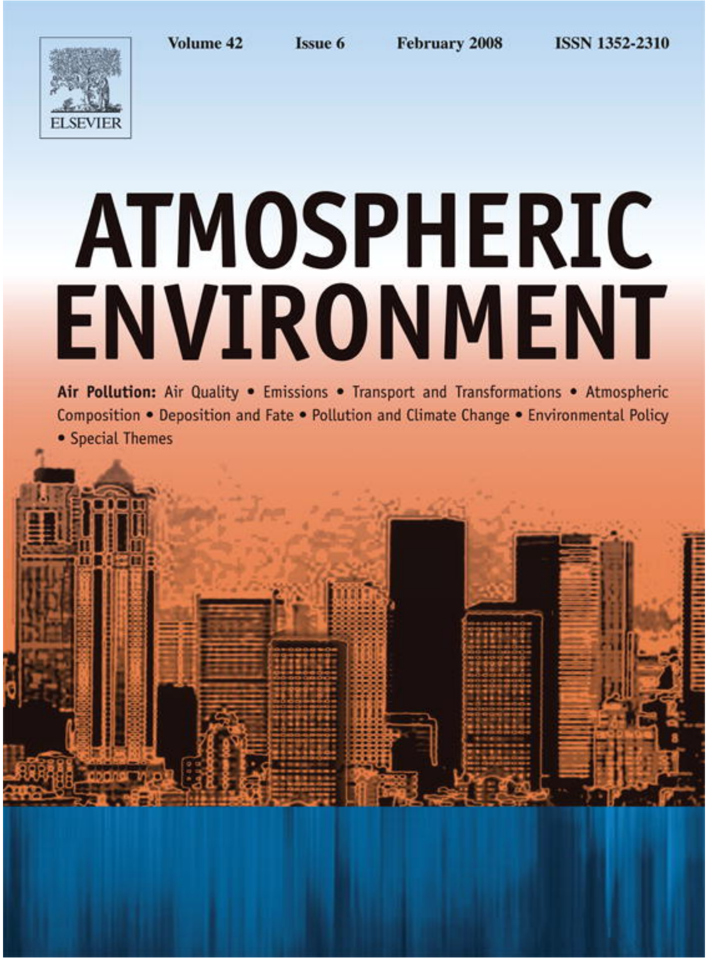

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Carbonaceous species emitted from handheld two-stroke engines

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Abstract

Small, handheld two-stroke engines used for lawn and garden work (e.g., string trimmers, leaf blowers, etc.) can emit a variety of potentially toxic carbonaceous air pollutants. Yet, the emissions effluents from these machines go largely uncharacterized, constraining the proper development of human exposure estimates, emissions inventories, and climate and air quality models. This study samples and evaluates chemical pollutant emissions from the dynamometer testing of six small, handheld spark-ignition engines—model years 1998–2002. Four oil–gas blends were tested in each engine in duplicate. Emissions of carbon dioxide, carbon monoxide, and gas-phase hydrocarbons were predominant, and the PM emitted was organic matter primarily. An ANOVA model determined that engine type and control tier contributed significantly to emissions variations across all identified compound classes; whereas fuel blend was an insignificant variable accounting for $<5\%$ of the observed variation in emissions. Though emissions rates from small engines were generally intermediate in magnitude compared with other gasoline-powered engines, numerous compounds traditionally viewed as motor vehicle markers are also present in small engine emissions in similar relative proportions. Given that small, handheld two-stroke engines used for lawn and garden work account for 5–10% of total US emissions of CO, CO_2, NO_x, HC, and $PM_{2.5}$, source apportionment models and human exposure studies need to consider the effect of these small engines on ambient concentrations in air polluted environments.

Keywords: Source apportionment; Profile; Two-stroke; Biofuel; Lawn and garden; PAH; VOC; PM

1. Introduction

Lawn and garden machines emit 6 million tons of pollutants annually, accounting for 5–10% of total US emissions of carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxides (NO_x), hydrocarbons (HC), and fine particulate matter ($PM_{2.5}$) (EPA, 2000). Two-stroke engines currently dominate the handheld segment of the lawn and garden equipment market (e.g., chain saws, leaf blowers, and string trimmers). Two-stroke small engines typically emit more smoke than engines running on gasoline only, because they burn an oil–gasoline mixture, can lack emissions controls, and are often not regularly maintained (Volckens et al., 2007). Operators of handheld engines—when without the proper protection—may be exposed to excessively high concentrations of these emissions; the analog emissions from gasoline-powered equipment (i.e., gasoline-powered vehicles) have become a serious public health issue (EPA, 2005).

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Despite their potential toxicity and contribution to atmospheric pollution, the emissions from handheld, two-stroke engines have been largely uncharacterized. The emissions are expected to be predominantly carbonaceous. This illuminates the importance of identifying and quantifying their individual gas- and particle-phase organic compounds and the particle-phase organic and elemental carbon fractions. Uses for these quantitative emissions measurements include estimating human exposures to small engine pollutants and developing source-receptor, air quality, and climate models (EPA, 2005). Improved receptor models are needed since PM is being monitored and regulated in the atmospheric environment. Model predictions of anthropogenic climate forcing require estimating secondary organic aerosol yields from photo-oxidation using gaseous organic compound emissions from combustion.

This study characterized the organic composition of the gas- and particle-phase emissions from two-stroke, handheld, gasoline-powered small engines used for lawn and garden work. Handheld small engines are classified according to their engine displacement: Class III engines have a displacement $<20\,\mathrm{cm}^3$, Class IV engines have displacement between 20 and $50\,\mathrm{cm}^3$, and Class V engines have a displacement $>50\,\mathrm{cm}^3$. Phase 1 engines represent model years 1997–2001 for Class III and IV and model years 1998–2003 for Class V engines. All newer engines, after 2001 for Class III, IV and after 2003 for Class V, are designated as Phase 2. EPA's Phase 2 rulemaking calls for a graduated phase-in of emission standards beginning in 2002 and completing in 2007. All Class III and IV engines must emit $<805\,\mathrm{g\,kWh}^{-1}$ of CO and $<50\,\mathrm{g\,kWh}^{-1}$ for the sum of $\mathrm{HC}+\mathrm{NO}_x$ by the 2005 model year. For Class V engines, emissions of CO must not exceed $603\,\mathrm{g\,kWh}^{-1}$ and $\mathrm{HC}+\mathrm{NO}_x$ must not exceed $72\,\mathrm{g\,kWh}^{-1}$ by model year 2007. We focus specifically on assorted phases 1 and 2, Class IV control tier engines—model years 1998 and onward with displacements of 20–50 cm^3—investigating the effect of different oil–gasoline fuel blends on gas- and particle-phase organic compound emissions (see http://www.epa.gov for more information on rulemaking and engine class designations). Small engine dynamometer testing is performed as a means to standardize duty cycles and also to ensure rigor when comparing across experimental controls and test variables. Gasoline-powered vehicles are expected to make substantial contributions to atmospheric volatile organic compound (VOC) levels, however, the possibility exists that atmospheric VOCs apportioned to motor vehicle exhaust also contain a significant contribution from small engine emissions.

2. Materials and methods

A total of six spark-ignition engines from model years 1998–2002 were tested in this study. These engines were obtained locally from consumers, pawnshops, and lawn service vendors. All engines were tested "as is", with minimal (if any) maintenance performed to get them to run properly on the dynamometer.

2.1. Dynamometer setup

The details of the dynamometer setup and testing procedure are provided elsewhere (Volckens et al., 2007). Briefly, engines were coupled to an eddy-current dynamometer and tested using a modified SAE J1088 certification duty cycle (Gabele, 2000). This J1088 cycle contains two operating modes: the first mode is run at 100% of rated torque and 85% of rated speed for 9 min; followed by 1 min at idle or no load. Our tests were run under the same torque/speed conditions as the J1088, except that we sampled continuously throughout the duration of the test (instead of separate samples for each mode). Engine exhaust generated during testing was diluted using a constant volume dilution technique ($13\,\mathrm{m}^3\,\mathrm{min}^{-1}$) that is described elsewhere (Volckens et al., 2007; Gabele, 2000). Contamination from both background air and interior surfaces of the tunnel were evaluated with daily blanks, which accounted for $<1\%$ of measured gas and particle pollutant emissions from any engine, on average.

2.2. Fuel and oil types

All engines were tested using two fuels and two oils for a total of four fuel/oil combinations. The two fuels (Haltermann Products Inc., Channelview, TX) consisted of a regular, unleaded summer gasoline, and a reformulated gasoline containing 10% ethanol. Target fuel specifications were chosen to be representative of the national average for these two types of fuel. These target specifications were not meant to agree with specifications for Indolene test fuel, which is used for most certification testing, but rather to mimic popular gasoline formulations used in the US. The two oils, a synthetic two-cycle oil (Genuine Factory Parts #147543) and a "low smoke" mineral, two-cycle oil (Pro-Mix #54001), were purchased at a local retailer. Routine laboratory analyses were conducted on each fuel and oil; the results of these analyses are provided elsewhere (Volckens et al., 2007). Oil was blended with the fuels in proportions recommended by the oil manufacturer, and each fuel/oil combination was given a unique code.

2.3. Emissions measurement

2.3.1. Aldehydes and ketones

Aldehydes and ketones were determined using ASTM Method D5197-92, which is a modified version of EPA method TO-11A (EPA, 1999). Compounds were sampled through a heated sample line (110 °C) at $1.0\,\mathrm{L\,min^{-1}}$ and collected on dinitrophenylhydrazine (DNPH)-coated silica gel cartridges. One background cartridge was drawn per day to represent the background levels for every test conducted that day. DNPH cartridges were extracted with acetonitrile and analyzed using high-performance liquid chromatography.

2.3.2. Volatile organic compounds (VOCs)

VOCs were collected in 60-L Tedlar bags for hydrocarbon and oxygenate speciation. All bag samples were analyzed within a few hours of collection. The C_3–C_{13} hydrocarbon analysis was performed on a pair of Hewlett-Packard Model 5890 GCs using a previously described protocol that quantifies 420 individual VOC compounds as individual chromatographic peaks (Siegl et al., 1993). Of these, 196 compounds have been identified while the identity of 224 remains unknown. A complete list of individual VOCs analyzed is provided as supporting information.

2.3.3. Particulate matter (PM) and semivolatile PAH

$PM_{2.5}$ samples were collected for the determination of mass, organic carbon (OC), elemental carbon (EC), and semivolatile polycyclic aromatic hydrocarbons (PAHs). Samples for the determination of mass and PAH content were collected on 47 mm Teflon filters (Teflo Pall Life Sciences, Ann Arbor, MI) followed by a two-stage polyurethane foam (PUF) plug. Samples for OC/EC were collected on quartz filters (2500QAOT Pallflex Products Corp., Putnam, CT) that had been pre-baked at 500 °C for 12 h. A backup quartz filter was placed behind a separate Teflon filter line to account for the adsorption of semivolatile OC to the front quartz filter (Turpin et al., 2000). All samples were collected by drawing diluted engine exhaust at $16.7\,\mathrm{L\,min^{-1}}$ through an isokinetic probe followed by a 2.5 μm cut-point cyclone (URG Corp., Chapel Hill, NC). Filters for gravimetric analysis were transferred to labeled Petri dishes and allowed to equilibrate for a minimum of 24 h. Weighings were conducted in a temperature and humidity controlled room using a Cahn balance with a 1.0 μg resolution. Filters and PUF samples for PAH analyses were spiked with a suite of deuterated internal standards, transferred to sealed Petri dishes and stored at −80 °C prior to analysis. Teflon filters and PUF samples were each extracted with a 1:1:1 volumetric solution of pentane/dichloromethane/methanol using high-pressure solvent extraction (ASE 200, Dionex Corp.). The extract was concentrated to a final volume of 250 μL under a stream of pure nitrogen and then reconstituted to 500 μL with additional solvent. Extracts were analyzed by gas chromatography/mass spectrometry (HP 5890/5972, Agilent Corp.) for 32 PAHs using select ion mode. Quartz filters for OC/EC analysis were stored in a −80 °C freezer prior to analysis using the NIOSH 5040 thermo-optical method (Birch and Cary, 1996). The amount of OC detected on the backup quartz filter was subtracted from that of the front quartz filter to account for the adsorption artifact. None of the samples showed any presence of carbonate, and the EC component was generally low. Analysis of backup PUF cartridges for evidence of compound breakthrough ($>20\%$ of total mass detected on backup) showed no PUF penetration except for dibenzothiophene. Therefore, the reported dibenzothiophene emissions, while minimal, are considered conservative due to potential breakthrough.

2.3.4. Regulated compounds

Analysis of regulated emissions included carbon monoxide (CO), total hydrocarbons (HC), and nitrogen oxides (NO_x). Additional emissions were also analyzed, including carbon dioxide (CO_2), sulfur dioxide (SO_2), and fine particulate matter mass ($PM_{2.5}$). The results of these analyses are reported elsewhere (Volckens et al., 2007).

2.3.5. Statistical analyses

A second objective of this study was to assess both precision and accuracy associated with emissions profiles (i.e., both inter- and intra-engine variability). The intent of this analysis was to assess whether a composite emissions profile was representative of small engine exhaust for the range of conditions tested, as well as to determine important factors affecting emissions from small engine exhaust. This contrasts with past studies that either combined samples collected from multiple experiments to increase detection (i.e., compositing) or studies that profiled only one or two sources such that insight into source variability is limited (Rogge et al., 1993; Schauer et al., 2002). Four sets of emissions tests were conducted on each of six engines, one set for each of the four fuel/oil combinations. Each experimental condition was repeated once, producing a total of 48 separate tests. Statistical analyses were completed for each compound class in order to include the entire range of chemicals that were measured, although key findings for specific species are noted where appropriate. Statistical analyses were conducted with SAS software (version 9.1, SAS Institute Inc., Cary, NC) using analysis of variance (ANOVA) and paired, two-tailed t-tests at the $\alpha = 0.05$ significance level. One ANOVA model assessed the variability of emissions between and within engines; a second model identified engine or experimental variables (e.g., fuel type, oil type, control tier, rpm, displacement) that significantly affected compound emission rates. Prior to the analysis, data were log-transformed using Box–Cox maximum-likelihood power transformations to normalize the distribution of variance across each pollutant dataset.

3. Results and discussion

3.1. Total emissions mass balance and summary

The average emissions budget for carbonaceous species in small engine exhaust is shown in Fig. 1; VOC emissions are further segregated by class and predominant compound names. This figure represents test-averaged emissions across all six engines and four oil–gas mixtures.

The GC–MS and HPLC analyses identified 238 individual organic compounds, accounting for 80% of the total hydrocarbon emissions. Of the remaining 20%, approximately 10% were resolved by GC–MS but were not specifically identified. The remaining 10% of the hydrocarbon mass, while unknown, is probably associated with C_2–C_3 compounds, which were not measured. Of the identified species, 210 are gas-phase: 10 *n*-alkanes, 38 branched alkanes, 19 alkenes, 30 branched alkenes, 4 alkynes and branched alkynes, 44 aromatics, 23 aldehydes, 25 cycloalkanes, 10 cycloalkenes, and 7 olefins. A total of 28 PAHs were identified. PAH emission rates are given as a gas- and particle-phase total, representing a composite of the four oil–gas fuel blends with each having been tested in duplicate. Individual compound emission rates for the 48 individual experiments are provided in Supporting Information as Table S1.

3.2. Emissions of gas-phase compounds

The majority of carbonaceous emissions (99.9%, w/w) from small engines are gas-phase, as is the case among other source profiles reporting both gas- and particle-phase emission factors (Schauer et al., 1999a, b, 2002; Hays et al., 2002). For measured hydrocarbons, the relative distribution among compound classes is as follows: 31% aromatics, 23% branched alkanes, 13% *n*-alkanes, and 8% cycloalkanes. As expected, the VOC emissions are closely related to composition of the base fuel: 40% aromatics, 23% branched alkanes, 12% *n*-alkanes, and 7% cycloalkanes for summer-grade gasoline. Comparison of the C_3–C_{13} compounds present in the fuel to those in the exhaust revealed a strong correlation between fuel consumption and VOC emission rates ($R^2 = 0.87$). This relationship is shown graphically in Fig. 2 (for the approximately 100 compounds identified in both fuel and exhaust) and provides evidence of *scavenging losses* within these engines (Nuti, 1998). Scavenging losses, which are inherent to two-stroke engines, represent unburned or partially burned fuel that short circuits the cylinder during the exhaust/intake stroke and exits the engine before the next compression/power stroke begins. Although data are presented in Fig. 2 as an average emission factor for each species, similar patterns were seen between fuel consumption and exhaust emissions across all experimental conditions ($R^2 > 0.60$ for most compounds). The slope of Fig. 2 indicates that as much as 17% of the raw gas/oil fuel mixture may exit the engine in this manner. Mitigation of this loss mechanism will likely decrease hydrocarbon emission factors and increase energy efficiency.

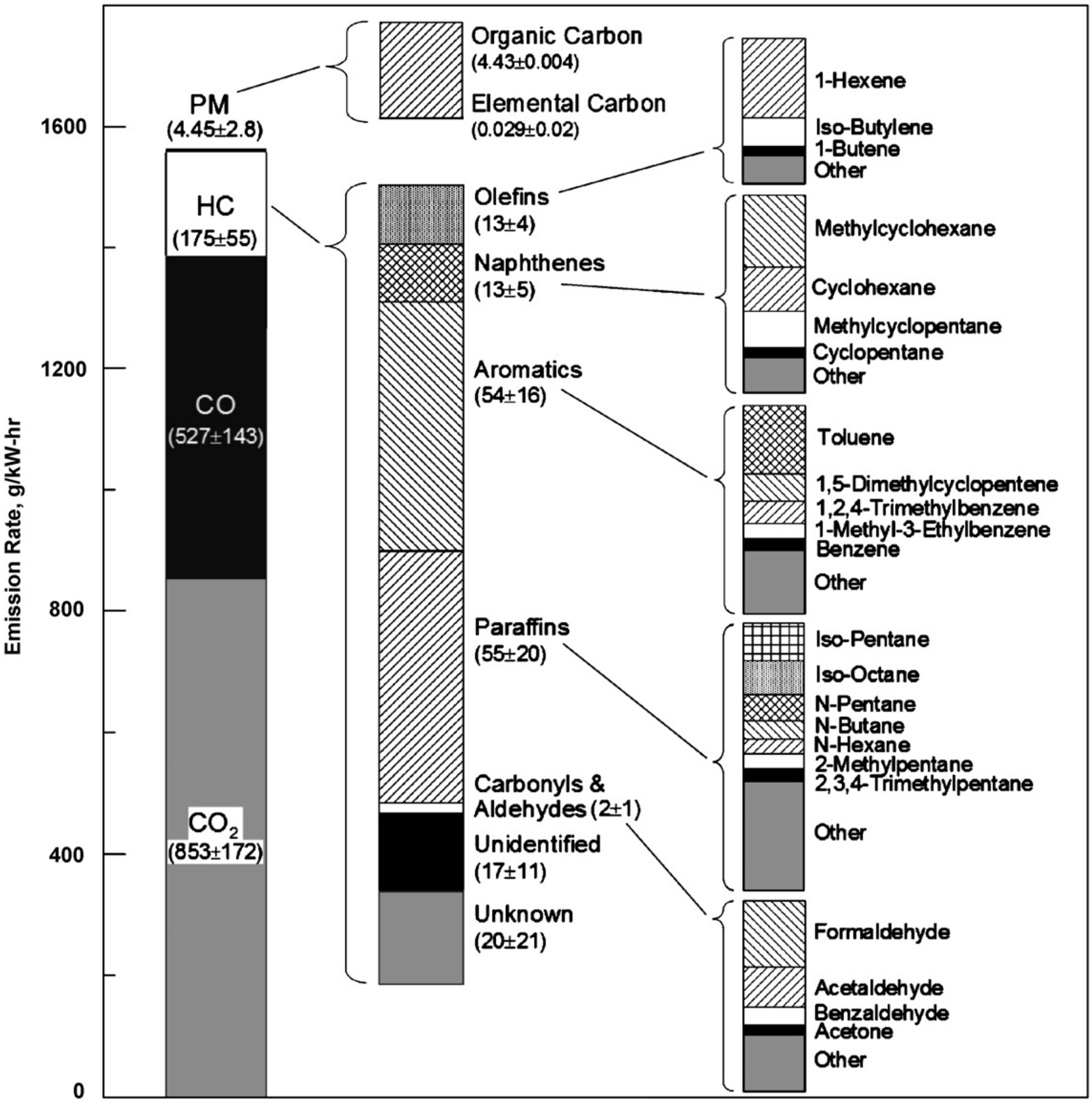

Fig. 1. Carbonaceous emissions from small engines organized by class and compound type. Values in parenthesis indicate the global average across all engines tested ± 1 S.D.

The hydrocarbon emissions are largely dominated by several compounds. For example, toluene emissions accounted for roughly 40% (w/w) of the gas-phase aromatics, *n*-pentane for 25% (w/w) of the *n*-alkanes, *iso*-pentane and *iso*-octane for 40% (w/w) of the branched alkanes, and 1-hexene for 80% (w/w) of the alkenes (Fig. 1). These five compounds represent approximately 50% of VOC species present in small engine exhaust.

Several olefinic compounds detected in the small engine exhaust were absent from the base fuel. These include 4 alkynes, 10 cycloalkenes, and 6 dienes (1,2-butadiene, 1,3-butadiene, 1,4-pentadiene, *cis*-1,3-pentadiene, cyclopentadiene, *trans*-1,3-pentadiene) comprising approximately 1% of the total hydrocarbon exhaust. Olefinic exhaust compounds that are not nascent to the fuel have been previously reported for catalyst-equipped gasoline motor vehicles (Schauer et al., 2002). The formation of olefins is of particular significance as several species (i.e., 1,3-butadiene) have known or suspected health effects (Henderson, 2001; Jackson et al., 2000). Past research has indicated that olefin formation may be caused by combustion of fuels containing alkenes (McEnally and Pfefferle, 2005)

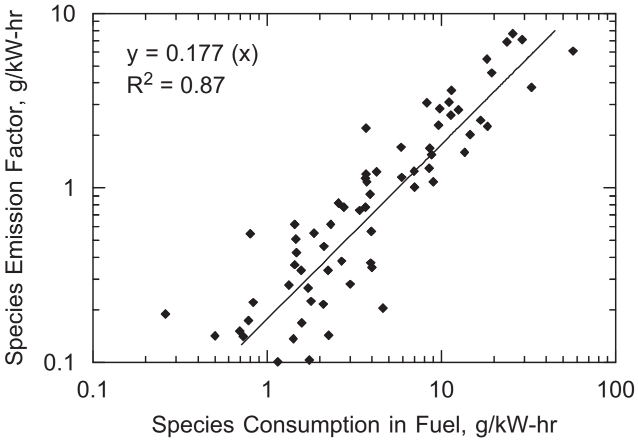

Fig. 2. Compound consumption rate (as fuel) vs. emission rate (as exhaust) for selected VOC compounds detected in the base gasoline fuel.

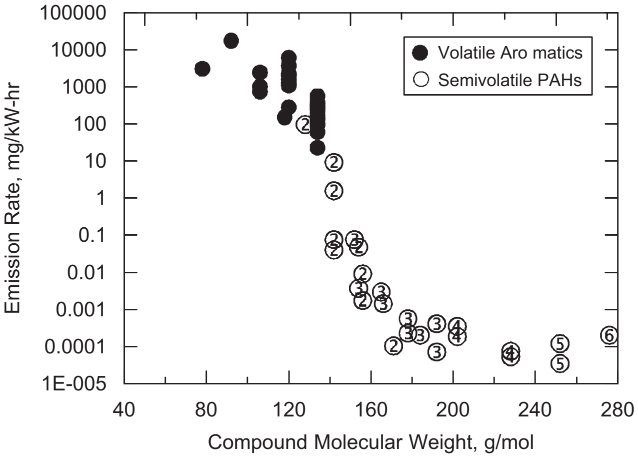

Fig. 3. Emission factors for volatile and semivolatile PAH compounds as a function of molecular weight. Numbers in open symbols represent the number of PAH rings present (sum of particle- and gas-phase).

and cycloalkanes (Hakansson et al., 2001), both of which were present in the two fuels tested.

A pattern evident from the test-averaged emission profiles shows that compound emission rates tend to decay exponentially with increasing compound molecular weight. This pattern is discerned from Fig. 3, showing average emission rates of volatile aromatics and semivolatile PAHs as a function of molecular weight. The plotted PAHs are semivolatiles distributed between the gas- and particle-phases (discussed in the following section), corresponding to low- and high-ring numbers, respectively. This result also confirms our earlier observation that gas-phase compounds dominate the overall emissions profile. Due to the numerous sampling artifacts associated with semi-volatile aerosol measurement (Turpin et al., 2000; Volckens and Leith, 2003), data from PUF and filter samples were combined together to represent total PAH emissions. The steepest decline in emissions falls somewhere between the 2- and 3-ring PAH structures. Only one 6-ring PAH was identified (indeno(1,2,3-*c*,*d*)pyrene); additional multi-ring, higher molecular weight PAHs were not detected.

3.3. Emissions of particle-phase compounds

Although particulate matter emissions from small engines are a minor component of the total mass (<0.1%, w/w), they are not insignificant. $PM_{2.5}$ emissions from small engines are roughly 10 times higher than those from light-duty automobiles (Volckens et al., 2007) and PAHs comprise approximately 5% of the $PM_{2.5}$ mass; these emissions may have important implications for human health and source apportionment.

As shown in Fig. 1, OC constitutes the vast majority of $PM_{2.5}$ emissions (>99.5%, w/w) with little variability (a factor of 1.2 was used to convert raw carbon counts to organic carbon mass). Some of the PM-derived OC is likely a result of direct emissions of unburned motor oil (i.e., a component of the fuel/oil scavenging loss) that volatilizes in the cylinder and recondenses into the particle-phase upon cooling. Other portions, such as the 4-6-ring PAH compounds, may be formed pyrolytically during combustion or may reside in the oil/fuel mix. Although black, or elemental carbon (EC) is a key component of radiative forcing and climate change (Andreae, 2001; Hansen et al., 2000), very little EC was detected in small engine PM.

Correction for the adsorption of gas-phase organics onto the quartz filters (OC subtraction from the quartz-behind-Teflon filter) resulted in an average OC reduction of approximately 20% per filter. After making this correction, excellent agreement was found between the gravimetric and thermo-optical measurement methods; the relative difference between total carbon (EC and an artifact-corrected OC) and PM mass were 4±2%, on average. Since only nanogram-level quantities of metals were detected via separate ICP-MS analyses, we conclude that the vast majority of small engine-derived PM is organic in nature.

3.4. Factors that affect emissions from small handheld engines

There are several engine design factors and details of operation that can help explain observed differences in the emission rates for the engines tested (e.g., engine displacement, oil–gas fuel mixture type and grade(s) burned, proportion of gas versus oil burned, control tier engine design or model year, and work load). We tried to obtain a wide variety of engines for this study to better characterize emissions, which afforded us the opportunity to examine changes in emissions as a function of several of these factors. Only the salient factors that significantly affected measured emission factors are discussed below.

The ANOVA determined that engine and control tier were significant variables ($p = 0.05$) for all compound classes and both gas- and particle-phases. In no case was the type of oil blend found to be a significant variable, accounting for $<5\%$ of the observed variation in emissions. Inter-engine variability (i.e., between engine) was assessed by comparing emissions between separate engines running on identical fuels, while intra-engine variability (within engine) was assessed by comparing the same engines across repeat tests. Inter-engine variability accounted for 67% of the observed variation in emissions, while intra-engine variability accounted for only 27%. Thus, the variability in emissions between different small engines is clearly more important than within the same engine, regardless of oil or fuel type, for the conditions tested in this study.

In addition, the highest emitting engines were all phase 1 (pre-2000 control phase). Although oil–gas fuel blend type generally has little effect on chemical species emission rates, one main exception to this pattern was increased aldehyde emissions when testing the oxygenated gasoline (approximately 10% ethanol). This is consistent with previous studies noting increased aldehyde emissions (especially formaldehyde and acetaldehyde) using ethanol-based fuels (Black et al., 1998; Knapp et al., 1998). Oxygenated fuel increased the average emission rates of acetaldehyde and valeraldehyde by $>300\%$ and 29%, respectively, and represented a statistically significant difference from the unleaded fuel exhaust emissions for these compounds. However, burning oxygenated fuel yielded average emissions increases of $<20\%$ for most other aldehyde forms.

3.5. Comparison to existing profiles

An objective of comparing emissions profiles is to evaluate whether small, handheld engines contribute to regional air quality relative to other sources. For example, small engine VOC emissions may contribute to the production of ground-level ozone and secondary aerosol formation. We constrain our comparative evaluation to petroleum-powered engines since such emissions will be most similar to the small handheld engines tested here. Given that numerous organic markers emitted from small engines are also motor vehicle markers (e.g., light molecular weight aromatics, olefins, and PAHs), such a comparison allows us to determine whether small engines have a confounding effect on source attribution in urban environments (Rogge et al., 1993).

There are numerous reports on the gas- and particle-phase organic and inorganic compounds in engine exhaust, covering the source testing of a variety of different gasoline- and diesel-powered engines found in light- and heavy-duty cars and trucks (Rogge et al., 1993; Schauer et al., 1999a, b, 2002; Hildemann et al., 1991; Siegl et al., 1999; Zielinska et al., 2004). Also available are aggregate vehicle emissions profiles estimated from on-road tunnel studies (Sawyer et al., 2000). Studies that measure only $PM_{2.5}$ mass or total hydrocarbons (Harley et al., 2005; Shi et al., 2000; Yanowitz et al., 2000) or focus on only a small number of chemical classes (Zielinska et al., 2004) are generally of limited use in source-receptor modeling and therefore disregarded in the following analysis.

Fig. 4 shows emissions of selected organic compounds from small engines compared with several other engines, including a two-stroke and four-stroke motorcycle engine (Tsai et al., 2003), a two-stroke outboard marine engine (Kado et al., 2000), a two-stroke chain saw (Magnusson et al., 2000), a catalyst-equipped gasoline-powered car (Schauer et al., 2002), and a medium-duty diesel truck (Schauer et al., 1999a, b). All profiles in Fig. 4 are given as a mass fraction of total gas- or particle-phase emissions (e.g., total VOC or PM mass) so that a common basis is used for comparisons. Although numerous source apportionment studies (Schauer and Cass, 2000; Schauer et al., 1996) use EC and OC as source markers, only source profiles from gasoline-powered cars (Schauer et al., 2002) and diesel trucks (Schauer et al., 1999a, b) report OC and EC and so these source markers were not used in this comparison.

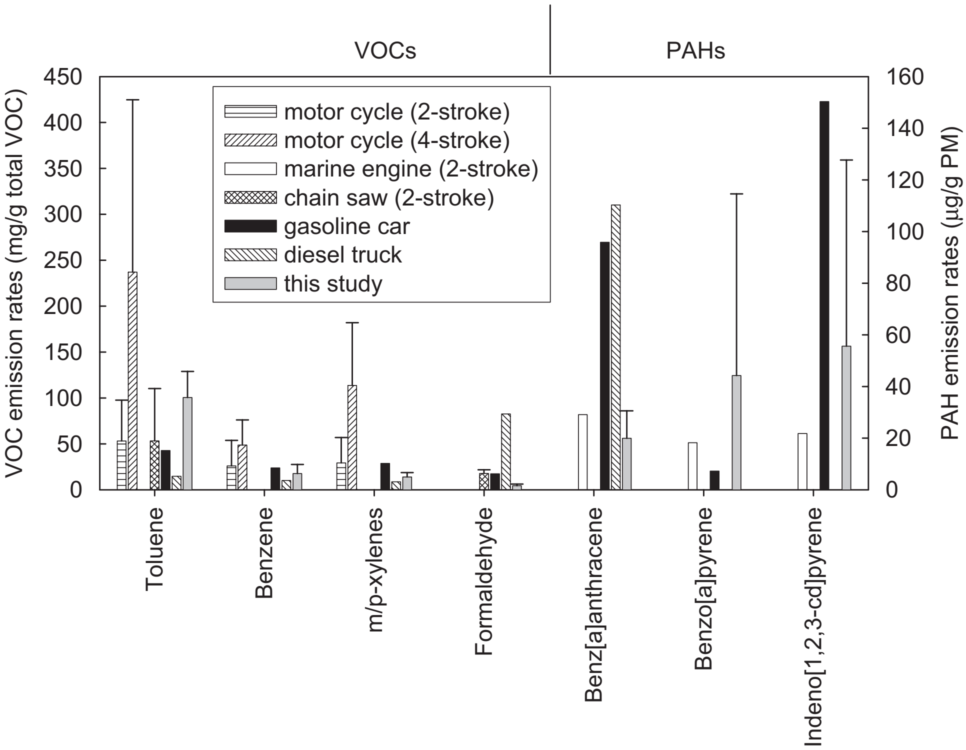

Fig. 4. Relative emission rates of select compounds as a function of source engine type.

For most of the compounds shown in Fig. 4, emission rates from small engines were generally intermediate in magnitude compared with other engines, although small engine emissions of PAHs (especially benzo[*a*]anthracene and indeno[1,2,3-*c*,*d*]pyrene) are among the highest. For source apportionment purposes, the overlap in PAHs shown in Fig. 4 may result in a commingling of these sources. The variability in emissions is not given for the other PAH sources as results from only one experiment were reported.

3.6. *Implications for source apportionment*

This study is one of the first to report the emission rates of both individual gas- and particle-phase organic compounds from small engines, and thus provides a potentially useful dataset for developing regional source-receptor models. One limitation of source emissions studies is that only a limited number of engines are tested, such that intra-source variability cannot be assessed. The comparatively large number of source tests completed for this study ($n = 48$) allowed us to assess both inter- and intra-engine variability.

Numerous source apportionment studies have identified motor vehicles as a major source of both VOCs and PM emissions in urban areas (Schauer and Cass, 2000; Schauer et al., 1996). Previous researchers have reported various techniques to better characterize motor vehicle emissions. Robinson et al. (2006) used ratio–ratio plots of various PAHs to compare ambient data and source profiles. For example, ratios of benzo(*g*,*h*,*i*)perylene/benzo[*e*]pyrene and indeno(1,2,3-*c*,*d*)pyrene/benzo[*e*]-pyrene typically range from between 0 and 5 for gasoline vehicles. Similarly, ratios of PAHs/benzo[*e*]pyrene for selected PAHs from the small engines in this study displayed ratios typically ranging between 0 and 10 (see box plot of PAH ratios; Fig. S1). Chang et al. (2006) reported five different alkanes (2,2-dimethylbutane, 3-methylpentane, methylcyclopentane, 2-methylhexane, and 3-methylhexane) that represented potential motor vehicle markers because of strong correlation with other known vehicle markers. All of these compounds are present in small engine emissions, constituting 12.8±2.3% of all paraffin emissions. Thus, small engines represent a potentially important emissions source being omitted typically from source apportionment studies. While the results discussed earlier in this section point to some differences in emission profiles between motor vehicle and small engines (especially between the distribution of gas- and particle-phase chemical classes), it is clear that numerous compounds traditionally viewed as motor vehicle markers (e.g., light molecular weight aromatics, olefins, and PAHs) are also present in small engine emissions. Future studies involving source apportionment of PM or VOCs should consider the effect of small engine emissions on ambient concentrations in urban and suburban environments as well as whether such emissions may be separated from those of larger gasoline and diesel-powered engines, since the majority of emitted compounds are chemically indistinguishable.

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Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.atmosenv.2007.10.032.

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