Community Air Toxics Study - Interim (Phase 1) Report

Assessment of the Effectiveness of New Mobile Source Air Toxics Regulations in Reducing Ambient Concentrations of Benzene and Other Air Toxics in Anchorage, Alaska

Summary

This report summarizes findings from the first phase of a two-phase study. This study investigates the effectiveness of new federal mobile source air toxics rules, known as MSAT2, that are expected to reduce the average benzene content in Anchorage gasoline about four-fold by 2012.

In the first phase of this study, ambient concentrations of volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), and carbon monoxide (CO) were monitored in an east Anchorage residential neighborhood for a one-year period between October 2008 and October 2009. During this same period Anchorage gasoline was sampled to determine the content of benzene and other VOCs in gasoline. A follow-up, second phase study is planned after the implementation of MSAT2 to measure differences in ambient concentrations that may result from these new rules.

Ambient benzene concentrations measured in Anchorage in Phase 1 of this study were among the highest in the U.S. (See Appendix). The data suggest that these high ambient concentrations were related to the high benzene content (5%) of Anchorage gasoline. Our Phase 1 analysis suggests that ambient benzene concentrations in Anchorage should decline by about 50% if the gasoline benzene content is reduced to 1.3% as a result of MSAT2.

Like benzene, ambient VOCs and PAHs were generally much higher in winter than in summer. Strong positive correlations of many ambient VOCs and PAHs with ambient CO suggest that motor vehicle tailpipe emissions (from uncombusted or partially combusted fuel) are mainly responsible for the production of these air toxics; evaporative emissions were not a significant source.

PAH data indicated that wood burning is often an important and even predominant source of ambient PAHs, especially on weekends and holidays in the winter.

Background

Motor vehicles are a major source of toxic air pollutants in urban areas, impacting air quality and risking the health of large populations nationwide. VOCs and PAHs are two major compound groups in urban air toxics, and many of them are known or suspected to cause cancer or serious health problems, although only a handful of them are recognized as Hazardous Air Pollutants (HAPs) by the Environmental Protection Agency

(EPA). Examples of VOCs are benzene, ethylbenzene, toluene, and xylene (BETX) and 1,3-butadiene, all of which are recognized HAPs. In Table 1, examples of air toxics that are commonly found in polluted air are shown.

Many of these HAPs found in ambient air are emitted as automobile exhaust. In fact, mobile sources are estimated to be responsible for 70-80% of national emissions of BETX and 60% of 1,3-butadiene[1].

Table 1. VOC and PAH commonly found in ambient air and the listing status as hazardous air pollutants (HAPs).

Group	Compound	Toxicity (reference chemical listing*)	Listed as HAP?
VOC	Benzene	Recognized: carcinogen (P65) Suspected: Neurotoxicant, Respiratory Toxicant (EPA-HEN)	Y
	Ethylbenzene	Recognized: carcinogen (P65) Suspected: Neurotoxicant, Respiratory Toxicant (EPA-HEN)	Y
	Toluene	Recognized: Developmental Toxicant (P65) Suspected: Neurotoxicant, Respiratory Toxicant (EPA-HEN)	Y
	Xylenes	Suspected: Cardiovascular or Blood Toxicant, Neurotoxicant, Respiratory Toxicant (EPA-HEN)	Y
	1,3-Butadiene	Recognized: carcinogen (P65) Suspected: Respiratory Toxicant (EPA-HEN)	Y
PAH	Naphthalene	Recognized: carcinogen (P65) Suspected: Developmental Toxicant, Neurotoxicant (EPA-HEN)	Y
	Anthracene	Suspected: Gastrointestinal or Liver Toxicant (ATSDR)	N
	Phenanthrene	Suspected: Respiratory Toxicant (NTP-HS)	N
	Pyrene	Suspected: Neurotoxicant, Skin or Sense Organ Toxicant (RTECS)	N
	Chrysene	Recognized: carcinogen (P65)	N
	Benzo (a) anthracene	Recognized: carcinogen (P65)	N
	Retene	Lacking data	N
	Benzo (a) pyrene	Recognized: Carcinogen P65 Suspected: Respiratory Toxicant (EPA-HEN)	N
	Benzo (b) fluoranthene	Recognized: carcinogen (P65)	N
	Benzo (k) fluoranthene	Recognized: carcinogen (P65)	N
	Indeno(1,2,3-cd)pyrene	Recognized: carcinogen (P65)	N
	Benzo (g,h,i) perylene	Lacking data	N
	Coronene	Lacking data	N

* Reference list legends: **ATSDR**= Agency for Toxic Substances and Disease Registry, **EPA-HEN**= EPA's Health Effects Notebook for Hazardous Air Pollutants, **NTP-HS**= National Toxicology Program's Chemical Repository of Health and Safety Data, **P65**= California's Proposition 65, **RTECS**= National Institute for Occupational Safety and Health's Registry of Toxic Effects of Chemical Substances.

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[1] National Research Council of the National Academies (2003) Managing carbon monoxide pollution in meteorological and topographical problem areas. National Academies Press, Washington DC, USA.

BETX are major components of gasoline, and a portion of VOCs in ambient air come from the evaporation of fuels. They can also be emitted when they pass through engines uncombusted. Studies have estimated that as much as 60% of the VOCs in vehicle exhaust are tailpipe emissions of uncombusted gasoline.[2]

Reducing the content of benzene and other aromatics in gasoline has been shown to produce significant reductions in tailpipe exhaust emissions of benzene. Benzene emission rates from gasoline-powered light-duty vehicles declined by 54% following the introduction of California Phase 2 Reformulated Gasoline in March 1996 when the ceiling benzene content in gasoline was cut in half to ≤0.8%[3, 4]. In this case the decline in benzene emissions was roughly proportionate to change in the benzene content of the gasoline.

PAHs are another group of air toxics that generally have a greater molecular weight than VOCs and are semi-volatile (e.g., naphthalene) or non-volatile (e.g., coronene). Higher molecular weight PAHs are often associated with fine particulate matter ($PM_{2.5}$). Although few are listed as HAPs, evidence for serious human health effects of PAHs has been accumulating in recent years. PAHs are not original components of gasoline or other fuels; they are byproducts of partial combustion and are commonly found in automobile exhaust or wood smoke[5,6]. Some PAHs are known to be source-specific. For example, retene is highly specific to coniferous-wood burning[7], whereas indeno (1,2,3-cd) pyrene, benzo (g,h,i) perylene, and coronene are associated with gasoline engine exhaust[8]. Additionally, a pyrene-to-benzo(a)pyrene ratio of greater than five is suggestive of an automobile source[9]. Thus, examination of the ambient PAH profile can provide insight into the sources of PAHs in ambient air.

To reduce human daily exposure to toxic VOCs and PAHs from motor vehicles, the Environmental Protection Agency (EPA) promulgated a new Mobile Source Air Toxics rule in 2007[10] targeting benzene. The rule has three primary provisions: (1) setting limits for refiners to produce gasoline with annual average benzene content ≤0.62%

[2] Schuetzle, D. et al. (1994) The Relationship between Gasoline Composition and Vehicle Hydrocarbon Emissions: A Review of Current Studies and Future Research Needs. *Environ. Health. Perspect.* 102, Supplement 4,

[3] Harley RA. (2006) Effects of reformulated gasoline and motor vehicle fleet turnover on emissions and ambient concentrations of benzene. Environ. Sci. Technol. 40:5084-5088.

Air Resources Board, California Environmental Protection Agency 92008) Cleaner-burning gasoline: an update http://www.arb.ca.gov/fuels/gasoline/cbgupdat.htm

[4] Health Assessment of 1,3-Butadiene (2002) by U.S. Environmental Protection Agency. EPA/600/P-98/001F http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=54499#Download

[5] Sapkpta A & Buckley T (2003) The mobile source effect on curbside 1,3-butadiene, benzene, and particle-bound polycyclic aromatic hydrocarbons assessed at tollbooth. J. Air & Waste Manage. Assoc. 53: 740-748.

Rosenbaum et al. (1999) National estimates of outdoor air toxics concentrations. J. Air & Waste Manage. Assoc. 50:2067-2072.

[6] Sheesleya RJ et al. (2007) Sensitivity of molecular marker-based CMB models to biomass burning source profiles. Atoms. Environ. 41:9050-9063.

[7] Ramdahl T. (1983) Retene—a molecular marker of wood combustion in ambient air. Nature 306:580-582.

[8] Sheesley et al. (2008) Source apportionment of elevated wintertime PAHs by compound-specific radiocarbon analysis. Atmos. Chem. Phys. Discuss., 8:20901–20924, and

Zechmeister et al. (2006) Pilot study on road traffic emissions (PAHs, heavy metals) measured by using mosses in tunnel experiment in Vienna, Austria. Environ. Sci. Pollut. Res. 13:398-405

[9] Korte N (1999) Polynuclear Aromatic Hydrocarbons (Chapter 4) *In* A guide for the technical evaluation of environmental data. pp.67-88. Technomic Publishing Company, Inc. Lancaster, PA, 17604, USA.

[10] Federal Register Vol. 72, No. 37. Rules and Regulations. (February 26, 2007)

beginning 2011[11]; (2) requiring vehicle manufacturers to meet new cold temperature emission standards (at 20 °F) starting 2010 for lighter vehicles (≤6000 lbs) and 2012 for heavier vehicles (>6000 lbs)[12]; and (3) limiting evaporation from and permeation through portable fuel containers to ≤0.3 g per gallon per day starting with those manufactured in 2009.

Anchorage is ideal for evaluating the effectiveness of the first provision of the rule for the following reasons:

- It has some of the highest ambient benzene concentrations in the U.S. and evidence suggests that gasoline-fueled motor vehicles are the source of these high concentrations. It also has very high ambient concentrations of other BETX components. (See comparison with other cities in Appendix).

- It is Alaska's largest city (2000 census population = 260,283) and is the center of economy and employment. The Anchorage vehicle population is largely gasoline-fueled. Less than 10% of vehicle miles traveled (VMT) is accrued by vehicles using non-gasoline fuels such as diesel or compressed natural gas.

- The benzene content of Anchorage gasoline is several times higher than most areas of the U.S. The implementation of the rule is expected to result in approximately four-fold reduction of benzene in gasoline compared to a less than two-fold reduction expected in most other areas.

- The largest emission source of air toxics is considered to be the motor-vehicle operation and related mobile sources, because there is no petroleum refining and little heavy industry in Anchorage that likely emits significant VOCs or PAHs. Furthermore, clean-burning natural gas rather than coal or oil serves as the primary energy source for electrical generation and space heating due to its relatively low cost in Anchorage. Motor vehicles account for an estimated 77% of all CO emissions.

- Previous studies in Anchorage have shown strong associations (R^2 >0.9) between ambient benzene and CO, which allows comparison of ambient benzene normalized for CO.

- Nearly all the gasoline supplied in Anchorage originates from a single refiner and the composition of gasoline is therefore relatively homogeneous.

- The effect of the MSAT2 rule on Anchorage air can provide insights into the dynamics of air toxics in other cities, particularly those in cold regions.

The goal of this two-phase study is to quantitatively evaluate the effectiveness of the new MSAT2 gasoline benzene limits on Anchorage air quality. In Phase 1 of the study, we aimed to obtain base information on ambient VOC, PAH, and CO concentrations in Anchorage air and their seasonal variations. We also wanted to characterize the composition of gasoline, particularly its benzene content, prior to the implementation of the rule. In Phase 2, we plan to repeat the same measurements and compare results from Phases 1 and 2 to assess the effectiveness of the rule.

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[11] The rule allows a nationwide averaging, banking, and trading. In addition to the 0.62 vol% standard, Refiners must also meet a maximum benzene standard of 1.3% beginning July 2012. Although the benzene reduction in Anchorage gasoline is yet to be determined, we have assumed that the post-rule benzene content will be approximately 1.3%.

[12] Non-methane hydrocarbon emissions from light-duty vehicles (≤6000LBs) must be ≤0.3g/mile and from heavy-duty vehicles (>6000 lbs) <0.5g/mile.

Methods

Gasoline

Regular and premium grade gasoline samples were collected bimonthly (Oct and Dec 2008; Mar, May, Jul, and Sep 2009) from selected gasoline stations within Anchorage bowl, shown in yellow in Figure 1, for one year. To obtain representative samples, 20 gasoline stations from 6 store brands were selected for the first sampling (Figure 1). We selected gasoline stations that were presumed to have high sales volumes; stations located on high volume roads were given preference in the selection process.[13] The gasoline station locations are indicated by the green dots in Figure 1. The number of gasoline stations was reduced to 10 (of 6 store brands) after Oct sampling, because the first round of sampling results showed that the chemical composition of gasoline was very similar among stations selling the same brand.

Figure 1. **Map of Anchorage bowl (yellow area) and sampling locations for the Phase 1 study**. All air samples were collected and monitored at Garden Station. The 20 green dots show locations of gasoline stations selected for initial sampling.

To ensure samples were fresh and/or to minimize cross-contamination of different grades, gasoline samples were collected by first purging >0.1 gallon of gasoline, if the pump had separate nozzles for two grades, and >2.0 gallons if the pump used one

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[13] Data from the Annual Traffic Volume Report (2006-2008), published by the Alaska Department of Transportation and Public Facilities were used to select gas stations adjacent to high volume roads.

nozzle to deliver multiple grades. Following purging, stainless steel fuel cans were pre-rinsed 3 times by pumping 50-100 mL of gasoline each time. Sample bottles were filled with a minimal headspace to minimize off-gassing and were immediately placed on ice in a cooler. Replicates were collected with more than 10% of these samples. Each sample was transferred to a GC vial and transported in an ice-chilled shipping container for VOC analysis to the Applied Science, Engineering and Technology (ASET) laboratory at University of Alaska, Anchorage. The samples were kept <5°C until analysis and were analyzed by GC within 48 hours of the end of sampling using 100 Meter Capillary High Resolution Gas Chromatograph Column.

Four duplicate gasoline samples were collected during each bi-monthly sampling round. The average absolute percent difference in the benzene content among the 24 sample pairs collected during the study was less than 0.1%. The single largest absolute benzene content difference in a sample pair was just 0.32%. Other BTEX components exhibited similar reproducibility.

Air sampling and monitoring

Ambient air was sampled and monitored for one year (Oct 2008-Oct 2009) at a long-term air quality monitoring station, "Garden", located in a typical residential area in northeast Anchorage (Figure 1).[14] The station is designated as an EPA State and Local Air Monitoring Station (SLAMS) and has served as a CO monitoring site for over 30 years. Monitoring was performed here for air toxics studies in Anchorage in 1993-94, 1994-96, and 2002.

VOC

Ambient VOC samples were collected at Garden Station and analyzed in accordance with Air Toxics Compendium Method TO-15. In short, evacuated (≤ -27"Hg) 6-L passive-fill SUMMA canisters equipped with an electronic timer and a mass-flow controller were used to collect 24-hr air samples at 3.5 mL/min air intake rate with frequency of once every 6 days for one year starting Oct 2008 (total = 62). After each collection, the canister was shipped to the EPA contract laboratory, ERG, in North Carolina where VOC concentrations were analyzed by GC/MS (gas chromatography/mass spectrometry). Over the course of the study six duplicate canisters were collected to assess precision. The average absolute difference in the ambient benzene concentration in the six paired samples was less than 0.1 ppb. The average relative difference in the ambient benzene concentration in replicate canisters was 17%. Other VOC compounds exhibited similar precision.

PAH

Ambient PAH samples were collected and analyzed according to modified Air Toxics Compendium Method TO-13, using two high-volume air samplers (Tisch TE-1000). Air was pumped through a glass fiber filter and a sorbent cartridge (a cylinder filled with polyurethane foam/XAD resin) at >0.139 m^3/min for 24 hrs every 6 days for one year (total = 60). After each collection, the filter and cartridge were retrieved, transferred to air-tight containers, and shipped to the ERG laboratory on ice via overnight express. When overnight shipment was not possible, the samples were kept frozen until shipment. Over the course of the study seven replicate samples were collected to assess precision. Over 90% of the analyte concentrations measured in these replicate

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[14] Physical address: Trinity Christian Reformed Church, 3000 East 16th Ave, Anchorage, AK 99508.

pairs had a relative percentage difference of less than 30% when concentrations were five times the minimum detection limit or higher for that analyte.

CO

Ambient CO was monitored continuously at Garden Station during the one-year study period using a trace level CO analyzer (TECO Model 48i-TLE). The instrument's performance and precision were tested bi-weekly with NIST-traceable zero air and challenge gases varying from 3.0 to 9.15 ppm in concentration. During the study the analyzer met all quality control requirements for SLAMS CO and successfully passed third party audits conducted by the Alaska Department of Environmental Conservation.

Results & Discussion

Gasoline composition

The annual mean benzene content of Anchorage gasoline was about 5% (w/w) (Regular grade 5.0%, 5.3% in premium grades).[15] Toluene was the largest component among the BETX compounds (annual mean 17.4% in regular grade and 19.3% in premium). All together, BETX compounds comprised nearly 40% of the gasoline by weight, and minimal differences in BETX composition were observed across seasons and store-brands. Premium grade gasoline contained slightly higher levels of all BETX compounds.

Table 2. BETX content of Anchorage gasoline (mean and 1 standard deviation).

regular grade (% w/w)							
	Oct-08	**Dec-08**	**Mar-09**	**May-09**	**Jul-09**	**Sep-09**	**Annual Average**
benzene	5.36 ± 0.13	5.12 ± 0.38	5.01 ± 0.41	4.63 ± 0.15	4.72 ± 0.54	5.11 ± 0.43	**5.04 ± 0.42**
ethyl benzene	2.35 ± 0.12	2.27 ± 0.26	2.28 ± 0.37	2.69 ± 0.16	2.09 ± 0.26	2.45 ± 0.30	**2.36 ± 0.29**
toluene	17.59 ± 0.54	18.25 ± 0.65	18.79 ± 1.36	16.96 ± 1.66	14.99 ± 1.39	17.62 ± 0.67	**17.37 ± 1.52**
total xylenes	13.21 ± 0.34	12.69 ± 0.51	12.63 ± 0.91	13.43 ± 0.44	11.7 ± 1.51	13.32 ± 0.90	**12.83 ± 0.96**

| premium grade (% w/w)							
	Oct-08	**Dec-08**	**Mar-09**	**May-09**	**Jul-09**	**Sep-09**	**Annual Average**
benzene	5.52 ± 0.09	5.43 ± 0.05	5.33 ± 0.06	5.36 ± 0.06	4.75 ± 0.55	5.54 ± 0.15	**5.32 ± 0.34**
ethyl benzene	2.89 ± 0.09	2.80 ± 0.10	2.84 ± 0.09	3.08 ± 0.09	2.80 ± 0.27	2.76 ± 0.11	**2.86 ± 0.16**
toluene	19.40 ± 0.53	19.74 ± 0.22	20.80 ± 0.52	19.28 ± 0.63	17.72 ± 1.04	18.91 ± 0.68	**19.31 ± 1.06**
total xylenes	16.29 ± 0.59	15.86 ± 0.45	16.17 ± 0.52	16.47 ± 0.37	15.06 ± 1.39	15.46 ± 0.71	**15.89 ± 0.85**

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[15] w/w = weight per weight

Ambient VOC, PAH, and CO concentrations in Anchorage

Ambient VOCs and PAHs were generally much higher in winter than in summer. The seasonal averages of total VOC, BETX, and total PAH were 2-3 times higher in the cold season (Oct-Mar) than in the warm season (Apr-Sep). In Figure 2, examples of seasonal fluctuation of VOC and PAH are shown along with CO. The concentrations of benzene, total BETX, total PAH and CO tracked each other closely, and all recorded their highest concentrations on Jan 7, 2009.

Ambient BETX and 1,3-butadiene concentrations were all strongly and positively associated with CO concentrations (Figure 3), and all of these VOC compounds were correlated among each other (R^2 >0.9, data not shown). Furthermore, many individual PAH compounds as well as total PAH correlated strongly with ambient CO, BETX, and total VOC. The strong correlations among BETX 1,3-Butadiene, PAHs and CO indicate that the emissions of these air pollutants are directly affected by the same factors that influence CO emissions, such as poor combustion of gasoline during vehicle cold-starts. PAHs were highly correlated with 1,3-butadiene (Table 3). PAHs and 1,3-butadiene are not components of gasoline but are products of incomplete combustion.

Figure 2. Seasonal fluctuations of (A) benzene, (B) total BETX, (C) total PAH, and (D) CO concentrations in Anchorage air. Annual medians are indicated as dotted lines.
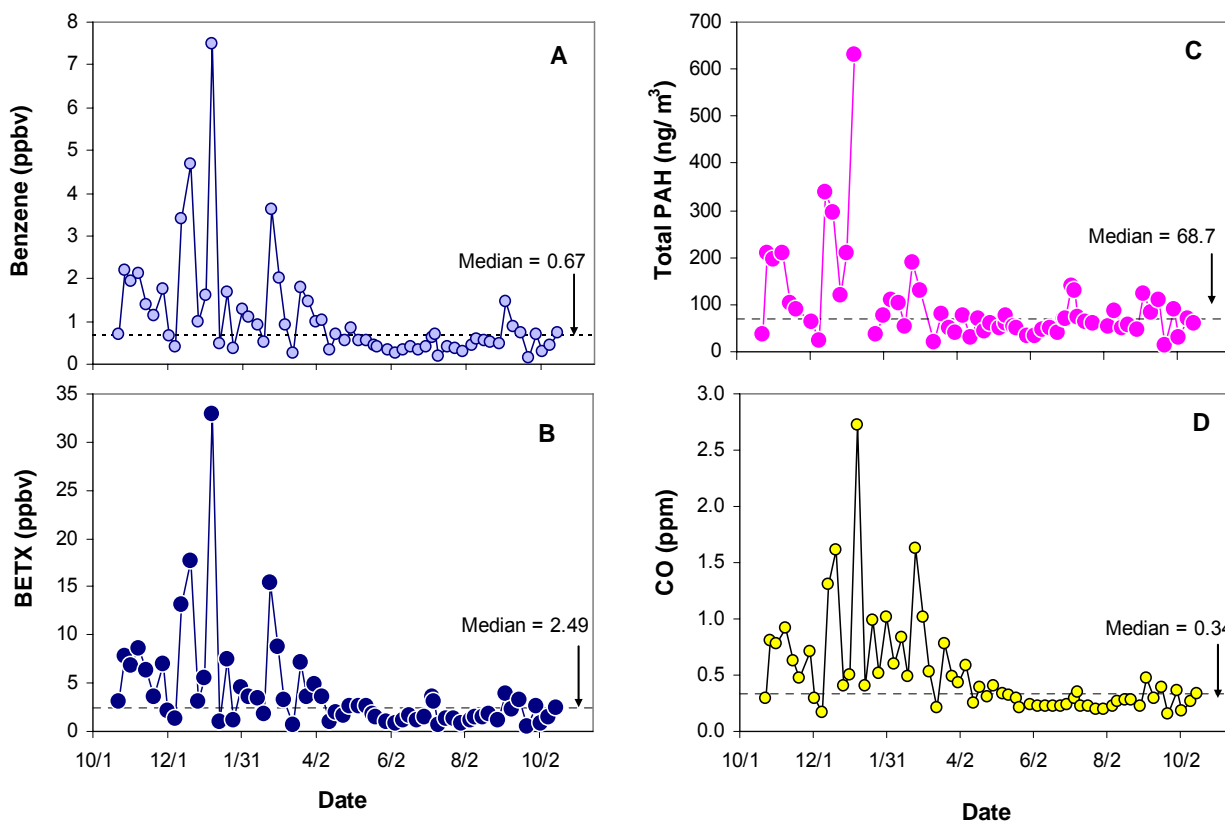
Figure 3. Positive associations of ambient BETX and 1,3-butadiene with CO during the study period (Oct 2008-Oct 2009).
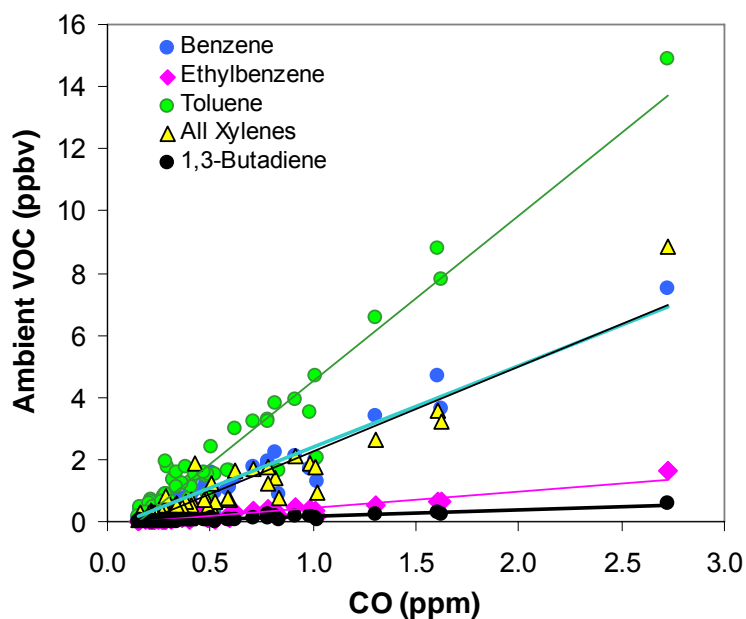
Table 3. Correlation matrix of ambient PAH vs. ambient CO, total VOC, and BETX.
Values shown are Pearson's R. The comparison was made for the samples collected on the same day (n=59 for PAH-CO comparison; n=14-55 for PAH-VOC comparison). Strong correlations ($R \geq 0.8$) are shown in bold letters.

Selected PAH in ambient air	known common source	Ambient			
		CO	Total VOC	Total BETX	1,3-Butadiene
Naphthalene		**0.897**	**0.914**	**0.939**	**0.951**
Anthracene		0.539	0.568	0.501	0.424
Phenanthrene	organic matter butning	0.475	0.545	0.560	0.530
Pyrene	gasoline engine exhaust	**0.805**	**0.816**	**0.873**	**0.886**
Chrysene		**0.808**	**0.829**	**0.834**	**0.900**
Benzo (a) anthracene	gasoline engine exhaust	**0.815**	**0.832**	**0.861**	**0.924**
Retene	coniferous wood burning	0.724	0.793	0.771	**0.805**
Benzo (a) pyrene		**0.813**	**0.829**	**0.862**	**0.929**
Benzo (b) fluoranthene		0.779	0.793	**0.811**	**0.882**
Benzo (k) fluoranthene		0.709	0.714	0.746	**0.804**
Indeno(1,2,3-cd)pyrene	gasoline engine exhaust	**0.830**	**0.821**	**0.858**	**0.923**
Benzo (g,h,i) perylene	gasoline engine exhaust	0.757	0.771	**0.810**	**0.904**
Coronene	gasoline engine exhaust	0.777	0.739	**0.801**	**0.890**
Total PAH		**0.886**	**0.908**	**0.933**	**0.945**

Increasing molecular weight (label along left side of PAH list, top to bottom)

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Implications of Ambient BETX-CO associations

Uncombusted gasoline VOCs (i.e.; gasoline components that pass through the engine and out the tailpipe unaltered) has been shown to account for about 60% of total VOCs in the exhaust during vehicle cold-starts[16]. This may be particularly true for benzene; one study showed that a greater proportion of benzene in gasoline passes through engine uncombusted than other BETX compounds under some conditions.[17]

A comparison of ambient benzene-CO associations across cities with different gasoline benzene contents supports the idea that lowering benzene concentration in gasoline may result in lower ambient benzene concentration. Figure 4 shows the relationship between ambient CO and benzene concentrations in Anchorage, El Paso, TX and Calexico, CA.[18] During the summer of 2008 the gasoline benzene content in El Paso was reported to be 2.24% and is estimated to have been 0.8% or less in Calexico. [19, 20], whereas Anchorage gasoline benzene content was 5% in the 2008-2009 period.

Figure 4. Comparison of 24-h average CO and benzene concentration relationships in Anchorage, El Paso and Calexico. The CO-normalized benzene concentrations at [CO] = 2 ppm are shown on y-axis. (Calendar year 2008 data for El Paso and Calexico, Oct 2008 – Oct 2009 data for Anchorage)

$y = 2.62x - 0.26$
$R^2 = 0.93$

$y = 1.87x + 0.03$
$R^2 = 0.94$

$y = 0.83x - 0.04$
$R^2 = 0.71$

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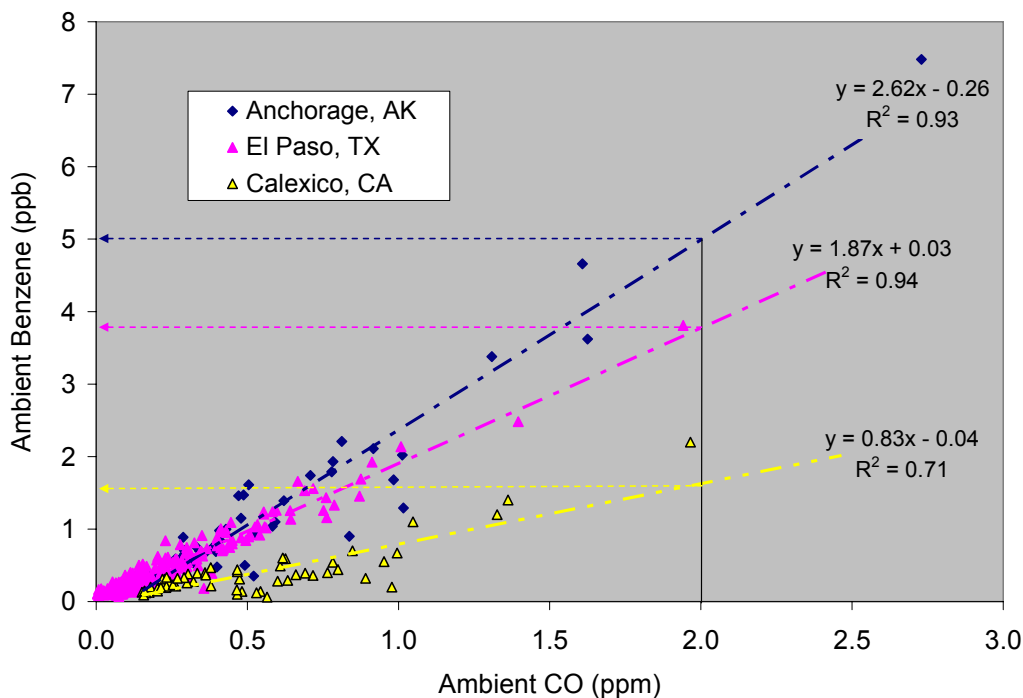
[16] Schuetzle D. et al. (1994) The relationship between gasoline composition and vehicle hydrocarbon emissions: a review of current studies and future research needs. *Environ. Health. Perspect.* 102, supplement 4

[17] Marshall, WF. (1988) Study to determine the fate of benzene precursors in gasoline. Final report. Office of Scientific and Technological Information OSTI ID: 6008233, report# PB-89-178883/XAB

[18] These data were obtained from the EPA AQS database using the Discoverer application. http://www.epa.gov/ttn/airs/airsaqs/aqsdiscover/

[19] "Sampling and Laboratory Analysis of Retail Gasoline and Diesel Fuel for Selected Texas Cities– Summer 2008," prepared for the Texas Commission of Environmental Quality, August 31, 2008.
[20] California reformulated gasoline requirements limit benzene content to 0.8% or less.

Calexico and El Paso were selected for comparison with Anchorage because, like Anchorage, they have some of the highest ambient CO concentrations in the U.S. Figure 4 can be used to predict the expected ambient benzene concentration in each community based on its CO concentration. For example, at a 24 h-CO concentration of 2 ppm, the expected benzene concentration in Anchorage is about 5.0 ppb, El Paso is about 3.8 ppb and Calexico is just 1.6 ppb. On a relative basis, these ambient benzene concentrations are roughly proportional to the gasoline benzene content in each community.

Using the CO–normalized ambient benzene concentrations computed above, the impact of MSAT2 implementation on ambient benzene concentrations may be estimated. In Figure 5, the gasoline benzene content and ambient benzene concentrations of the three cities listed above are compared when 24-hour CO concentration is 2.0 ppm. The figure indicates that if Anchorage's gasoline benzene content is reduced from the current 5.0% to 1.3%, ambient benzene should decline from about 5.0 ppb to 2.5 ppb when the 24-hour CO concentration is 2.0 ppm. This suggests that if the benzene content in gasoline is reduced to 1.3%, Anchorage can expect about a 50% decline in ambient benzene.

Figure 5. Anticipated impact of MSAT2 implementation on CO-normalized ambient benzene concentration in Anchorage. Data shown are from Anchorage, El Paso and Calexico at 24-h [CO] = 2.0 ppm
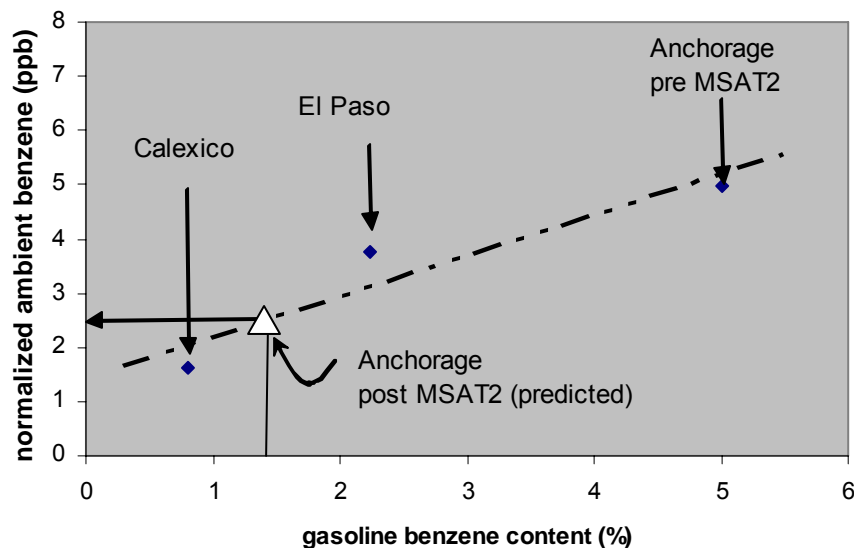
The change in the CO-normalized ambient benzene concentration between Phase1 (before MSAT2) and Phase 2 (after MSAT2) will be a key indicator of the effectiveness of the rule in reducing ambient benzene in Anchorage. The slope of the benzene-CO regression line has remained nearly the same in Anchorage for many years, presumably because the benzene content in gasoline has remained relatively constant. In 1992-93 the slope of the regression line was 2.8; in this 2008-09 study the slope was 2.6. We anticipate seeing a large reduction in this slope when the benzene content in Anchorage gasoline is reduced in 2011 or 2012.

We will also examine any changes in the relationship (slope) between CO and other BETX compounds. Ambient toluene, ethylbenzene and xylene concentrations were also highly correlated with CO. Although there may be some changes in the content of these gasoline components as a consequence of MSAT2, these changes are likely to be less significant than benzene. Thus, the slope of the regression line between these other BTEX components and CO is not expected to change nearly as much as benzene.

The relationship between ambient 1, 3- butadiene and CO

As noted earlier, Anchorage experiences some of the highest ambient CO and benzene concentrations in the U.S. If 1,3-butadiene is correlated with CO, and CO concentrations are among the highest in the nation, one would expect that ambient 1,3-butadiene, like benzene, would also be quite high. However, the ambient concentrations of 1,3- butadiene measured during Phase 1 of this study were not particularly high in Anchorage relative to other communities. The ambient benzene concentration at the Garden site in Anchorage was more than four times higher than the median 1.06 ppb vs. 0.25 ppb) but less than twice the median for 1,3-butadiene (0.07 ppb vs. 0.04 ppb). (See Appendix).

We examined the relationships between CO and 1,3-butadiene for the same three communities (Anchorage, El Paso, and Calexico) examined earlier for benzene (Figure 6). Curiously, the CO-normalized 1,3-butadiene concentration relationships are the reverse of those observed for benzene. For 1,3-butadiene we see the highest CO-normalized concentrations in Calexico and the lowest in Anchorage. Normalized concentrations in Calexico were roughly four times higher than Anchorage.

Figure 6. Comparison of 24-h average CO and 1,3-butadiene concentration relationships in Anchorage, El Paso and Calexico. The CO-normalized 1,3-butadiene concentrations at [CO] = 2 ppm are shown on y-axis. (Calendar year 2008 data for El Paso and Calexico, Oct 2008 – Oct 2009 data for Anchorage)
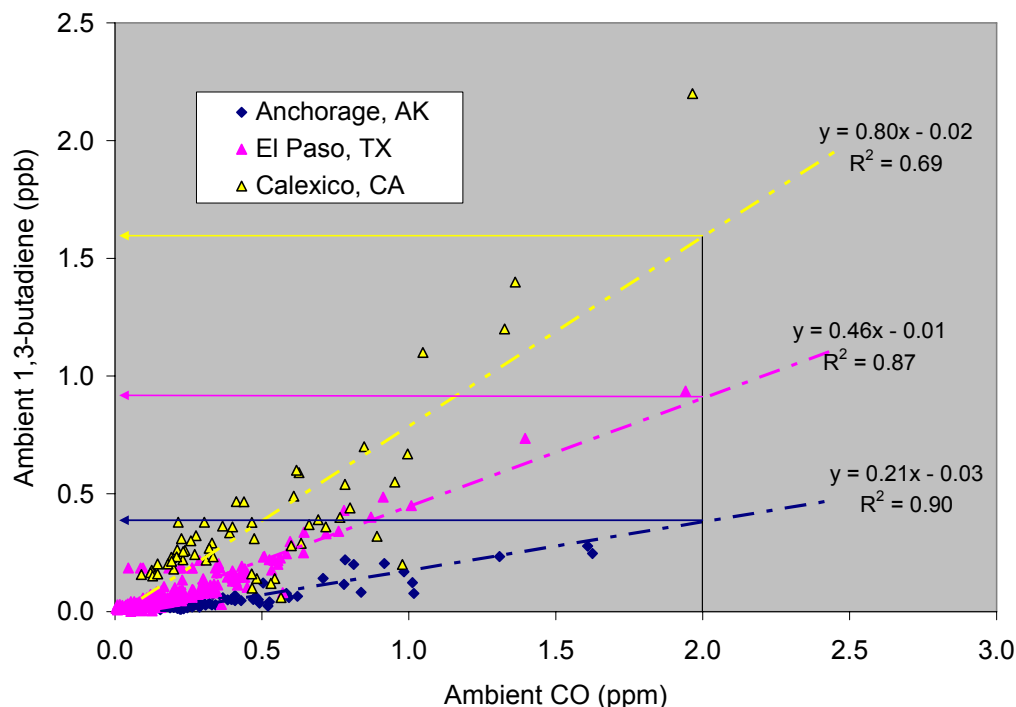
It is unclear why 1,3-butadiene concentrations would be lower in Anchorage relative to the two other communities examined here. We do not know whether climate, fleet characteristics, fuel composition and/or other variables are the source of these differences. We plan to re-examine these 1,3- butadiene relationships in Phase 2 of this study to determine whether fuel composition changes resulting from the implementation of MSAT2 will have an effect on ambient 1,3-butadiene.

PAH profiles – temporal changes of source indicators

The profiles of PAH in Anchorage's air differed across sampling dates and seasons. Naphthalene was the predominant PAH compounds in ambient air throughout the year, making up 59-88% of total PAHs, and the fluctuations of non-naphthalene PAHs tracked closely that of naphthalene (R =0.96, data not shown).

In Figure 7 and 8, seasonal trends in PAHs are shown along with several source indicators. Total PAH excluding naphthalene is plotted in Figure 7 along with retene, which is indicative of a coniferous wood burning. The pyrene-to-benzo(a)pyrene ratio, which suggests a vehicular emission source when greater than five, is also provided for each sample in Figure 7 . Naphthalene was excluded from total PAH to elucidate seasonal fluctuations of other PAHs; inclusion of naphthalene would mask trends of other PAHs because it was such a dominant component of the total PAH. Samples collected on weekends and holidays during the winter months (Oct–Mar) are indicated with yellow highlight. The pink vertical bar indicates approximate duration during which smoke from the wildfire affected Anchorage air quality. Three PAHs that are associated with gasoline-fueled motor vehicles (indeno(1,2,3-c,d) pyrene, benzeo (g,h,i) perylene, and coronene) are shown in Figure 8.

The ambient non-naphthalene PAH concentration was generally higher during the coldest time of the year (Oct –Feb) with the highest concentration found around Christmas-New Year holidays (Figure 7). Retene concentrations tracked non-naphthalene PAH, and both non-naphthalene PAH and retene showed small but significant spikes in early July 2009 when the smoke from a Kenai Peninsula wildfire reached Anchorage raising the $PM_{2.5}$ concentration to 28 μg/m^3, well above typical levels (mean annual $PM_{2.5}$ of the study period was 7.5 μg/m^3).

The pyrene:benzo(a)pyrene ratio was relatively low between October and January, occasionally dropping to below 5, but the ratio exceeded the threshold value indicative of auto exhaust greatly in the spring and summer (Figure 7). This suggests that the contribution of automobile exhaust to ambient PAHs is relatively strong in warmer months. In contrast, retene concentration was high in the October-January period when pyrene:benzo(a)pyrene ratio was often less than 5. The contrasting trends of the pyrene:benzo(a)pyrene ratio vs. retene concentration indicates a significant contribution from wood burning (i.e.; fireplaces and wood stoves) to ambient PAH in cold months.

Figure 7. Non-naphthalene PAH concentrations and PAH source indicators over time. Total non-naphthalene PAHs is shown in the histogram, retene and a pyrene:benzo(a)pyrene ratio and are shown in lines.
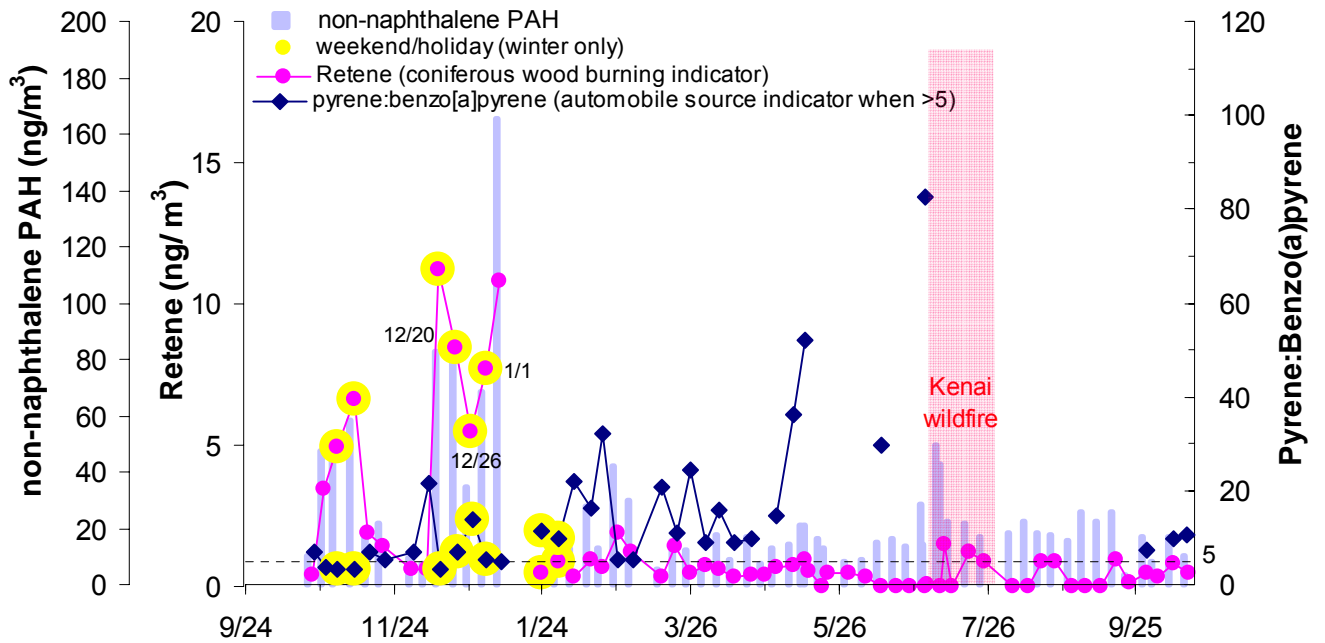
Figure 8. PAHs indicative of gasoline-powered automobiles over time.
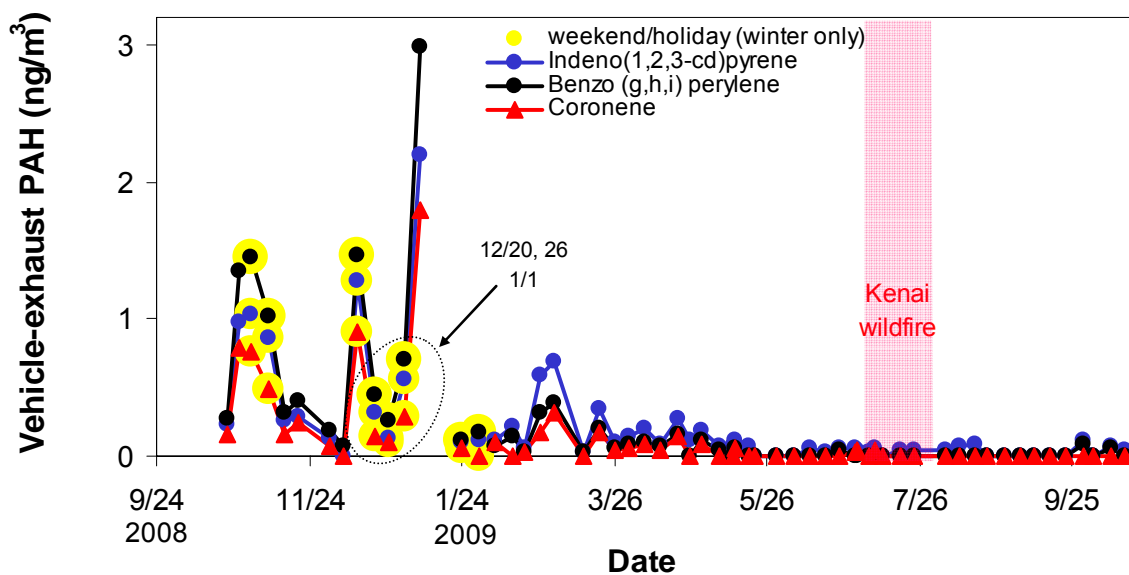
A closer look at the concentrations of retene and the three "vehicle exhaust PAH" indicators (indeno (1,2,3-c,d) pyrene, benzeo (g,h,i) perylene, and coronene) provides further insight into the sources of the high ambient PAH concentrations in winter. The concentration of retene was always high when non-naphthalene PAH was high and was high on most weekends and holidays during the winter (Figure 7). In contrast, the vehicle exhaust PAH concentrations were not always high when both retene and other PAHs were high. For example, vehicle exhaust PAHs were relatively low on the weekends and holiday around Christmas and the New Year's Day (Dec 20, 26, and Jan 1), whereas retene and total non-naphthalene PAH recorded some of the highest concentrations on the same dates (Figure 7 & 8). Thus, wood burning is likely a predominant source of ambient PAHs on weekends and holidays near Christmas and New Year's Day.

Conclusions and Recommendations for Phase 2

In Anchorage, all air toxics were generally much higher in winter than in summer. Many of the air toxics listed as HAPs (BETX, 1,3-butadiene, naphthalene) were strongly correlated with CO concentrations, suggesting that incomplete combustion of gasoline is the major source of these HAPs. Because nearly 80% of CO in ambient air in Anchorage is estimated to originate from vehicle exhaust, we suspect that it also plays a major role in the emissions of these HAPs.

This study revealed that Anchorage air has some of the highest concentrations of ambient benzene in the nation. We suspect that the same persistent winter atmospheric temperature inversions that contribute to high CO concentrations also contribute to high levels of air toxics. For ambient benzene, this situation is exacerbated by the high content of benzene in Anchorage gasoline. Ambient concentrations of ethyl benzene, toluene and xylenes were also among the highest in the U.S., presumably because of the same factors. Our analysis suggests that a four-fold lowering of the gasoline benzene content from 5.0% to 1.3% should reduce ambient benzene concentrations in Anchorage by about 50%.

A close look at the PAH profiles and source indicators in Anchorage air consistently implicated wood burning as a major source especially in winter. Although there is evidence that vehicle exhaust contributes to PAHs, it seems to be a less important source than wood burning in winter. Wood burning PAH-source indicators were particularly strong on weekends and holidays near Christmas and New Year's Day, as well as during a period of wildfire in summer.

We plan to perform a follow-up study after the implementation of the new benzene rule to assess the effect of the MSAT2 rule on air toxics in Anchorage air. As noted earlier, we plan to follow the same basic protocols in the next phase (post MSAT2 implementation) of this study with some minor modifications.

We offer the following recommendations for Phase 2:

- Because both VOCs and PAHs were relatively low between Apr 1 and Sep 30, reduce the frequency of sampling from a 1-in-6 to a 1-in-12 day schedule. Increase the sampling frequency to a 1-in-3 day schedule during the Oct 1- Mar 31 period when VOC and PAH concentrations are highest. Perform some supplementary PAH

sampling on holiday weekends in the winter when wood burning activity is expected to be high.

- Reduce the frequency of gasoline sampling from bi-monthly to quarterly. Phase 1 of the gasoline sampling study indicated very little variation in gasoline composition among stations over the course of the year.

- Further explore the relationship between CO and 1,3-butadiene in Anchorage and other communities and determine why ambient concentrations of this pollutant seem to be relatively low in Anchorage.

Appendix

Comparison of Anchorage VOC, PAH with other locations

Ambient VOC and PAH concentrations in Anchorage were compared with the concentrations in other monitoring sites in the U.S. that were available from the Hazardous Air Pollutant Report on EPA's AirData website (www.epa.gov/air/data/index/html). The most recent data available from this report were from 2008. We compared annual mean values measured at sites across the U.S. to mean values measured at the Garden site in Anchorage between Oct 2008 and Oct 2009.

These data suggest that Anchorage has some of the highest ambient BETX levels in the country. Among monitoring sites nation-wide, Anchorage ranked in the 98th percentile or higher for benzene, ethyl benzene, toluene and o-xylene.

Anchorage ranked in the 82nd percentile for 1,3-butadiene and 56th percentile for naphthalene.

Table A-1(a-f). National rankings of selected ambient VOC and PAH. Anchorage data were collected between Oct 2008 and Oct 2009. All other data were collected in 2008.

(a) Benzene

Rank	Percentile	Site Address	City	State	Annual Mean (ppb)
1	100%	Ab Tech College	Asheville	NC	3.68
2	100%	618 Logan St.	Steubenville	OH	2.63
3	99%	520 Grand Island Blvd	Tonawanda	NY	2.59
4	99%	520 Grand Island Blvd	Tonawanda	NY	2.50
5	99%	520 Grand Island Blvd	Tonawanda	NY	2.02
6	99%	201 H.O.Mills Blvd.	Port Arthur	TX	1.88
7	98%	304 Stewart Street	Galena Park	TX	1.12
8	98%	Yorkville		GA	1.07
	98%	**Garden Street**	**Anchorage**	**AK**	**1.06**
9	98%	Gregg Co. Airport Near Longview		TX	1.02
10	97%	1001 B Lynchburg Road	Houston	TX	0.99
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34	90%	1504 Haden Road	Houston	TX	0.53
84	75%	Mt. View: 3500 Cabarton Ln	Boise City	ID	0.35
34	50%	2842 Wyoming	Dearborn	MI	0.25
253	25%	649 Fifth Street	St. Paul Park	MN	0.18

(b) Ethyl benzene

Rank	Percentile	Site Address	City	State	Annual Mean (ppb)
1	100%	803 N. Loren Ave., Azusa	Azusa	CA	0.30
2	100%	New Jersey Turnpike Interchange 13	Elizabeth	NJ	0.23
3	99%	228 W. Palm Ave., Burbank	Burbank	CA	0.21
4	99%	2443 South Jackson Avenue	Tulsa	OK	0.21
5	99%	700 West San Francisco Ave	El Paso	TX	0.20
6	98%	228 W. Palm Ave., Burbank	Burbank	CA	0.19
	98%	**Garden Street**	**Anchorage**	**AK**	**0.18**
7	98%	702 Light Co. Service Road	Pasadena	TX	0.18
8	98%	1029 Ethel St, Calexico High School	Calexico	CA	0.18
9	97%	2443 South Jackson Avenue	Tulsa	OK	0.18
10	97%	Cleveland Ave. At Clark Dr.	El Paso	TX	0.18
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32	90%	1630 N Main St, Los Angeles	Los Angeles	CA	0.13
79	75%	Harrison Av	Boston	MA	0.10
32	50%	Abraham Lincoln Jr High Grofftown Rd	Lancaster	PA	0.06
232	25%	900 Fm 667 Ellis County	Italy	TX	0.04

(c) Toluene

Rank	Percentile	Site Address	City	State	Annual Mean (ppb)
1	100%	100 E. 2nd St.	Parachute	CO	2.29
	100%	**Garden Street**	**Anchorage**	**AK**	**1.85**
2	100%	228 W. Palm Ave., Burbank	Burbank	CA	1.76
3	99%	2900 Community College Avenue	Cleveland	OH	1.70
4	99%	228 W. Palm Ave., Burbank	Burbank	CA	1.63
5	99%	803 N. Loren Ave., Azusa	Azusa	CA	1.61
6	98%	Canal And Blue Bell, Sports Complex		SD	1.59
7	98%	New Jersey Turnpike Interchange 13	Elizabeth	NJ	1.57
8	98%	1029 Ethel St, Calexico High School	Calexico	CA	1.43
9	97%	3355 Grandview Ave. & 32nd St.	Port Arthur	TX	1.40
10	97%	1155 Redwood Ave., El Cajon	El Cajon	CA	1.40
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32	90%	2552 Jefferson Ave., Napa	Napa	CA	0.95
79	75%	1340 Sixth Street	Berkeley	CA	0.66
32	50%	Bahnson Ave, Hilltop Site	Sioux Falls	SD	0.40
237	25%	Denton Airport South Cams 56	Denton	TX	0.26

(d) o-Xylene

Rank	Percentile	Site Address	City	State	Annual Mean (ppb)
1	100%	803 N. Loren Ave., Azusa	Azusa	CA	0.34
2	100%	228 W. Palm Ave., Burbank	Burbank	CA	0.31
3	99%	228 W. Palm Ave., Burbank	Burbank	CA	0.29
4	99%	1029 Ethel St, Calexico HS	Calexico	CA	0.23
5	99%	New Jersey Turnpike Interch 13	Elizabeth	NJ	0.23
6	98%	158b Jackson St, San Jose, Ca	San Jose	CA	0.23
	98%	**Garden Street**	**Anchorage**	**AK**	**0.22**
7	98%	700 Zaragosa St.	Laredo	TX	0.20
8	98%	897 Barron Ave., Redwood City	Redwood City	CA	0.19
9	97%	Frontier Ave At 55th Street	Niagara Falls	NY	0.19
10	97%	1630 N Main St, Los Angeles	Los Angeles	CA	0.19
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32	90%	Cleveland Ave. At Clark Dr.	El Paso	TX	0.14
78	75%	Harrison Av	Boston	MA	0.10
32	50%	911 Old Hwy 90 West	San Antonio	TX	0.06
236	25%	1703 Roberts Rd	Loudon	TN	0.03

(e) 1,3-butadiene

Rank	Percentile	Site Address	City	State	Annual Mean (ppb)
1	100%	1225 Merriman St., Port Neches	Port Neches	TX	1.00
2	100%	10th St. & Vine St. Davenport	Davenport	IA	0.41
3	99%	650 Newtown Pike, Fayette Co Health Dept	Lexington-Fayette (	KY	0.36
4	99%	3355 Grandview Ave. & 32nd St.	Port Arthur	TX	0.36
5	99%	2900 Community College Avenue	Cleveland	OH	0.35
6	98%	9401 1/2 Manchester Street	Houston	TX	0.29
7	98%	Grant & Grove Streets	Beaumont	TX	0.29
8	98%	Ballpark Road	Calvert City	KY	0.27
9	97%	Ballpark Road	Calvert City	KY	0.27
10	97%	3903 1/2 Old Highway 146	La Porte	TX	0.25
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31	90%	Camp Webb Grayson Lake		KY	0.12
	82%	**Garden Street**	**Anchorage**	**AK**	**0.07**
77	75%	9511 Avenue V 1/2	Galveston	TX	0.06
31	50%	171 West 1370 North, Bountiful, Utah	Bountiful	UT	0.04
229	25%	1532 W. Michigan St.	Duluth	MN	0.02

(e) naphthalene

Rank	Percentile	Site Address	City	State	Annual Mean (ng/m^3)
1	100%	618 Logan St.	Steubenville	OH	4727
2	98%	7300 Superior	Cleveland	OH	794
3	97%	520 Grand Island Blvd	Tonawanda	NY	640
4	95%	2900 Community College Avenue	Cleveland	OH	553
5	94%	Bonita & St John	Middletown	OH	410
6	92%	S.R. 676 Washington Career Center	Marietta	OH	405
7	90%	Korbel Ave.	Columbus	OH	381
8	89%	7629 Broadway	Cleveland	OH	337
9	87%	2547 St Tikhon	Cleveland	OH	332
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16	76%	750 Dundee Road	Northbrook	IL	94
	56%	Garden Street	Anchorage	AK	71
32	50%	4103 Beacon Hill S, Seattle, Wa	Seattle	WA	55
47	25%	Utoy Creek, 736 Selig Dr.		GA	39