June mobile sampling program in Spokane is shown in Figure 42 through Figure 46.

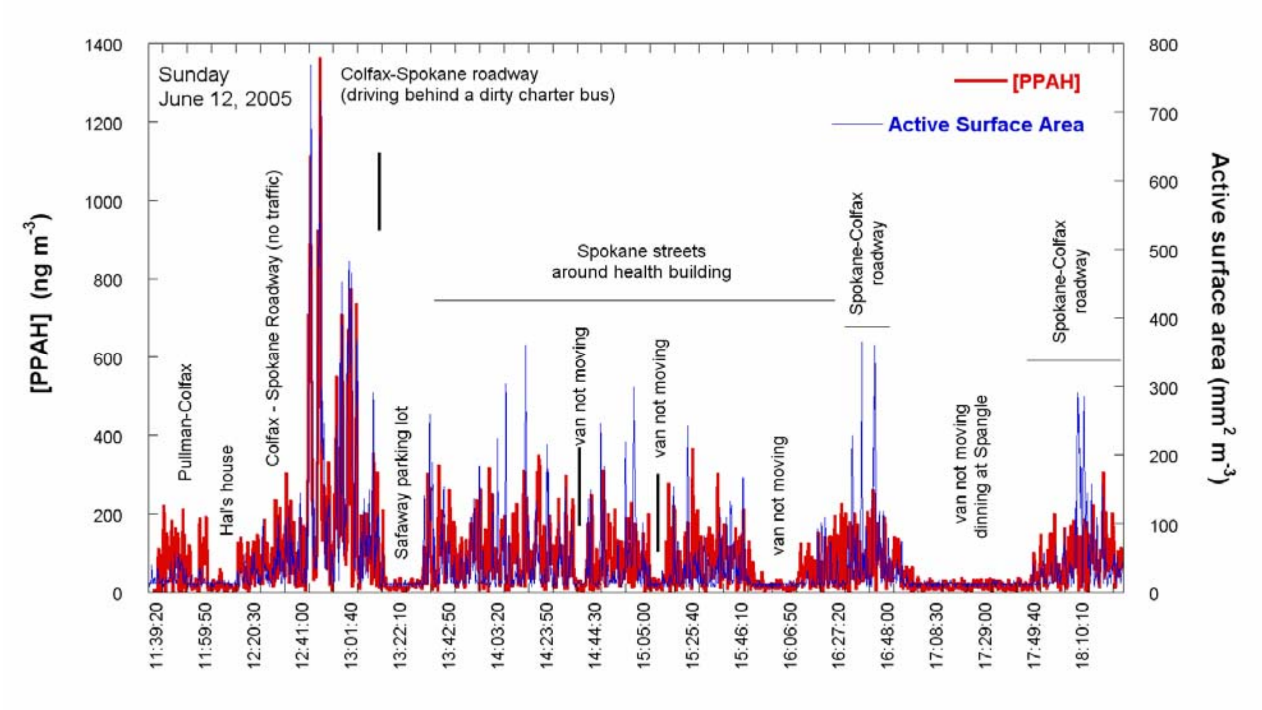


Figure 42. Time series of PPAH concentration and total active surface area during the mobile sampling period on June 12, 2005.

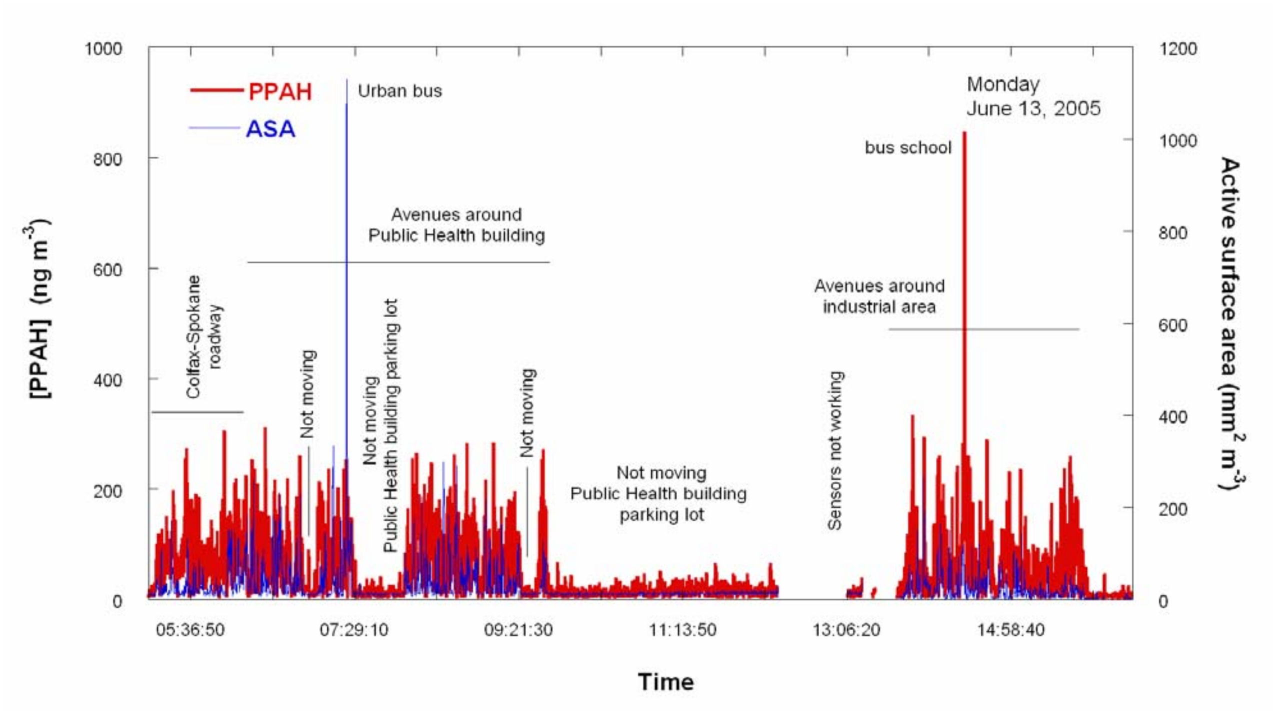


Figure 43. Time series of PPAH concentration and total active surface area during the mobile sampling period on June 13, 2005.

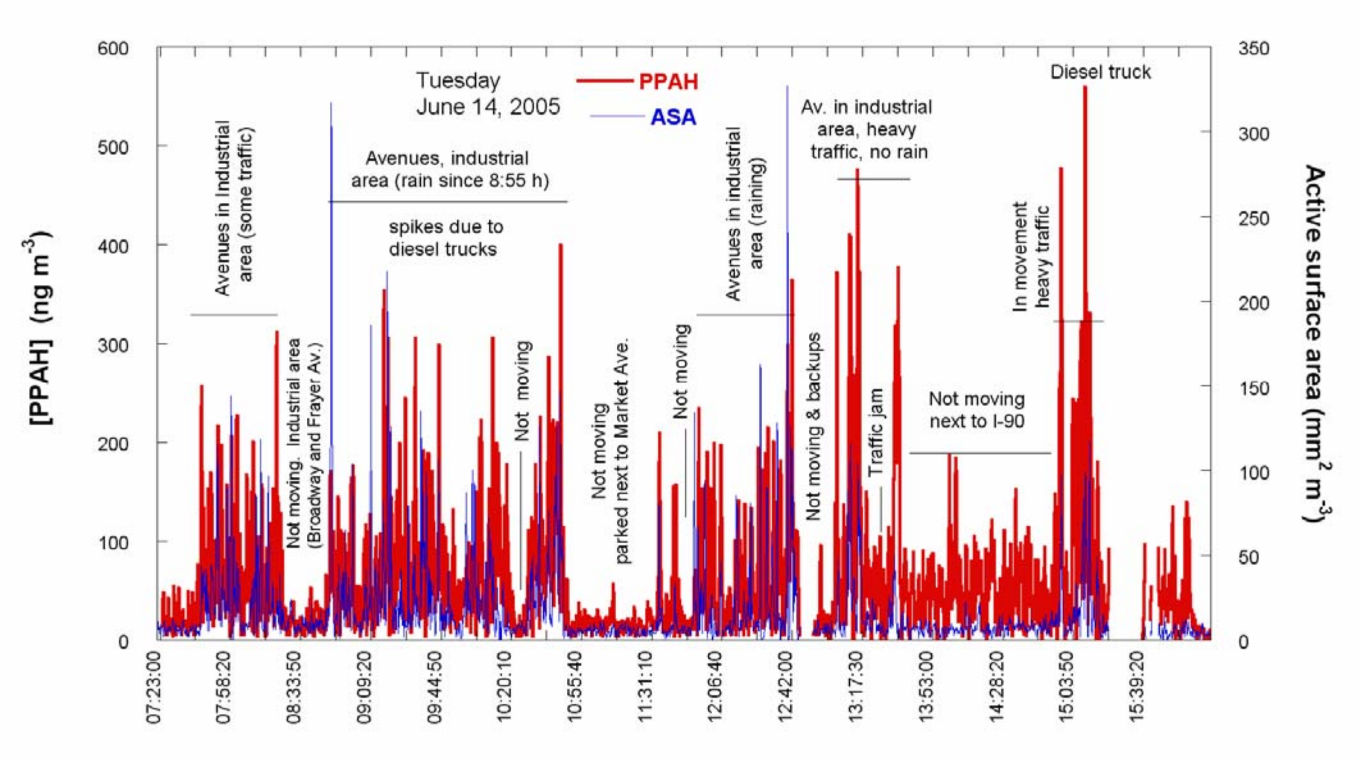


Figure 44. Time series of PPAH concentration and total active surface area during the mobile sampling period on June 14, 2005.

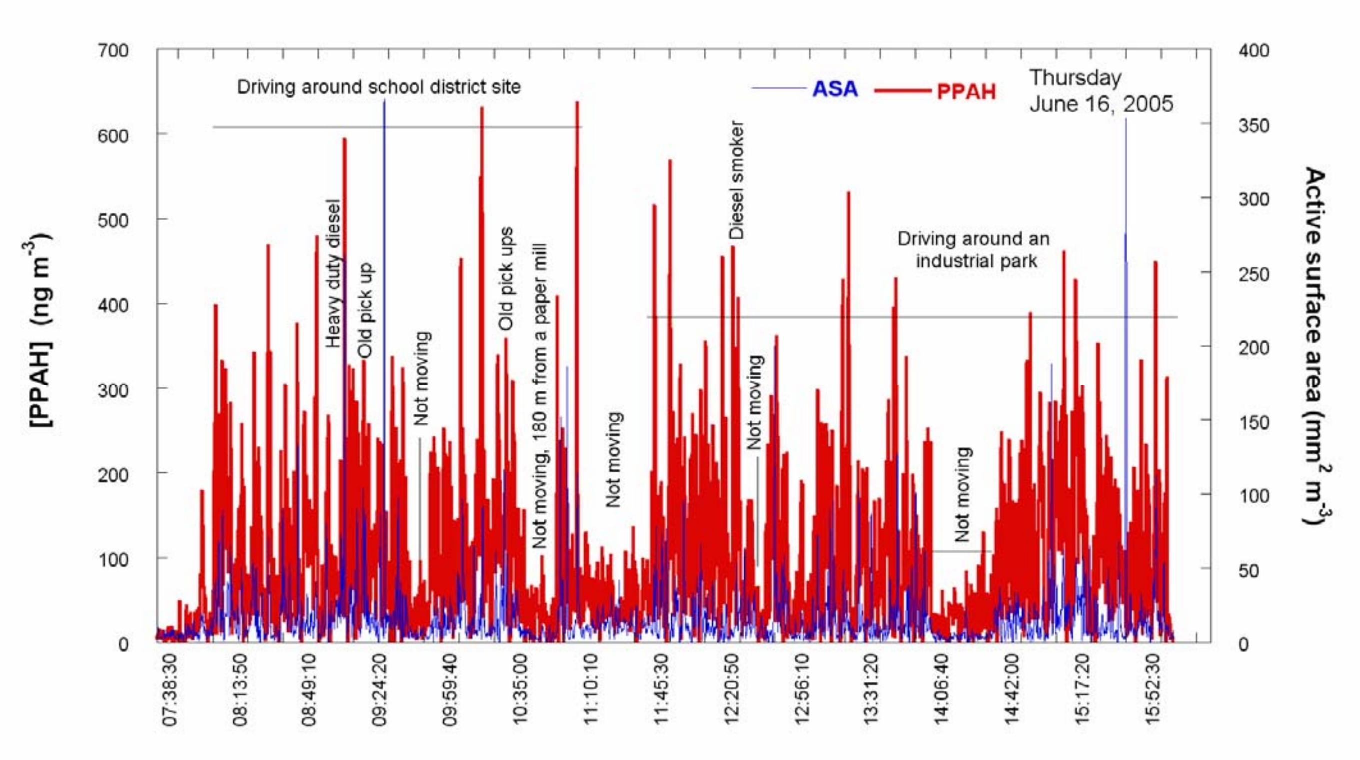


Figure 45. Time series of PPAH concentration and total active surface area during the mobile sampling period on June 16, 2005.

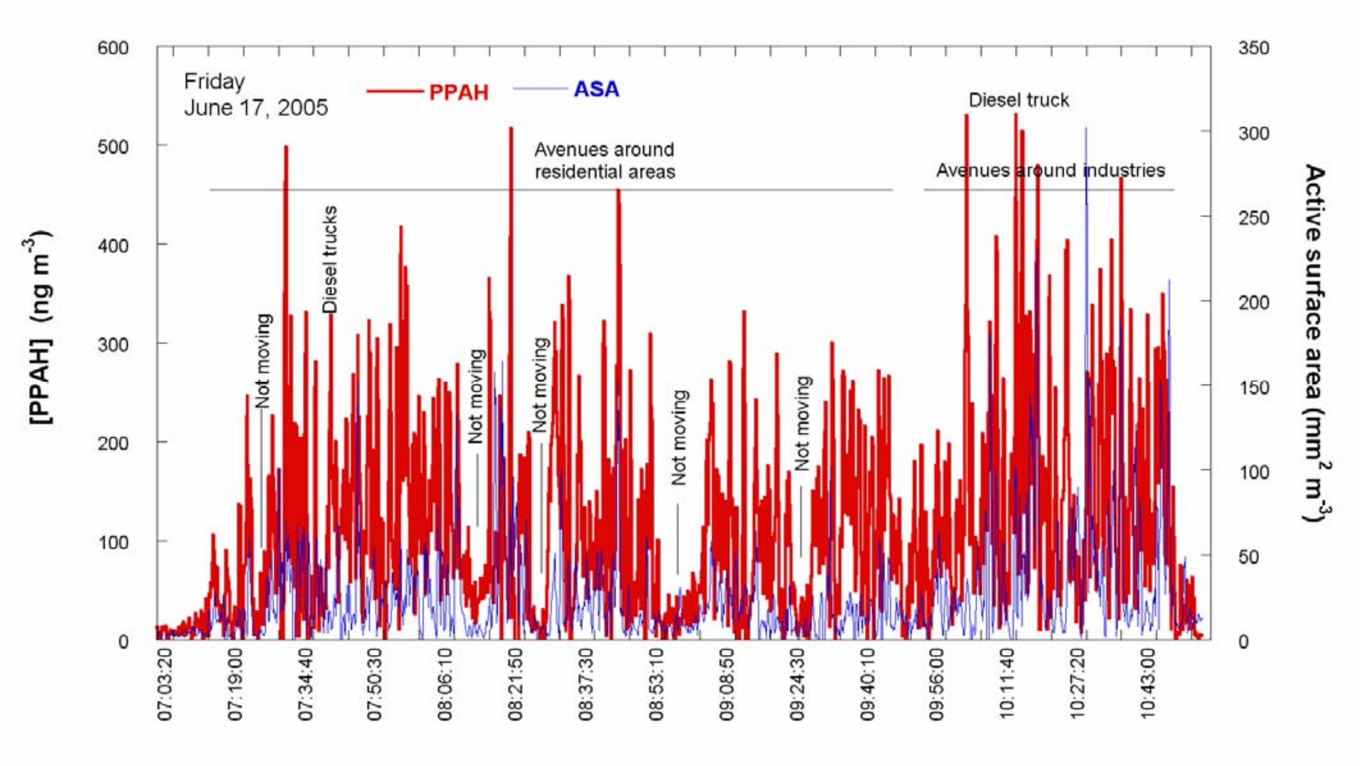


Figure 46. Time series of PPAH concentration and total active surface area during the mobile sampling period on June 17, 2005.

For all percentile plots of PPAH concentrations and active surface area presented on the following pages, each box encloses 90% of the data. The bottom and top of each box represent 5% and 95% of the data. Three lines are drawn inside each box. The middle line represents the median value, while the lower and upper dashed lines represent 25% and 75% of the data, respectively. The red dots indicate the mean values.

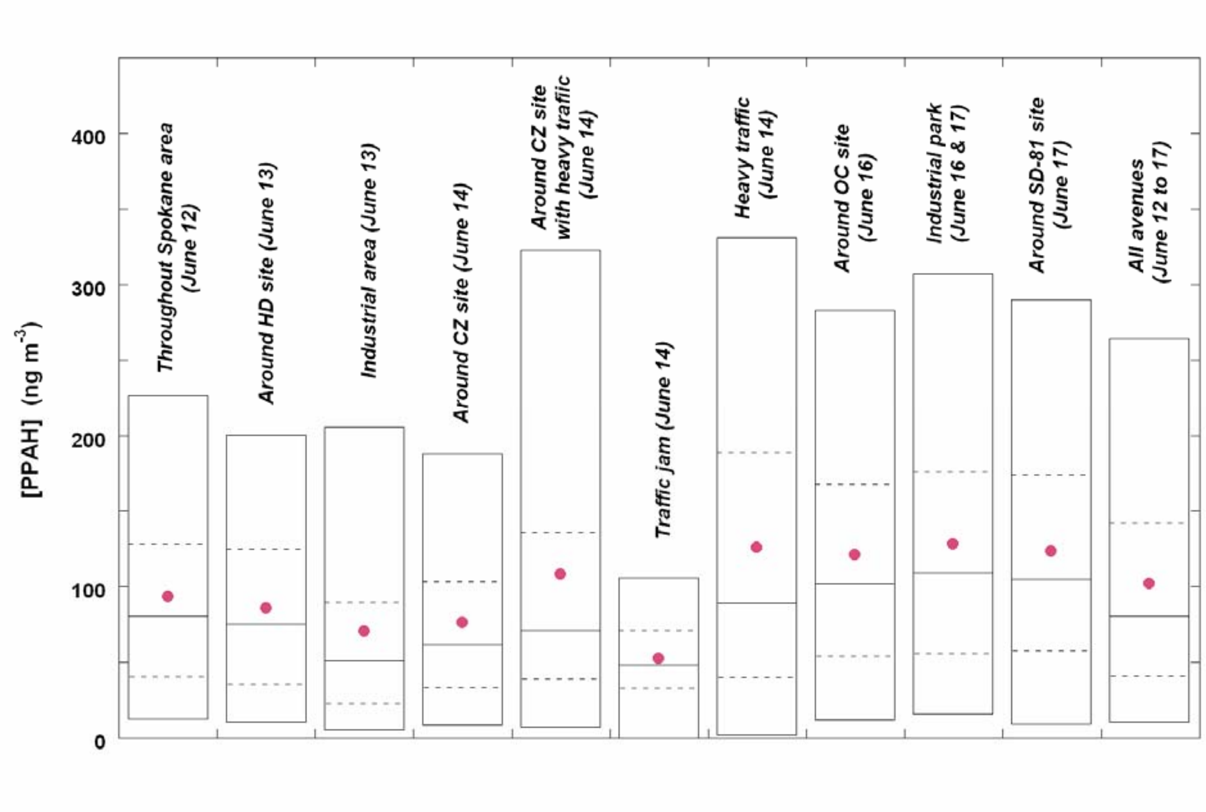


Figure 47. Percentile plot of PPAH concentrations measured along different Spokane. Avenues.

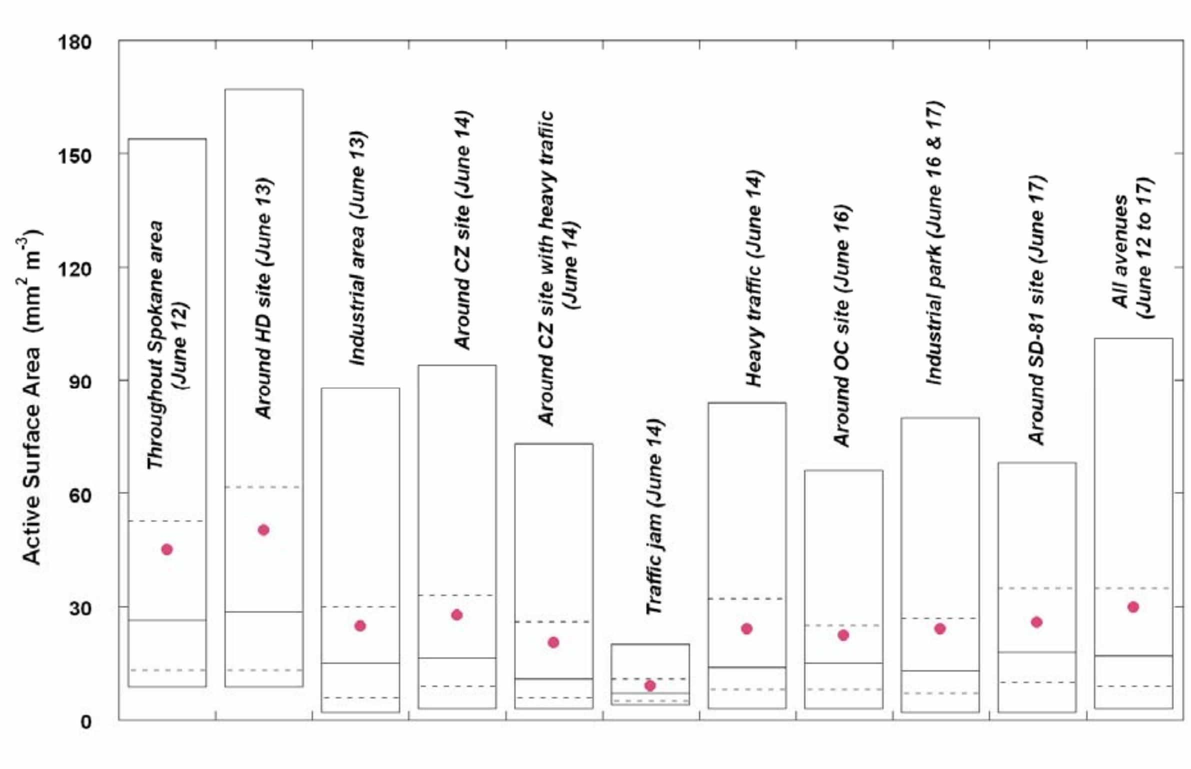


Figure 48. Percentile plot of active surface areas measured along different Spokane avenues.

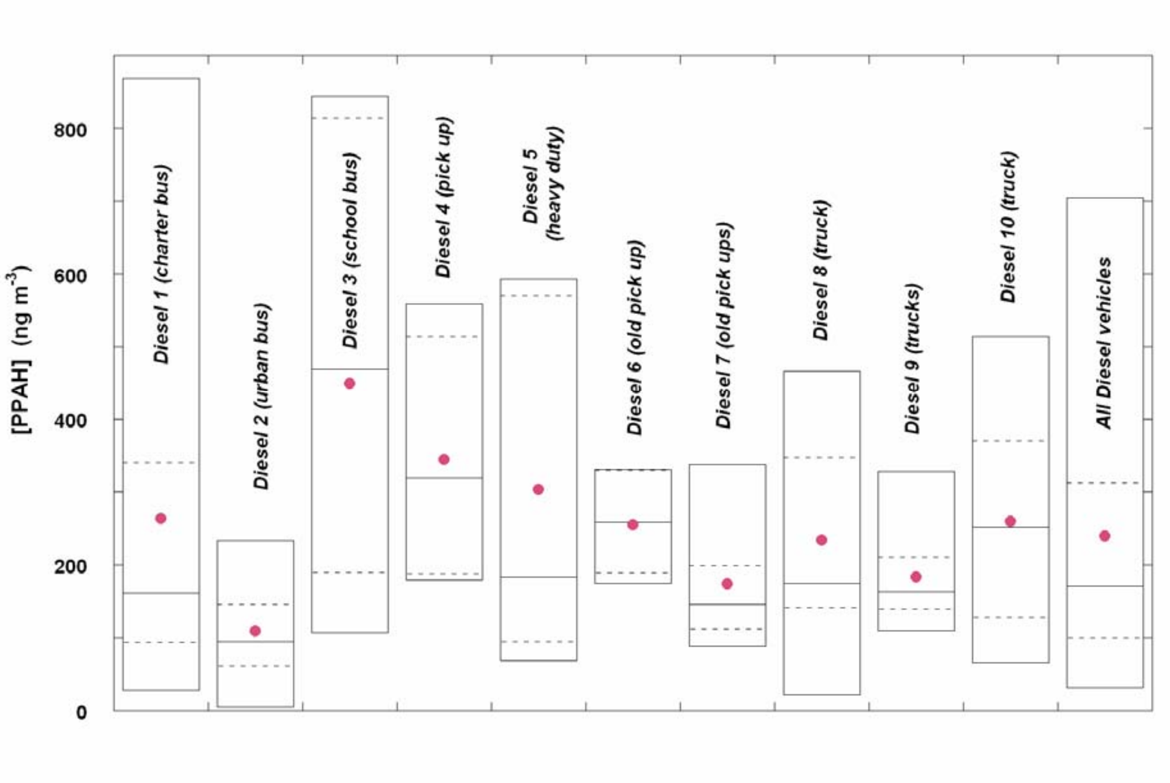


Figure 49. Percentile plot of PPAH concentrations from diesel vehicles measured during chase experiments.

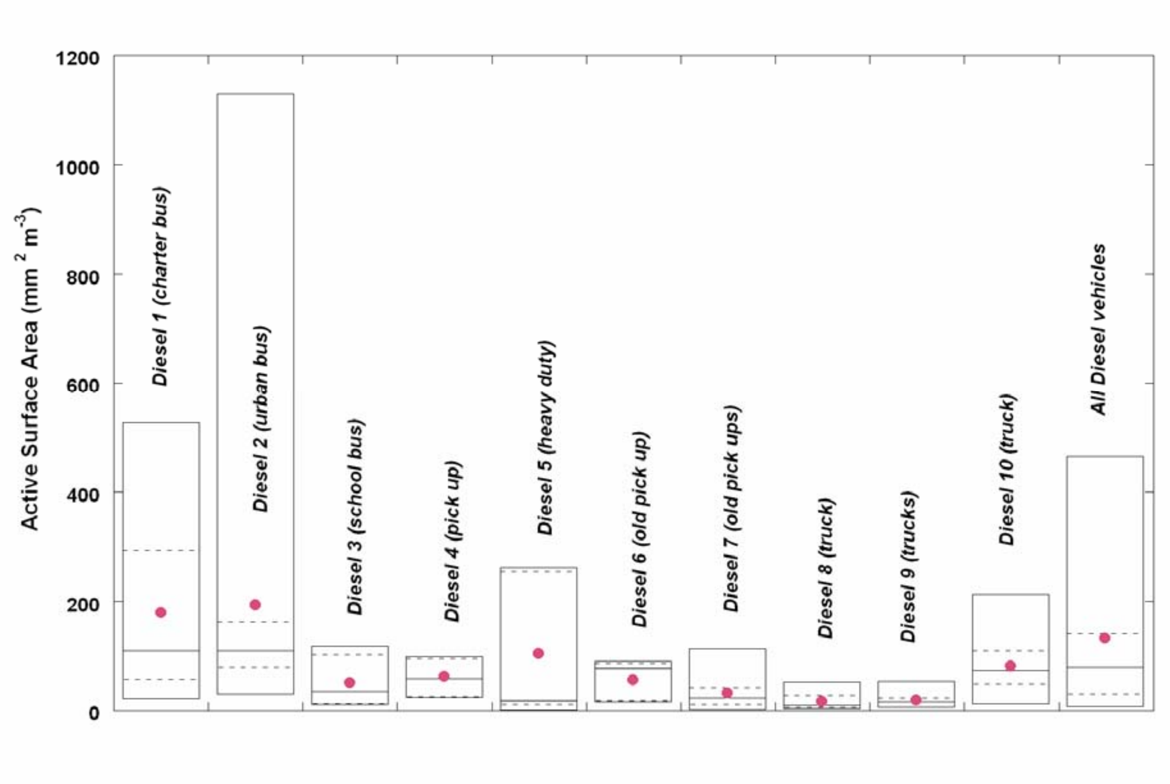


Figure 50. Percentile plot of active surface areas from diesel vehicles measured during chase experiments.

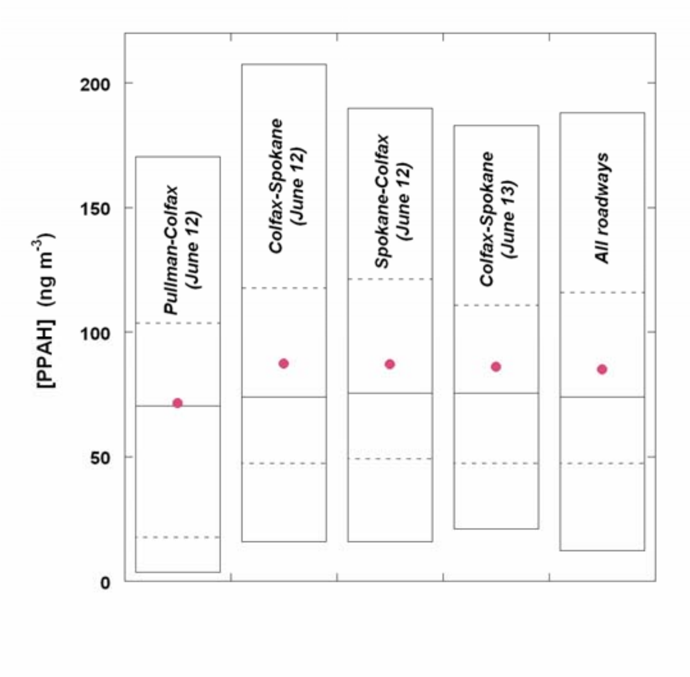


Figure 51. Percentile plot of PPAH concentrations measured on interstate roadways around Spokane.

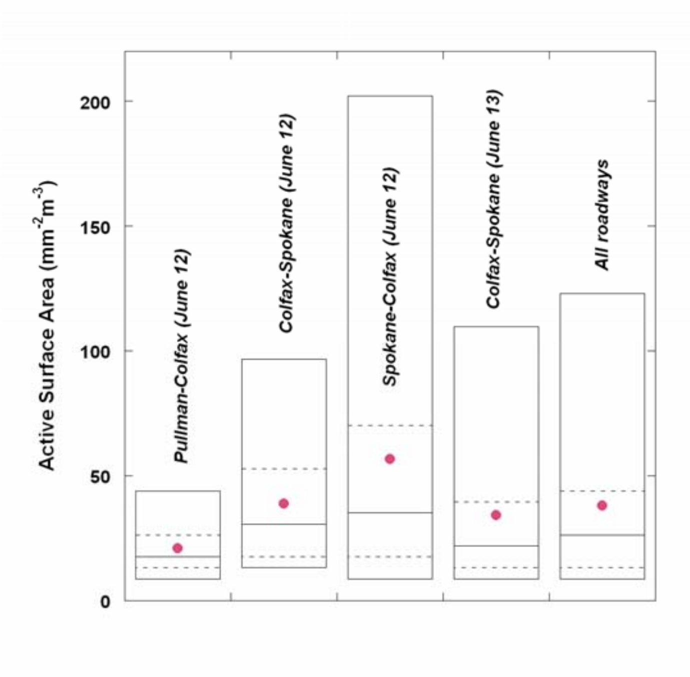


Figure 52. Percentile plot of active surface areas measured on interstate roadways around Spokane.

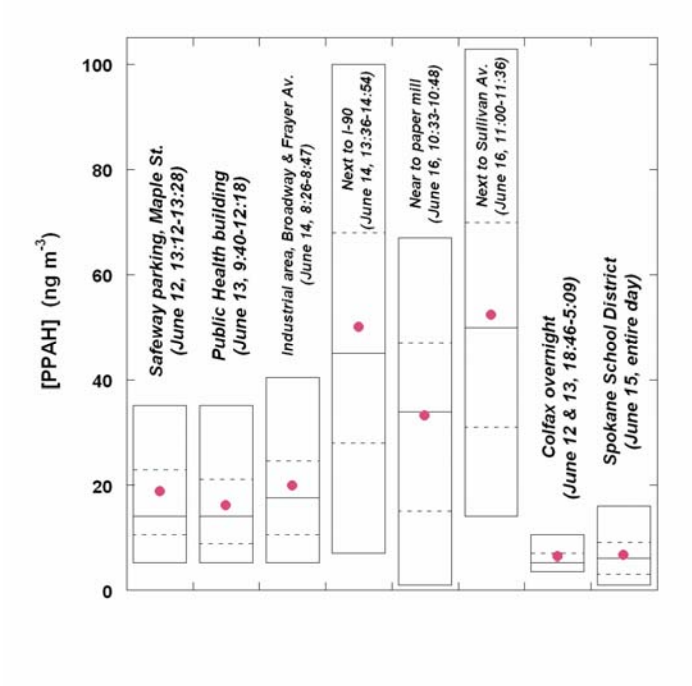


Figure 53. Percentile plot of PPAH concentrations measured at fixed sites.

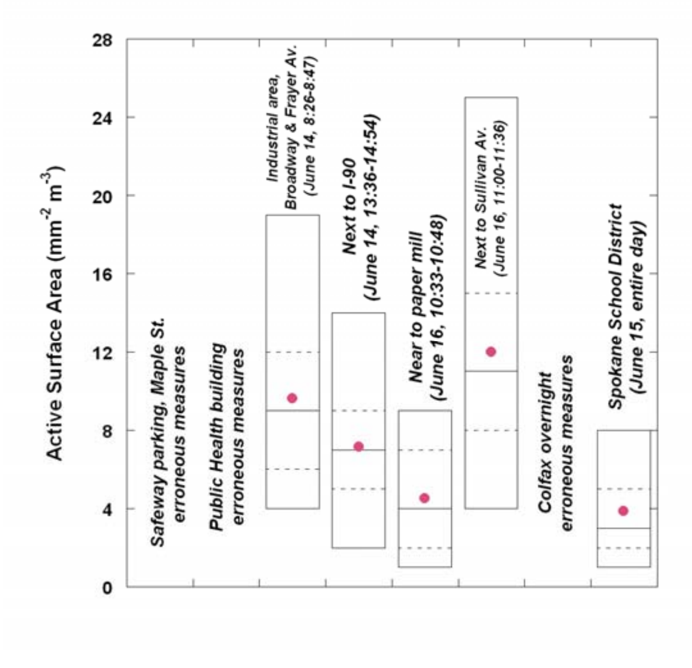


Figure 54. Percentile plot of active surface area measured at fixed sites.

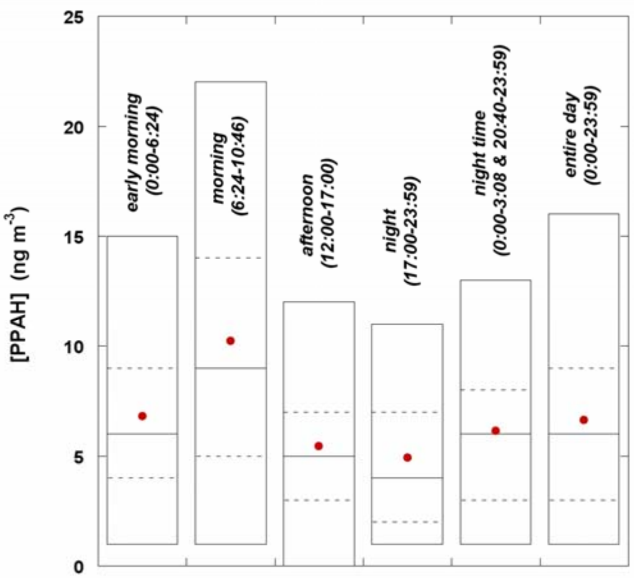


Figure 55. Percentile plot of PPAH concentrations measured while stationary at the SD site on June 15, 2005.

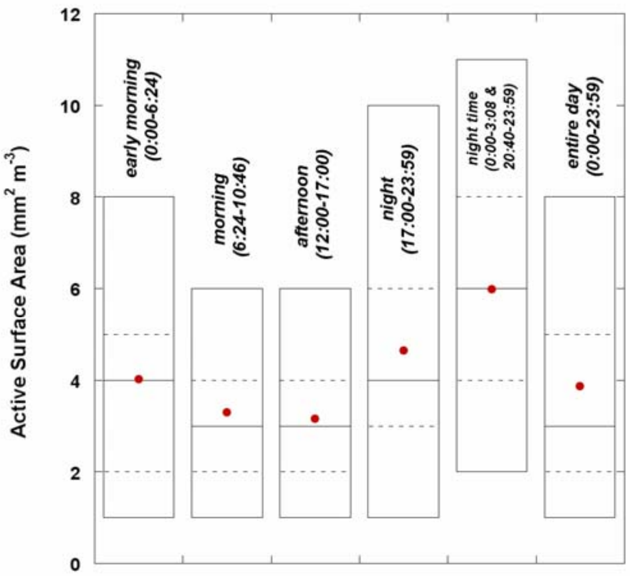


Figure 56. Percentile plot of active surface area measured while stationary at the SD site on June 15, 2005.

4.5 Particle Size Distribution

Of the particles with an aerodynamic diameter smaller than 20 μm measured with the APS 3320 sensor at fixed sites and along roadways, it was found that on average 90% existed in the submicron range. Figure 57 shows the cumulative size distribution of particles measured on streets around the OC site during the morning rush period (7:10 to 9:45 h). 71% of the particles had an aerodynamic diameter smaller than 0.523 μm and 91% smaller than 1 μm. For the fresh emission of a diesel bus it was found that 85% of the particles were smaller than 0.523 μm and 97% smaller than 1 μm

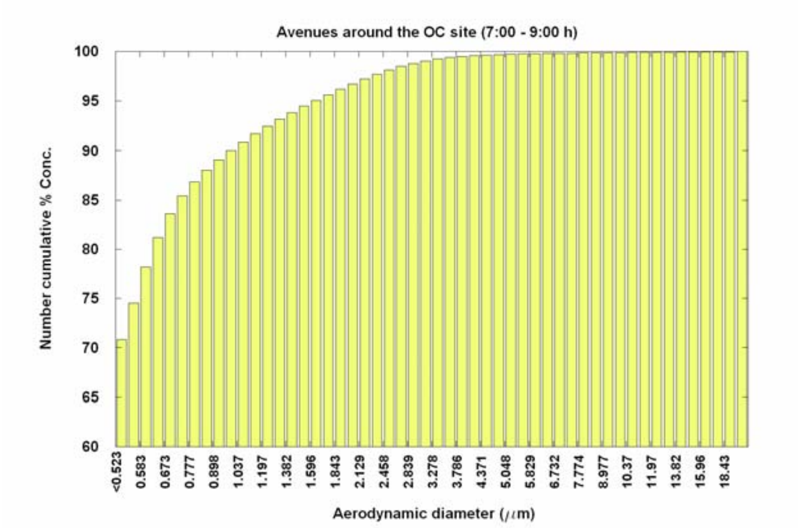


Figure 57. Cumulative size distribution of particles with aerodynamic diameter smaller than 20 μm in avenues around the OC site measured on June 17 between 7:10 and 9:45 h.

Additional size distribution data for measurements made during this field campaign are listed in the following graphs and tables.

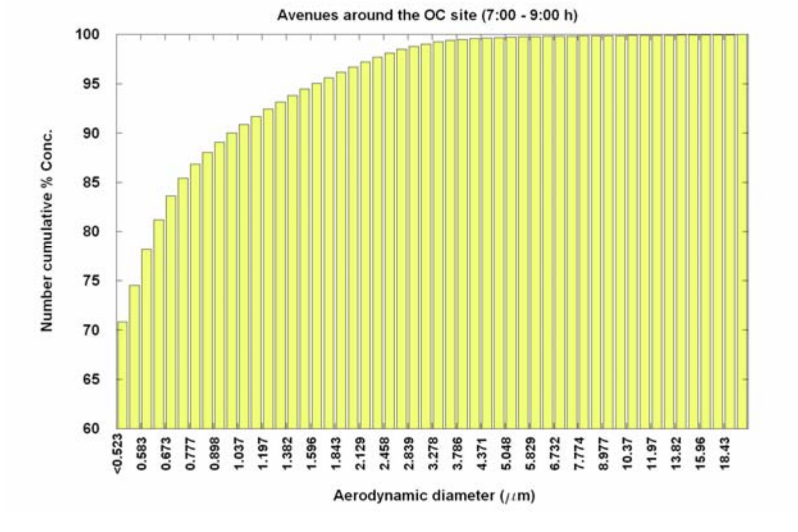


Figure 58. Cumulative size distribution of particles for avenues around the OC site measured on June 17 between 7:20 and 9:45 h

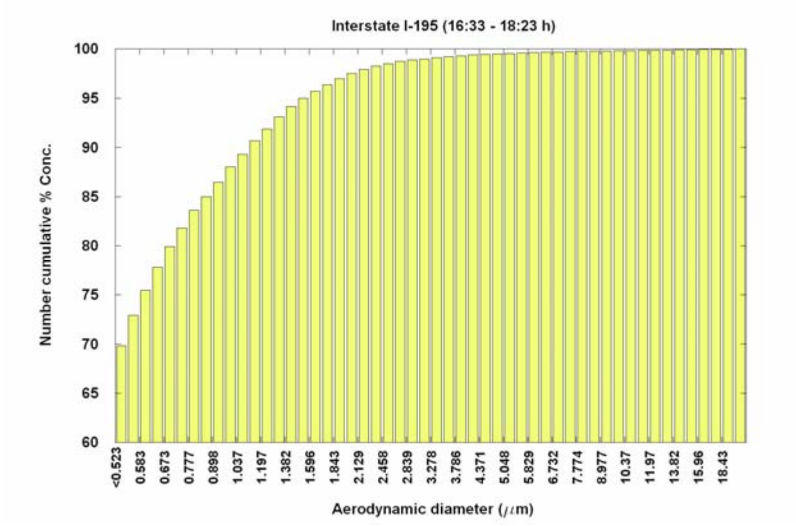


Figure 59. Cumulative size distribution of particles measured in the interstate roadway I-195 on June 12 between 16:33 and 18:23 h.

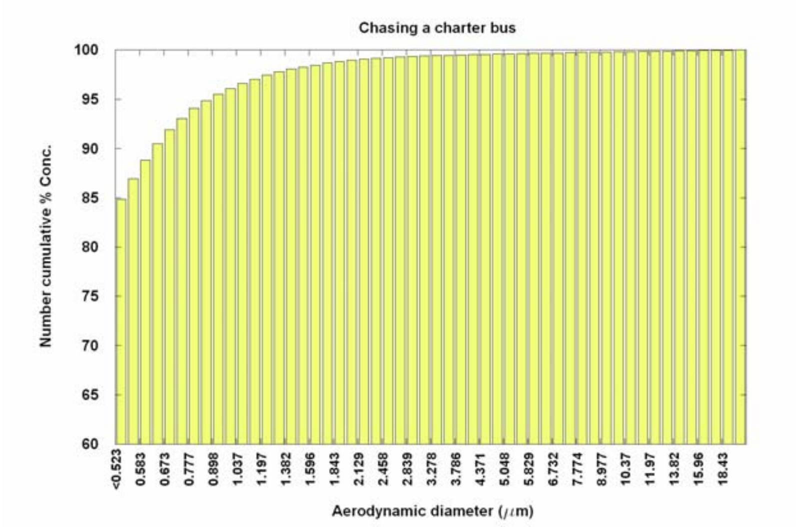


Figure 60. Cumulative size distribution of particles from a plume emitted by a charter bus.

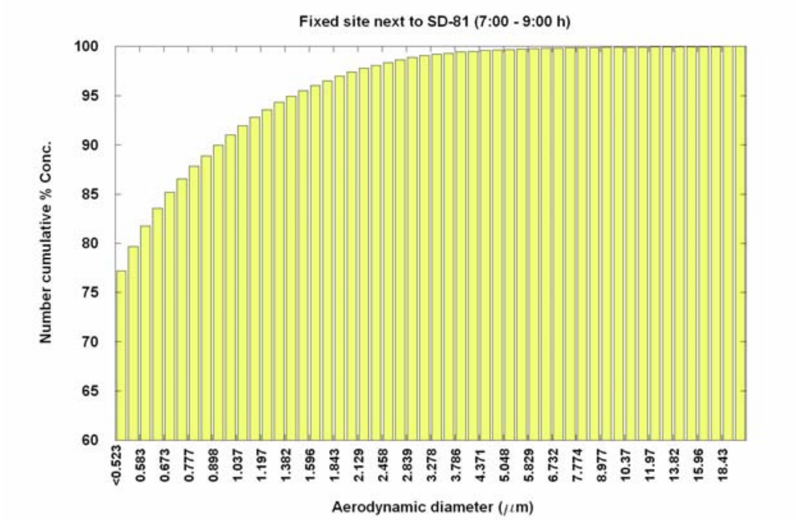


Figure 61. Cumulative size distribution of particles measured at the SD site on June 15 during the morning rush hours (7:00 and 9:00 h).

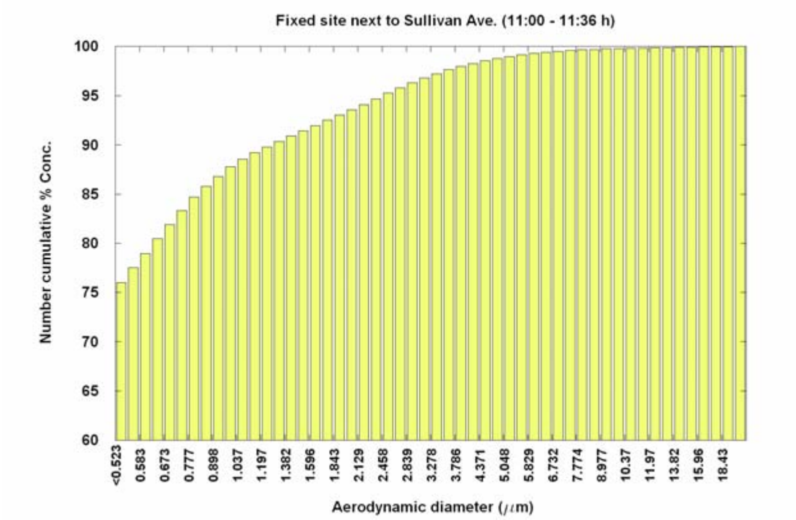


Figure 62. Cumulative size distribution of particles measured in the fixed site next to Sullivan avenue on June 16 between 11:00 and 11:36 h.

4.6 VOC Measurements with the PTR-MS

The Proton Transfer Reaction Mass Spectrometry identifies VOCs in ambient air as their molecular mass plus one. This technique creates ions by transferring a H^+ from H_3O^+ to the VOCs followed by mass spectroscopy detection of the product ions (Lindinger et al., 1998). The PTR-MS does not employ a column, so response times are short (seconds) and automated, continuous measurements can be made over extended periods of time. Specificity in the PTR-MS is achieved by the soft ionization (minimal fragmentation) and response is limited to species with a greater proton affinity than water. In cases where several VOCs produce the same M+1 ion, individual species quantitation is not possible. For example, the signal at mass 121 (C_3-benzenes) is comprised of i- and n-propylbenzene, three ethyltoluenes and three trimethylbenzenes. Validation of PTR-MS measurements have been performed by de Gouw et al. (2003) and Warnake et al. (2003) to determine the set of VOCs that are suitable for measurement with this technique.

During the Spokane field campaigns, a PTR-MS instrument belonging to Montana State University (MSU) was housed in our mobile laboratory. Of the "core" air toxics, the PTR-MS can measure benzene and acetaldehyde without interference from other VOCs. In addition, it is a good monitoring technique for other low molecular weight oxygenated hydrocarbons (methanol and acetone), other aromatics (toluene, xylenes, etc) and some sulfur containing species (methyl mercaptan, dimethyl sulfide, etc). In the data summary that follows, we have presented benzene, acetaldehyde, methanol, and acetone concentrations in daily graphs with notations as to location, plumes, etc. This format is similar to that employed with the PPAH data. Acetone is a good indicator of area sources that emit solvents and is usually accompanied by elevated levels of toluene and higher molecular weight aromatics. Thus, acetone measurements can be used to pinpoint release points for several VOCs.

Figure 63 through Figure 70 summarize PTR-MS data for the June sampling period and Figure 71 through Figure 76 summarize the PTR-MS data collected during the winter 2005 sampling period.

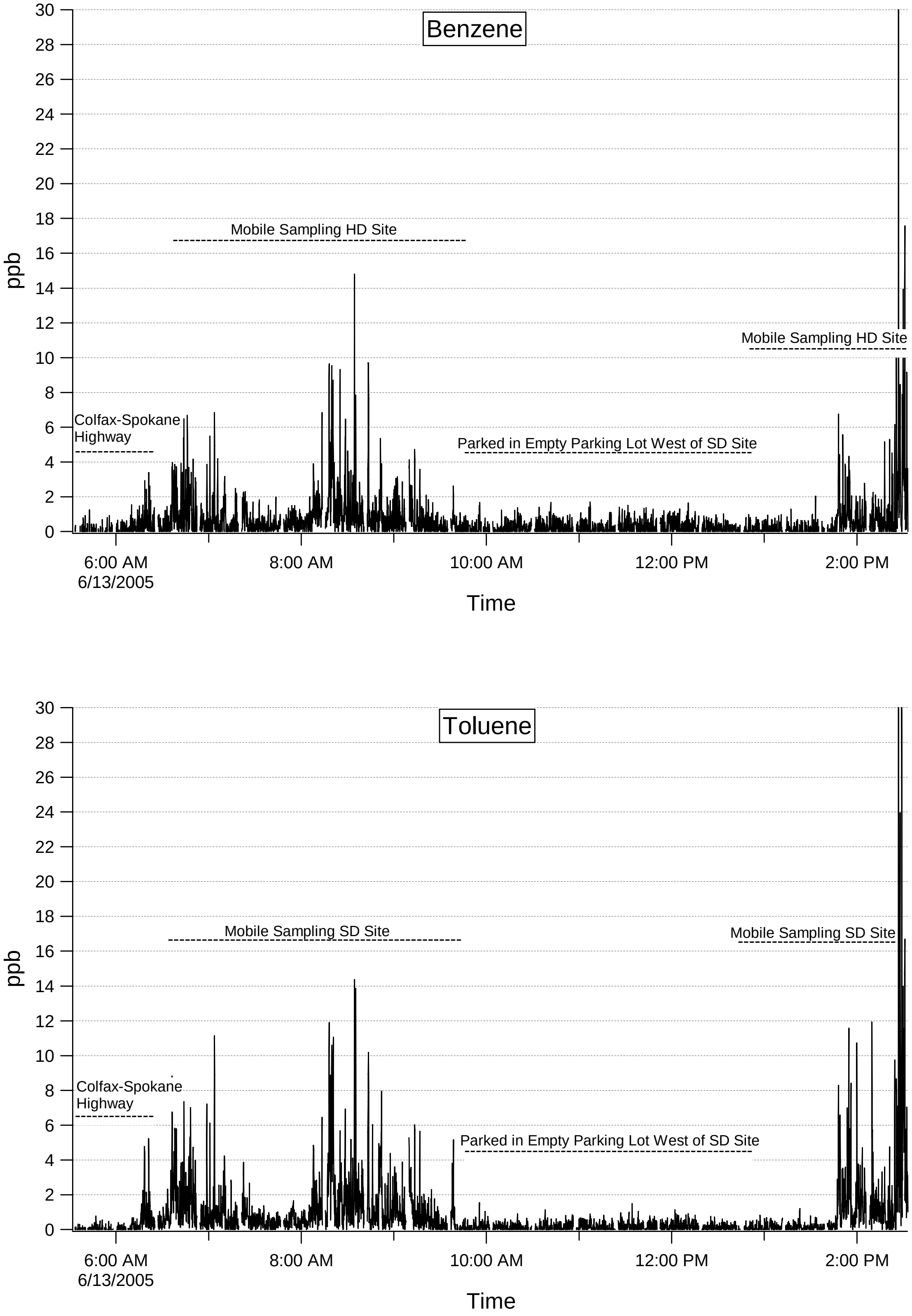


Figure 63. PTR-MS data collected on June 13, 2005.

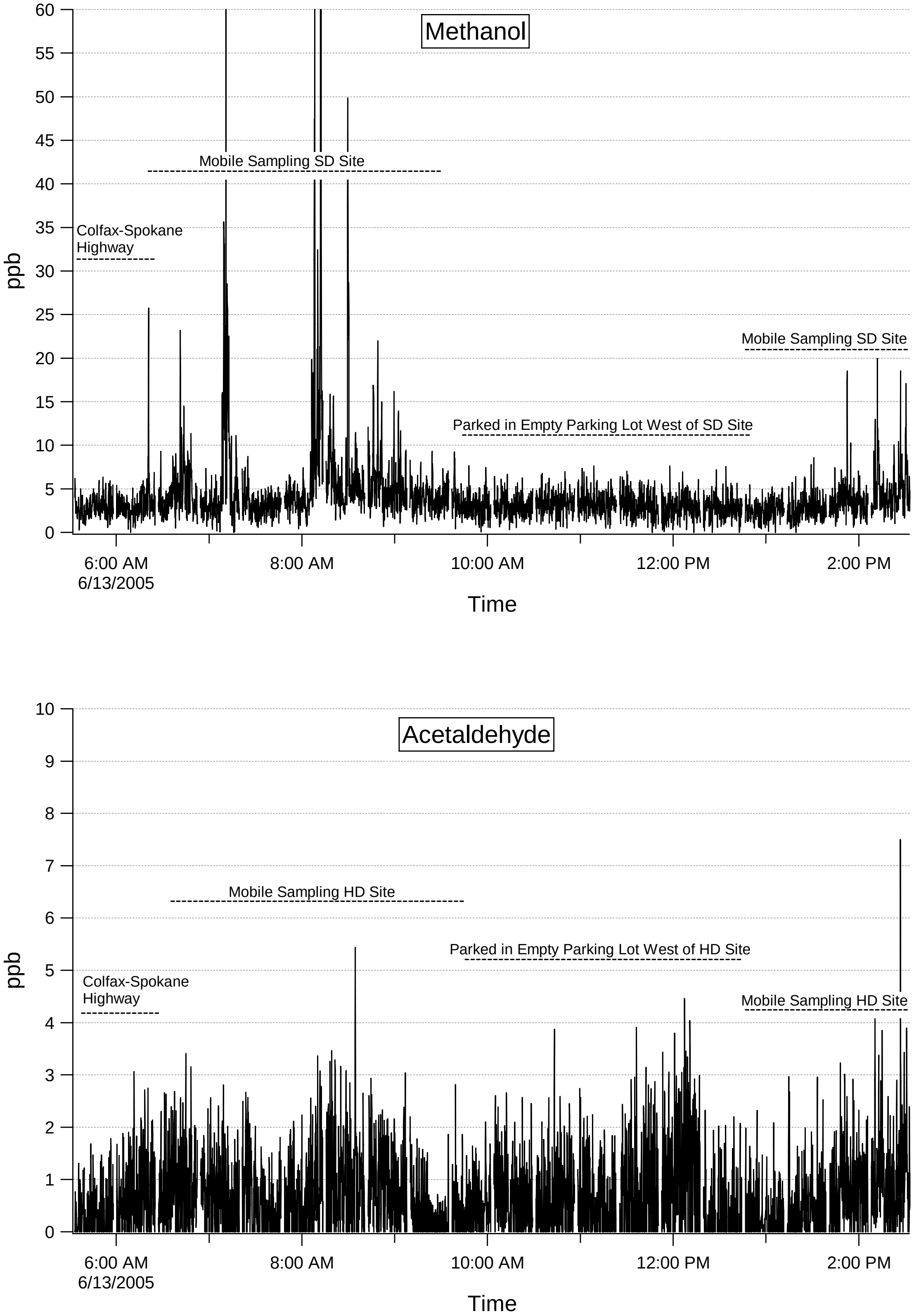


Figure 64. PTR-MS data collected on June 13, 2005.

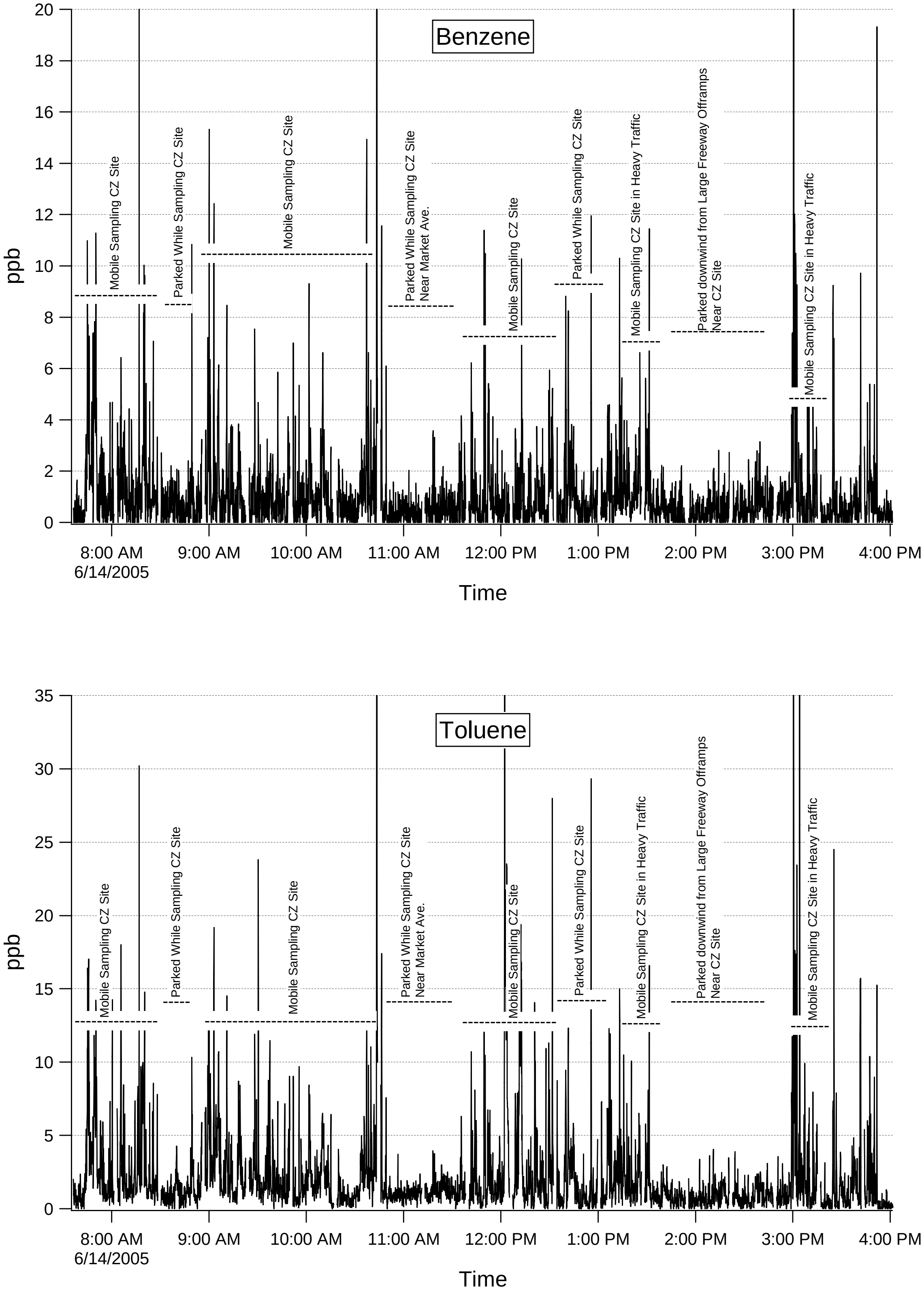


Figure 65. PTR-MS data collected on June 14, 2005.

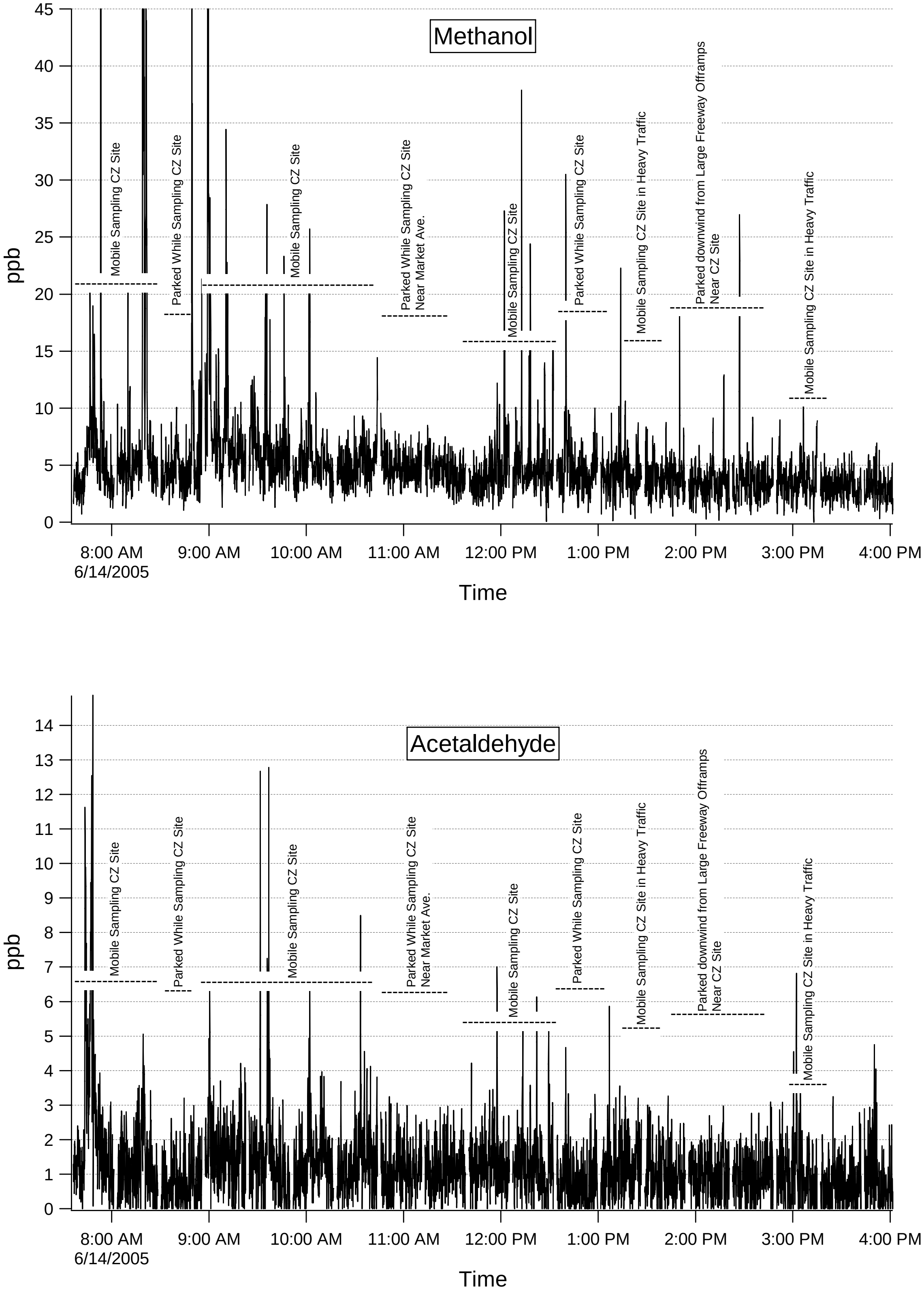
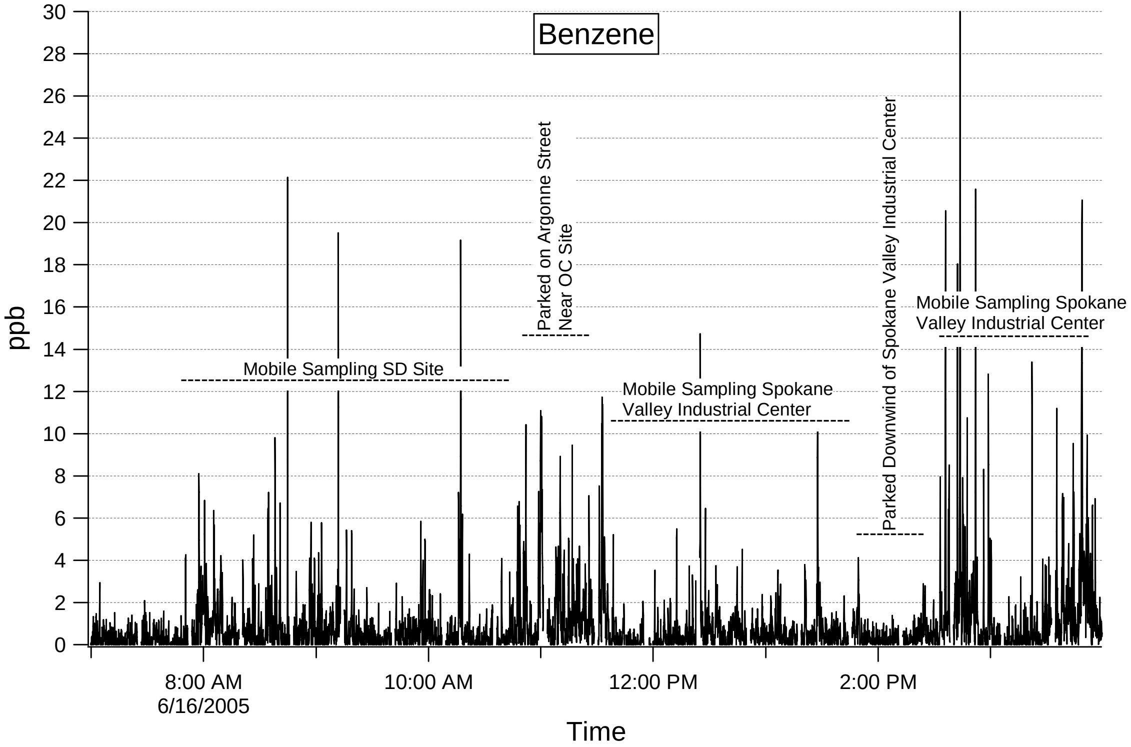


Figure 66. PTR-MS data collected on June 14, 2005.



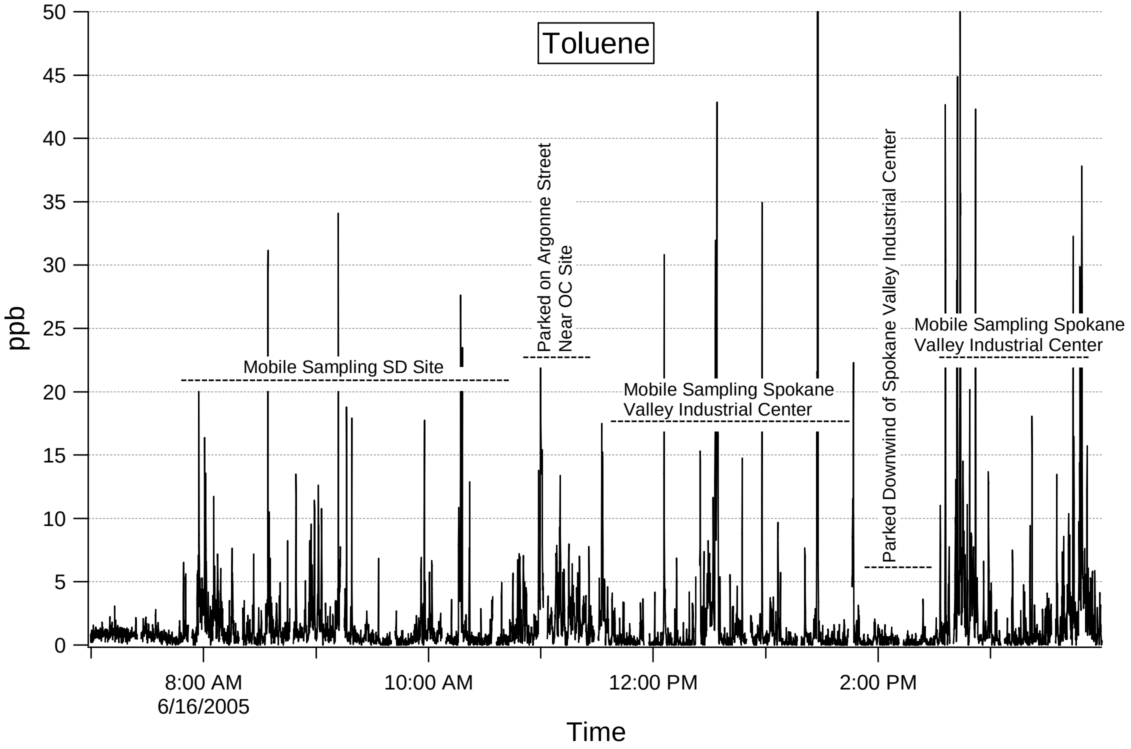
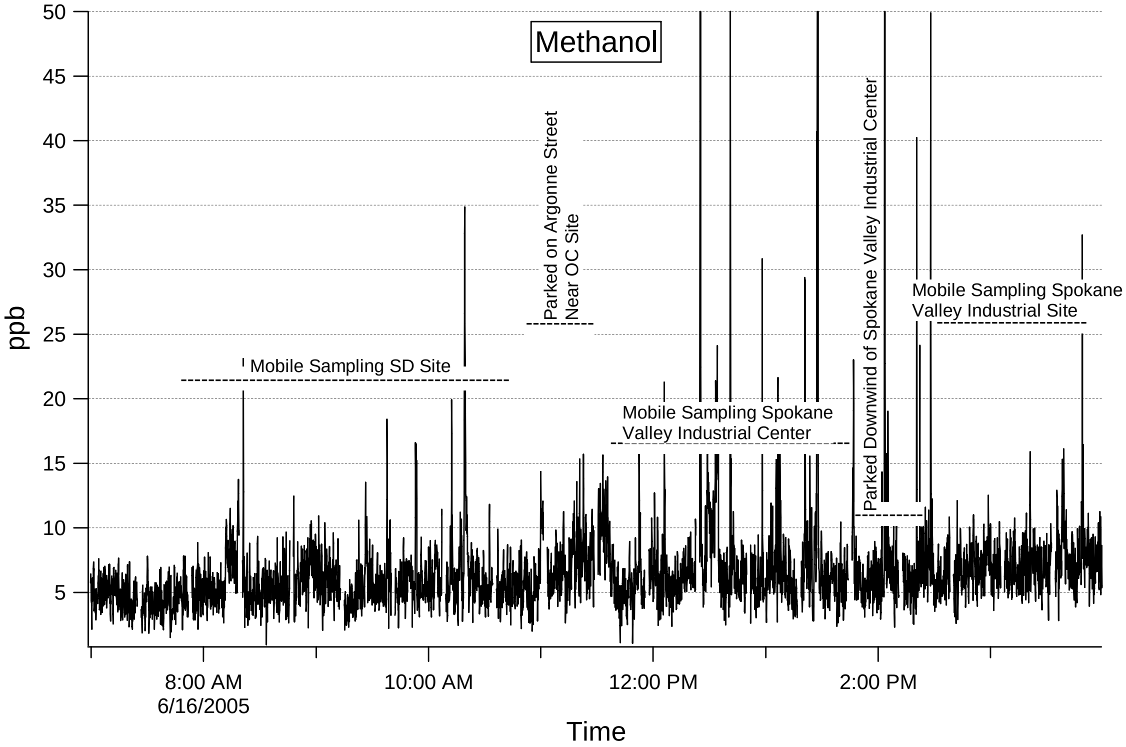


Figure 67. PTR-MS data collected on June 16, 2005.



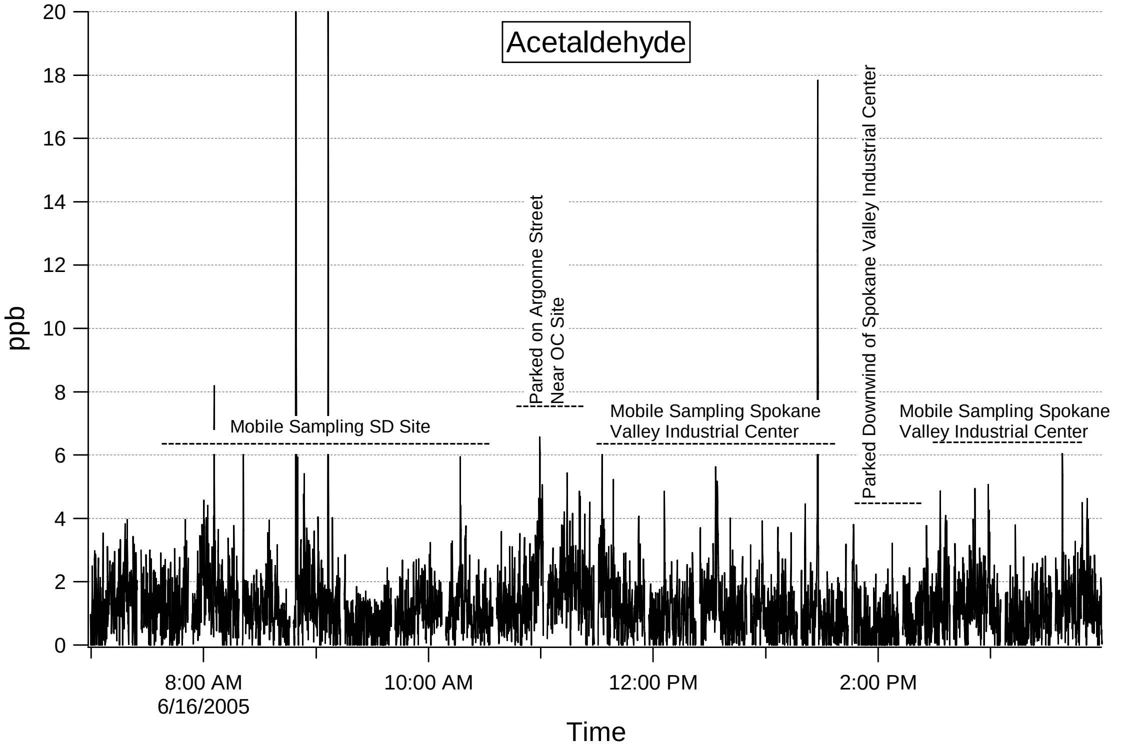


Figure 68. PTR-MS data collected on June 16, 2005.

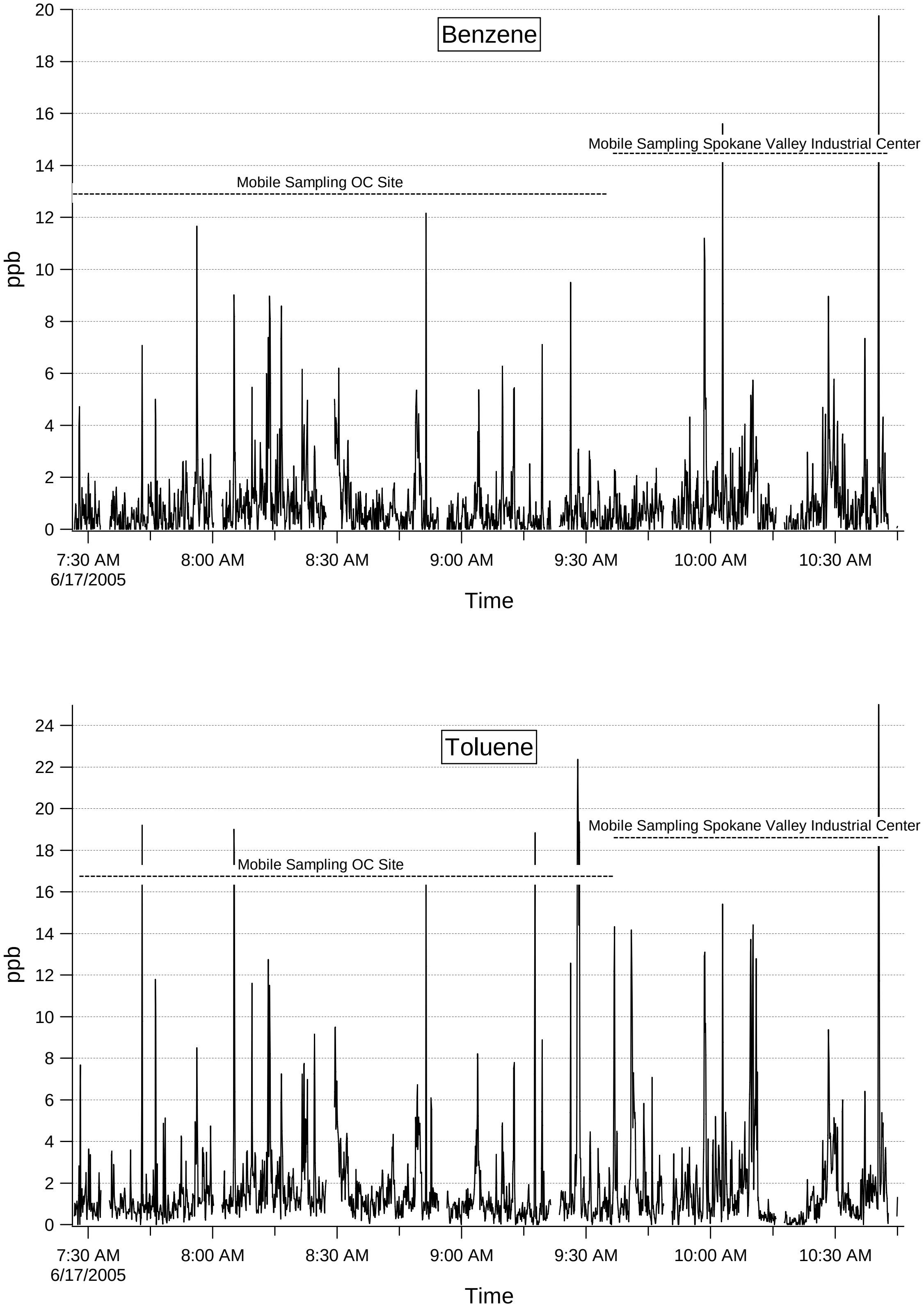
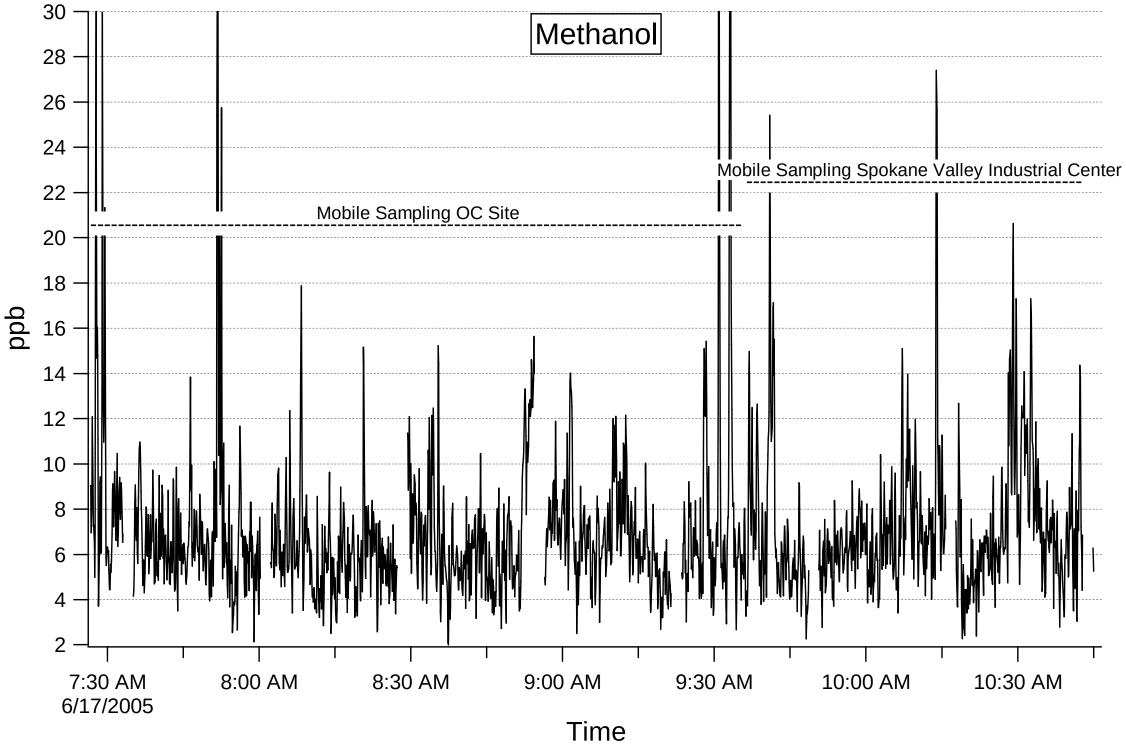


Figure 69. PTR-MS data collected on June 17, 2005.



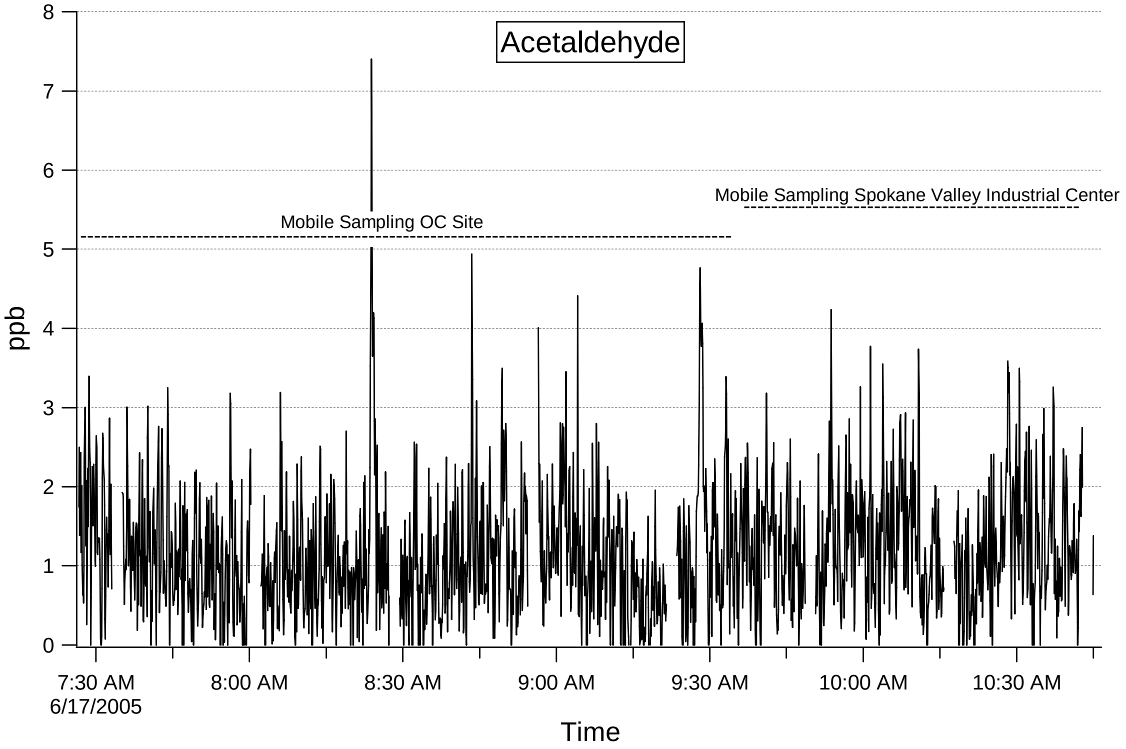
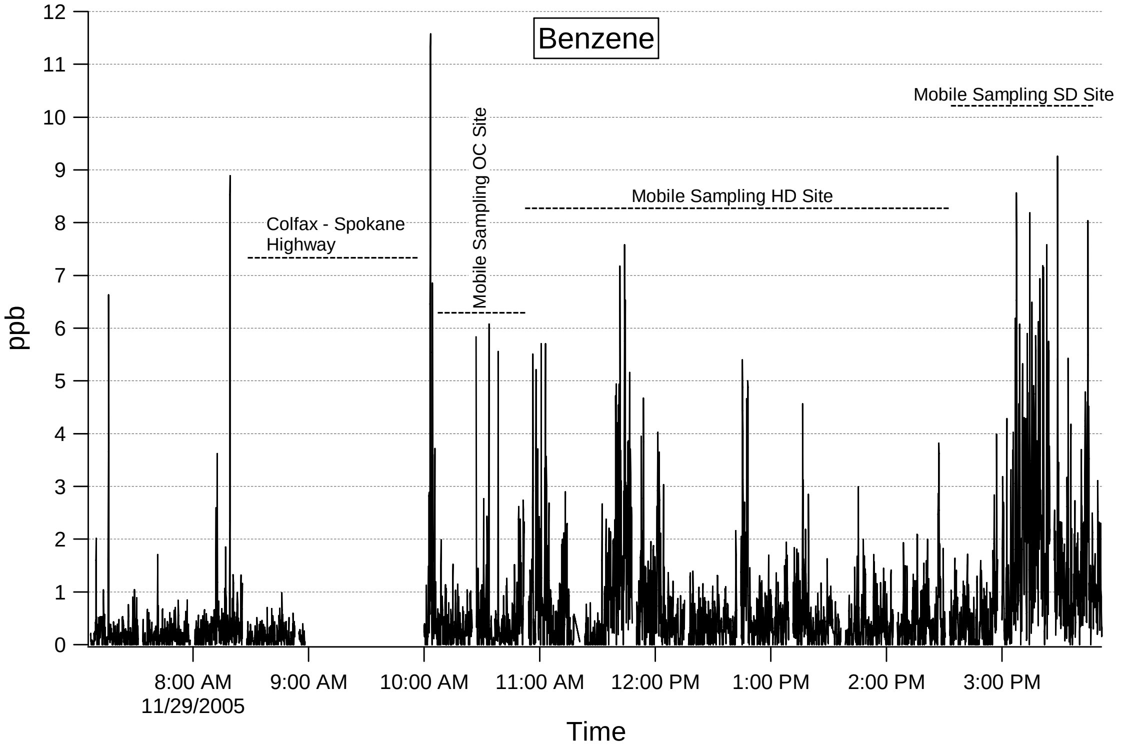


Figure 70. PTR-MS data collected on June 17, 2005.



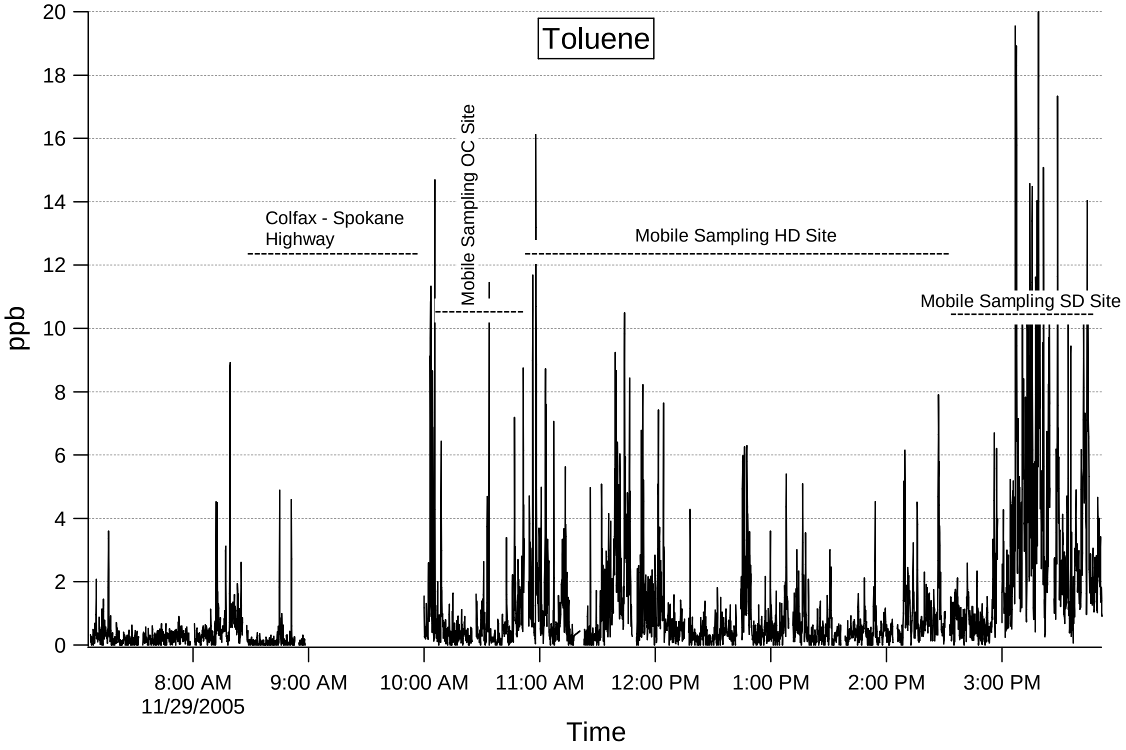
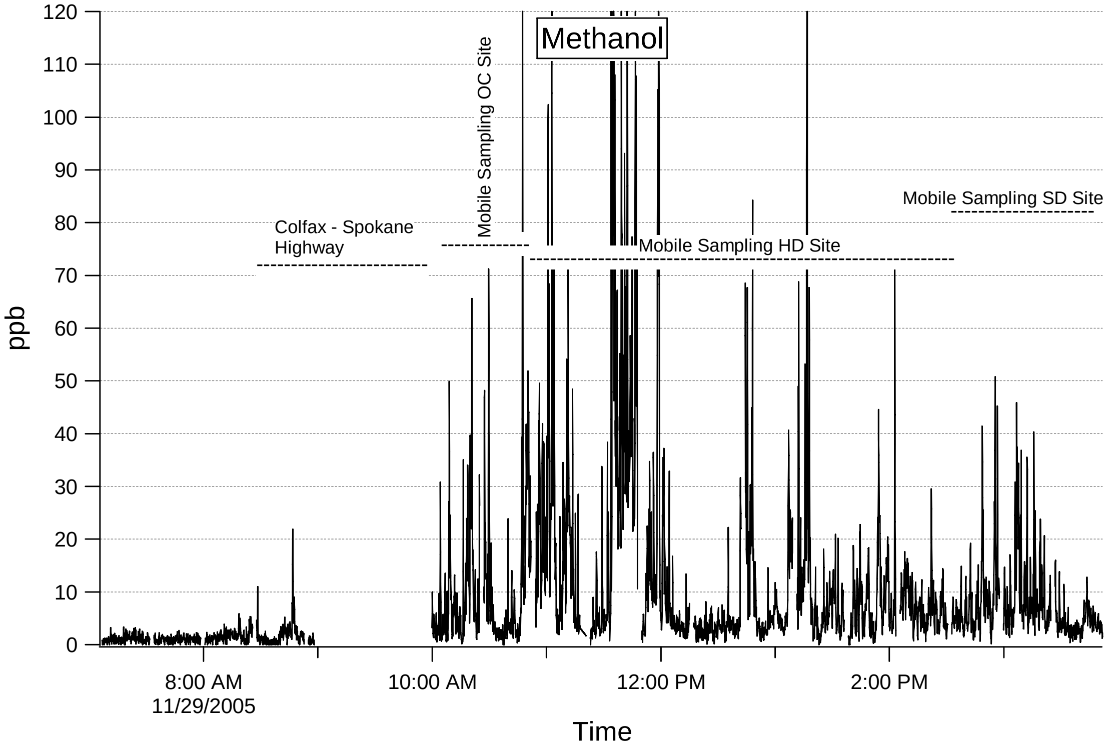


Figure 71. PTR-MS data collected on November 29, 2005.



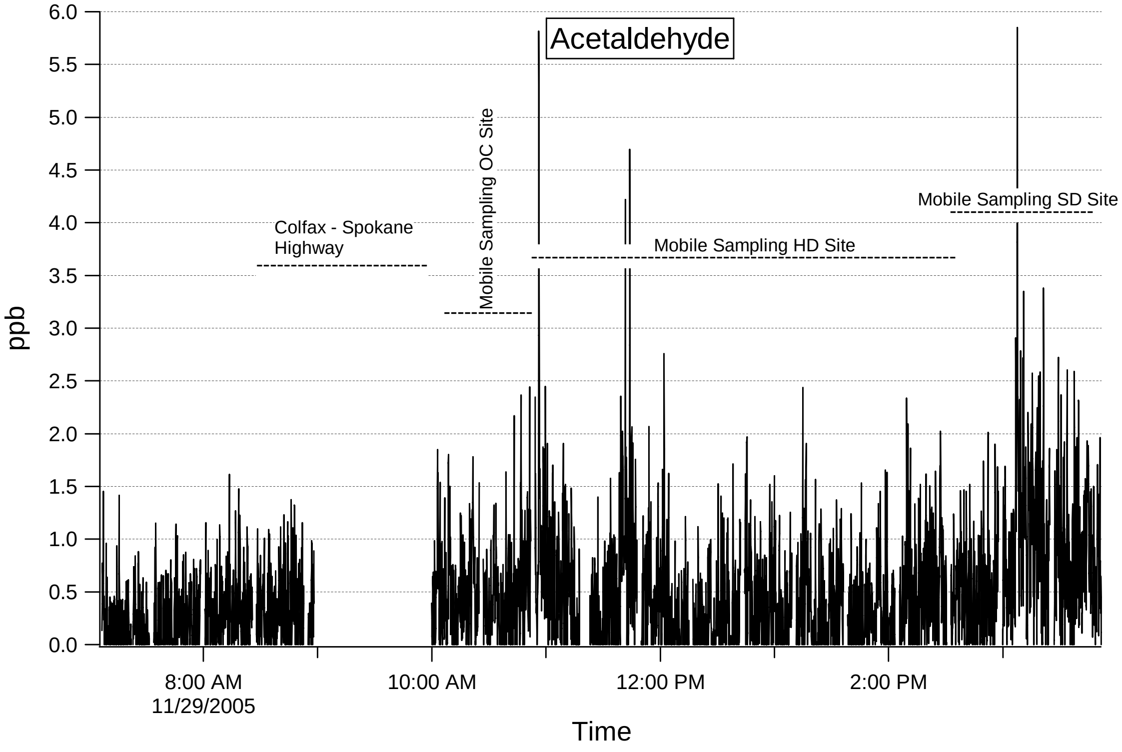
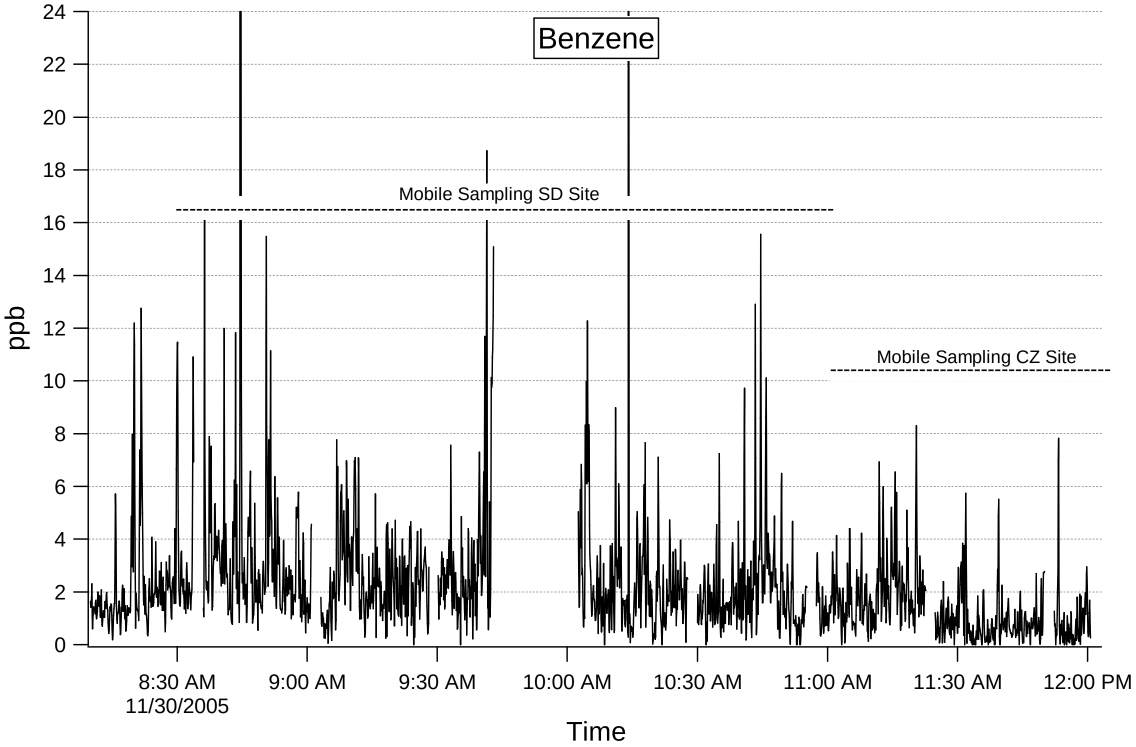


Figure 72. PTR-MS data collected on November 29, 2005.



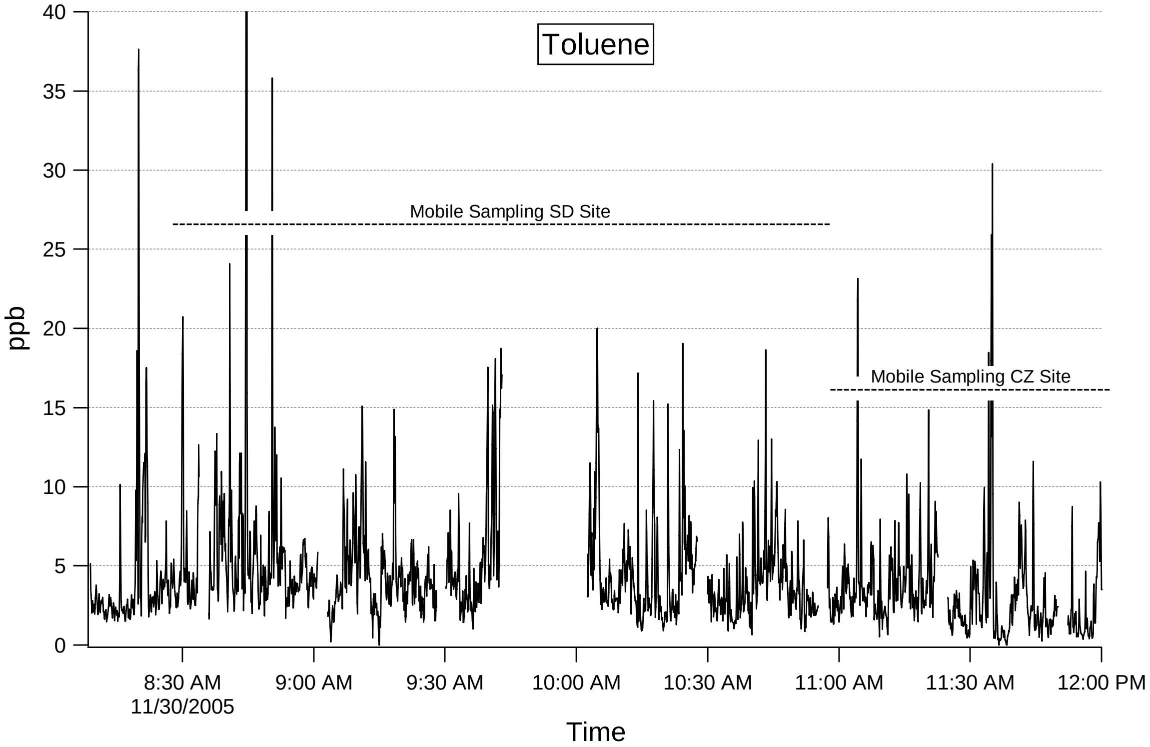


Figure 73. PTR-MS data collected on November 30, 2005.

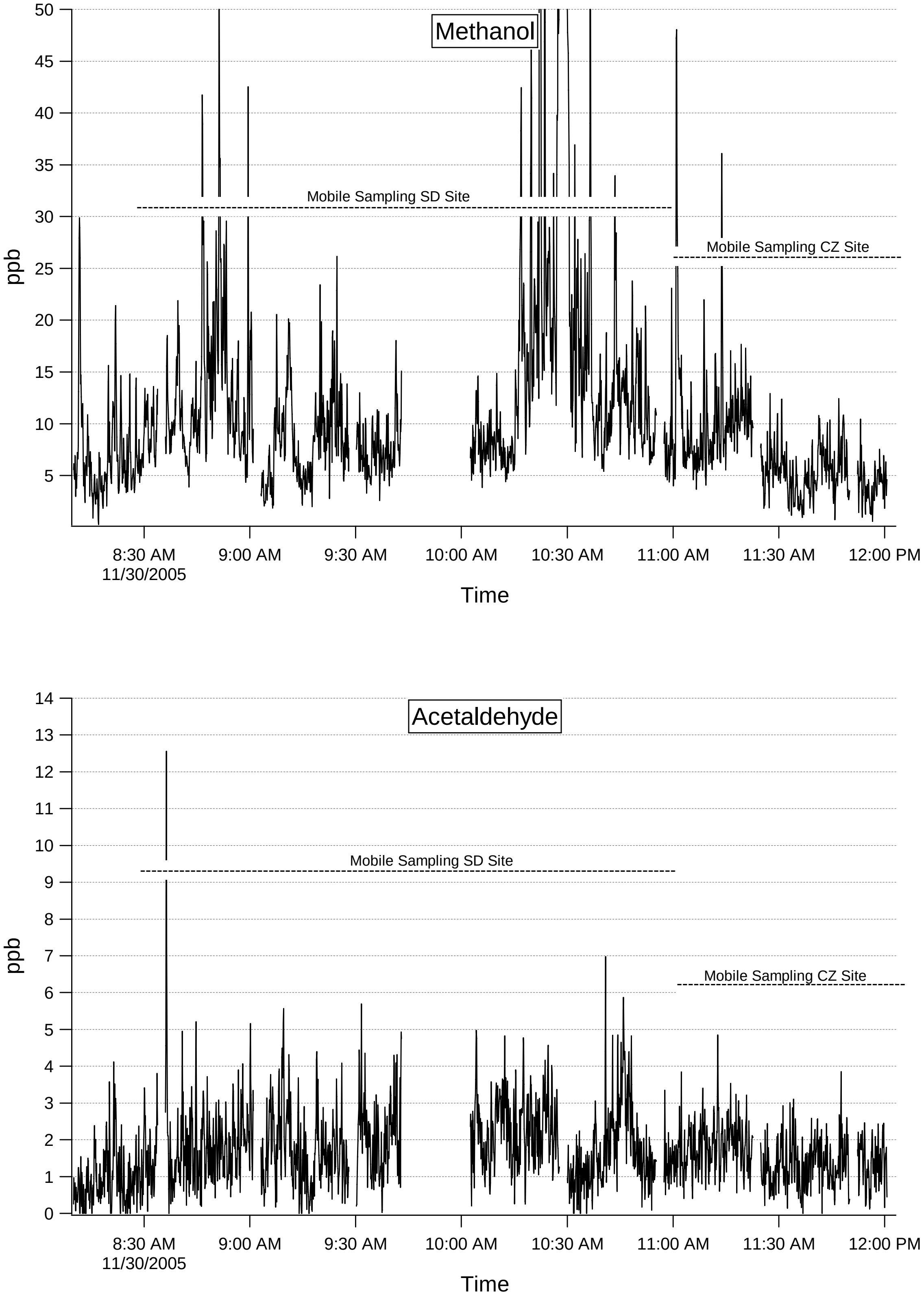
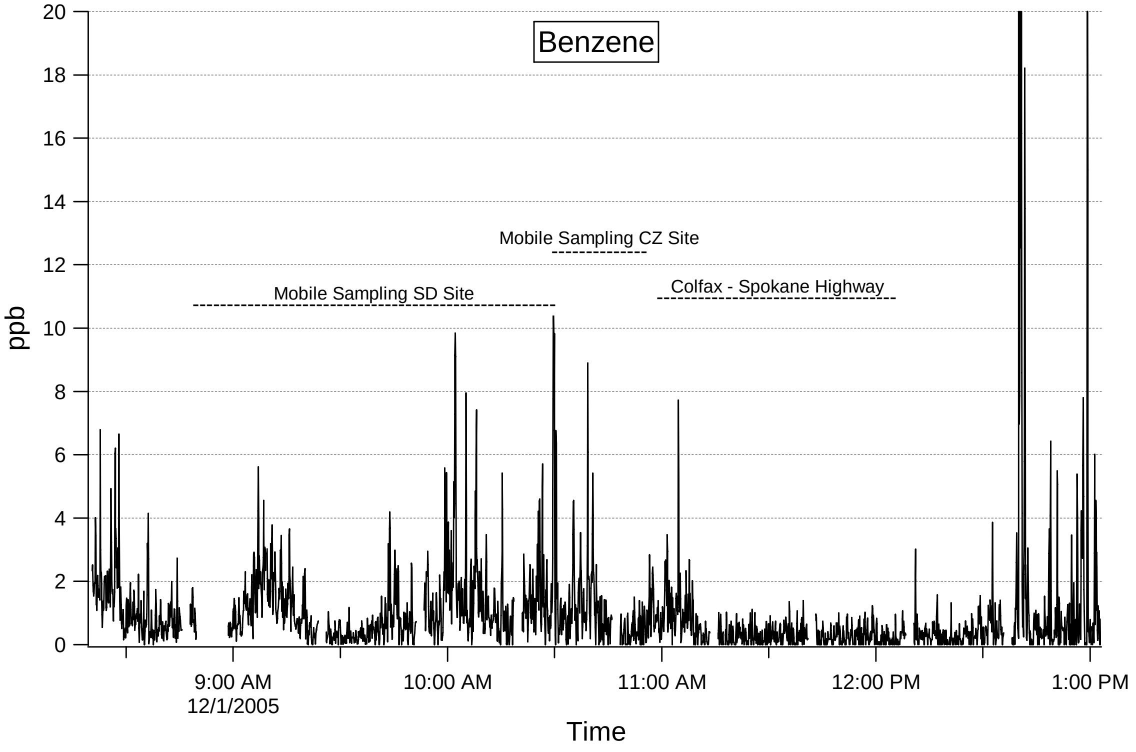


Figure 74. PTR-MS data collected on November 30, 2005.



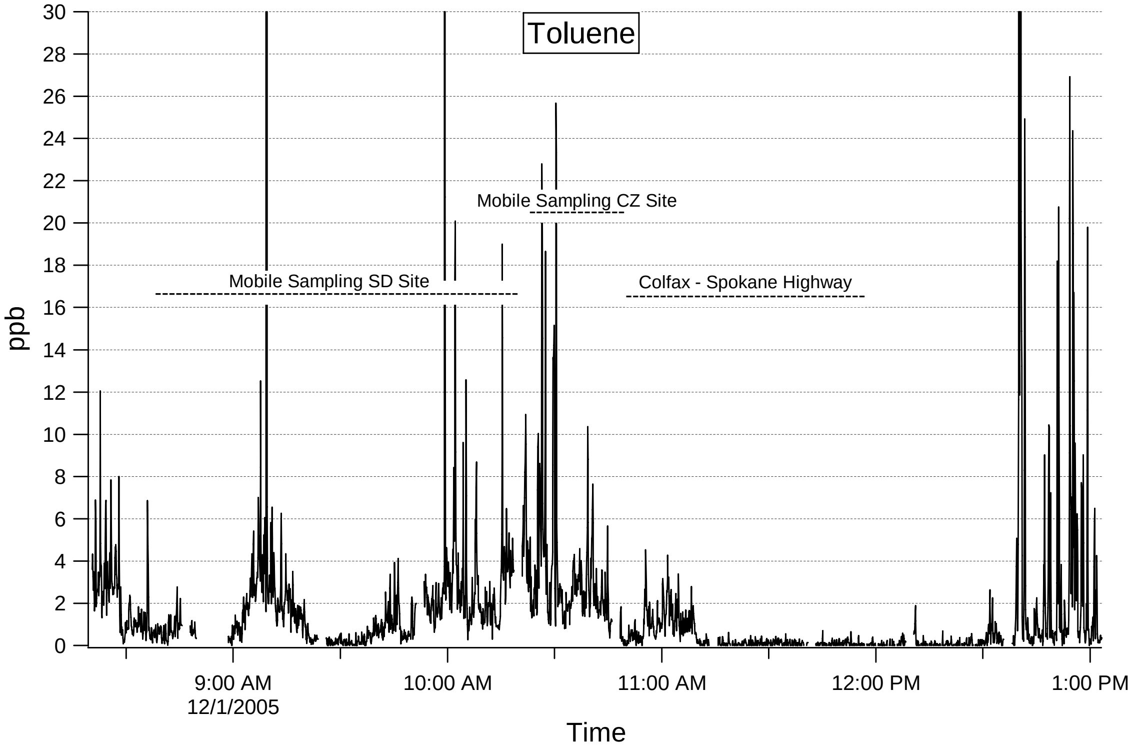
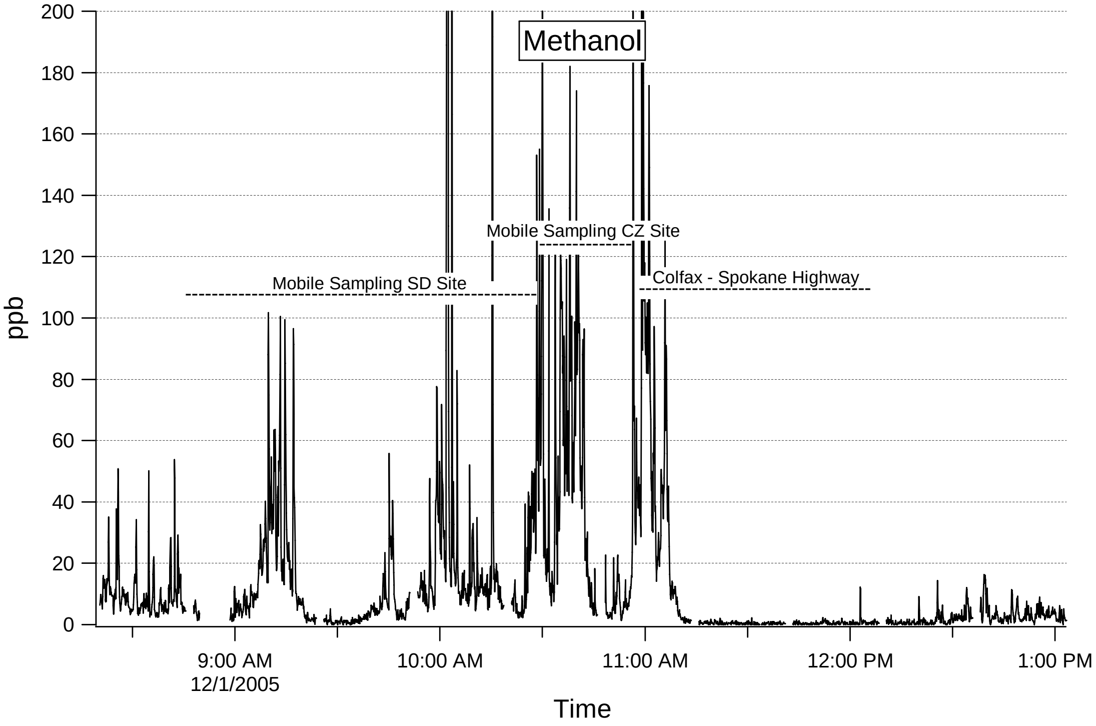


Figure 75. PTR-MS data collected on December 1, 2005.



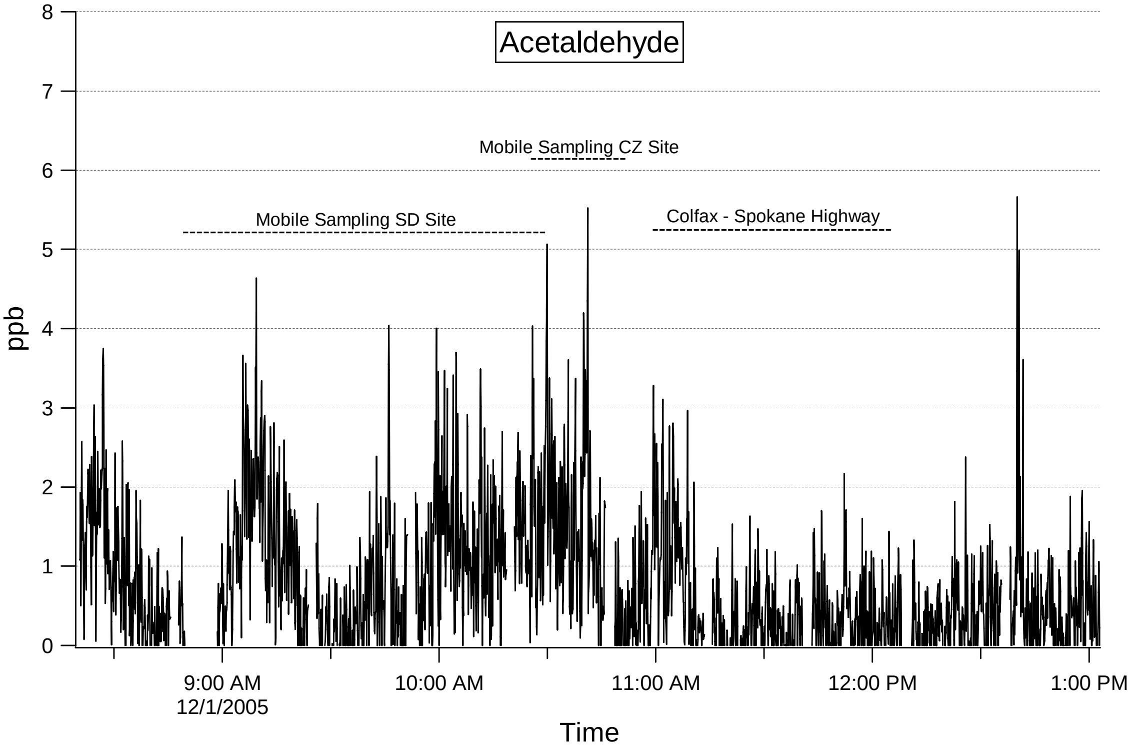


Figure 76. PTR-MS data collected on December 1, 2005.

4.7 Positive Matrix Factorization (PMF) Modeling

In a real sense, PMF uses multiple tracers to identify source categories since none of those tracers are unique for a specific source. The key issue for this type of source-receptor characterization is relating the "tracer groups" identified by the model with expected local source categories. Two PMF studies based on chemical analyses of particulate matter have been reported for Spokane. From data collected at a site in north Spokane, Kim, et al. (2003) assigned 7 source categories of $PM_{2.5}$. Figure 77 shows the PM source apportionment assigned by Kim, et al. Their analysis shows vegetative burning to be the major contributor to $PM_{2.5}$ in Spokane. More recently, Shaltanis (2006) has completed a PMF analysis of $PM_{2.5}$ sources in Spokane using a larger data set collected at the same north Spokane site. The source apportionment is illustrated in Figure 78.

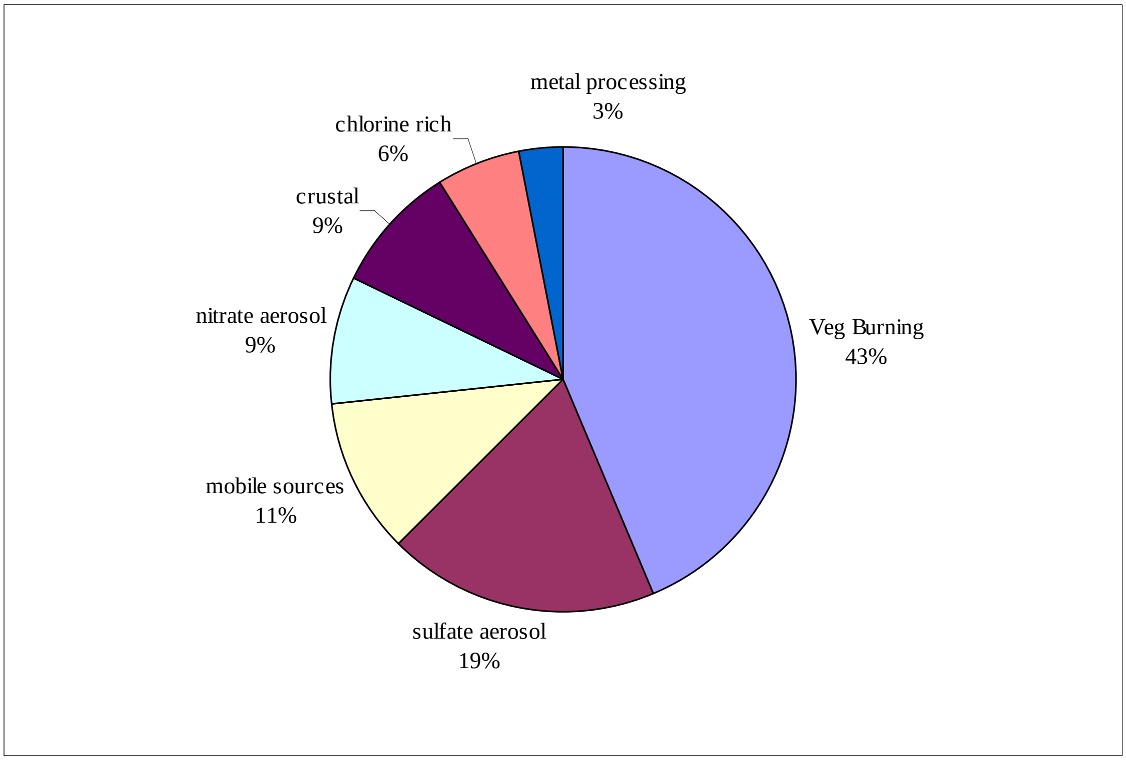


Figure 77. $PM_{2.5}$ sources assigned by Kim et al. (2003) for Spokane.

The source categories are similar in these two PMF modeling studies with the exception that there is no sulfate aerosol category in the Shaltanis analysis. Comparing the two shows the Kim et al. analysis to have a much larger vegetative burning component and a lower mobile contribution.

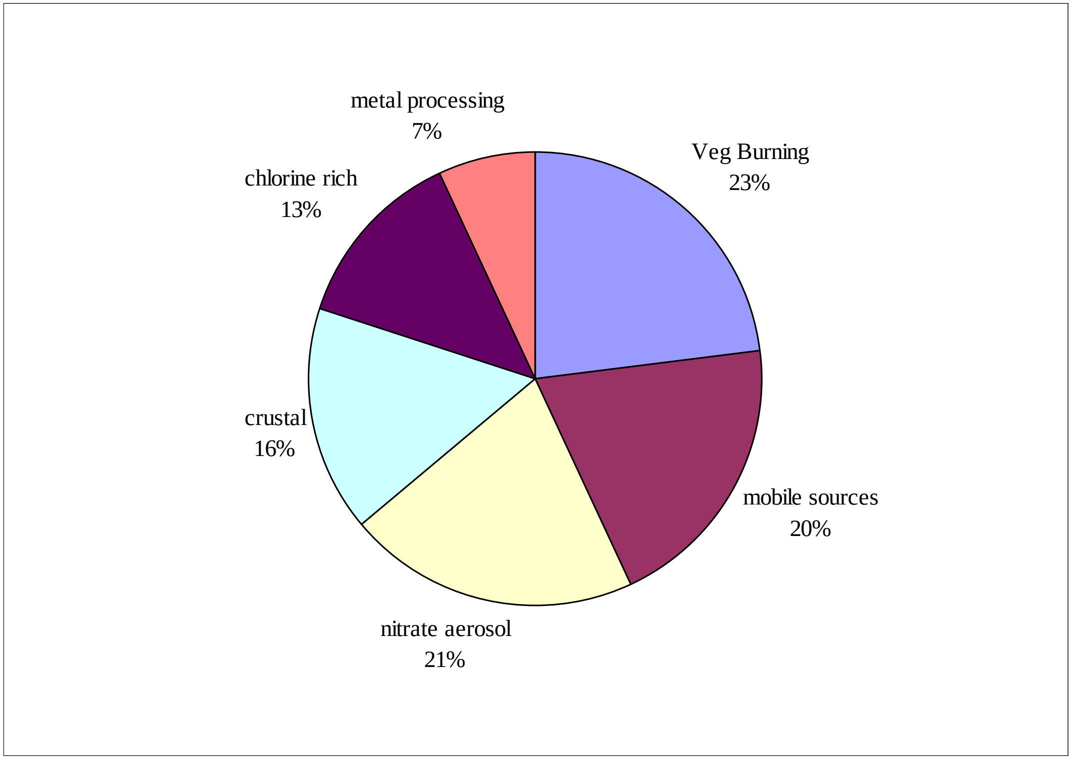


Figure 78. $PM_{2.5}$ sources assigned by Shaltanis. (2006) for Spokane.

We measured Al, As, Be, Cd, Cr, Fe, Mn, Ni, and Pb in PM_{10} at four sites in Spokane during 2005. This gave us 236 samples to use for PMF modeling. In addition, there was concurrently collected VOC data that can be employed in the analysis. Al, Fe and to a lesser extent Mn and Pb serve as tracers for soil sources. Combustion sources are rich in benzene, Pb, As, Cd and almost all of the other trace metals. The elevated levels of chromium and nickel at the CZ site are evident in the PMF analysis and can be assigned to an industrial (metal processing) source. Using the current EPA PMF model (version 1.1), we have identified five source categories for PM_{10} in Spokane. As seen in Figure 79 through Figure 83, these factors (source categories) can be assigned to crustal, combustion and industrial sources. Factor #1 is rich in crustal elements and is most prominent during a late summer period when stable meteorological conditions prevailed. Factor #1 likely represents re-suspended particulate matter. Factor #2 is rich in cadmium and other combustion related species. Cadmium is emitted during incineration of plastics and other waste materials. Factor #3 comprises the largest percentage of the PM_{10} (48%) is clearly associated with crustal sources. Its timeline shows a peak on June 21 when hot, windy meteorological conditions contributed to a wind blown dust event. Factor #4 is combustion related and most likely connected with mobile and vegetative burning sources. Chromium and nickel dominate Factor #5 implying an industrial metal processing source. The average PM_{10} apportionment for these five factors is illustrated in Figure 48.

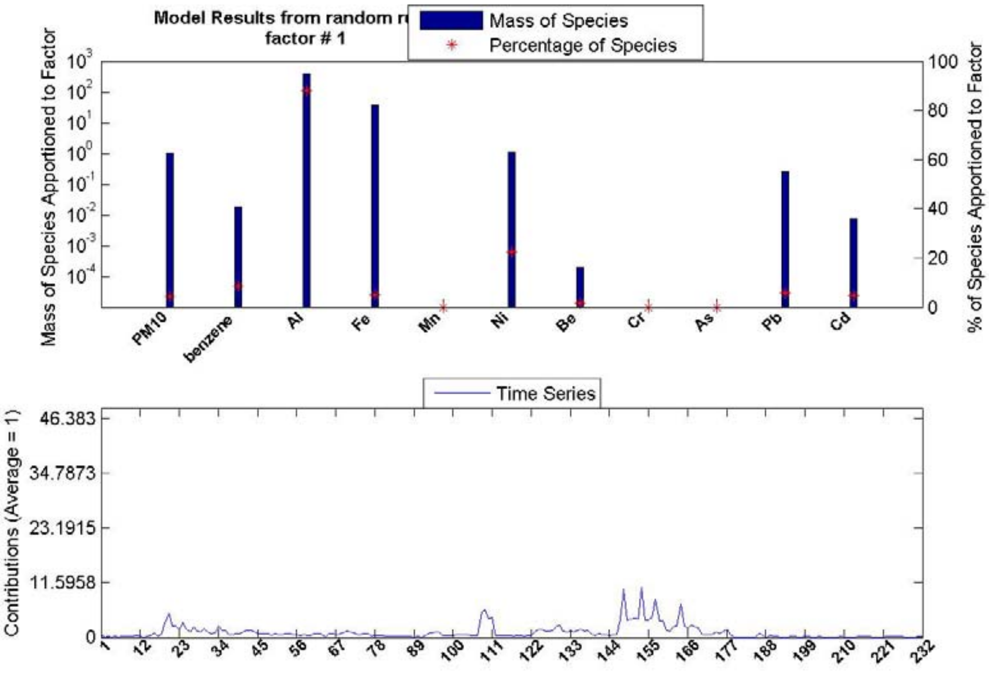


Figure 79. PMF random factor #1 most likely related to a crustal source.

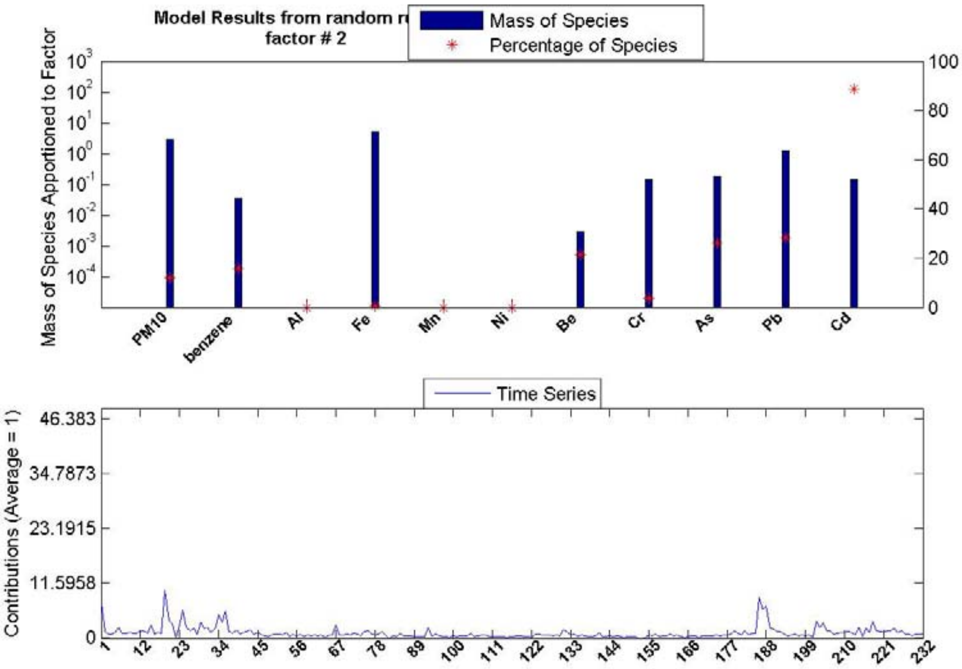


Figure 80. PMF random factor #2 associated with incineration.

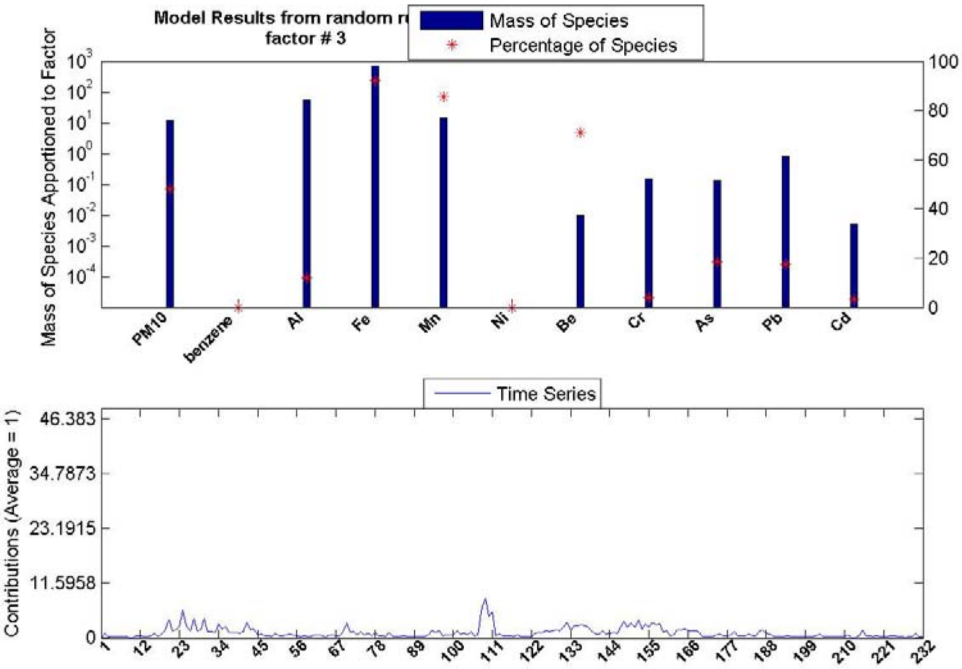


Figure 81. PMF random factor #3 associated with wind blown dust..

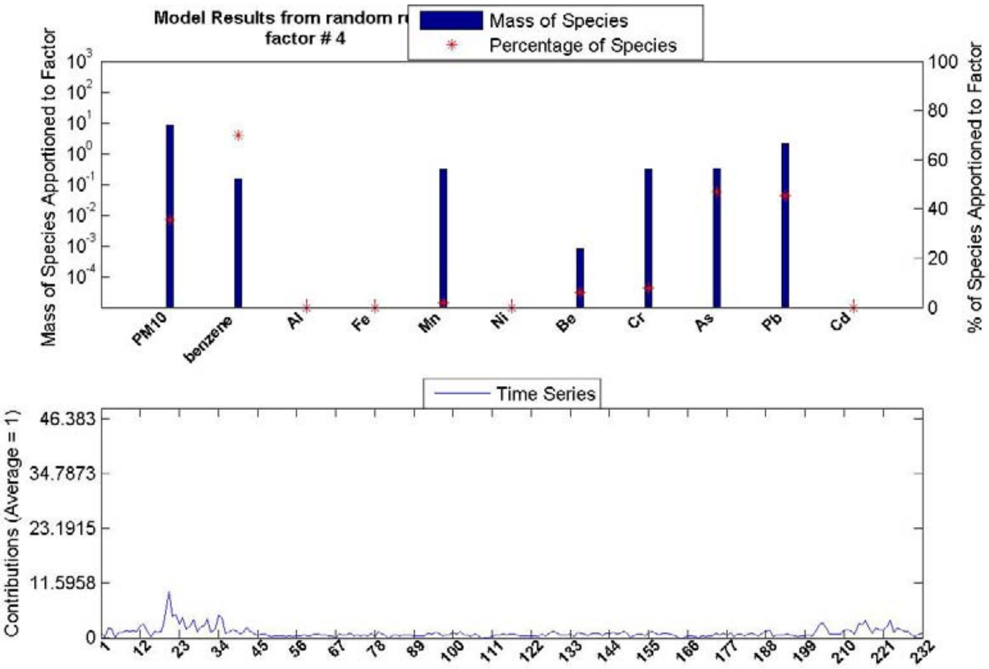


Figure 82. PMF random factor #4 associated with combustion sources.

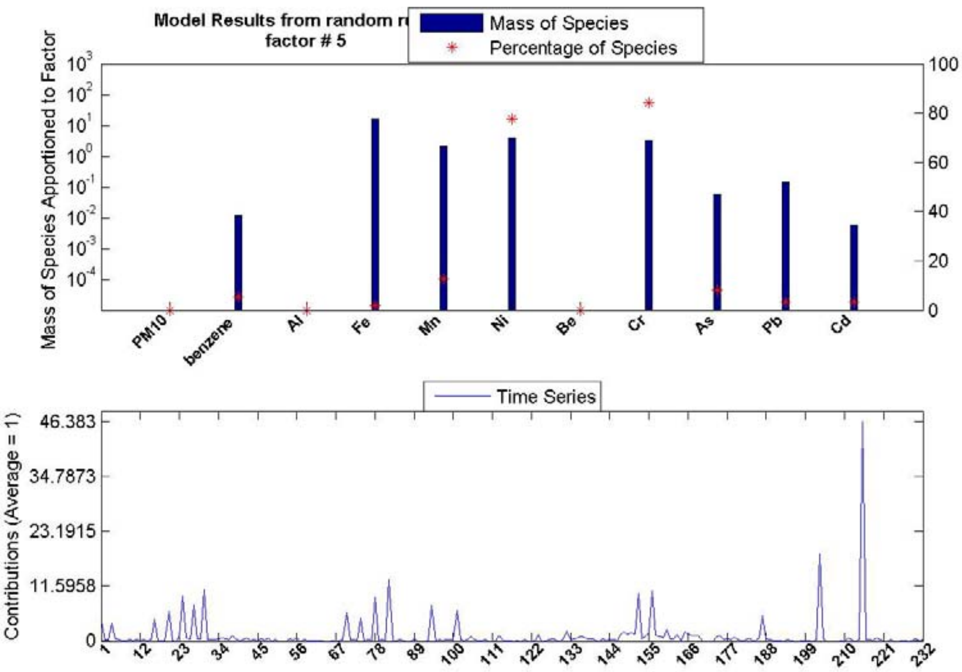


Figure 83. PMF random factor #5 associated with industrial metal processing.

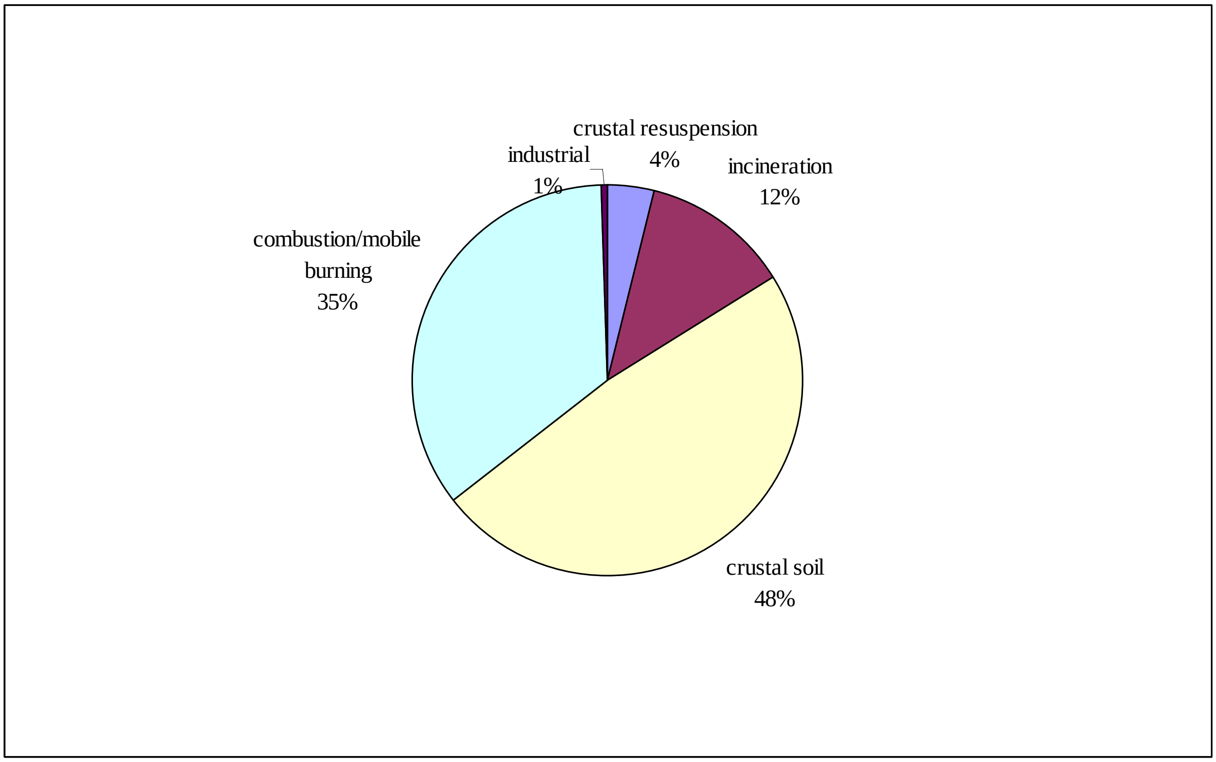


Figure 84. Pie chart showing PM_{10} apportionment in Spokane.

A direct comparison of source apportionments assigned by the Kim et al. (Figure 77), Shaltanis (Figure 78) and the present study (Figure 84) is not possible because of differing source categories utilized in each study. Our PMF analysis has a higher crustal component than the other two due, in part, to the fact that we did not measure the components of secondary aerosol (nitrate and sulfate). Secondary aerosol accounted for about 25% in the Kim et al. and Shaltanis apportionments. If we assumed a similar percentage in Spokane particulate matter in 2005, our crustal percentage would decrease and be more comparable to the other two studies.

5.0 Measurement-Model Comparison

WSU's Laboratory for Atmospheric Research provides daily air quality predictions in the Pacific Northwest through the AIRPACT air quality modeling system (www.airpact-3.wsu.edu). The model used in AIRPACT is the CMAQ Chemical Transport Model (CCTM, version 4.6). The model accounts for chemical interactions for compounds in gas, aqueous and aerosol phases. The gas-phase chemical mechanism applied in the model is SAPRC99. The aerosol module contains aerosol process dynamics for nucleation, coagulation, condensation and dry deposition. Wet depositions of both aerosol and gas-phase compounds are included in cloud processes that scavenge chemical species via aqueous chemistry. CMAQ represents aerosols via the modal approach with overlapping log-normal aerosol size distributions for three modes: Aitkin mode, accumulation mode and coarse mode. To convert the log-normal distribution representation to size-resolved mass concentration units, the PMx program is used to post process model output for $PM_{2.5}$ mass concentrations for individual aerosol species.

The forecast meteorology for the AIRPACT system comes from the Mesoscale Meteorological model (MM5 version 3.7.3) (Grell et al., 1994). It is operated in the forecast mode by the Weather Forecast Group at the University of Washington (http://www.atmos.washington.edu/mm5rt). This real-time MM5 forecast system provides hourly, 3-dimensional, gridded meteorological variables over the Pacific Northwest region at 36-, 12- and 4-km grid resolutions with 37 vertical levels for the next 48 to 72 hours (Mass et al., 2003). The AIRPACT system uses the 12-km MM5 output initialized with the 00Z-hour data from the National Center for Environmental Prediction (NCEP) GFS model results. The AIRPACT system is initialized nightly right after the meteorological data from MM5 becomes available. The Meteorology-Chemistry Interface Processor (MCIP version 3.1) pre-processes the MM5 model results and collapses the vertical level from 37 sigma layers to 21 layers while retaining key parameters such as PBL heights, cloud cover, incoming solar radiation, and momentum and heat fluxes for CMAQ.

Accurate emission inventory information is critical for meaningful air quality forecast results. The AIRPACT emission subsystem includes a series of emission processing steps to generate gridded, hourly emission data required by the CMAQ model. The subsystem is initiated at the beginning of each forecast day to process emissions from anthropogenic and biogenic sources, ammonia gas from dairy operations, and wild and prescribed fires. The SMOKE processor is scripted to process area, on-road mobile, non-road mobile and point source emission categories for each simulation day. Area and non-road mobile emissions are base on the 2002 EPA National Emission Inventory (NEI-2002) dataset and grown to year 2005 by county and source specific projection factors from the EPA EGAS software. On-road mobile emissions are generated using EPA MOBILE6 emission factors with 2005 mobile activity data from individual states in the domain. Point source inventory is also based on the NEI-2002 dataset. The inventory was updated to reflect 2005 operation activities for states of Washington, Idaho and Oregon by the Washington State Department of Ecology. The biogenic emissions inventory system version 3 (BEIS3) from EPA is used to estimate daily biogenic emissions for the AIRPACT system.

The BEIS3 model is part of the SMOKE processor. Emissions include soil and vegetative NOx, isoprene, terpenes and other non-specific biogenic VOC.

The AIRPACT domain includes the entire states of Washington, Oregon and Idaho and portions of Southern British Columbia, northern California, Nevada and Utah. The large domain allows the system to better capture pollutant transport over longer distances and lessens the influence of model boundary condition uncertainties on forecast results. The domain is made up of 95 by 95 horizontal grids with grid resolution of 12 km by 12 km. Vertically there are 21 layers. There are 12 layers in the lower 1,000 meters and an additional 9 layers up to the tropopause (10 km).

Timing of model output is important for forecast products such as AIRPACT. In order for the system to be usable, model output has to be available before the start of each day. In the current configuration, the system provides 24-hour air quality forecast beginning at 08-hour GMT (0-hour PST) for the next day. The system is initiated daily at midnight and is able to complete the entire simulation and post processes in less than 4 hours with graphical outputs available by 04-hour local time. The model provides hourly average predicted air toxic concentrations for benzene, 1,3-butadiene, acetaldehyde, formaldehyde and PM_{10}. In order to compare model with measured air toxic data in Spokane, we have selected the 12 km grid that best encompasses the 4 sampling sites. The AIRPACT hourly predicted concentrations were average over the same 24-hr period that an integrated canister or filter was collected. Table 26 shows a comparison of modeled and measured results for the five sampling days in December 2005.

Table 26. Measured and Modeled Concentrations

	Benzene (ppbv)	1,3-Butadiene (ppbv)	Acetald. (ppbv)	Formald. (ppbv)	PM_{10} (ug/m^3)
12/6 mod	1.81	0.04	0.14	0.91	30.4
12/6 mea	0.93	0.21	1.80	3.61	35.1
12/12 mod	4.06	0.09	0.26	0.99	69.5
12/12 mea	0.27	0.06	1.28	1.77	31.4
12/18 mod	1.67	0.04	0.17	1.11	29.9
12/18/mea	0.41	0.12	1.48	2.31	23.7
12/24 mod	1.54	0.03	1.11	0.77	34.4
12/24 mea	0.55	0.11	1.16	1.42	16.4
12/30 mod	1.75	0.04	0.14	0.20	12.4
12/30 mea	0.15	0.04	0.82	0.90	9.4

The model over predicts benzene and an evaluation of the reason for the difference indicated a problem with the model's benzene emission inventory. In a similar vein, the model greatly under predicted the carbonyl concentrations. The reason for this is most likely unrealistically low boundary/initial conditions employed for acetaldehyde and formaldehyde in the model. Attempts are being made to correct these deficiencies in the AIRPACT-3 model predictions.

6.0 Exposure Assessment Screening

EPA's Region 4 has described a risk-based screening approach that can be applied to air toxic data sets (www.epe.gov/region4/air/airtoxic/athera1.htm). The screening methodology is designed to provide an easy means of identifying which air toxics may be of specific concern in a particular area. We have applied this screening approach with the 2005 Spokane data set as a means of identifying the air toxics of greatest concern. We determined annual average and maximum concentrations for each air toxic species and compared these values to chronic inhalation levels deemed to be harmful to human health. Table 27 shows the results of this screening exercise.

Table 27. Risk-Based Screening Assessment for Air Toxic Data Collected in Spokane.

"Core" Air Toxic	Annual Ave. Concentration (ug/m^3-voc) (ng/m^3-metal)	Max Detected Concentration (ug/m^3-voc) (ng/m^3-metal))	Chronic Screening (ug/m^3-voc) (ng/m^3-metal)	Annual Ave. > chronic	Max > Chronic % of Detections Exceeding( )
Benzene	0.77	6.19	0.13	Yes	Yes(97)
1,3-Butadiene	0.11	0.86	0.03	Yes	Yes(75)
CCl_4	0.63	0.63	0.07	Yes	Yes(100)
Chloroform	0.05	0.34	9.80	No	No
PCE	0.27	2.85	0.17	Yes	Yes(36
TCE	0.11	0.64	0.50	No	Yes(0.4)
Acetaldehyde	2.5	5.6	0.45	Yes	Yes(100)
Formaldehyde	2.5	11	0.98	Yes	Yes(86)
Arsenic	0.90	5.92	0.23	Yes	Yes(89)
Beryllium	0.02	0.17	0.42	No	No
Cadmium	0.20	1.56	0.56	No	Yes(5)
Chromium	1.00	6.91	0.08	Yes	Yes(96*)
Lead	0.49	30.2	150	No	No
Manganese	19.0	125	5.00	Yes	Yes(66)
Nickel	2.10	32.1	2.10	Yes	Yes(26*)

Of the 15 air toxics listed in Table 27 all but chloroform, beryllium and lead exhibited maximum concentrations that exceeded the chronic screening value (column 6). The number of trichloroethylene and cadmium detections exceeding the screening concentration were small and their annual average concentrations were below the toxic screening value. The screening concentrations are based on the cancer risk level of 1 x 10^6. Most of the other air toxics had concentrations that exceeded the chronic screening value more than 50% of the time.

A Spokane resident is not subjected to the measured annual average or higher ambient concentrations all of the time. Their day-to-day activities normally include considerable time spent indoors. For this reason, EPA has developed the Hazardous Air Pollutant Exposure Model (HAPEM) as a more accurate means of predicting "apparent" inhalation exposure of selected population groups to air toxics.

Thus, more robust risk assessment is warranted for many of the "core" air toxics observed in Spokane. The HAPEM assessment includes ambient air concentration data, indoor-outdoor concentration relationships, population data, and population activity patterns to estimate the "apparent" exposure level for various groups of individuals.

6.1 Exposure Modeling

We applied HAPEM5 in Spokane using annual average air toxic concentrations recorded at each of the four sites. The exposure levels for ten population groups that reside in the neighborhood surrounding each sampling site are shown in Table 28 through Table 31. Chloroform, trichloroethylene, beryllium and lead are not in the tables because the initial screening described previously showed they were not a risk to human health in Spokane. In addition, carbontetrachloride is omitted because use of this chlorinated compound has been discontinued and the levels recorded in Spokane and elsewhere in the U.S. represent current global background concentrations. Following the exposure tables (Table 28 through Table 31) are several figures (Figure 85 through Figure 94) that compare the modeled exposure levels with the chronic screening value (CSV). Graphs are shown for the 0-4, 5-11, 12-17, >65 male age groups and the 18-64 male and female categories. In all age divisions except for the 18-64 age range, male and female exposures are nearly identical.

HAPEM exposure estimates differ little for male and female residents in the 0-4, 5-11, 12-17 and over 65 age groups. For all residents in these age groups, calculated exposure levels for benzene, 1,3-butadiene, acetaldehyde and formaldehyde exceeded their chronic screening value by a significant amount (Figure 85, Figure 87, Figure 89, and Figure 95). Human exposures to benzene and 1,3-butadiene were greatest in the CZ and SD neighborhoods while residents living in the SD and OC areas had the highest exposures to acetaldehyde and formaldehyde. Trace metals were most troublesome in the CZ district. Exposures estimated for arsenic, chromium, manganese and nickel all exceeded the chronic screen value (Figure 86, Figure 88, Figure 90, and Figure 96). In the other three neighborhoods, chromium exposures exceeded the CSV, estimated manganese exposures were about the same as the CSV and nickel was below the CSV.

In the 18-64 age grouping, male and female exposure estimates differed for some of the air toxics. For example, exposure to arsenic and manganese appears to be more troublesome for female residents in this age group. Female exposure to these two metals exceeds the CSV in all four neighborhoods while male exposures were about the same as or below the CSV in the regions around the HD, SD and OC sites (Figure 92 and Figure 94). As with the other age classifications, benzene, 1,3-butadiene and the two carbonyls posed a problem for 18-64 males and females. In addition, tetrachloroethylene exposure estimates exceeded the CSV for 18-64 year olds residing in the vicinity of the CZ and SD sites, but were below the screening value in the less commercial HD and OC neighborhoods.

Thus, this Spokane exposure assessment showed chloroform, beryllium, cadmium, lead, and nickel to be below danger levels, while benzene, 1,3-butadiene, carbon tetrachloride, tetrachloroethylene, trichloroethylene, acetaldehyde, formaldehyde, arsenic, chromium, and manganese exceeded their 1 x 10^6 risk of disease level.

Table 28. Air toxic concentration exposures (ppbv and ng/m^3) for residents living in the neighborhood surrounding the HD site.

Age Group Male/Female	**0-4 male**	**5-11 male**	**12-17 male**	**18-64 male**	**65 + male**	**0-4 fem**	**5-11 fem**	**12-17 fem**	**18-64 fem**	**65 + fem**
Benzene	0.46	0.47	0.43	0.33	0.46	0.47	0.46	0.44	0.37	0.45
1,3-Butadiene	0.06	0.06	0.05	0.04	0.06	0.06	0.06	0.05	0.05	0.05
PCE	0.17	0.18	0.16	0.12	0.17	0.17	0.17	0.17	0.14	0.17
Acetaldehyde	1.84	1.88	1.73	1.32	1.84	1.86	1.81	1.77	1.47	1.79
Formaldehyde	1.56	1.60	1.47	1.12	1.56	1.58	1.55	1.51	1.25	1.53
As	0.18	0.24	0.24	0.15	0.21	0.16	0.28	0.21	0.22	0.23
Cd	0.04	0.06	0.06	0.03	0.05	0.04	0.06	0.05	0.05	0.05
Cr	0.36	0.49	0.48	0.29	0.43	0.31	0.55	0.42	0.45	0.46
Mn	4.90	6.58	6.44	3.92	5.74	4.20	7.42	5.60	6.02	6.16
Ni	0.76	1.02	1.00	0.61	0.89	0.65	1.15	0.87	0.93	0.95

Table 29. Air toxic concentration exposures (ppbv and ng/m^3) for residents living in the neighborhood surrounding the CZ site.

Age Group Male/Female	**0-4 male**	**5-11 male**	**12-17 male**	**18-64 male**	**65 + male**	**0-4 fem**	**5-11 fem**	**12-17 fem**	**18-64 fem**	**65 + fem**
Benzene	0.81	0.83	0.77	0.58	0.81	0.82	0.80	0.78	0.65	0.79
1,3-Butadiene	0.11	0.12	0.11	0.08	0.11	0.11	0.11	0.11	0.09	0.11
PCE	0.29	0.29	0.27	0.21	0.29	0.29	0.28	0.28	0.23	0.28
Acetaldehyde	2.14	2.19	2.02	1.54	2.14	2.17	2.12	2.07	1.71	2.09
Formaldehyde	1.88	1.92	1.77	1.35	1.88	1.90	1.86	1.81	1.50	1.83
As	0.49	0.65	0.64	0.39	0.57	0.42	0.74	0.56	0.60	0.61
Cd	0.07	0.09	0.09	0.06	0.08	0.06	0.11	0.08	0.09	0.09
Cr	5.57	7.47	7.31	4.45	6.52	4.77	8.43	6.36	6.84	7.00
Mn	10.85	14.57	14.26	8.68	12.71	9.30	16.43	12.40	13.33	13.64
Ni	5.46	7.33	7.18	4.37	6.40	4.68	8.27	6.24	6.71	6.86

Table 30. Air toxic concentration exposures (ppbv and ng/m^3) for residents living in the neighborhood surrounding the SD site.

Age Group Male/Female	0-4 male	5-11 male	12-17 male	18-64 male	65 + male	0-4 fem	5-11 fem	12-17 fem	18-64 fem	65 + fem
Benzene	0.65	0.67	0.61	0.47	0.65	0.66	0.64	0.63	0.52	0.64
1,3-Butadiene	0.09	0.10	0.09	0.07	0.09	0.09	0.09	0.09	0.08	0.09
PCE	0.29	0.29	0.27	0.21	0.29	0.29	0.28	0.28	0.23	0.28
Acetaldehyde	2.14	2.19	2.02	1.54	2.14	2.17	2.12	2.07	1.71	2.09
Formaldehyde	2.61	2.67	2.45	1.87	2.61	2.64	2.58	2.52	2.09	2.55
As	0.32	0.43	0.42	0.25	0.37	0.27	0.48	0.36	0.39	0.40
Cd	0.06	0.08	0.08	0.05	0.07	0.05	0.09	0.07	0.07	0.07
Cr	0.35	0.47	0.46	0.28	0.41	0.30	0.54	0.40	0.43	0.44
Mn	5.46	7.33	7.18	4.37	6.40	4.68	8.27	6.24	6.71	6.86
Ni	0.63	0.85	0.83	0.50	0.74	0.54	0.95	0.72	0.77	0.79

Table 31. Air toxic concentration exposures (ppbv and ng/m^3) for residents living in the neighborhood surrounding the OC site.

Age Group Male/Female	0-4 male	5-11 male	12-17 male	18-64 male	65 + male	0-4 fem	5-11 fem	12-17 fem	18-64 fem	65 + fem
Benzene	0.62	0.64	0.59	0,45	0.62	0.63	0.62	0.60	0.50	0.61
1,3-Butadiene	0.08	0.08	0.07	0.05	0.08	0.08	0.07	0.07	0.06	0.07
PCE	0.17	0.18	0.16	0.12	0.17	0.17	0.17	0.17	0.14	0.17
Acetaldehyde	2.60	2.66	2.45	1.87	2.60	2.63	2.57	2.51	2.08	2.54
Formaldehyde	2.40	2.46	2.26	1.72	2.40	2.43	2.37	2.31	1.92	2.34
As	0.27	0.36	0.35	0.21	0.31	0.23	0.40	0.30	0.33	0.33
Cd	0.07	0.10	0.10	0.06	0.09	0.06	0.11	0.08	0.09	0.09
Cr	0.36	0.48	0.47	0.29	0.42	0.31	0.55	0.41	0.44	0.45
Mn	5.01	6.72	6.58	4.00	5.86	4.29	7.58	5.72	6.15	6.29
Ni	0.83	1.12	1.09	0.67	0.98	0.71	1.26	0.95	1.02	1.05

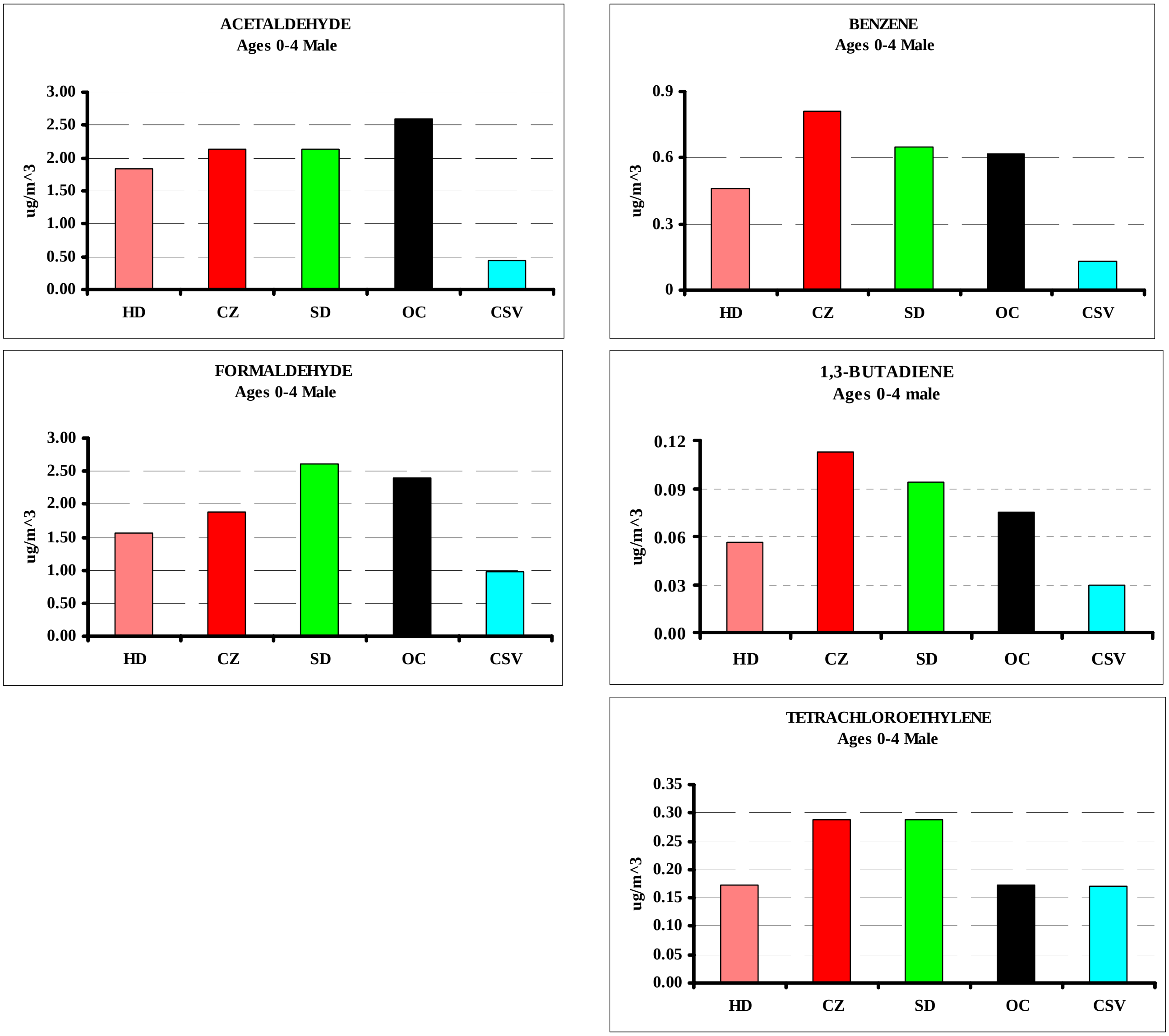


Figure 85. Air toxic VOC exposures ($\mu g/m^3$) for male residents in the 0-4 age group.

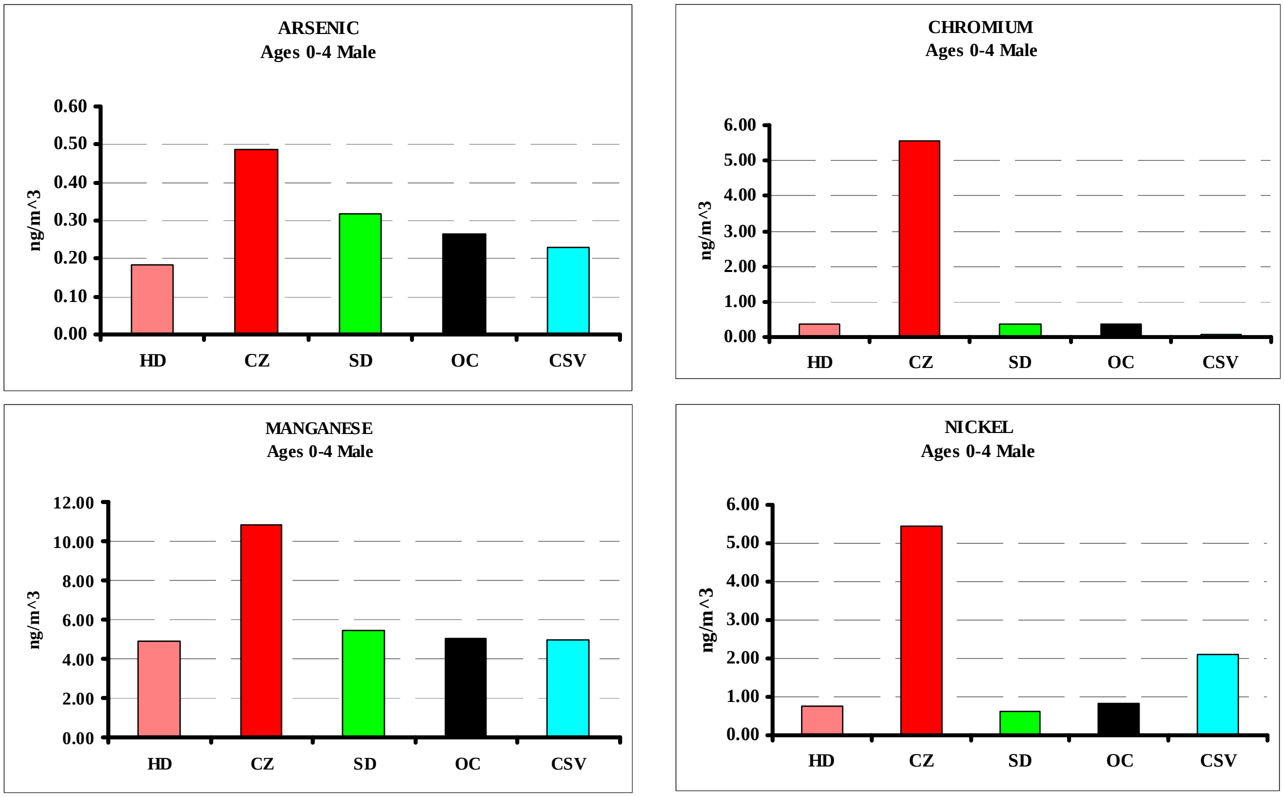


Figure 86. Air toxic trace metal exposures (ng/m^3) for male residents in the 0-4 age group.

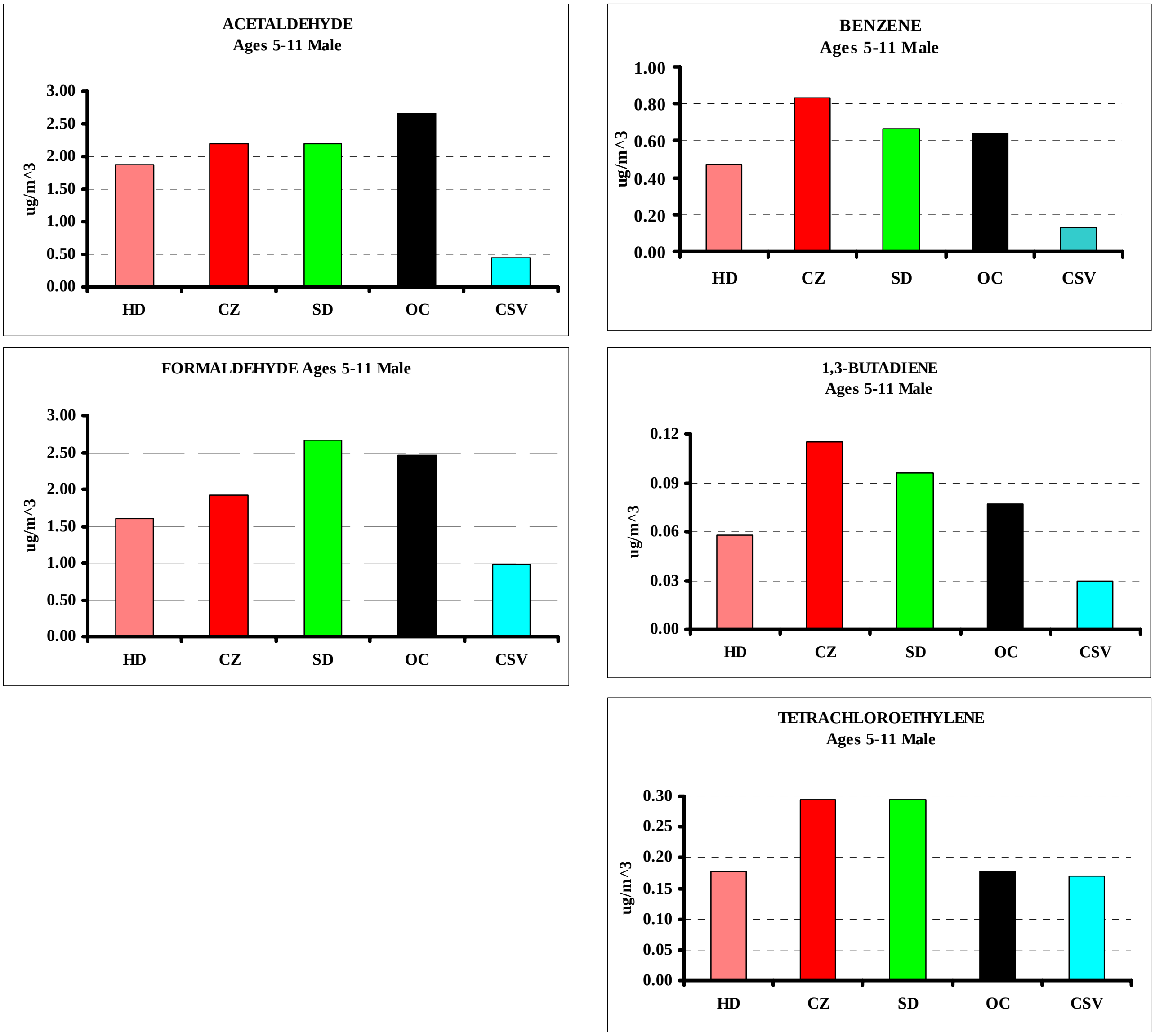


Figure 87. Air toxic VOC exposures (μg/m^3) for male residents in the 5-11 age group.

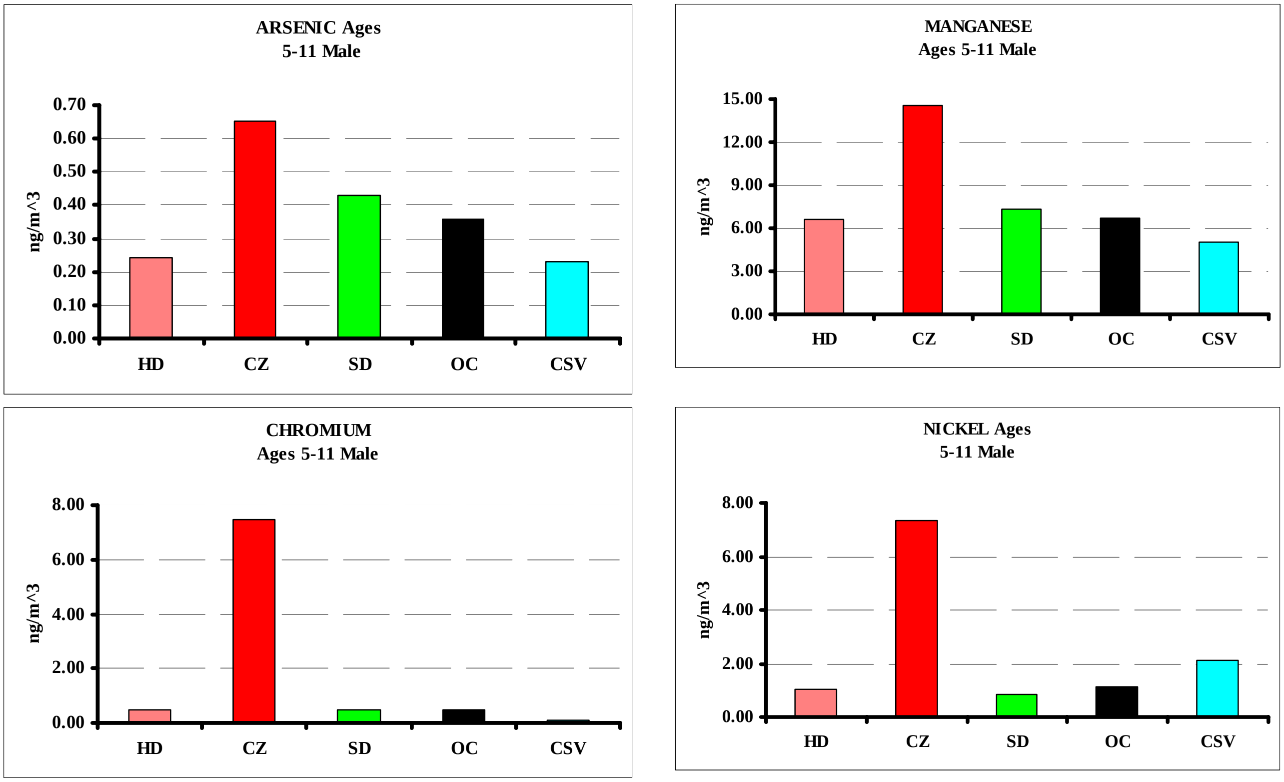


Figure 88. Air toxic trace metal exposures (ng/m^3) for male residents in the 5-11 age group.

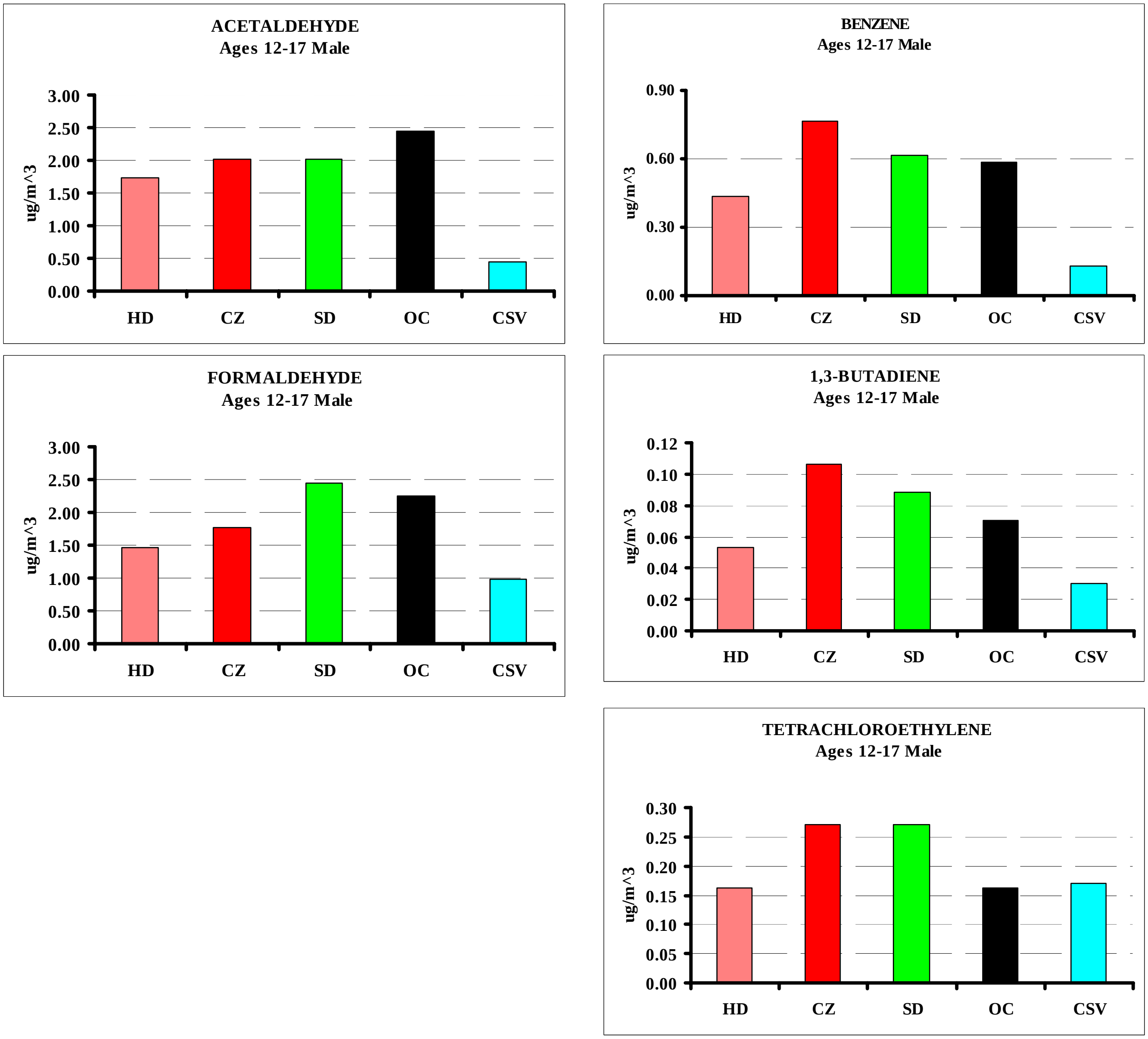


Figure 89. Air toxic VOC exposures (μg/m^3) for male residents in the 12-17 age group.

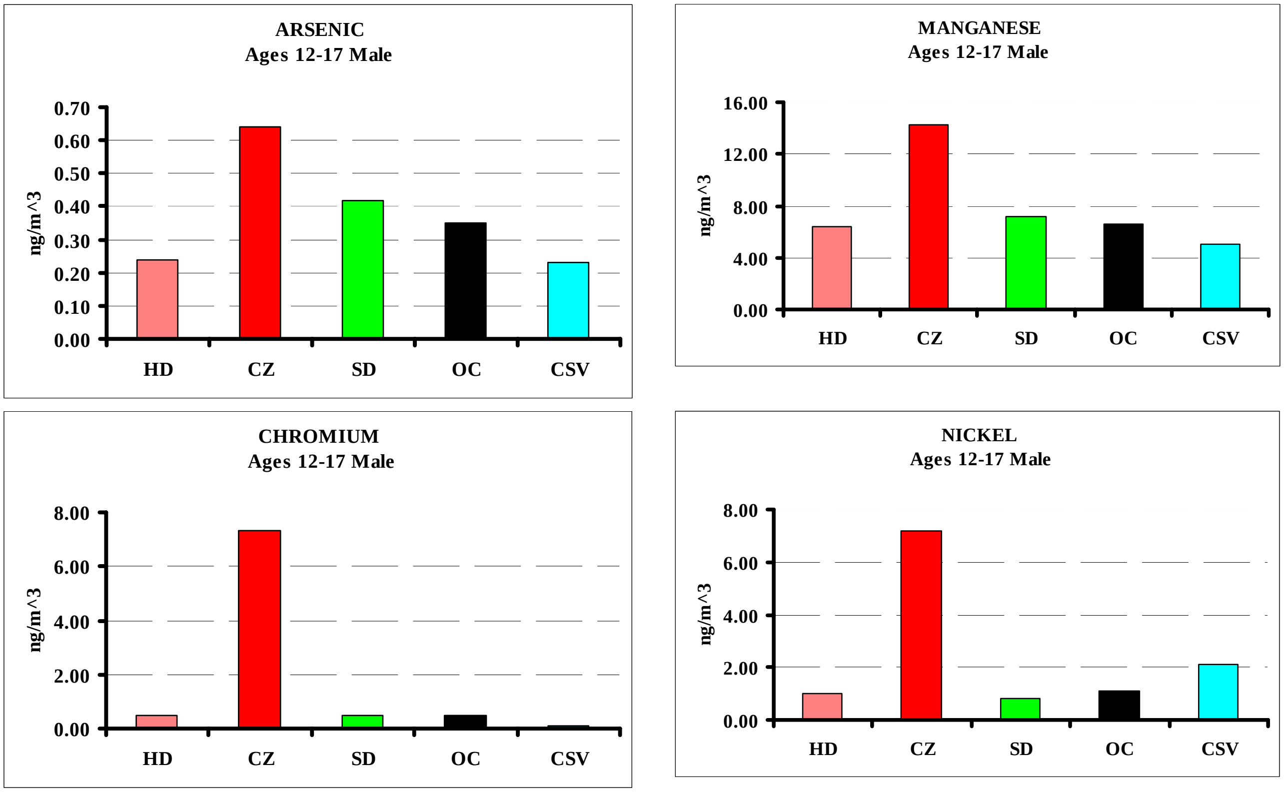


Figure 90. Air toxic trace metal exposures (ng/m^3) for male residents in the 12-17 age group.

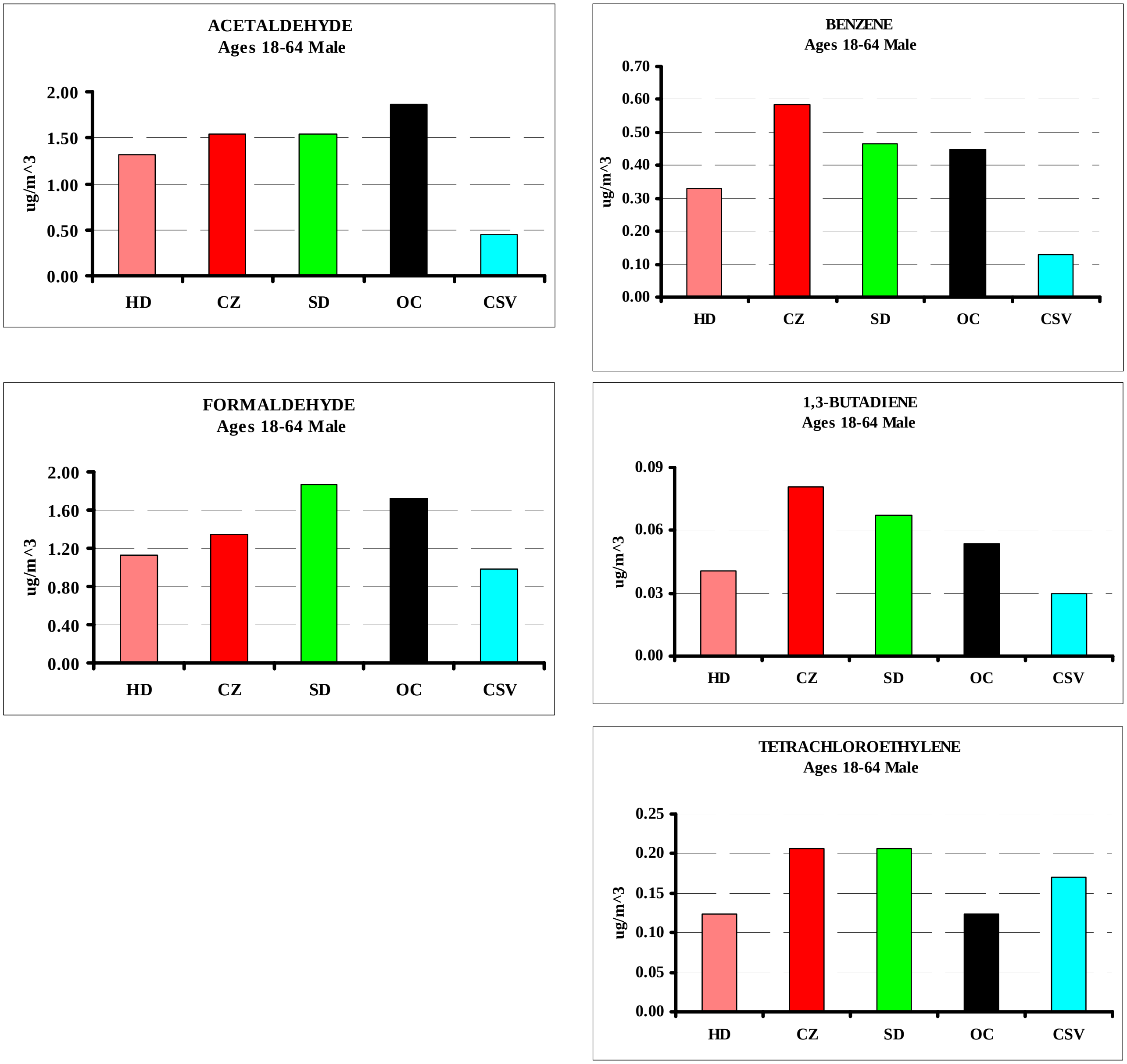


Figure 91. Air toxic VOC exposures (µg/m^3) for male residents in the 18-64 age group.

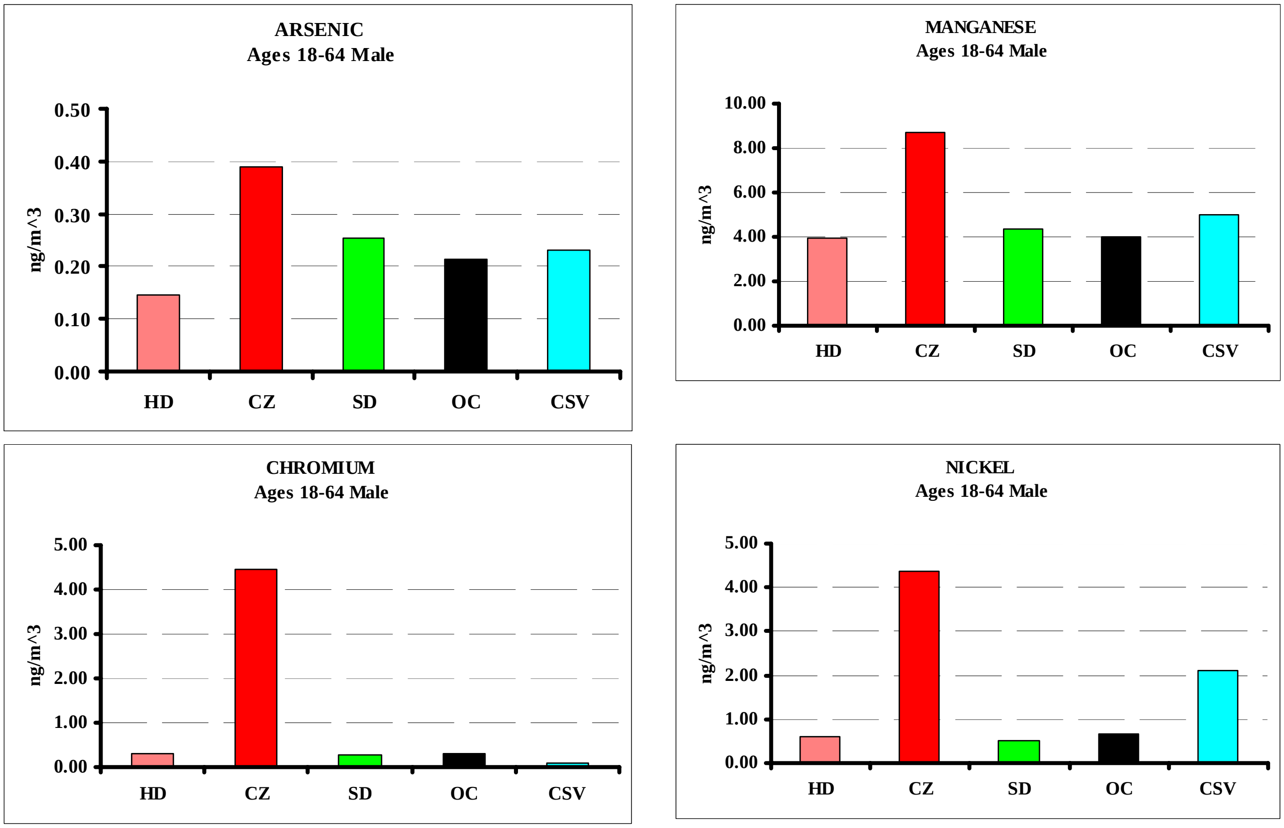


Figure 92. Air toxic trace metal exposures (ng/m^3) for male residents in the 18-64 age group.

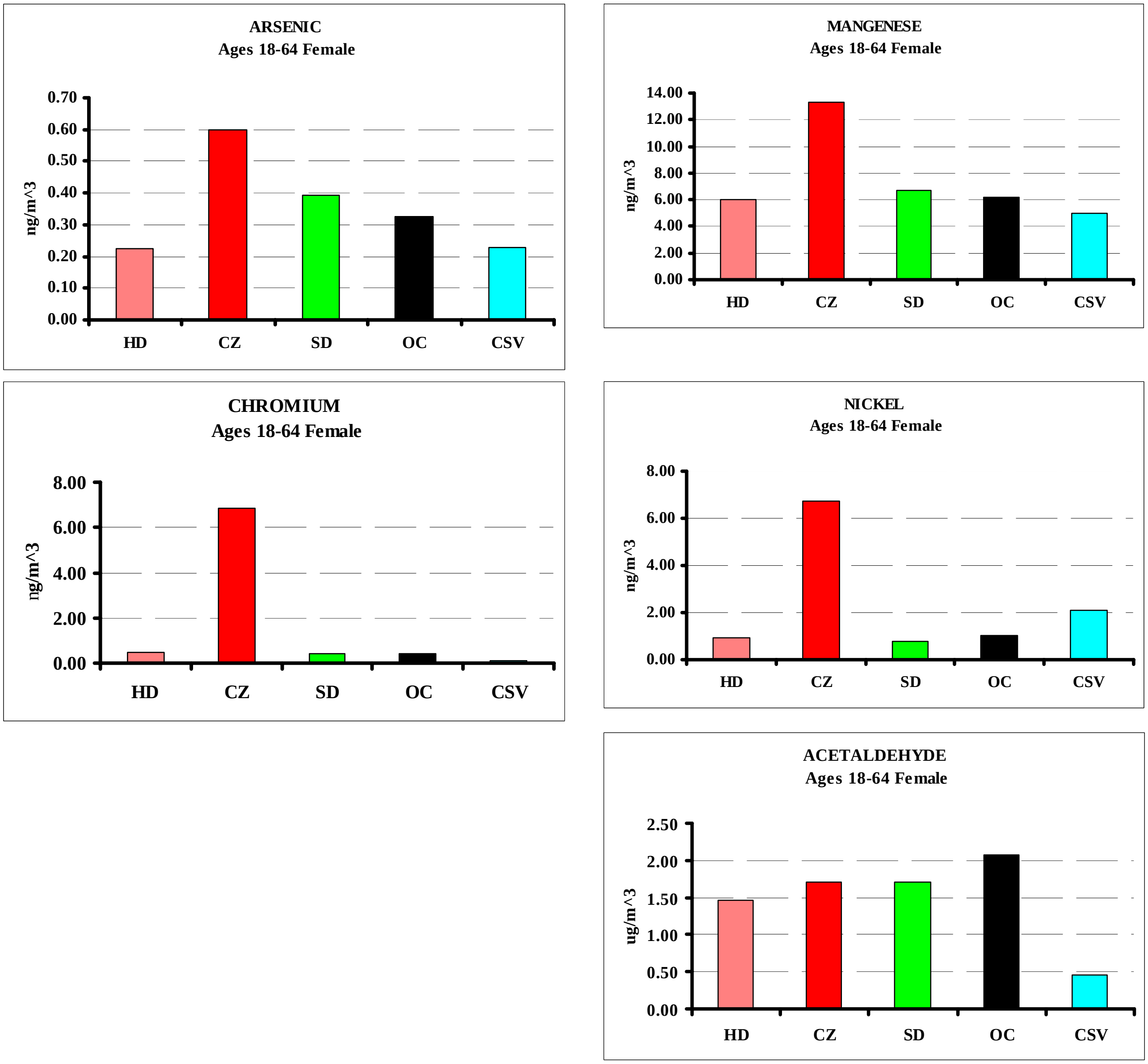


Figure 93. Air toxic VOC exposures (µg/m^3) for female residents in the 18-64 age group.

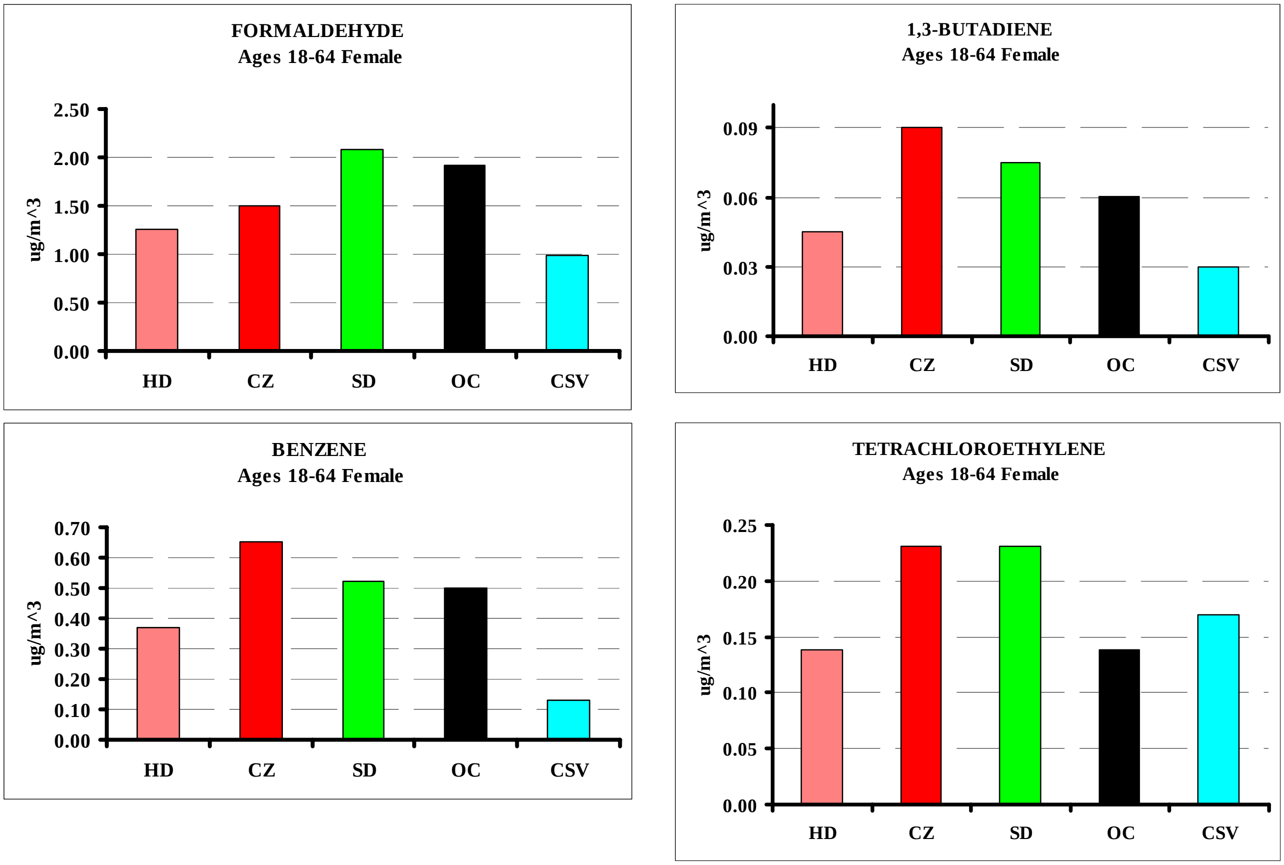


Figure 94. Air toxic trace metal exposures (ng/m^3) for female residents in the 18-64 age group.

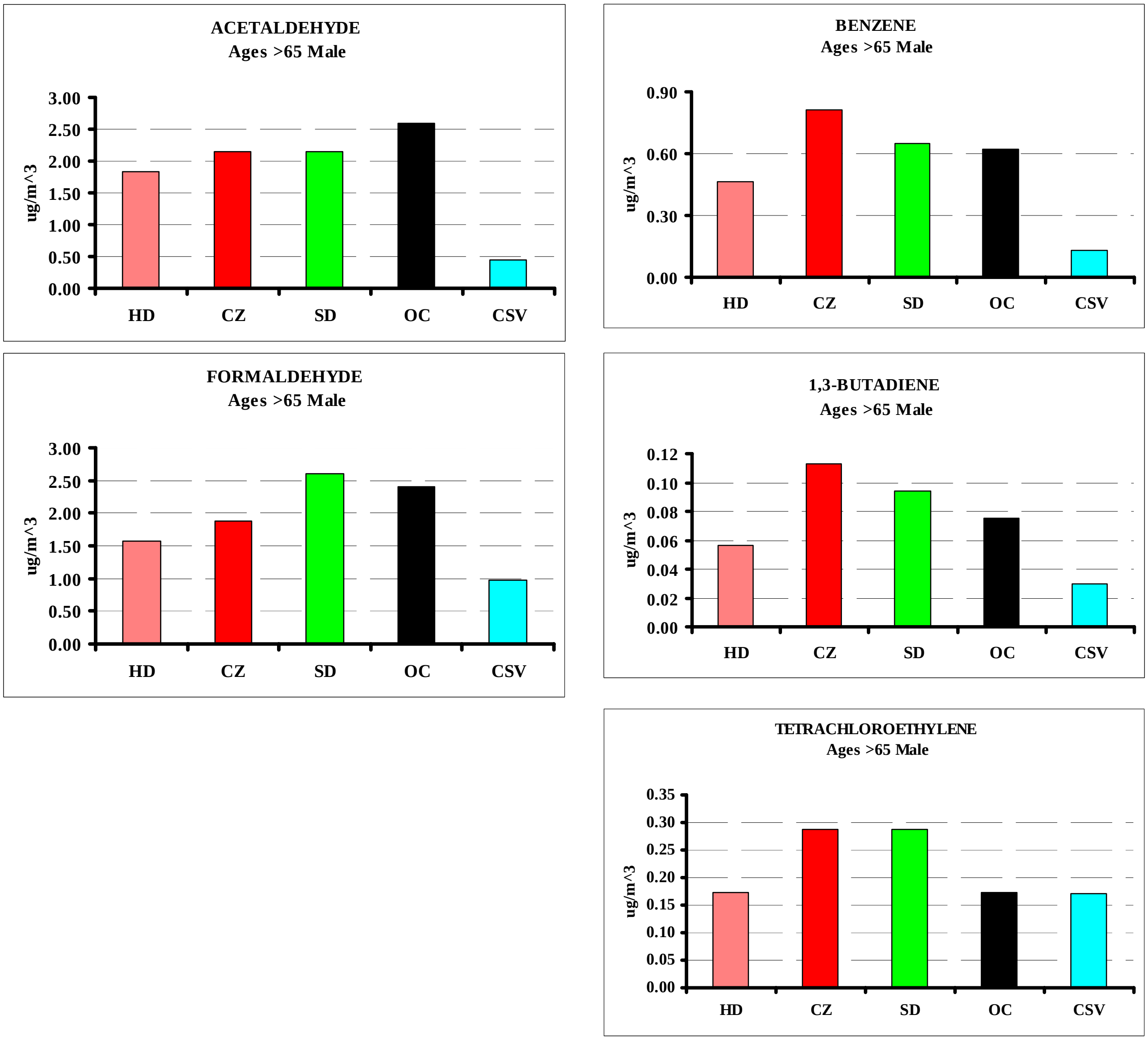


Figure 95. Air toxic VOC exposures ($\mu g/m^3$) for male residents in the >65 age group.

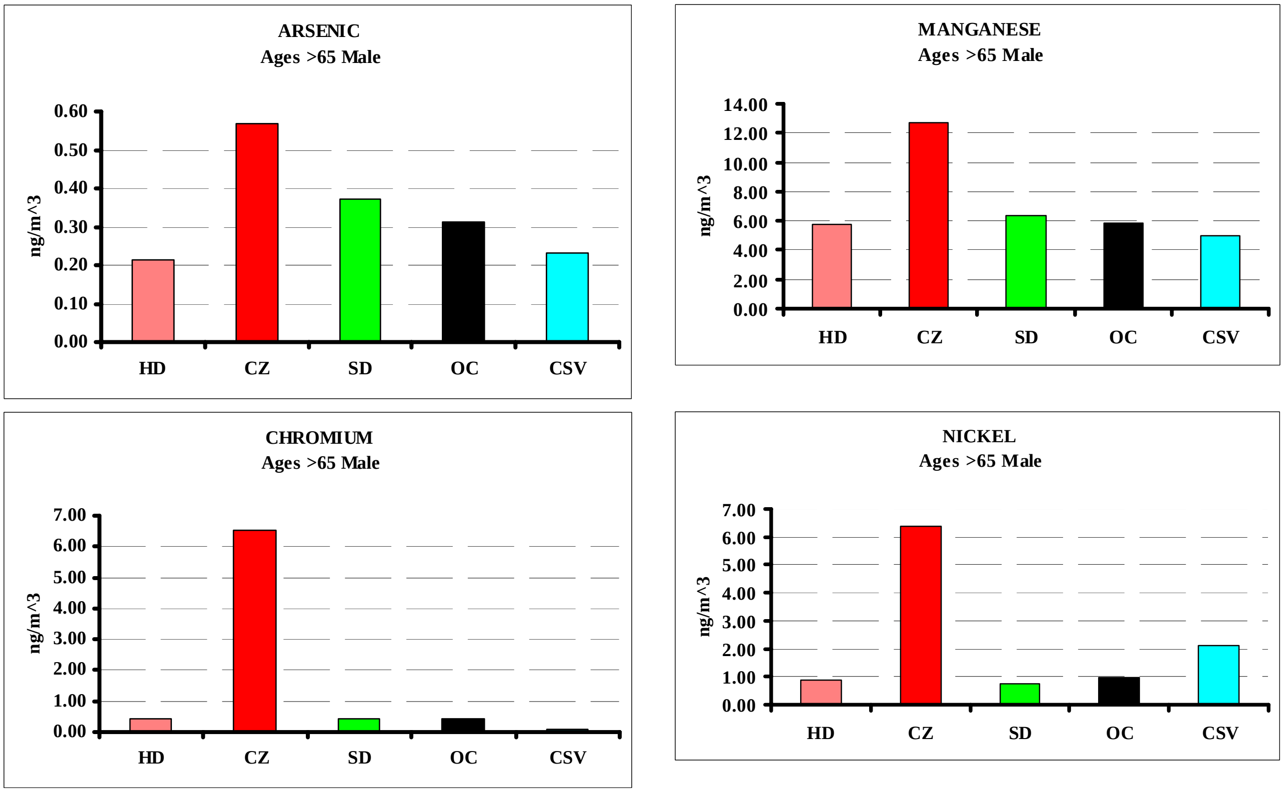


Figure 96. Air toxic trace metal exposures (ng/m^3) for male residents in the >65 age group.

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8.0 Appendix

This appendix contains a summary of baseline concentration data for BTEX compounds that were measured in Spokane but are not included on EPA's "core" air toxic list.

8.1 Toulene

Table 32. Toluene statistics determined at Spokane area sites in 2005

Site	Mean (ppbv)	95% CI	Median (ppbv)	Min (ppbv)	Max (ppbv)	n
HD	0.67	0.10	0.61	0.15	2.18	61
CZ	1.34	0.25	1.11	0.24	6.03	61
SD	1.20	0.18	1.09	0.29	0.3.37	57
OC	0.92	0.13	0.88	0.10	2.53	60

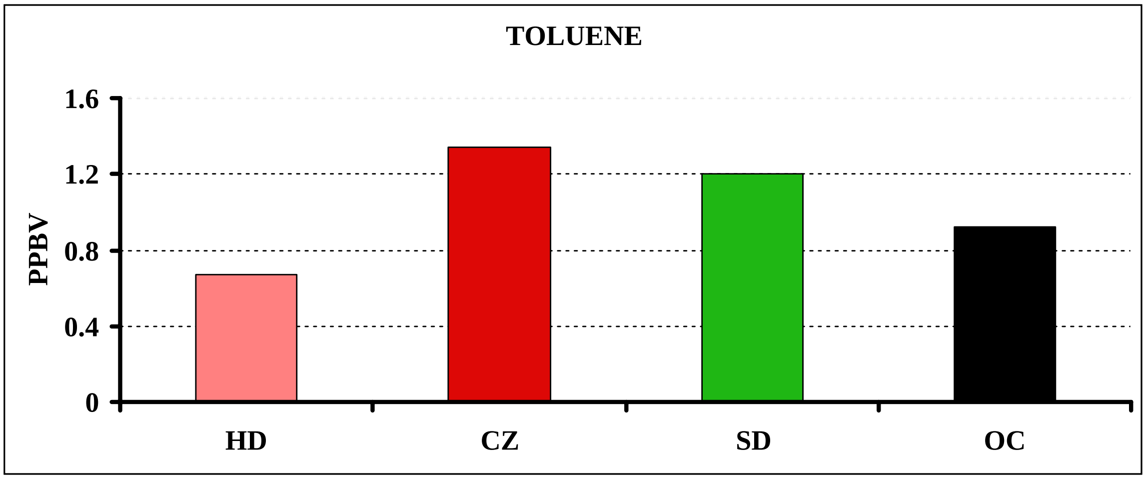

Figure 97. Annual average toluene concentrations at the four Spokane sites in 2005.

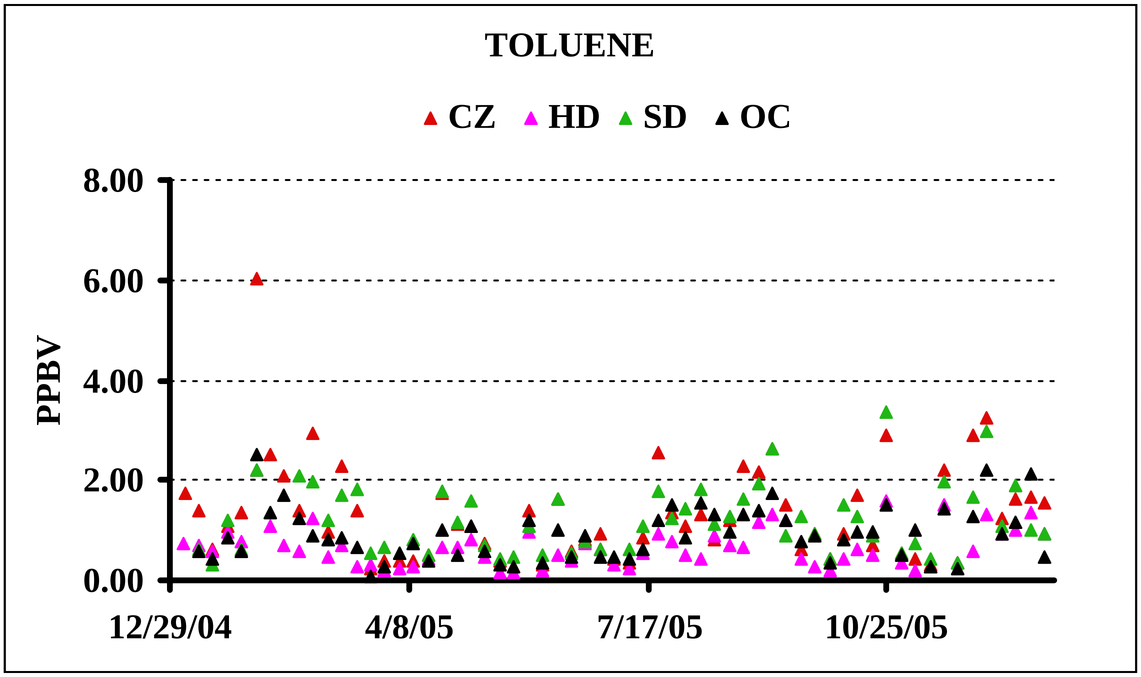

Figure 98. Toluene temporal behavior at the four Spokane area sites.

8.2 Ethylbenzene

Table 33. Ethylbenzene statistics determined at Spokane area sites in 2005

Site	Mean (ppbv)	95% CI	Median (ppbv)	Min (ppbv)	Max (ppbv)	n
HD	0.11	0.02	0.10	0.03	0.35	61
CZ	0.20	0.04	0.17	0.04	0.88	61
SD	0.18	0.03	0.16	0.04	0.55	57
OC	0.14	0.02	0.13	0.02	0.43	60

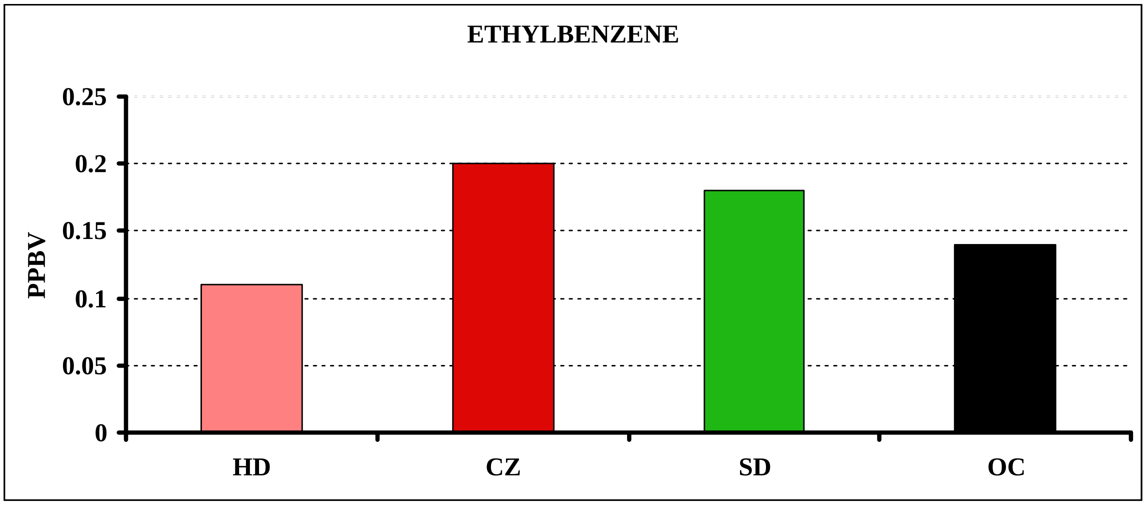

Figure 99. Annual average ethylbenzene concentrations at the four Spokane sites in 2005.

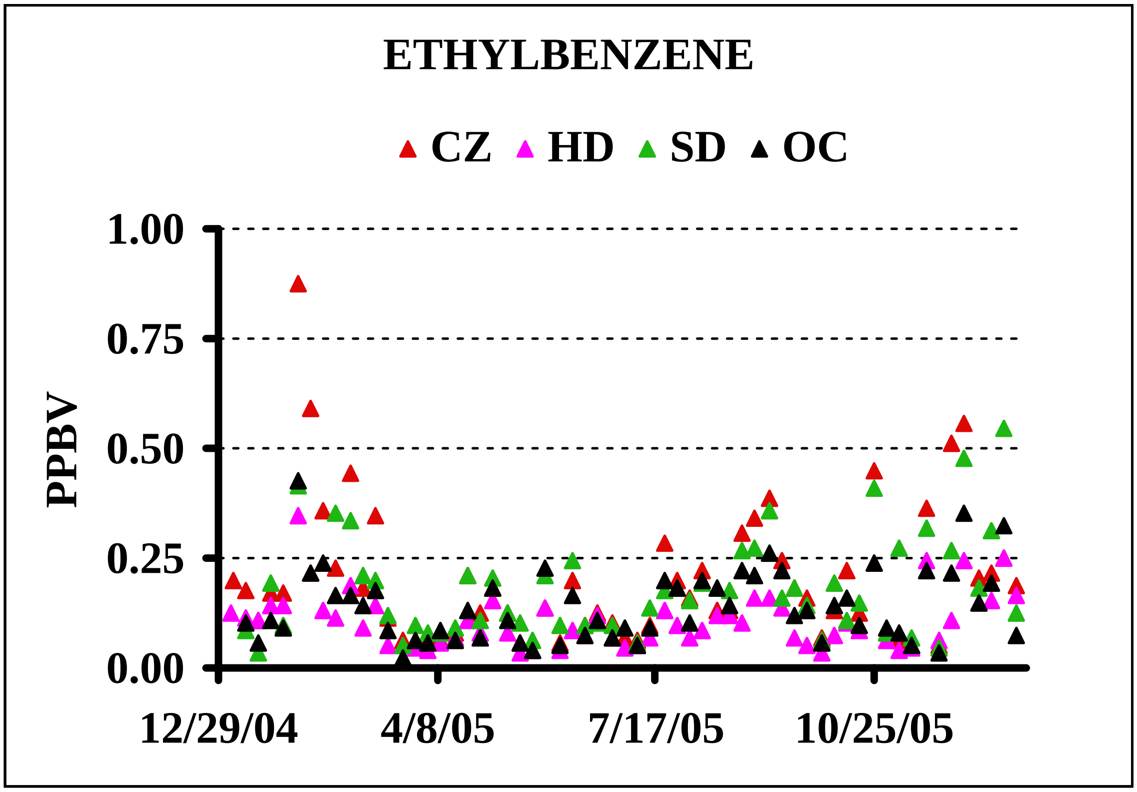

Figure 100. Ethylbenzene temporal behavior at the four Spokane area sites.

8.3 m- & p-Xylene

Table 34. m & p-Xylene statistics determined at Spokane area sites in 2005

Site	Mean (ppbv)	95% CI	Median (ppbv)	Min (ppbv)	Max (ppbv)	n
HD	0.44	0.06	0.39	0.13	1.39	61
CZ	0.82	0.15	0.72	0.18	3.24	61
SD	0.67	0.10	0.58	0.17	1.76	57
OC	0.56	0.08	0.50	0.10	1.58	60

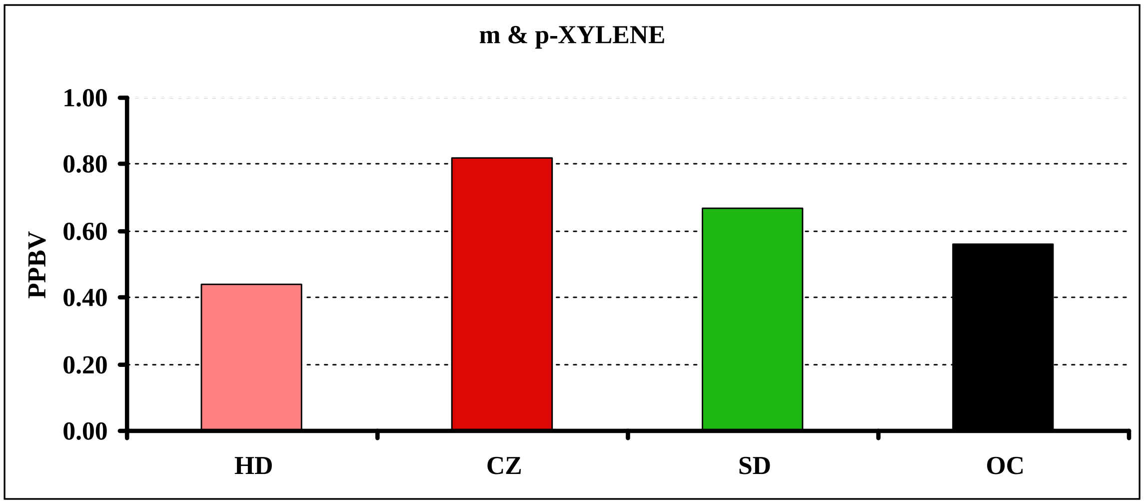

Figure 101. Annual average m & p-xylene concentrations at the four Spokane sites in 2005.

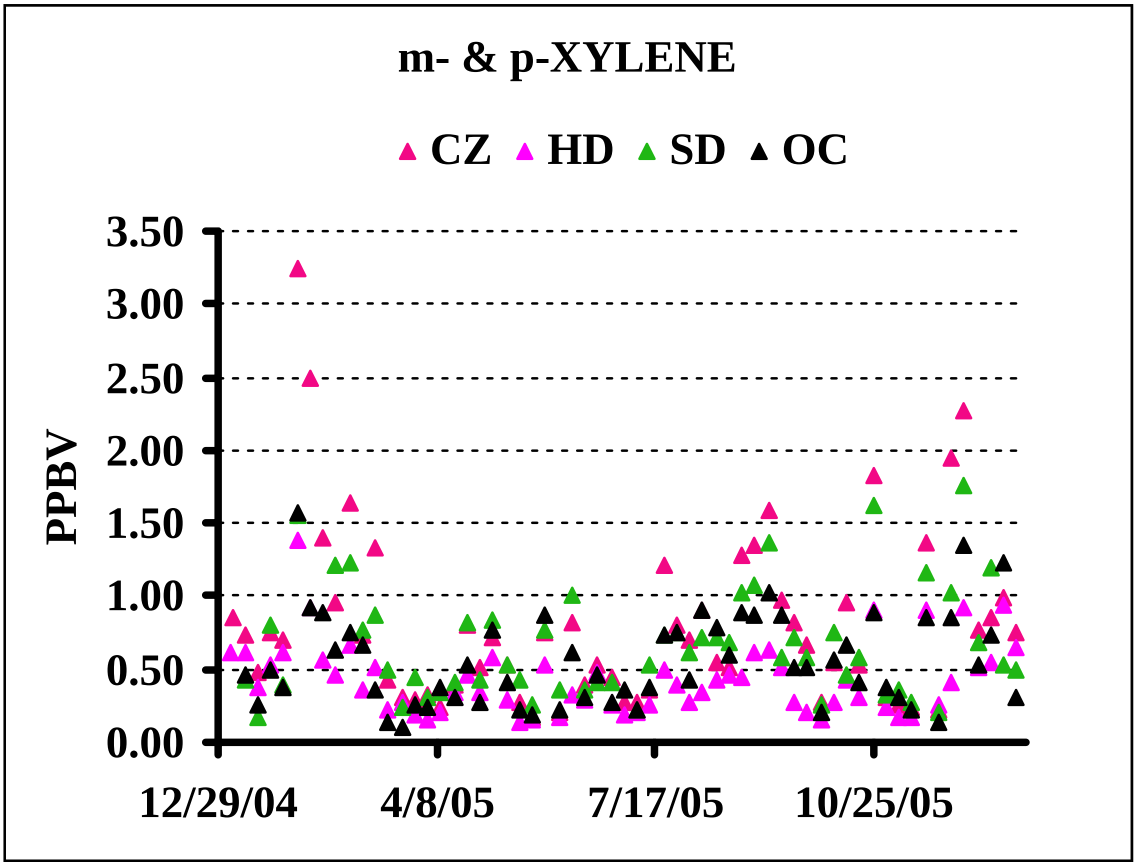

Figure 102. m- & p-Xylene temporal behavior at the four Spokane area sites.

8.4 Styrene

Table 35. Styrene statistics determined at Spokane area sites in 2005

Site	Mean (ppbv)	95% CI	Median (ppbv)	Min (ppbv)	Max (ppbv)	n
HD	0.08	0.01	0.06	0.03	0.38	61
CZ	0.12	0.02	0.09	0.02	0.47	61
SD	0.12	0.03	0.09	0.02	0.55	57
OC	0.22	0.05	0.15	0.04	1.02	60

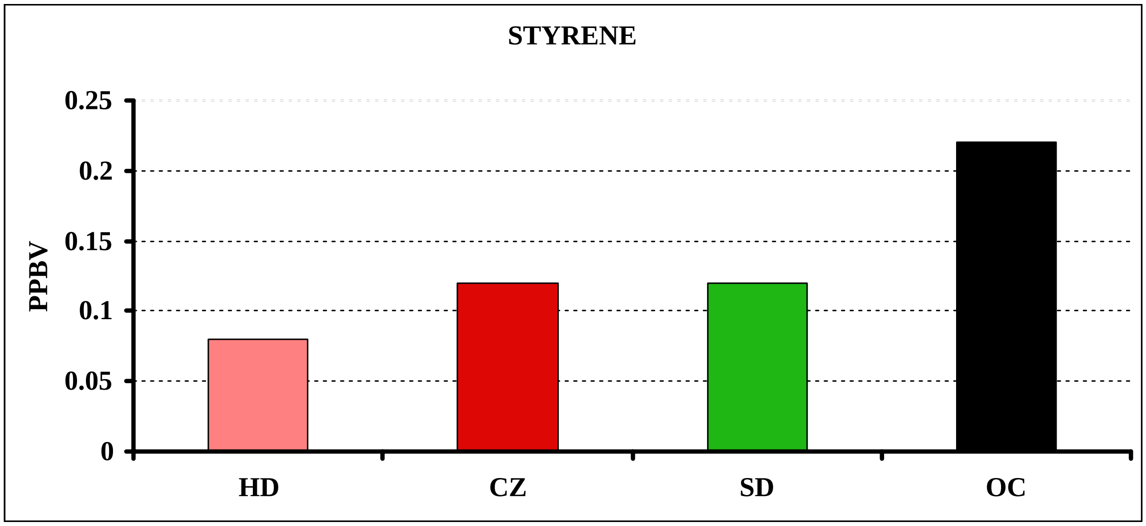

Figure 103. Annual average styrene concentrations at the four Spokane sites in 2005.

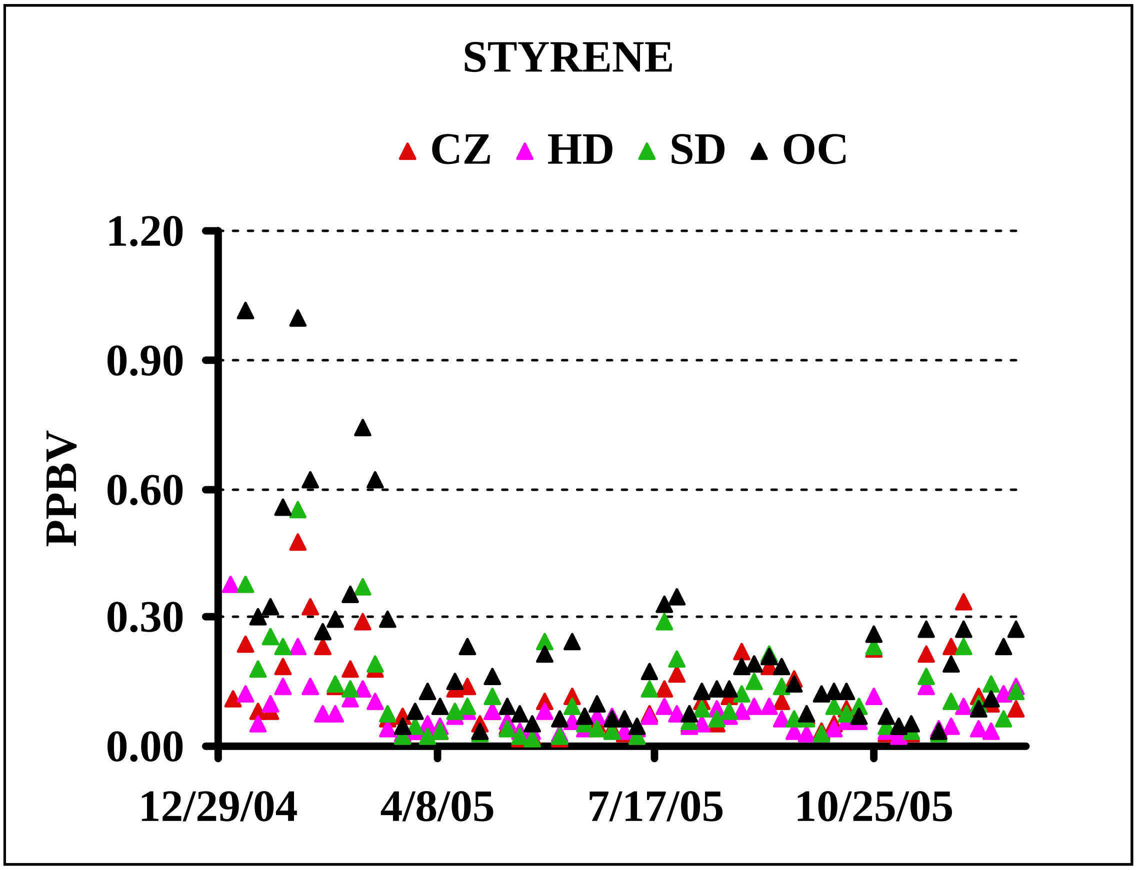

Figure 104. Styrene temporal behavior at the four Spokane area sites.

8.5 o-Xylene

Table 36. o-Xylene statistics determined at Spokane area sites in 2005

Site	Mean (ppbv)	95% CI	Median (ppbv)	Min (ppbv)	Max (ppbv)	n
HD	0.14	0.02	0.13	0.03	0.41	61
CZ	0.27	0.05	0.22	0.05	1.07	61
SD	0.22	0.03	0.19	0.06	0.62	57
OC	0.19	0.03	0.17	0.02	0.57	60

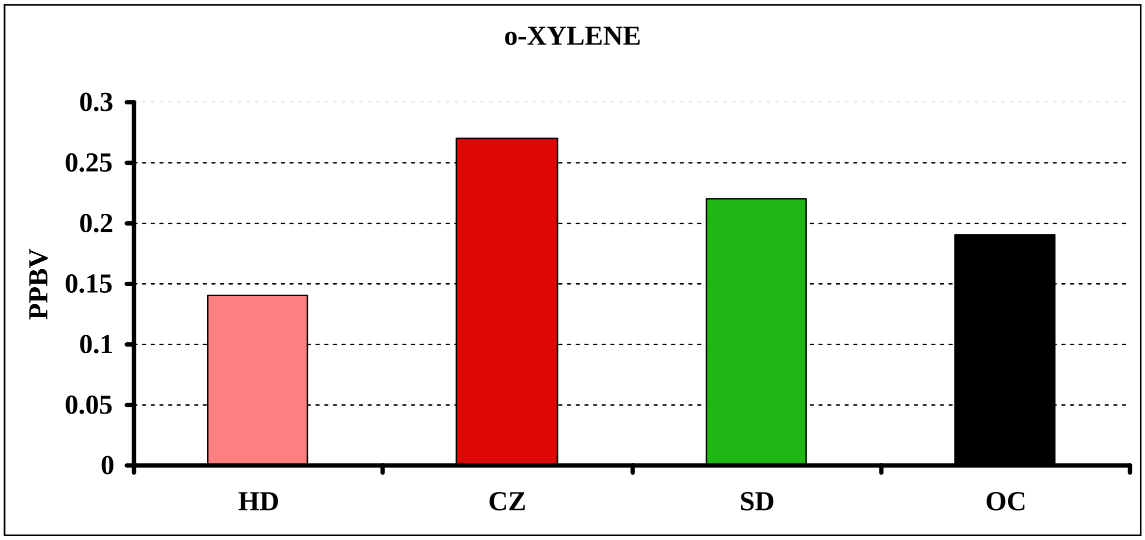

Figure 105. Annual average o-xylene concentrations at the four Spokane sites in 2005.

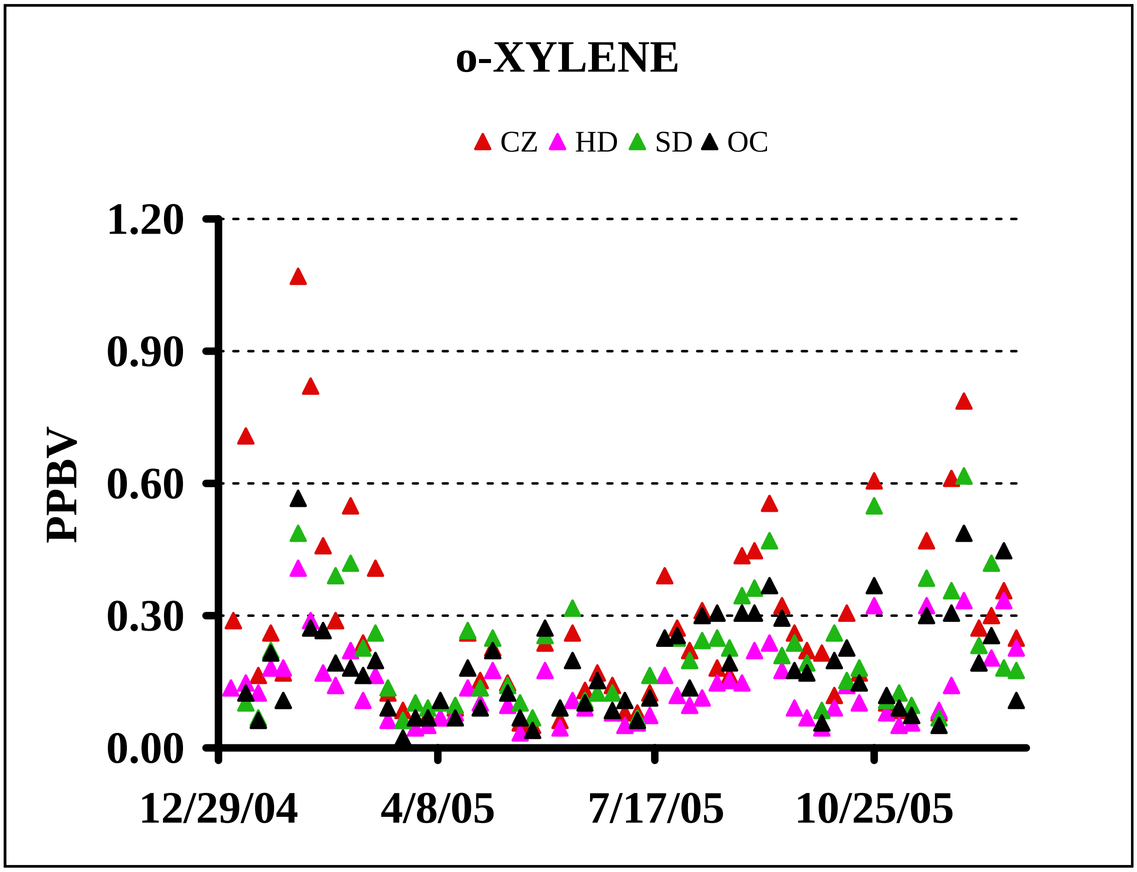

Figure 106. o-Xylene temporal behavior at the four Spokane area sites.