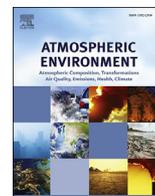




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Impact of a new gasoline benzene regulation on ambient air pollutants in Anchorage, Alaska

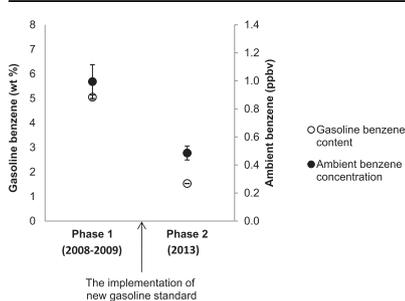
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HIGHLIGHTS

- The impact of a new EPA limit on benzene in gasoline on ambient air was evaluated.
- Average gasoline benzene content was reduced by 70% as a result of the new limit.
- The new benzene limit alone reduced the ambient benzene concentration by 46%.

GRAPHICAL ABSTRACT



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ABSTRACT

The purpose of this study was to quantify the impact of a new U.S. Environmental Protection Agency (EPA) standard that limits the amount of benzene allowed in gasoline on ambient benzene concentrations. This new standard, together with two companion regulations that limit cold-temperature automotive emissions and the permeability of portable fuel containers, was expected to lower the levels of ambient benzene and other volatile organic compounds (VOCs) nationwide. In this study the impact of the gasoline benzene standard was evaluated in Anchorage, Alaska in a two-phase ambient air monitoring study conducted before and after the new gasoline standard was implemented. Gasoline sold by Anchorage retailers was also evaluated in each phase to determine the content of benzene and other gasoline components. The average benzene content in Anchorage gasoline was reduced by 70%, from 5.05% (w/w) to 1.53% (w/w) following the implementation of the standard. The annual mean ambient benzene concentration fell by 51%, from 0.99 ppbv in Phase 1 to 0.49 ppbv in Phase 2. Analysis suggests the change in gasoline benzene content alone reduced benzene emissions by 46%. The changes in toluene, ethylbenzene, and xylene content in gasoline between Phase 1 and 2 were relatively small and the differences in the mean ambient concentrations of these compounds between phases were modest. Our results suggest that cold winter communities in high latitude and mountainous regions may benefit more from the gasoline benzene standard because of high benzene emissions resulting from vehicle cold start and a tendency to develop atmospheric stagnation conditions in the winter.

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1. Introduction

Volatile organic compounds (VOCs) are major urban air pollutants: many are known carcinogens, mutagens, or are suspected to cause serious health problems (Kampa and Castanas, 2008). Among

these VOCs, exposure to benzene is known to cause acute leukemia and increase the risk for developing other cancers (NATA, 1999; National Toxicology Program, 2014; Smith, 2010; Snyder et al., 1993). Furthermore, recent studies suggest potential non-cancerous health impacts (e.g., endocrine disruption) from benzene, toluene, ethylbenzene, and xylene isomers (BTEX) even at low, ambient-level exposure (Reviewed in Bolden et al., 2015). Motor vehicle exhaust is the major source of BTEX in urban air (Kopczynski et al., 1972; Parrish et al., 2009; von Schneidmesser et al., 2010) because the compounds are major components of gasoline and because they are emitted from tailpipes as unburned gasoline as well as secondary products of combustion (Baker et al., 2008; Harley et al., 2001; Kirchstetter et al., 1999a; Parrish, 2006; Schuetzle et al., 1994).

As part of the nation-wide effort to reduce ambient benzene and total VOCs from motor vehicle sources, the U.S. Environmental Protection Agency (EPA) promulgated a new regulation in 2007 (“gasoline benzene standard” hereafter), which was to be implemented in two steps. The first step required gasoline refineries to meet a lower benzene content (0.62% v/v) beginning in 2011, although averaging, banking and trading were allowed. The second step limited individual refineries to a maximum average gasoline benzene content of no more than 1.3% (v/v) beginning July 2012, regardless of banking and trading (EPA, 2007). The gasoline benzene standard was accompanied by two additional regulations: the establishment of new cold-temperature tailpipe emission standards for motor vehicles and a new limit on the permeability of portable fuel containers. Nationally, the EPA projected that the three components of the regulatory package (gasoline benzene standard, cold temperature emission standards and portable fuel container standard) together would provide a 33,206 ton reduction in benzene emissions in 2015. The gasoline benzene standard itself was projected to account for about 49% of the total reduction and the cold temperature emission standards a similar proportion (49%) of the reduction (EPA, 2007). In contrast, the new fuel-container permeability standard was projected to provide only 2% of the total benzene reduction. The gasoline benzene standard was not expected to contribute to quantifiable reductions of total VOCs (EPA, 2007).

In this study, the impacts of the new gasoline benzene standard on gasoline composition and ambient air quality were evaluated in Anchorage, AK. Ambient concentrations of BTEX were compared with carbon monoxide (CO) before (2008–2009) and after (2013) the benzene content of Anchorage gasoline was lowered as a result of the implementation of the standard. We also investigated whether the reduction of benzene was associated with increases in other VOC components in gasoline, especially toluene, ethylbenzene, and xylene. Anchorage was ideal for testing the effectiveness of the standard because it had some of the highest ambient benzene concentrations in the U.S. and because the benzene content of Anchorage gasoline prior to the rule implementation (~4%, v/v) was three to four times higher than that commonly found in gasoline elsewhere in the U.S. (EPA, 2012). Furthermore, an emission inventory compiled in 1999 suggested that emissions from fuel-combustion engines (predominantly gasoline-fueled) accounted for 96% of total benzene emissions in Anchorage. (Alaska Department of Environmental Conservation; ADEC, 2001a). These conditions, combined with Anchorage's geographic isolation from other large urban areas (the closest city with a population >100,000 is well over 3000 km in any direction), provided a unique environment to test the effectiveness of the gasoline benzene standard. Because the initial benzene content of Anchorage gasoline was relatively high, and large reductions in gasoline benzene were required by the new standard, we expected to observe a significant decline in ambient benzene concentration.

2. Materials and methods

2.1. Sampling timeline

Liquid gasoline and ambient air samples were collected in two sampling phases. Phase 1 was conducted during a 12-month period (Oct 22, 2008–Oct 16, 2009) shortly before the implementation of the gasoline benzene standard, and Phase 2 (Jan 4, 2013–Dec 30, 2013) afterwards. Tesoro Alaska Refining provides the largest share of the gasoline sold in Anchorage. They completed the necessary refinery modifications and began producing gasoline to meet the 1.3% (v/v) benzene limit in July 2012 (pers. comm. Tesoro Alaska).

2.2. Liquid gasoline VOC composition

Gasoline samples were collected bimonthly during Phase 1 and quarterly during Phase 2. We selected six gasoline retailers that had multiple fuel stations on high-volume roads in Anchorage. For each sampling round, regular- and premium-grade gasoline samples were collected separately from one to three stations among each retail brand (i.e., total of 6–15 samples per collection). Each sampling round included two sets of duplicate samples per gasoline grade. The total number of gasoline samples, not including the number of duplicated samples, was 70 regular grade and 69 premium grade in Phase 1, and 35 each for premium and regular grades in Phase 2.

Regular- and premium-grade gasoline samples were collected individually in 850-mL stainless steel fuel bottles with minimal headspace. To ensure samples were fresh and/or to minimize cross-contamination of different grades, samples were collected by first purging at least 0.8 L of gasoline, if the pump had separate nozzles for two grades, and at least 8 L if the pump used one nozzle to deliver multiple grades. Following purging, stainless steel fuel cans were rinsed three times by dispensing 50–100 mL of gasoline each time. Sample bottles were immediately placed on ice in a cooler and transferred to the Applied Science and Engineering Technology Laboratory at the University of Alaska, Anchorage, where each gasoline sample and a laboratory blank (5% pentadecane in dichloromethane) was transferred into a glass vial with air-tight septa, and stored at 4 °C until analysis for VOCs could take place. There were 142 target analytes. One laboratory blank, analyzed as an unknown sample, accompanied every 20 gasoline samples. The weight percent of each target analyte in all blanks was less than 0.1%. In addition, a quality control standard (International NIST standard SRM[®] 2297 Reformulated Gasoline, 10% Ethanol) was analyzed; all results were within ±15% of the true value. The gasoline samples were analyzed within 48 h of sample collection using the PIANO standard and a 100 Meter Capillary High Resolution Gas Chromatograph Column and an analytical procedure based on ASTM Method D6729-14 (2009).

2.3. Ambient air pollutants

2.3.1. Monitoring location

All air pollutants were monitored and collected at a CO monitoring site located in a residential neighborhood in central Anchorage known as the Garden Street site. The Garden Street site was one of two residentially-oriented CO monitoring sites operating in Anchorage during Phase 1 and 2 of this study. Previous monitoring at five other residential sites (since discontinued) has demonstrated that the CO concentrations measured at the Garden Street site were generally representative of other urban neighborhoods in Anchorage (MOA, 1998). The study also demonstrated that, unlike other urban areas in warmer regions, both residential neighborhood and high-volume roadways of Anchorage contribute

similarly to overall CO emissions (MOA, 1998). The Garden Street site is located 6 km or more away from significant emission sources such as electrical generation facilities and major airports. Emission inventory analysis suggests that vehicle cold start and warm-up idling emissions are substantial contributors to CO emissions in urban residential neighborhoods in Anchorage (MOA, 1998). CO concentrations measured at the Garden Street site are generally among the highest 2% of country (EPA, AirData). Previous VOC monitoring at this site suggested that ambient benzene concentrations were also very high relative to the rest of the country (MOA, 1996; Taylor and Morris, 1995).

2.3.2. Ambient VOCs

Ambient air samples for BTEX were collected continuously over 24 h every six days, using 6-L evacuated (−686 mm Hg) SUMMA[®] canisters that were cleaned and certified according to TO-15 canister cleaning procedures by Eastern Research Group (ERG; Morrisville, NC). A duplicate sample was collected bimonthly and a field blank sample was collected monthly to ensure sample quality. The canisters were shipped to ERG for analysis by GC/MS in accordance with the EPA Method TO-15 (EPA, 1999). The acceptance criteria for VOC analysis used by ERG were approved by EPA.

2.3.3. CO

Carbon monoxide was monitored continuously using a trace-level CO analyzer (Thermo Electron Corporation Model 48i-TLE). The instrument was configured in accordance with the US-EPA Federal Reference and Federal Equivalent Methods for CO (RFCA-0981-054). Daily average concentrations of CO were calculated from hourly measurements.

2.4. Data analysis

Average BTEX content of gasoline across premium and regular grades was calculated as sales-volume weighted average, using a premium-to-regular ratio of 0.09: 0.91 (pers. comm. Tesoro Alaska.). We used a paired *t*-test to assess whether chemical constituents in gasoline differed between Phases 1 and 2. Gasoline VOC content was reported as weight percentage, however, we also estimated the volume percentage of benzene for comparison with the gasoline benzene standard. For the conversion calculation, we used annual average gasoline density of 0.7285 g/mL (pers. comm. Tesoro Alaska) and benzene density of 0.885 g/mL at 15.6 °C.

To minimize the potential interference from a large wildfire 100 km south of Anchorage (Santa Creek Fire), two ambient observations in Phase 1 (July 8 and 11, 2009) were excluded from the analysis. Additionally, one winter observation in Phase 1 (Jan 7, 2009) was excluded from the analysis because of unusually high ambient CO and BTEX concentrations following an uncommonly long streak of extremely cold temperatures when maximum daily temperatures remained below −18 °C (the eleven-day long streak was the longest since 1961, Cassell, 2009).

Changes in ambient BTEX before and after the implementation of the gasoline benzene standard were evaluated by examining changes in the ratios of individual BTEX to CO between the two phases. The use of ratios normalizes for changes in the individual BTEX concentrations that result from factors that control mobile source emissions but are unrelated to the gasoline benzene standard, such as ambient temperature, motor vehicle fleet turnover and atmospheric mixing conditions. For example, the EPA mobile source emissions model known as MOVES estimates that CO and VOC emission rates both approximately double between 20 °C and −10 °C (Choi et al., 2011). Motor vehicle fleet turnover would also reduce CO and VOC emissions in a similar manner, as has been observed nationwide since the mid 1990s (Bishop and Stedman,

2008; Warneke et al., 2012). Additionally, differences in atmospheric mixing conditions would affect the relative concentration of CO and ambient VOCs in a similar way. Carbon monoxide, emitted as a result of incomplete combustion, is commonly used as a marker for motor vehicle emissions and shows a strong correlation with urban air VOCs (e.g., Baker et al., 2008; Gentner et al., 2009; von Schneidmesser et al., 2010; Warneke et al., 2012). Thus, ambient VOCs emitted primarily from mobile sources (e.g., benzene) were expected to have strong associations with CO. Our data confirmed a strong association between ambient benzene and CO concentrations: the benzene-CO correlation coefficient (*R*) exceeded 0.92 in both phases. Although it is difficult to use *in situ* measurements to separate the effect of gasoline benzene standard from other factors, examining the benzene:CO ratio can help distinguish the effect of the gasoline benzene standard from other factors that may have also influenced the ambient benzene concentration between phases. In this study, the ratios of benzene and other BTEX compounds to CO were determined as the slopes of the correlation plots, and the differences in the ratios between phases were evaluated by testing whether an interaction between CO and phase was significant.

In our analysis we assert that evaporative emissions of individual BTEX compounds from motor vehicles in Anchorage were relatively insignificant in comparison with exhaust emissions. Ambient temperatures in Anchorage are cool even in the summer and evaporative emissions decline with ambient temperature (Rubin et al., 2006). The 24-h average ambient temperature ranged from −22 to 20 °C during the study period, with average temperatures 2.4 °C in Phase 1 and 3.6 °C in Phase 2. Emissions modeling (EPA MOVES) suggests that motor vehicle exhaust emissions comprise between 80% (summer) and 90% (winter) of total VOC emissions in Anchorage.

3. Results and discussion

3.1. Liquid gasoline VOC composition

As a consequence of the gasoline benzene standard, the average annual benzene content in Anchorage gasoline was reduced by 70%, from 5.05% (w/w) in Phase 1 to 1.53% (w/w) in Phase 2 (Fig. 1, Table 1). These are equivalent to 4.16% (v/v) and 1.26% (v/v), respectively. The mean benzene content in Phase 1 was more than

Table 1

The content of major VOC components of liquid gasoline in Phases 1 and 2. Mean (1 standard error) of six retail stores. The means were estimated by a premium-to-regular sales ratio of 0.09: 0.91. The means listed are those >2% (w/w) of total VOC in the both phases. The asterisks indicate BTEX compounds. Unaccounted refers to the sum of compounds that were not identified.

Compounds	Mean VOC content (% w/w)	
	Phase 1	Phase 2
Benzene*	5.05 (0.09)	1.53 (0.01)
Toluene*	17.85 (0.32)	16.06 (0.14)
Ethylbenzene*	2.38 (0.09)	2.21 (0.02)
Xylene*	13.07 (0.21)	11.01 (0.07)
2-Methylbutane	11.12 (0.11)	16.85 (0.14)
Unaccounted	8.04 (0.19)	6.66 (0.11)
2-Methylpentane	5.51 (0.18)	6.65 (0.07)
n-Butane	5.16 (0.10)	7.54 (0.03)
Pentane	4.15 (0.48)	3.17 (0.18)
3-Methylpentane	3.63 (0.13)	3.92 (0.05)
Methylcyclopentane	3.04 (0.06)	3.62 (0.05)
3-Methylhexane	2.67 (0.13)	2.87 (0.04)
Hexane	2.66 (0.09)	1.11 (0.05)
2-Methylhexane	2.26 (0.11)	2.40 (0.03)
Heptane	2.06 (0.06)	2.27 (0.02)

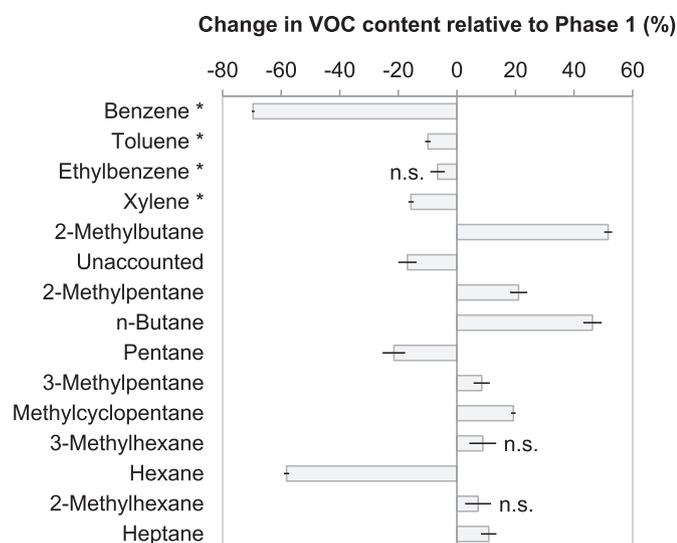


Fig. 1. Changes in the content of major VOC components of local gasoline in Anchorage, AK between Phases 1 and 2. The percentages are calculated as: $100 \times (\text{Phase 2} - \text{Phase 1}) / (\text{Phase 1})$. The error bars indicate ± 1 standard error (SE); n.s. indicates the change in VOC content between Phases 1 and 2 not significantly different ($P > 0.05$). The asterisks indicate BTEX compounds.

four-fold greater than the national average for the same time period (0.94%, EPA, 2012). The average gasoline benzene content measured in Phase 2 was below the 1.3% (v/v) limit stipulated by the gasoline benzene standard (EPA, 2007). There were reductions in the amount of other BTEX compounds but in relative terms they were small in comparison with benzene. There was a large relative reduction in gasoline hexane content but the absolute reduction was only 1.5% (Fig. 1, Table 1). Reductions in these gasoline VOCs were offset by increases in other gasoline components such as isobutane, n-butane, and 2-methylbutane.

3.2. Ambient pollutant concentrations

The annual mean benzene concentration in ambient air fell by 51%, from 0.99 ppbv in Phase 1 to 0.49 ppbv in Phase 2 (Table 2). This drop in the annual mean was the largest absolute and relative decline among all BTEX compounds (Table 2). The absolute changes in the ambient concentrations of toluene, ethylbenzene, and xylene were all small (< 0.07 ppbv, Table 2). However, the ambient concentrations of all the BTEX compounds except benzene increased slightly between Phases 1 and 2, even though the amount of each of these components in gasoline decreased marginally, or remained unchanged (Fig. 1). As is discussed further below (section 3.3.), we have explored possible reasons for this and have not found a plausible explanation.

Table 2

Mean air temperature and the concentrations of ambient air CO and BTEX in Anchorage AK during Phases 1 and 2. SE = 1 standard error.

	Mean (1 SE)		Change in means ^a	
	Phase 1	Phase 2	Difference	(%)
Air temperature (°C)	2.4	3.6	1.15	–
CO (ppm)	0.48	0.41	–0.06	–13
VOC (ppbv)				
Benzene	0.99	0.49	–0.51	–51
Toluene	1.68	1.73	0.05	3
Ethylbenzene	0.17	0.20	0.03	22
Xylene	0.77	0.83	0.07	8

^a Change in percent was calculated as: $100 \times (\text{Phase 2} - \text{Phase 1}) / (\text{Phase 1})$.

The annual mean CO declined by 13% in Phase 2, but it seems unlikely that the relatively modest changes in gasoline composition between the phases would have had much impact on CO emissions. Instead, we attribute the decline in ambient CO to a number of other factors that could have influenced CO emission rates. Emissions from the motor vehicle fleet in Anchorage would be expected to decline slightly during the three-year period between phases as a result of fleet turnover. Indeed, the new cold temperature emission standards that accompanied the gasoline benzene standard, and phased-in beginning with model year 2010 vehicles, would be expected to reduce both CO and benzene emissions. Weather differences between phases could have also influenced ambient benzene. Because cold temperatures contribute to higher CO emissions (Singer et al., 1999) and because the annual mean temperature was 1.2 °C higher in Phase 2, CO emissions during this phase may have also decreased slightly as a result. However, as we discuss in the following section, our data suggest that the effect of these factors on the ambient benzene concentration was relatively small in comparison with reductions due to the gasoline benzene standard.

3.3. Ambient air VOC:CO ratios

There are strong associations ($R > 0.9$) between ambient benzene concentrations and CO (Fig. 2, Table 3), suggesting that benzene originates mainly from gasoline-fueled motor vehicles. The other BTEX compounds also exhibit strong correlations with CO. While residential wood burning and other biomass burning can also contribute to CO and benzene emissions (Schauer et al., 2001; Watson et al., 2001), the wood burning contribution to benzene is likely much less important than mobile sources in Anchorage.

Previous emission inventories in Anchorage suggest that a high proportion of both CO (79%) and benzene (96%) emissions originate from gasoline-fueled engines (ADEC, 2001b). Our findings are consistent with other studies which have concluded that benzene and CO in urban ambient air originate predominantly from gasoline combustion by motor vehicles (Baker et al., 2008; Harley et al., 2006). We therefore assume that in Anchorage, ambient CO serves as a good surrogate for other motor vehicle emissions like benzene. Thus, changes in the ratio of a particular motor vehicle pollutant (e.g., benzene) with CO indicate a change in the emission rate of that pollutant relative to aggregate motor vehicle emissions.

The benzene:CO ratio was significantly reduced by 46% following the implementation of the gasoline benzene standard: from 2.43 in Phase 1 to 1.31 in Phase 2 ($P < 0.001$, Table 3). The benzene:CO ratio appeared to have remained relatively constant over a decade prior to the implementation of the gasoline benzene standard: in an earlier study conducted over 14 months (1994–1996) using the same monitoring site as in this study, a mean ambient benzene:CO ratio was 2.33, similar to the ratios observed during Phase 1 (2.43). This implies that the changes in gasoline formulation alone contributed to reducing ambient

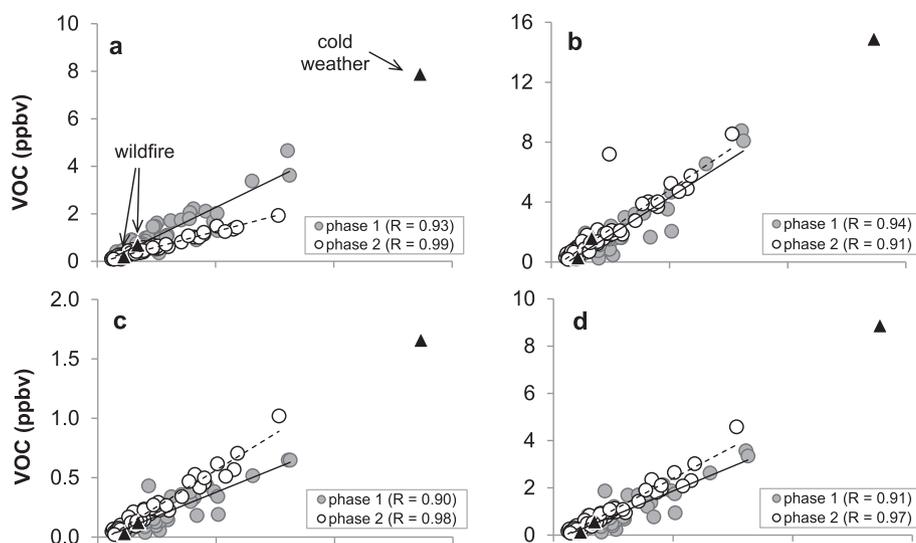


Fig. 2. Correlations between ambient air VOC and CO. (a) benzene, (b) toluene, (c) ethylbenzene, and (d) xylene. The triangles indicate data points collected in Phase 1 that were excluded from correlation analysis: two observations during the wildfire in the summer (July 8 & 11, 2009), and one following a stretch of unusually cold weather (Jan 7, 2009; see text for details). $n = 58$ (Phase 1) and 60 (Phase 2).

Table 3

Associations between ambient air pollutants and CO during Phases 1 and 2 in Anchorage, AK. Individual BTEX:CO ratios were determined as slopes of correlation plots. Significant differences in individual BTEX:CO ratios between the two phases were found at $p < 0.05$.

	R		Ratio to CO		Change in ratio ^a	
	Phase 1	Phase 2	Phase 1	Phase 2	(%)	p
Benzene	0.929	0.987	2.43	1.31	-46	<0.001
Toluene	0.937	0.912	4.99	5.26	5	0.498
Ethylbenzene	0.899	0.978	0.40	0.62	53	<0.001
Xylene	0.912	0.974	2.10	2.68	27	<0.001

^a Change in percent was calculated as: $100 \times (\text{Phase 2} - \text{Phase 1}) / (\text{Phase 1})$.

benzene levels by roughly 46%. The slightly larger reduction in the observed mean ambient concentrations (51%, Table 2) implies that factors such as fleet turnover and the differences in meteorological conditions between the phases contributed to the additional reduction (5%).

The ethylbenzene:CO and xylene:CO ratios increased significantly between Phase 1 and 2, and there was a small but insignificant increase in the toluene:CO ratio (Table 3). As noted earlier, the amount of each of these gasoline components dropped slightly or was unchanged between phases (Fig. 3). It is possible that compositional changes of gasoline between the phases, although relatively small, resulted in greater secondary production of ethylbenzene and xylene during combustion. Studies have shown that fuel composition affects the production of secondary VOC (Perry and Gee, 1995) and that a greater fraction of secondary products are C₆–C₉ aromatics, such as ethylbenzene and xylenes (Nordin et al., 2013; Odum et al., 1997). While increases in wood burning can be an additional source of ambient BTEX and alter the ratio of individual BTEX compounds with CO (Gaeggeler et al., 2008; Schauer et al., 2001), evidence suggests that this was unlikely the case. During our study period, indicators for wood burning such as ambient PM_{2.5} (particulate matter <2.5 μm) and polycyclic aromatic hydrocarbons (PAHs) decreased from Phase 1 to 2 by 26% (PM_{2.5}) and by 8% (PAHs) (data not shown), suggesting a decrease in wood burning. Neither increases in evaporative emissions from industrial sources or decreases in photooxidation of ambient

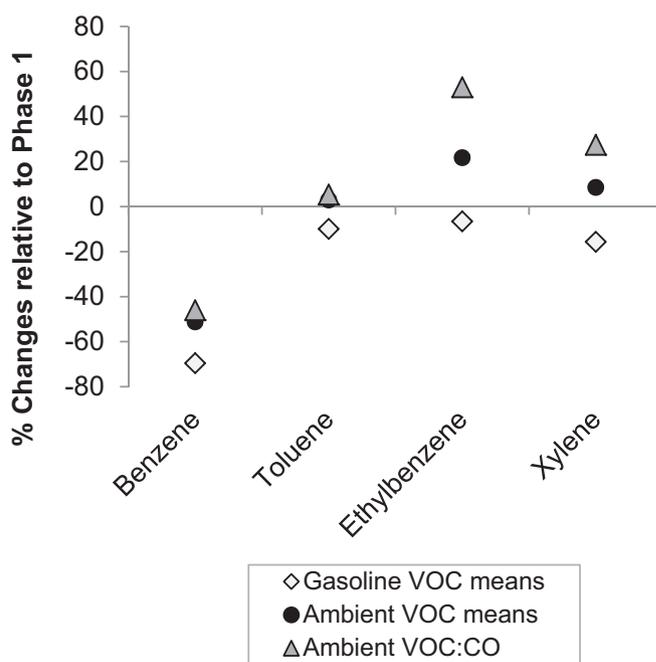


Fig. 3. Comparison of changes in mean gasoline VOCs, mean ambient air VOCs, and VOC:CO ratios relative to Phase 1.

ethylbenzene and xylene was likely. The strong linear associations of each compound with CO (Fig. 2, Table 3) and with ambient 1,3-butadiene ($R > 0.9$, data not shown), a compound produced strictly via combustion processes, suggest a strong combustion source rather than evaporative source. Furthermore, considerably more favorable conditions for photooxidation of VOCs in Phase 2 than Phase 1 (i.e., longer presence of snow cover on the ground in spring (Edwards et al., 2014; Polissar et al., 2001)) should have contributed to lower ethylbenzene:CO and xylene:CO ratios and not increased as observed (Fig. 2, Table 3).

The observed declines in ambient benzene (51%) and the benzene:CO ratio (46%) were smaller than relative decline of the gasoline benzene content (70%). Benzene can be formed from other

gasoline components such as toluene, ethylbenzene, and xylene during the combustion process and contribute a portion of total benzene emissions (Nordin et al., 2013; Zervas et al., 1999). The amount of each of these non-benzene components in gasoline changed relatively little between phases (Fig. 1, Table 1). Thus, we would expect the contribution of benzene formed secondarily through the combustion process to be more or less the same in Phases 1 and 2 and independent of gasoline benzene content. This may explain why the relative decline in ambient benzene was not proportionate with the relative reduction of benzene in gasoline.

3.4. Effectiveness of the gasoline benzene standard

Our results indicate that the gasoline benzene standard reduced benzene content in gasoline by 70%. Based on the changes in the benzene:CO ratio, our observations suggest that the new standard effectively reduced benzene concentrations by 46% in Anchorage air. This reduction is about four times greater than the 12% reduction projected nationwide for 2015 from the implementation of the gasoline benzene standard (EPA, 2007). This is reasonable given the fact that the benzene reduction in Anchorage gasoline (from 5% to 1.5%, w/w) was much greater than most communities in the U.S. (EPA, 2012). The contribution of gasoline benzene standard

estimated in this study (46%) is comparable to the values reported by Kirchstetter et al. (1999b), who estimated that California's fuel reformulation in 1995–1996 contributed to a 73% reduction in gasoline benzene and 30–40% reduction in ambient benzene concentrations.

We suspect that the contribution of fleet turnover was much less important than the gasoline benzene standard. For California's fuel reformulation, in which gasoline benzene concentration was reduced by a similar magnitude as in this study, Harley et al. (2006) estimated that fleet turnover contributed to 4% of the ambient benzene reduction immediately following the changes in gasoline formula. Although the portable fuel container standard was in effect during our study period, it is unlikely that its contribution was significant. The impact of the gasoline benzene standard on benzene emissions is projected to be more than 20 times greater than the portable fuel container standard in 2015 (EPA, 2007).

The benzene:CO ratio did not differ across season within each phase, regardless of large seasonal changes in air temperature (Fig. 4). The stable ratio across season suggests that relative benefit (i.e., percentage reduction in ambient concentration) of the gasoline benzene standard was similar across season. However, because ambient benzene concentrations are generally much higher on cold days than warm (Fig. 4), the absolute magnitude of the reductions in ambient benzene was the greatest on cold days. Between Phases 1 and 2, on days when the ambient temperature was below -10°C , the average benzene concentration fell by 0.73 ppbv (from 1.79 to 1.07 ppbv). In contrast, when temperatures were greater than 10°C , the average concentration fell by 0.30 ppbv (from 0.52 to 0.22 ppbv). Cold start emissions of CO and VOCs increase with decreasing air temperature, and some cold-climate communities in high latitudes (Anchorage, Fairbanks AK) and cold mountainous areas (Salt Lake City, Ogden, UT) have a propensity to develop pollution-trapping air stagnation conditions in the winter (Lareau et al., 2012). This suggests that communities in cold, high latitude and mountainous regions may benefit more from the gasoline benzene standard than counterparts in warmer and/or less mountainous regions.

The gasoline benzene standard may also be of more benefit in communities with high ambient CO. Because CO serves as a good surrogate for motor vehicle pollution (Baker et al., 2008; Gentner et al., 2009; von Schneidmesser et al., 2010), communities with high ambient CO would also have a tendency to have high benzene concentrations. Thus, these communities may experience greater absolute reductions in ambient benzene concentration following the implementation of the gasoline benzene standard.

4. Conclusion

The implementation of EPA's new gasoline benzene standard resulted in a reduction of benzene content in Anchorage gasoline of 70%. The gasoline reformulation helped to reduce local ambient benzene concentration, lowering the annual mean by 51%. Some of this decrease appeared to result from factors unrelated to the gasoline benzene standard (i.e., fleet turnover and warmer temperatures in Phase 2), because CO concentrations also dropped by 13% during the same period. However, observed changes in the benzene:CO ratio suggest that the gasoline benzene standard alone effectively reduced the ambient benzene concentration in Anchorage by 46%. This reduction is roughly four times greater than projected at a national level. The greater effectiveness of the gasoline benzene standard observed in this study was likely due to the high benzene content in Anchorage's gasoline prior to the rule implementation and the large reduction required to meet the 1.3% (v/v) maximum benzene requirement. Although it is difficult to accurately quantify the contribution of the gasoline benzene

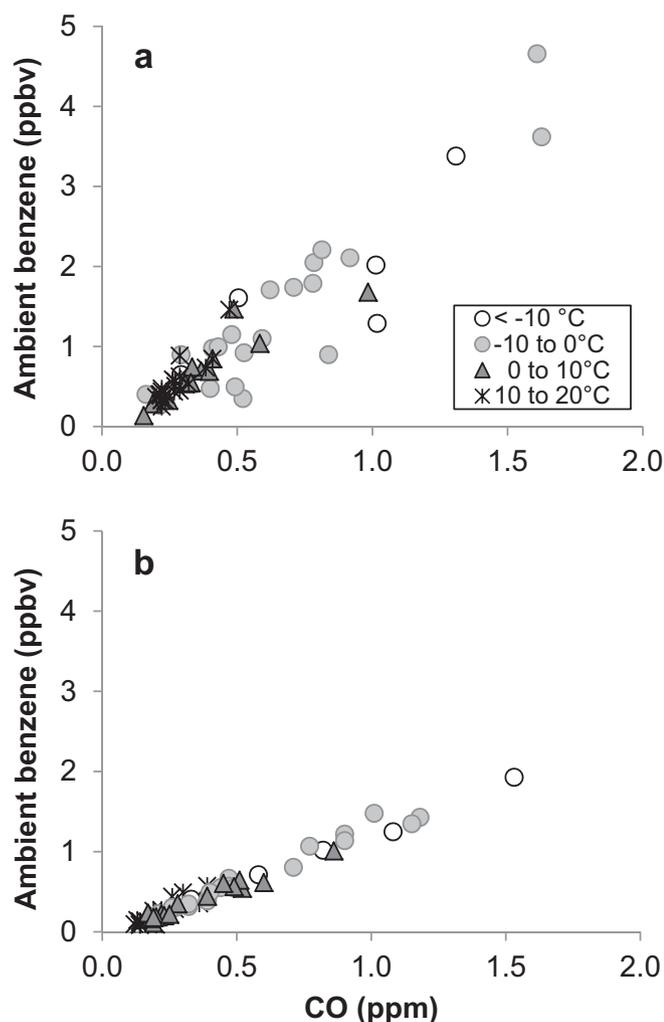


Fig. 4. Relationships between benzene and CO in ambient air of Anchorage, AK with respect to seasonal temperature changes. (a) Phase 1, and (b) Phase 2. Slope did not differ across seasons within each Phase ($p > 0.05$).

standard itself from *in situ* measurements, it is apparent from our results that the benzene standard contributed significantly to the reduced ambient benzene concentrations.

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