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VOC composition of current motor vehicle fuels and vapors, and collinearity analyses for receptor modeling

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Abstract

The formulation of motor vehicle fuels can alter the magnitude and composition of evaporative and exhaust emissions occurring throughout the fuel cycle. Information regarding the volatile organic compound (VOC) composition of motor fuels other than gasoline is scarce, especially for bioethanol and bio-diesel blends. This study examines the liquid and vapor (headspace) composition of four contemporary and commercially available fuels: gasoline (<10% ethanol), E85 (85% ethanol and 15% gasoline), ultra-low sulfur diesel (ULSD), and B20 (20% soy-biodiesel and 80% ULSD). The composition of gasoline and E85 in both neat fuel and headspace vapor was dominated by aromatics and *n*-heptane. Despite its low gasoline content, E85 vapor contained higher concentrations of several VOCs than those in gasoline vapor, likely due to adjustments in its formulation. Temperature changes produced greater changes in the partial pressures of 17 VOCs in E85 than in gasoline, and large shifts in the VOC composition. B20 and ULSD were dominated by C₉ to C₁₆ *n*-alkanes and low levels of the aromatics, and the two fuels had similar headspace vapor composition and concentrations. While the headspace composition predicted using vapor–liquid equilibrium theory was closely correlated to measurements, E85 vapor concentrations were underpredicted. Based on variance decomposition analyses, gasoline and diesel fuels and their vapors VOC were distinct, but B20 and ULSD fuels and vapors were highly collinear. These results can be used to estimate fuel related emissions and exposures, particularly in receptor models that apportion emission sources, and the collinearity analysis suggests that gasoline- and diesel-related emissions can be distinguished.

Keywords

Biofuels; Collinearity; Diesel; Evaporative emissions; Gasoline; Volatile organic compounds (VOCs)

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2011.11.017.

1. Introduction

A diverse and evolving set of motor vehicle fuels is available in the US and other countries. Recent changes to gasoline-like fuels include additions of methyl tert-butyl ether (MTBE) followed by ethanol as oxygenates, and the increased availability of E85, an 85% ethanol/15% gasoline blend. The ethanol in gasoline and E85 are “bioethanol,” produced from agricultural feedstocks such as corn and providing an at least partly renewable fuel. Recent changes to diesel fuels include dramatic reductions in sulfur content, now at 15 ppm and forming ultra-low sulfur diesel (ULSD), and additions of methyl ethers derived from soybeans and other feedstocks to form biodiesel blends B5, B10 and B20, containing 5%, 10% and 20% fractions, respectively, of biodiesel in ULSD for use in unmodified diesel engines.

The fuel formulation affects the magnitude and composition of both evaporative and exhaust emissions occurring throughout the fuel cycle (Hill et al., 2006; Blottnitz and Curran, 2007; Lapuerta et al., 2008). In the US, reformulated gasoline, in which the Reid vapor pressure, aromatics, olefins and other reactive volatile organic compounds (VOCs) are controlled to limit emissions of ozone precursors, is required in cities with the worst ozone problems (US EPA, 2008a). Biofuels can reduce tailpipe emissions, however, the higher vapor pressure of ethanol-containing fuels can increase evaporative emissions (da Silva et al., 2005). Some biofuels can degrade some elastomers and metals used in vehicle fuel systems, which can also increase permeation rates and evaporative emissions (US DOE, 2009, 2010). The fuel formulation also affects emissions from inadvertent spills, in which all fuel components fully evaporate, as well as situations in which the more volatile and permeable components are preferentially emitted, e.g., losses from storage tanks, refueling, and fuel system components (US DOE, 2009).

Fuel compositions vary widely, and an up-to-date understanding of fuel and vapor compositions is needed to estimate fuel-related emissions, exposures and health risks. For example, a typical composition of gasoline ca. 1989 was 25–40% isoalkanes, 20–50% total aromatics (including 0.5–2.5% benzene), 4–8% alkanes, 3–7% cycloalkanes, 2–5% alkenes and 1–4% cycloalkenes (all% volume) (ATSDR, 1995b). Compositions rapidly changed between 1995 and 1996 in California when both aromatics and alkenes were reduced (Harley and Kean, 2004). Nowadays, gasoline contains mostly (55–77%) saturated hydrocarbons, 9–36% aromatics, some unsaturated hydrocarbons, less than 10% ethanol (US EPA, 2008b), and the benzene content has been reduced (as described later). While the compositions of pure biodiesel and ethanol fuels are well known, information regarding the compositions of the diesel and gasoline fuels prior to blending is limited. Thus, little compositional information is available for the new bioethanol and biodiesel blends, especially for speciated VOCs.

Knowledge of fuel and vapor compositions are critical for receptor models, which apportion measured air pollutant levels to different emission sources (Watson et al., 2001; Brown et al., 2007). These models are especially valuable for apportioning VOC sources due to large uncertainties in VOC emission inventories (Kenski et al., 1995). To distinguish among source types, such models require that each has a unique “profile” (composition).

Collinearity among profiles, a common problem, degrades receptor model results by causing errors, inflating variances among predicted apportionments, and diminishing the robustness of results.

This study investigates fuel and vapor compositions of current and commercially available fuels, including two conventional petroleum-based diesel and gasoline (<10% of ethanol) fuels, and two biofuel blends. Vapor measurements are compared to predictions based on the fuel's composition and vapor-liquid equilibrium theory. The collinearity among fuel and vapor profiles is evaluated using variance decomposition analyses, and a set of profiles for use in receptor modeling is suggested.

2. Materials and methods

2.1. Fuel and headspace sampling

The four commercial fuels tested were “regular” conventional gasoline (containing <10% of ethanol), E85, conventional ULSD, and B20. 1 L of each fuel was purchased from a Marathon fuel station in Michigan in December 2007 and stored in a glass bottle placed in a laboratory safety cabinet.

Fuel composition was measured by diluting each fuel in pentane to 50 and 100 $\mu\text{L mL}^{-1}$, and then injecting 2 μL into an adsorbent-packed thermal desorption tube (TDT) for analysis. These dilution levels were established in pilot tests that responses fell within calibration curves. Two samples at each dilution level were collected and analyzed. The TDTs (Scientific Instrument Services, Inc., Ringoes, NJ, USA) were packed with 160 mg Tenax GR and 70 mg Carbosieve SIII, and loaded using a stainless-steel loader (Scientific Instrument Services, Inc., Ringoes, NJ, USA). Cleaning, storage, shipping and analysis protocols for these TDTs have been described elsewhere (Peng and Batterman, 2000).

Headspace vapors were sampled and measured at 5, 20 and 40 °C also using TDTs, thus allowing full comparability between liquid and vapor measurements. 10 mL of each fuel was placed into a 60 mL amber glass vial that was then sealed with a screw cap and Teflon-lined septum. Vials of each fuel were maintained at the desired temperature (within 0.1 °C) in a water bath for at least 30 min. The sampling sequence went from low to high temperature. A gas-tight syringe was used to sample and transfer 50–1000 μL of vapor, depending on fuel and temperature and established in pilot tests, into a TDT for analysis using the loader described earlier. Three to seven samples were taken for each fuel and temperature.

2.2. VOC analysis

The TDTs were analyzed after spiking with 2 μL of an internal standard (1 ng μL^{-1} each of fluorobenzene and p-bromofluorobenzene) using an automated short-path thermal desorption system (Model 2000, Scientific Instrument Services, Ringoes, NJ, USA), on-column cryofocusing, gas chromatography and mass spectrometry (GC/MS, Model 6890/5973, Chemstation, G1701BA, Hewlett Packard, Palo Alto, CA, USA). The method and its performance are detailed elsewhere (Peng and Batterman, 2000; Batterman et al., 2002; Jia et al., 2006). Analyses included 97 target compounds, each calibrated using

authentic standards, that were selected based on their health significance and frequency of occurrence. The limit of detection (LOD) was established for each VOC using seven low concentration spiked samples, and ranged from 0.024 to 10 ng, depending on the compound (Supplemental Data Table A.1). The method detection limit (MDL) was defined as the LOD divided by the sample volume, which depended on the fuel and temperature.

Quality assurance activities included blanks, spiked and duplicate samples for each test. All laboratory and field blanks were clean. A spiked standard (VOC standard mixture) was analyzed daily to check calibration, and all compounds were within 20% of the expected values. Replicate precisions were below 20%, thus replicates ($n = 3-7$) were averaged. The total target VOC (TTVOC) concentration was calculated as the sum of target VOCs.

2.3. Collinearity analysis

Pearson correlation coefficients and singular value variance-decomposition (SVD) analyses were used to investigate collinearity among the fuel and vapor profiles. The SVD procedure obtains condition indexes (CIs) and variance-decomposition proportions from the decomposition of the source profiles (Belsley et al., 1980; Belsley, 1991). (Details of the procedure are provided in the Supplemental data.) The largest CI is the condition number (CN) of the matrix, and indicates the overall degree of dependencies or collinearity. If the CN exceeds 10 to 30, the matrix is ill-conditioned and potentially difficult to invert (Callaghan and Chen, 2008). In a variance proportion table, adverse collinearity is detected also associated with high variance-decomposition proportions (>0.5) for at least two coefficients. This situation represents a “competing dependency”. In contrast to correlation coefficients which show only pair-wise dependencies, the SVD procedure can diagnose dependencies involving multiple profiles.

3. Results and discussion

3.1. Composition of neat gasoline

In neat gasoline, 29 target VOCs were detected, of which toluene, *n*-heptane, 1,2,4-trimethylbenzene, cyclohexane and *p*-,*m*-xylene were the five most prevalent compounds, accounting for 51% of the TTVOC concentration (Table 1). The 29 measured compounds accounted for only a portion (15% wt) of gasoline since the target VOC species covered only a limited range (C_6-C_{16}). Gasoline compositions in recent literature that have reported similar target species as those in the present study are summarized in Supplemental Table A. 2. Fuel compositions have been reported in various units, e.g., mass fraction (e.g., ppm or percent), mole fraction, carbon fraction (ppbC), and fraction of quantified compounds. Harley and Kean (2004) provide one of the most complete analyses, including 315 species from C_2-C_{15} . The top five VOCs in 1990 Atlanta, GA, US gasoline were toluene, 2-methylbutane, *p*-,*m*-xylene, 1,2,4-trimethylbenzene and *n*-butane, which accounted for 30% of the total nonmethane hydrocarbons (NMHC; ppbC basis) (Conner, 1995). In 2001 California gasoline, 2-methylbutane, toluene, *p*-,*m*-xylene, MTBE and 2,2,4-trimethylpentane were the top five compounds, accounting for 31% (wt) (Harley and Kean, 2004). In ca. 1996 Vancouver, Canada gasoline, toluene, 2-methylbutane, *p*-,*m*-xylene, *n*-pentane and 2-methyl pentane were the top five compounds, accounting for 34% of NMHC

(McLaren et al., 1996). In Washington State, US gasoline from the same period, toluene, 2-methylbutane, p-,m-xylene, *n*-pentane and 2,2,4-trimethylpentane were the top five compounds, accounting for 33% of NMHC (McLaren et al., 1996). In a 2003 study, the top five compounds in South Korea gasoline were 2-methylbutane, toluene, 2-methylpentane, *n*-pentane and p-,m-xylene, accounting for 42% (wt) (Na et al., 2004).

In comparison to the literature just described, we found toluene, ethylbenzene, and p-m-xylene at levels 3 to 6 times lower; cyclohexane, methyl cyclohexane and *n*-heptane levels were similar to the Californian reformulated gasoline (which was relatively high); and a higher naphthalene concentration. The comparison fuels were relatively old (1989–2003), and compositional differences likely reflect the lower levels of aromatic compounds found in the newer reformulated gasoline. While this analysis shows that VOC compositions can vary widely, the target compounds in this study are commonly found in fuels, and concentrations of at least some VOCs appear to be representative of current US fuels. For example, the benzene concentration in the test gasoline, 6140 mg L⁻¹ (Table 1) or 0.96% by volume, reflects the current national average for gasoline production from US refineries, which is expected to fall from 1.05 vol.% in 2007 to 0.62 vol.% in 2015 (US EPA, 2010).

3.2. Composition of E85

In E85, 27 target VOCs were detected, and p-, m-xylene, toluene, *n*-heptane, 1,2,4-trimethylbenzene and o-xylene were the top compounds, accounting for 59% of the TTVOCs (Table 1). TTVOc comprised 4.5% of the weight of E85, or 29.6% of the VOCs excluding ethanol. Given that E85 is an 85% bioethanol/15% gasoline blend, the VOC composition was expected to resemble that of gasoline, but with VOC concentrations (other than ethanol) approximately 85% lower. While both E85 and gasoline contained the same compounds, VOC abundances differed considerably (Table 1): In E85, the TTVOc concentration was 31% of gasoline's (rather than the expected 15%); ethylbenzene, p-,m-xylene, o-xylene, *n*-octane and *n*-nonane had higher fractions (>50%), while *n*-tetradecane, cyclohexane, and methyl cyclohexane had lower fractions (<10%). Benzene, naphthalene, *n*-decane, *n*-undecane, *n*-dodecane and *n*-tridecane had the “expected” fraction (15 ± 5%).

Many factors affect fuel composition. First, refineries adjust the base gasoline properties to meet fuel vapor pressure requirements. Ethanol contents below about 40% show an increased vapor pressure (about 1 psi), which is compensated by lowering the volatility of the base gasoline; the opposite is seen for high ethanol blends like E85, where higher volatility gasoline is needed to increase vapor pressure (US DOE, 2010). This helps to explain the abundance of aromatics (other than benzene) in the E85, which are adjusted to maintain the fuel's vapor pressure. Other factors affecting composition include: seasonal changes to attain desired (and mandated) volatility limits; variation in the ethanol content of commercial E85; differences in blending, feedstocks and production method; and the use of additives, oxygenates and small amounts of dye (ATSDR, 1995a; Marathon Oil Corporation, 2009; US DOE, 2010). Composition can vary by both batch and brand, and since only a single winter sample of each fuel was tested, the results in Table 1 cannot reflect the variation expected among commercial fuels.

3.3. Composition of neat ULSD and B20

Of the 28 VOCs detected in neat ULSD and B20, C₉–C₁₆ straight-chain alkanes were dominant and accounted for 90% of TTVOCs (Table 1). Among the aromatic VOCs, naphthalene and 1,2,3-trimethyl benzene were the top species, accounting for 4–6% of the TTVOC. The target VOCs accounted for only a small fraction of the fuel, specifically, 10% and 6% (wt) of ULSD and B20, respectively.

As a blend of 20% soy-based methyl esters and 80% petroleum diesel blend, B20 would have 80% of the petroleum-derived VOCs of conventional ULSD if the base fuel was unaltered. However, the TTVOC concentration of B20 was only 36% of that in ULSD; *n*-butylbenzene, naphthalene and cyclohexane had fractions below 40%; and many C₉–C₁₄ straight-chain alkanes and benzene had fractions of around 60%. In contrast, *p*-isopropyltoluene, 1,2,4-trimethylbenzene, *n*-heptane and *n*-pentadecane had the expected fraction (80 ± 5%), while ethylbenzene, *p*-,*m*-xylene, *o*-xylene, isopropylbenzene, *n*-propylbenzene, *sec*-butylbenzene, and *n*-octane had high fractions (>110%). These data indicate that the composition of the ULSD used in B20 differed from conventional ULSD.

As noted, VOC compositions of diesel and biodiesel blends have been rarely reported. In a 2006 study of diesel fuel in Taiwan, the top five VOCs were C₁₃–C₁₆ and C₁₈ straight-chain alkanes, accounting for 46% of the target compounds (Peng et al., 2006). In comparison, we found that levels of *n*-decane and *n*-undecane were 2.5 and 1.4 times higher, *n*-dodecane and *n*-tridecane were similar, and *n*-tetradecane, *n*-pentadecane and *n*-hexadecane were 39–50% lower (Supplemental Table A.3). VOC compositions in diesel fuels vary for the same reasons stated for gasoline and E85. Petroleum diesel also contains paraffins, cycloparaffins, and some aromatics (Song et al., 2000; Marathon Oil Corporation, 2010). Pure soy biodiesel contains mainly linoleic acid methyl ester, oleic acid methyl ester, palmitic acid methyl ester and stearic acid methyl ester, which collectively accounted for 89% (wt) of the Taiwan fuel (Peng et al., 2006).

3.4. Vapor composition of gasoline

Concentrations of headspace vapors measured for the four fuels at 5, 20 and 40 °C are listed in Table 2. For gasoline, 17 target VOCs were detected at 5 °C, and 20 VOCs at 40 °C, and five VOCs accounted for nearly all (95–96%) of TTVOC at each temperature: toluene (25–28%), benzene (19–20%), *n*-heptane (18–20%), cyclohexane (17–18%), and methyl cyclohexane (11–12%). The TTVOC concentration ranged from 16.1 g m⁻³ at 5 °C to 63.9 g m⁻³ at 40 °C. The headspace vapor was dominated by high volatility compounds, and the vapor fraction of several of the most prevalent VOCs in the liquid fuel (e.g., *p*-, *m*-xylene and 1,2,4-trimethylbenzene) was low.

Supplemental Table A.4 lists VOC compositions (as the fraction of TTVOC) of gasoline vapor measured in four studies reporting compounds similar to those measured here. Benzene, toluene, *p*-,*m*-xylene, cyclohexane and *n*-heptane were the top five VOCs (among our target VOCs) measured in Chicago (Doskey et al., 1992), Atlanta (Conner, 1995) and South Korea (Na et al., 2004), while toluene, cyclohexane, methyl cyclohexane, *n*-heptane and benzene were the top VOCs in California reformulated gasoline vapor (Harley et al.,

2000). Gasoline in Michigan had cyclohexane, methyl cyclohexane and *n*-heptane at similar fractions to the California reformulated gasoline vapor, but levels were 6–7 times higher than those in Chicago and Atlanta; and benzene had similar fractions across the studies with the exception of California, which had levels less than half those elsewhere. As noted for the liquid fuels, results can vary by brand, season, location, formulation and year. Vapor compositions are also affected by test conditions, e.g., temperature and measured compounds.

Gasoline vapor contains very volatile organic compounds (VVOCs) that were not measured in the present study, e.g., *n*-butane, isobutane, *n*-pentane and 2-methylbutane, which collectively accounted for 60–77% (wt) as measured in Chicago (Doskey et al., 1992), Atlanta (at 24 and 32 °C) (Conner, 1995) and South Korea (0 °C) (Na et al., 2004). In California reformulated gasoline (with ethanol), 2-methylbutane, 2-methylpentane, ethanol, *n*-pentane and 2,2-dimethylbutane together accounted for 62% (wt) of the headspace vapor (at 38 °C) (Harley et al., 2000). These studies also show significant variation in vapor concentrations.

3.5. Vapor composition of E85

The vapor composition of E85 was similar to that of gasoline, although concentrations of the more prevalent VOCs (e.g., cyclohexane, methylcyclohexane toluene) were several times lower (Table 2). For E85, the top five VOCs in headspace vapor were *n*-heptane (34–36%), cyclohexane (13–18%), toluene (13–14%), methylcyclohexane (8–10%) and benzene (8–9%), which collectively accounted for 77–85% of TTVOG in the headspace, depending on temperature. The TTVOG concentration in E85 vapor was 5.7 g m⁻³ at 5 °C or 35% of that of gasoline vapor, and 33 g m⁻³ at 40 °C or 52% of gasoline vapor, both well above the 15% expected if the gasoline composition was unchanged. Several VOCs, including *n*-octane, ethyl benzene, *p*-, *m*-, *o*-xylene and *n*-nonane, accounted for most of this increase (their concentrations exceeded levels gasoline by a factor of 1.3 to 1.9 at 5 °C, and by 2.4 to 2.9 at 40 °C). Headspace concentrations of cyclohexane, methylcyclohexane and toluene were also higher than the 15% expected (18–33% at 5 °C, 28–40% at 40 °C). Only the benzene concentration was close to 15% (15% at 5 °C, 20% at 40 °C). As seen for gasoline, several of the most prevalent VOCs in liquid E85 had low relatively vapor concentrations, e.g., 1,2,4-trimethylbenzene and 4-ethyl toluene.

3.6. Vapor composition of ULSD and B20

B20 and ULSD had similar VOC headspace compositions (Table 2). The top five target VOCs were cycloalkanes (methylcyclohexane, cyclohexane) and alkanes (*n*-octane, *n*-nonane, *n*-heptane), which together accounted for 63–76% of TTVOG (depending on temperature). The most abundant aromatics were toluene (7% of TTVOG), *p*-, *m*-xylene (3–6%), and benzene (2–4%). ULSD had slightly higher TTVOG headspace concentrations (0.99–6.16 g m⁻³ at temperatures of 5 and 40 °C, respectively) than ULSD (0.81–5.80 g m⁻³). Concentrations of most VOCs in the two fuels were similar (within 20%) at each temperature, although B20 showed higher concentrations of *n*-octane, ethyl benzene, *n*-nonane, 4-ethyl toluene at 5 °C and *n*-tridecane and *n*-tetradecane at 40 °C, but lower concentrations of cyclohexane. As seen earlier, vapor and liquid compositions differed

considerably, e.g., liquids were dominated by C₉–C₁₆ straight-chain alkanes, and vapors by cyclo-alkanes and C₇–C₉ straight-chain alkanes.

Few studies have reported the speciated VOC composition of diesel and biodiesel fuels. A 2006 study from Taiwan identified the top 20 VOCs in headspace vapors for conventional diesel and pure soy biodiesel at 25 °C, and the top five in conventional diesel vapor were *n*-octane, ethyl benzene, *p*-xylene, *n*-decane and toluene (together accounting for 39% of TTVOCs) (Peng et al., 2006). We had 13 VOCs in common with the Taiwan study (Supplemental Table A.5). The Michigan diesel vapor (measured at a slightly lower temperature of 20 °C) had much higher levels of 11 VOCs and little correlation with levels in the Taiwan diesel. As noted, the Taiwan diesel fuel did not list methyl cyclohexane and other aromatics among the top 20 VOCs.

The top five VOCs in Taiwan pure soy biodiesel vapor were linoleic acid methyl ester, oleic acid methyl ester, palmitic acid methyl ester, 1-penten-3-ol and capric acid methyl ester, which together accounted for 72% of TTVOCs (Peng et al., 2006). The biodiesel vapor also contained small amounts of aromatics (6.4%) and alkanes (4.8%), which suggests that the “pure” soy biodiesel was actually a blend containing conventional petroleum diesel. More generally, a portion of the biodiesel vapor results from oxygenated compounds (23% of target compounds in the Taiwan diesel vapors) (Peng et al., 2006), excess alcohol produced during the transesterification process (US DOE, 2009), and oxidized soy bio-diesel constituents; these compounds have higher volatility than methyl ethers. Future studies might be designed to evaluate the origin of these compounds and address oxidized constituents as well as oxidization stability.

3.7. Temperature dependence of vapor compositions

The partial pressures of VOCs in E85 showed greater variation with temperature than the VOCs in gasoline. As examples: E85 had 6 VOCs at higher concentrations than gasoline at 5 °C, and 15 VOCs at 40 °C; VOC concentrations in E85 vapor increased 4.4–15.4 times from 5 to 40 °C, compared to 3.8–5.8 times for gasoline (Fig. 1); and while the TTVOC concentration in neat E85 was only 30% of gasoline's, E85's TTVOC vapor concentration was 50% of that of gasoline's at 40 °C. Changes were especially large for the lower volatility VOCs in E85, e.g., 1,2,3-trimethyl benzene.

As mentioned, ULSD and B20 had similar vapor profiles, and these fuels showed similar and greater temperature dependencies than gasoline. Concentration increases from 5 to 40 °C (expressed as a ratio) were within 25% for most VOCs in ULSD and B20 vapors, although five VOCs (*n*-nonane, isopropylbenzene, *n*-propylbenzene, 4-ethylbenzene and sec-butylbenzene) had greater temperature dependencies for ULSD (13–17 times increase from 5 to 40 °C) than for B20 (8.4–11 times increase, Fig. 1).

The contrasting results for gasoline and E85 fuels suggest interactions associated with ethanol that may depend on temperature. Harley et al. (2000) notes that activity coefficients increase with ethanol fraction. Bennett et al. (1993) showed only small differences for temperatures from 25 to 60 °C. Our results were reproducible, and no experimental errors or biases are known.

From the perspectives of air quality and exposure assessment, changes in VOC composition due to temperature represent variation and uncertainty in fuel-related evaporative emissions. For receptor modeling, such changes can adversely affect results since profiles are typically assumed to be constant. As a practical matter, it may be sufficient to utilize seasonal analyses, which can account for some of the temperature effect. While vapor concentrations at different temperatures are correlated (see below), temperature-specific information pertaining to the vapor composition of motor vehicle fuels is scarce.

3.8. Prediction of headspace vapor composition

Headspace compositions can be predicted using the fuel's composition, vapor–liquid equilibrium theory and activity coefficients (as detailed in the Supplemental materials). Predicted and measured target VOC concentrations in headspace vapors were closely correlated for gasoline and E85 ($r = 0.88$ – 0.94 , depending on fuel and temperature), but differences between predicted and measured concentrations were sometimes large (Supplemental Fig. A.1). Results for E85 showed systematic underprediction of all target VOCs, suggesting that appropriate activity factors are from 1.5 to 2.0, a range containing the estimate from Harley et al. (2000). ULSD and B20 had lower correlation between predicted and observed vapor concentrations than gasoline, and predicted versus observed concentrations showed more scatter (Supplemental Fig. A.1).

Differences between the predicted and measured concentrations can arise from many factors, e.g., experimental errors, approximations in the Antoine equation, and missing or uncertain activity coefficients (Bennett et al., 1993; Guo et al., 2007). Several studies have shown good agreement ($r > 0.9$) between predicted and measured headspace compositions of gasoline (Conner, 1995; Kirchstetter et al., 1999; Na et al., 2004). No such studies have been identified for E85, ULSD and B20. Because we do not know the full composition of the tested (market) fuels or the fuels prior to being blended, our analysis cannot be used to evaluate the theoretical approaches used to predict vapor–liquid equilibrium.

3.9. Collinearity analysis

Because the headspace compositions of each fuel at the three temperatures were highly correlated ($r = 0.92$ – 1.00 ; Supplemental Table A.6), compositions at the three temperatures were averaged to obtain a single headspace composition profile. Correlation coefficients among the other profiles ranged widely, e.g., ULSD and B20 fuels had negative (though not significant) correlation with gasoline and E85 profiles.

The initial SVD analyses used eight profiles (four fuels and their headspace compositions), and the corresponding CIs and variance decomposition proportions are shown in Table 3. While both fuel and vapor compositions were included in the SVD analysis, the magnitudes of evaporative emissions generally exceed leaks. Still, the inclusion of both fuel and vapor profiles does not degrade the collinearity analysis for vapors alone. CIs range up to 24.8, and several of the CIs show possible collinearity problems, e.g., the 7th CI (16.2) shows competing dependencies between ULSD and B20 neat fuel profiles, and the 8th CI (24.8) shows dependencies between ULSD and B20 vapor profiles. Although the 6th CI (7.8) is less than the cut-off of 10, the variance-decomposition proportions suggest competing

dependencies (described in Supplemental data) between gasoline fuel, E85 fuel and gasoline vapor. This set of eight profiles is too collinear to use simultaneously in chemical mass balance (CMB) receptor models.

The high correlation between ULSD and B20 fuel profiles ($r = 0.98$) and vapors ($r = 0.92$ – 0.99) suggest that it is appropriate to combine these profiles. Therefore, profiles for ULSD and B20 liquid fuels (expressed as percentage of TTVOC) were averaged. Similarly, the ULSD and B20 headspace vapor profiles were averaged. The SVD analysis using the resulting six profiles (Table 4) does not show degrading collinearity, e.g., CIs range to 7.1. This suggests that ULSD and B20 neat fuel, ULSD and B20 headspace, and E85 headspace can be distinguished. However, the 6th CI (7.1) still shows competing dependencies involving gasoline fuel, E85 fuel and gasoline headspace. Since little E85 is used currently relative to gasoline, the E85 profile might be omitted, at least in areas where this is true. Collinearity problems might be further reduced using additional VOCs, although this may require more laboratory work and statistical analyses to determine if this resolves the collinearity concerns.

This analysis shows that receptor modeling should be able to distinguish diesel and gasoline fuels and their vapors without the adverse effects from collinearity. Importantly, VOCs related to evaporative emissions from diesel fuel normally would be present at much lower concentrations, e.g., the TTVOC concentrations in neat diesel was 30% lower than in gasoline, and the TTVOC concentration in diesel headspace was about ten times lower. Collinearity is only one of several sources of errors in receptor models, and the other assumptions must be valid. In any case, however, profiles that minimize collinearity will provide more accurate and stable results.

3.10. Limitations

The fuel samples used in this study represent a snapshot of four commercial fuels, which do not account for the variation in fuel composition, which can vary by brand, season and location. Compositions were determined for target VOCs that represent a subset of VOCs present. Quantification did not include ethanol or methyl ethers, which constitute large fractions of E85 and B20, respectively. Other oxygenated compounds also were not quantified, nor the oxidation stability of the fuel itself. The use of laboratory-blended fuels with known compositions would help to resolve questions concerning activity factors associated with ethanol additions. The comparisons with the literature were based on the VOCs that are reported in the open literature and that used similar target compounds as in this study.

4. Conclusion

Motor vehicle fuels contain hundreds of VOCs and can differ widely in composition. This study characterized VOCs in four current and commercially available fuels. Conventional gasoline showed liquid and vapor compositions that were comparable to earlier reports. The dominant VOCs in gasoline and E85 included aromatic compounds (e.g., toluene, 1,2,4-trimethylbenzene, p-mxylene) and alkanes (n-heptane, cyclohexane and methylcyclohexane). Headspace vapors were “enriched” in the fuel's more volatile

components (e.g., benzene, cyclohexane, methylcyclohexane and *n*-heptane). In ULSD and B20, for which little VOC information is available, the dominant VOCs included alkanes and several aromatics (e.g., 1,2,3-trimethyl benzene and naphthalene). Vapors of these fuels contained toluene, p-,m-xylene and benzene at concentrations much lower than gasoline's. Depending on temperature, E85 vapor had higher concentrations of several or many VOCs than gasoline, and vapor pressures of the 17 measured VOCs in E85 increased considerably faster with temperature than those in gasoline. B20 and ULSD had similar VOC compositions in headspace vapors. Measured and predicted vapor concentrations correlated closely, although predictions for fuels other than gasoline showed large biases. An analysis of collinearity showed that receptor models should be able to distinguish gasoline and diesel fuels using appropriately selected profiles, however, three combinations of profiles are too collinear to separate, namely, ULSD and B20 neat fuels, ULSD and B20 vapors, and gasoline fuel, E85 fuel and gasoline vapor.

The liquid and vapor compositions reported in this study can be used to help describe leaks and emissions from fuel- and vehicle-related sources (e.g., storage tanks, vehicle refueling, hot soaks, running and evaporative losses), define source profiles for receptor models aimed at apportioning emission sources, and estimate exposures and risks related to fuels. Because motor fuels continue to evolve, there will be a continuing need to update VOC speciation of liquid fuel and their vapors. In the US, for example, the allowable (but not required) content of ethanol in gasoline has just (2011) been increased to 15 vol.% from 10 vol.% (US EPA, 2011). The use of E15, along with the variation of VOCs demonstrated in commercial fuels, suggests a need to expand testing and reporting for speciated VOCs in vehicle fuels that goes beyond those parameters currently required in the reformulated fuels program (e.g., benzene, total aromatics, total olefins, and other parameters) (US EPA, 2008a).

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1.
Ratio of vapor concentrations at 40 and 5 °C for the four fuels.

Table 1

Composition of target VOCs in neat gasoline, E85, diesel and B20, and ratios comparing concentrations of gasoline and diesel fuels.

Fuel Unit	Gasoline (mg L ⁻¹)	E85 (mg L ⁻¹)	E85/Gasoline (%)	Diesel (mg L ⁻¹)	B20 (mg L ⁻¹)	B20/Diesel (%)
<i>Aromatics</i>						
Benzene	6140	862	14	67	37	55
Toluene	15,400	4110	27	238	214	90
Ethylbenzene	3080	1990	65	124	186	150
p-Xylene,m-xylene	9120	6980	76	420	496	118
o-Xylene	4610	2790	60	185	212	115
Isopropylbenzene	351	156	45	44	70	160
n-Propylbenzene	2110	665	32	115	167	146
p-Isopropyltoluene	88	29	33	112	83	75
4-Ethyl toluene	8380	2650	32	400	464	116
2-Ethyl toluene	3460	928	27	194	264	136
1,3,5-Trimethylbenzene	4060	1030	25	202	150	74
1,2,4-Trimethylbenzene	10,600	3270	31	720	575	80
1,2,3-Trimethylbenzene	3950	975	25	2120	961	45
sec-Butylbenzene	159	65	41	90	117	130
n-Butylbenzene	822	198	24	375	111	30
Styrene	14	4	32	<0.02	<0.02	–
Naphthalene	2240	378	17	3000	1220	41
<i>Alkanes</i>						
n-Heptane	12,800	3330	26	174	138	79
n-Octane	2870	1550	54	481	612	127
n-Nonane	1790	1050	59	7020	4120	59
n-Decane	1390	262	19	7690	4310	56
n-Undecane	1120	121	11	7730	4560	59
n-Dodecane	822	85	10	8370	5000	60
n-Tridecane	644	80	12	13,400	7620	57
n-Tetradecane	213	19	9	10,100	7130	71
n-Pentadecane	62	<0.02	–	9030	7580	84
n-Hexadecane	18	<0.02	–	9300	5550	60
Cyclohexane	9830	880	9	191	69	36
Methyl cyclohexane	8280	778	9	426	270	63
Total target VOCs	114,000	34,900	31	80,700	51,600	64

<: Below method detection limit, limit of detection is listed in supplemental data Table A.I.

Table 2

Headspace vapor composition (mg m^{-3}) of gasoline, E85, ULSD and B20 at three temperatures.

Fuel	Gasoline			E85			ULSD			B20		
	5 °C	20 °C	40 °C	5 °C	20 °C	40 °C	5 °C	20 °C	40 °C	5 °C	20 °C	40 °C
Cyclohexane	3120	6010	11,800	1020	1610	4540	267	477	905	146	213	808
Benzene	3170	6940	13,000	498	1060	2660	38	74	146	24	38	129
<i>n</i> -Heptane	3020	6840	12,800	2050	4340	11,300	101	221	526	81	140	473
Methyl cyclohexane	1860	3940	6900	542	1050	2770	255	534	1190	191	306	1130
Toluene	4280	9910	15,900	756	1810	4370	68	158	402	58	108	378
<i>n</i> -Octane	106	275	491	198	537	1420	70	180	588	90	180	600
Ethyl benzene	58	148	283	92	284	745	14	37	133	17	38	129
<i>p</i> -m-Xylene	182	466	924	312	1000	2650	37	102	350	37	84	321
<i>o</i> -Xylene	69	167	356	92	307	836	13	36	129	14	31	119
<i>n</i> -Nonane	9	16	66	16	33	189	55	167	678	71	176	667
Isopropylbenzene	2	3	12	2	4	26	2	6	27	3	8	27
<i>n</i> -Propylbenzene	15	32	86	9	37	115	3	10	47	5	12	45
4-Ethyl toluene	64	131	368	33	141	445	9	28	127	11	28	117
1,3,5-Trimethylbenzene	23	46	135	12	52	166	3	11	42	3	7	38
2-Ethyl toluene	20	41	116	9	41	133	4	12	61	6	15	59
1,2,4-Trimethylbenzene	66	130	392	30	135	446	10	31	133	8	23	117
<i>n</i> -Decane	<0.6	4	27	<0.6	2	25	25	77	363	24	66	346
sec-Butyl benzene	<0.6	<0.6	<1.0	<0.6	<0.6	<1.0	1	3	20	2	5	20
1,2,3-trimethyl benzene	16	29	94	6	29	97	4	12	51	3	8	46
<i>p</i> -Isopropyltoluene	<0.7	<0.7	1	<0.7	<0.7	2	1	2	9	1	2	9
<i>n</i> -Butyl benzene	<1.0	2	12	<1.0	1	11	1	3	16	1	3	15
<i>n</i> -Undecane	<0.8	<0.8	8	<0.8	<0.8	8	11	29	162	10	24	151
Naphthalene	<1.0	2	14	<1.0	<1.0	21	<0.2	<0.2	1	<0.2	<0.2	0.71
<i>n</i> -Dodecane	<0.6	<0.6	2	<0.6	<0.6	5	3	6	39	4	6	41
<i>n</i> -Tridecane	<0.5	<0.5	<1.0	<0.5	<0.5	<1.0	1	1	12	1	2	15
<i>n</i> -Tetradecane	<0.4	<0.4	<0.8	<0.4	<0.4	<0.8	0	0	3	0	0	4
Total target VOCs	16,100	35,100	63,900	5680	12,500	33,000	995	2220	6160	810	1520	5800

<: Below method detection limit, limit of detection is listed in supplemental data Table A.I.

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Table 3

Singular value variance-decomposition proportions of 8 compositional profiles.

Variable	Singular value							
Rank order	1	2	3	4	5	6	7	8
Eigenvalue	4.38	1.69	0.98	0.64	0.21	0.07	0.02	0.01
Condition index	1.00	1.61	2.11	2.63	4.54	7.80	16.22	24.79
Variance decomposition proportions								
Gasoline	0.004	0.000	0.012	0.001	0.090	0.76	0.004	0.128
E85	0.004	0.005	0.055	0.123	0.007	0.58	0.009	0.217
ULSD	0.001	0.008	0.004	0.000	0.000	0.002	0.96	0.023
B20	0.001	0.008	0.005	0.000	0.000	0.000	0.97	0.019
HS-Gasoline	0.006	0.003	0.006	0.103	0.189	0.69	0.003	0.000
HS-E85	0.010	0.004	0.020	0.058	0.81	0.095	0.000	0.005
HS-ULSD	0.000	0.001	0.002	0.001	0.000	0.000	0.003	0.99
HS-B20	0.000	0.001	0.003	0.002	0.000	0.003	0.002	0.99

HS = headspace using average of profiles measured at 5, 20, and 40 °C. Bold proportions show possibility of degrading collinearity.

Table 4

Singular value variance-decomposition proportions of 6 profiles.

Variable	Singular value					
Rank order	1	2	3	4	5	6
Eigenvalue	3.56	0.99	0.66	0.50	0.21	0.07
Condition index	1.00	1.90	2.32	2.66	4.10	7.09
Variance decomposition proportions						
Gasoline	0.008	0.002	0.008	0.000	0.101	0.88
E85	0.010	0.070	0.114	0.043	0.008	0.76
ULSD+B20	0.017	0.269	0.67	0.007	0.023	0.012
HS-Gasoline	0.011	0.022	0.002	0.090	0.198	0.68
HS-E85	0.017	0.016	0.004	0.060	0.81	0.094
HS-ULSD+B20	0.022	0.132	0.075	0.71	0.001	0.063

HS = headspace using average of profiles measured at 5, 20, and 40 °C. ULSD + B20 = average of ULSD and B20 profiles. Bold proportions show possibility of degrading collinearity.