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Combustion-Related Organic Species in Temporally Resolved Urban Airborne Particulate Matter

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Abstract

Accurate characterization of the chemical composition of particulate matter (PM) is essential for improved understanding of source attribution and resultant health impacts. To explore this we conducted ambient monitoring of a suite of 15 combustion-related organic species in temporally resolved PM_{2.5} samples during an ongoing animal exposure study in a near source environment in Detroit, MI. All of the 15 species detected were above the method detection limit in 8 hour samples. This study focused on two molecular classes: Polycyclic Aromatic Hydrocarbons (PAHs) and Hopanes measured in samples. Of the 12 PAHs studied, benzo[b]fluoranthene (169 pg m⁻³), benzo[g,h,i]perylene (124 pg m⁻³), and benzo[e]pyrene (118, pg m⁻³) exhibited the three highest mean concentrations while 17 α (H),21 β (H)-Hopane (189 pg m⁻³) and 17 α (H),21 β (H)-30-Norhopane (145 pg m⁻³) had the highest mean concentrations of the 3 Hopanes analyzed in samples. Ratios of individual compound concentrations to total compound concentrations (15 compounds) showed the greatest daily variation for 17 α (H),21 β (H)-Hopane (11–28%) and 17 α (H),21 β (H)-30-Norhopane (8–20%). Diagnostic PAH concentration ratios ([IP]/[IP + BP] (range 0.30 – 0.45), [BaP]/[BaP+BeP] (range 0.26 – 0.44), [BaP]/[BP] (range 0.41 – 0.82), [Bb]/[Bk] (range 2.07 – 2.66), in samples reflected impacts from a mixture of combustion sources consistent with greater prevalence of petroleum combustion source emissions (gasoline, diesel, kerosene, and crude oil) compared to coal or wood combustion emissions impacts at this urban site. Results from this study demonstrate that short duration sampling for organic speciation provides temporally relevant exposure information.

Keywords

Particulate matter; PAH; Hopane; point source; mobile source; urban environment

Introduction

Particulate matter, (PM) is a complex heterogeneous mixture of particles and droplets including acids (sulfates, nitrates), soil, dust, trace metals, and carbon-based components (Chow et al. 2015). Atmospheric particles have long been recognized as a detriment to air

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quality (Larson et al. 1989), human health (Solomon et al. 2012), and climate (Boucher et al. 2013). In the U.S., PM mass is regulated by the Environmental Protection Agency according to size and air concentration and is subject to the National Ambient Air Quality Standards (NAAQS) (Chow et al. 2015). Spatial and temporal variability in the size, morphology, and chemical composition of PM in regions, counties and states across the U.S. is well-known (Solomon et al. 2012). It has been suggested that such variability may result in variation in health effects resulting from exposure to PM (Solomon et al. 2012). Currently important evidence is emerging regarding the association between exposure to organic carbon emissions and health effects (Solomon et al. 2012). Therefore, accurate characterization of the organic chemical composition of PM is crucial to epidemiological studies that seek to identify associations between exposure to such chemicals and resultant health effects.

Carbon is known to be a sizable (30 to 50%) component of PM_{2.5} mass concentration monitored at Supersites in the United States (U.S. EPA TTN 2017). The carbon fraction of PM_{2.5} is composed of elemental carbon, (EC) and organic carbon, (OC) fractions which are known to be released from various sources (fossil fuel combustion, meat cooking, biomass burning, and mobile sources) (Schauer et al. 1996) as well as produced in the atmosphere via chemical oxidation of gas phase precursors (Heo et al. 2013). Carbonaceous emissions have been associated with adverse respiratory, cardiac, mutagenic, and carcinogenic health outcomes (Solomon et al. 2012). In particular, the OC component, which is much larger than the EC component (Solomon et al. 2012), consists of both primary (POA) and secondary (SOA) organic aerosols (Lewandowski et al. 2008; Heo et al., 2013).

Organic aerosols are diverse compounds of varying density, volatility, polarity, functional groups, aromaticity, and reactivity. Compared to knowledge regarding inorganic species in PM_{2.5}, there are still considerable knowledge gaps regarding organic speciation in carbonaceous aerosols. Characterization of specific compounds in carbonaceous aerosols will help inform in addition to facilitating further understanding of source-to-receptor pathways that lead to adverse health effects. Increased insight will furnish information to policy makers as they implement remediation strategies to ensure attainment with the NAAQS for PM.

The objective of this study was to quantify a selected suite of combustion-related organic compounds (polycyclic aromatic hydrocarbons (PAHs), and Hopanes) in airborne fine particulate matter (PM_{2.5}) collected during a whole-body air pollution inhalation study on rats (Sun et al. 2013) at an urban site known to be impacted by industrial emissions as well as mobile sources. This monitoring site located near southwest Detroit is known to have the highest PM_{2.5} levels in the state of Michigan because of its proximity to a variety of point and mobile sources (Michigan DEQ, 2011). PM levels in this area of Detroit have been demonstrated to adversely impact respiratory health in children and animal models (Lewis et al. 2013; Morishita et al. 2004), as well as cardiovascular health in adults and animal models (Morishita et al. 2015; Sun et al. 2013; Wagner et al. 2014). Previous characterizations of PM_{2.5} concentrations and the identification of responsible emission sources in southwest Detroit have been carried out (Gildemeister et al. 2007; Hammond et al. 2008; Pancras et al. 2013). These studies reported that southwest Detroit experiences impacts from both regional and local emission sources. They concluded that combustion point sources (oil and coal),

iron and steel production, and mobile sources (vehicles) were more correlated with local emissions and consistent with known locations of oil refineries, coal-fired utilities, integrated steel mills and two major interstate highways in southwest Detroit.

Recently, organic species were measured in the near-road exposures and effects of urban air pollutants (NEXUS) study in Detroit (Vette et al., 2013). PAH levels in concentrated air particles, (CAPS) were monitored at the Dearborn Chemical Speciation Network, (CSN), site (Morishita et al. 2009). However, many previous studies of species have used 24-hour sampling approaches (Schauer et al. 1996; Vasilakos et al. 2007; Bi et al. 2008; Giri et al. 2013; Heo et al. 2013; Kmal et al. 2013; Wiriya et al. 2013; Górka et al. 2014; Wang et al. 2016). In support of the 8-hr duration of animal whole-body inhalation exposures conducted at the site (Sun et al. 2013), the current study utilized 8-hour integrated exposure characterization. Sun et al. 2013 reported significantly higher levels of markers of inflammation and oxidative stress during exposure periods with higher levels of PM_{2.5} mass and the organic carbon fraction of PM_{2.5}. Therefore in an attempt to investigate speciation of the combustion-related organic fraction as well as the potential impact of specific emission sources during the study period, this manuscript provides the first characterization of two molecular classes of compounds, PAHs (12) and Hopanes (3), in short-duration (8-hour) PM_{2.5} samples collected in a near-source urban environment.

Our intent in collecting samples of eight-hour duration was to accurately capture the variation in combustion-related organic compound concentrations in the ambient air during an animal exposure study that was also occurring at the same time at this sampling site (Sun et al. 2013; Wagner et al. 2014). The animal exposure study used a rodent model to investigate the human health effects of exposure to complex mixtures of pollutants in an urban environment. Furthermore, our monitoring effort was not in support of regulatory measures where daily (i.e. 10224 hour) sampling is required. Longer sampling times may obscure the temporal resolution of maximum exposures and impacts of source emissions, thus constraining further insight regarding associations between sources of emissions and resultant health effects. The compounds that we characterized in these short duration samples are representative tracers diagnostic for combustion emissions especially traffic related exhaust. Exposure to traffic related exhaust specifically has been demonstrated to cause adverse respiratory and cardiovascular health outcomes (Solomon et al. 2012).

Materials and methods

Study site

The Dearborn, Michigan air monitoring site (42.3075°N, 83.1496°W) was located in a mixed industrial, commercial, residential area containing multiple point sources of PM_{2.5} emissions, the largest of which are iron and steel production (522,538 Kg year⁻¹), oil refining (71,668 Kg year⁻¹), and electric power generation (63,530 Kg year⁻¹) as reported in the 2011 National Emissions Inventory (U.S. EPA NEI, 2011). Mobile sources arise from traffic on interstates 94 and 75 located to the south and 96 located to the north. Heavy-duty truck depots and service railroad traffic also contribute to the air pollution. This study was conducted concurrent with a whole-body air pollution inhalation study on rats at the site during this time (Sun et al. 2013; Wagner et al. 2014).

A map (Figure S1) shows there are nine major PM sources (U.S. EPA120NEI, 2011) within 5 km of the study site.

Sampling Technique

Integrated 8-hr PM_{2.5} samples (7:30 am –3:30 pm) were collected on selected days over a 4-week period (July 26th –August 25th, 2011) using a TISCH Environmental (Clevs, OH) Model TE-1241000 sampler. We utilized identical sampling durations and sampling days in support of and to be concurrent with an animal inhalation exposure also occurring at the site during this time and described in Wagner et al., 2014. That study conducted inhalation exposures for eight hours per day on selected weekdays using protocols approved by the Association for Assessment and Accreditation of Laboratory Animal Care (AAALAC) (Wagner et al. 2014). Weekly flow checks were conducted using a National Institute of Standards and Technology (NIST) traceable (BGI, Inc, Butler, NJ) Delta primary flow calibrator, and a nominal flow rate of 250 liters per minute (LPM) was used to calculate concentrations collected on filters. A total of 17 PM_{2.5} samples and 2 field blanks were collected on Pall Corporation (Port Washington, NY) 102-mm diameter quartz fiber filters.

In preparation for sample collection the filters were prebaked at 550°C in a muffle furnace for four hours. Upon removal from the furnace the filters were cooled under chromatographic grade helium in a stainless steel chamber, packed in prebaked aluminum foil, and stored in a laboratory freezer at –30°C. Filters were shipped to the field in aluminum foil for deployment. After sampling, filters were sealed in aluminum foil and stored in a laboratory freezer until shipped back to EPA for analysis.

Sample Preparation and Analysis

Samples, field blanks, and laboratory blanks were spiked with deuterium labelled surrogates to monitor extraction efficiency. Sample filters collected at the Dearborn site were extracted in equal volumes (1:1:1) of dichloromethane, hexane and methanol using a Dionex (Sunnyvale, CA) Model ASE 200 Accelerated Solvent Extractor. A Zymark (Portland, OR) TurboVap Evaporator was used to concentrate samples to 0.2 mL using nitrogen purge gas. Extracts were subsequently subjected to solid phase extraction (SPE) on silica gel sorbent cartridges with a 1% acetone + 1% dichloromethane in hexane eluent. The SPE eluates were further purged with nitrogen to a volume of 0.1 mL and spiked with deuterium labelled internal standards. Prior to GC-MS analysis, the SPE eluates were diluted to 0.3 mL with dichloromethane.

Organic compounds in the extracts were analyzed by gas chromatography-mass spectrometry, GC-MS, using a Hewlett Packard model 6890 GC and Hewlett Packard model 5973 MSD (Mass Selective Detector, MSD) equipped with an inert ion source. During GC operation, pressure pulsed (30 psi) splitless injections and a pulse hold time of 0.5 min were implemented to assure that samples were transferred with minimized molecular weight discrimination. Sample volumes of 1.0 µl were injected into the inlet (temperature at 300°C) with a split time of 0.75 min using an Agilent (Santa Clara, CA) single-taper, deactivated inlet liner (part # 5181–3316) without glass wool. The interface temperature was set to

315°C while source and quadrupole temperatures were set to 300°C and 200°C, respectively. The MSD was run in selective ion mode (SIM) for optimal sensitivity and detection. An Agilent J&W DB-17 (50%-phenyl)-methylpolysiloxane mid polarity capillary column with a 0.25 mm inner diameter and 0.25 µm film thickness was used to separate the organic source markers in the eluate. The helium carrier gas flow rate was 1.0 mL min⁻¹ during GC operation. The GC temperature program ramp was 45°C for 1 min; to 225°C at 20°C/min hold 1 min; to 310°C at 2°C min⁻¹ hold 20 min.

Materials and Supplies

Chemical materials used in the preparation of calibration, surrogate, internal standard, quality control, and matrix spike solutions were purchased from Absolute Standards, AccuStandard, Chiron and the National Institute of Standards and Technology (NIST). GC² or high purity grade organic solvents were acquired from Honeywell Burdick and Jackson (Morris Plains, NJ) for all solution preparations, extractions, and SPE cleanup procedures.

Calibration and Quality Control

Internal standard calibration curves ranging from 5–200 pg µL⁻¹ were established, in triplicate, for the 12 PAHs, and 3 Hopane isomers using HP ChemStation software. Calibration curves, continuing calibration verification checks, and quality control (QC) solution evaluation procedures used were identical to those previously described (Turlington et al. 2010).

Ancillary Data

Hourly meteorological data and hourly ambient organic carbon concentration data from the Dearborn site were obtained from the Michigan Department of Environmental Quality, (MDEQ) (www.michigan.gov/deq, Sun et al., 2013). Ambient organic carbon concentrations were measured using a semi-continuous OC-EC field analyzer (Sunset Laboratory, Tigard, OR, USA)

Statistical Analysis

Data processing and all statistical analyses were performed using R statistical software (Rversion 3.2.2).

Results

Organic Compound Concentrations in Particulate Samples

Samples were analyzed for a suite of 15 combustion-related organic species . Method detection limit, (MDL), and percentage of samples above the MDL are provided in Table 1. All samples were above the MDL consistent with previous observations at sites in urban Detroit (Vette et al. 2013). Levels of organic species in field blanks were mostly non detectable. However, chrysene, benzo[b]fluoranthene, benzo[e]pyrene, 17α(H),21β(H)-Hopane, 17α(H),21β(H)-22S-Homohopane, indeno[1,2,3]pyrene, and benzo[g,h,i]perylene were sometimes detected in field blanks. For those compounds that were detected in blank filters, sample concentrations were a factor to 9 to 500 times greater than concentrations in

field blanks as shown by the range of sample/field blank concentrations in Table 1, and, therefore, no blank subtraction was deemed necessary.

Summary statistics as well as number of carbon atoms and number of rings for organic compounds are provided in Table 2. Overall, concentrations in 8-hour samples varied over two orders of magnitude in both PAH and Hopane compounds. For the PAH compounds, benzo[b]fluoranthene (447 pg m^{-3}), benzo[g,h,i]perylene (373 pg m^{-3}), and benzo[e]pyrene (303 pg m^{-3}) exhibited the three highest maximum concentrations. For the Hopanes, 17 α (H),21 β (H)-Hopane (452 pg m^{-3}) and 17 α (H),21 β (H)-22S-Homohopane (286 pg m^{-3}) displayed the highest and second highest maximum concentrations, respectively. Many of these 15 compounds have been previously detected in ambient samples at urban monitoring sites worldwide (Vasilakos et al. 2007; He et al. 2008; Olson et al. 2009; Piletic et al. 2013; Giri et al. 2013; K $\ddot{u}$ mal et al. 2013; G $\acute{o}$ rka et al. 2014; Wiriya et al. 2013; Wang et al. 2015; Wang et al. 2016), residential indoor and outdoor samples (Olson et al. 2008), near-roadway samples (Turlington et al. 2010), concentrated ambient particles, CAPS, (Morishita et al., 2009), and on-roadway in-vehicle cabin samples (Greenwald et al., 2014). Mean concentrations (8-hour) for PAH's were similar to those reported for daily DEARS study samples (Turlington et al. 2010) but considerably lower than daily samples collected in suburban Athens, Greece (Vasilakos et al. 2007). Mean concentrations for the three Hopane compounds ranged from 117 to 189 pg m^{-3} and were of similar magnitude to daily DEARS study samples (110–150 pg m^{-3}) collected at the CSN Trends site in Allen Park, Detroit in Feb-March 2005 (Turlington et al. 2010). Compared to measurements made in Guangzhou, China (Wang et al. 2016) and in Brno, Czech Republic (K $\ddot{u}$ mal et al. 2013), maximum concentrations of 17 α (H),21 β (H)-30-Norhopane and 17 α (H),21 β (H)-Hopane observed in the 8-hour samples in Dearborn were generally lower by a factor of 2. However the maximum concentration of 17 α (H),21 β (H)-22S-Homohopane in Brno was a factor of 17 higher compared to Dearborn, MI.

Previous studies in other Midwestern U.S. cities have examined primary and secondary organic carbon contributions to PM_{2.5} (Lewandowski et al. 2008; Piletic et al. 2013). Piletic et al. 2013 reported PAH and Hopane concentrations measured at an urban site (G.T. Craig site in downtown) and rural site (Chippewa Lake in Medina County) during the Cleveland Multiple Air Pollutant Study, CMAPS in 2009. In Dearborn, average 2011 summertime PAH (12 compounds) and Hopane (3 compounds) concentrations were a factor of 3.5 and 1.9 higher, respectively, compared to those in urban Cleveland in 2011, (Table 3). One reason for this difference may be due to the fact that the Cleveland samples were collected over a 24-hour period while those collected in Dearborn were collected over an 8-hour period. Average OC concentrations were higher in Dearborn, $4.40 \text{ } \mu\text{g m}^{-3}$ vs $2.6 \text{ } \mu\text{g m}^{-3}$ in Cleveland (Table 3) (Piletic et al., 2013), the ratio of PAH/OC was higher in Dearborn compared to Cleveland but the ratio of Hopanes/OC was the same at both sites. Weighted annual mean PM_{2.5} concentrations for Cleveland and Dearborn sites tend to be similar e.g. in 2011 they were 12.2 and 11.2 $\mu\text{g m}^{-3}$, respectively (U.S. EPA Airdata). A recession in 2009 resulted in lower industrial output from a steel mill in downtown Cleveland (Lynam et al. 2016) and may explain why a lower PAH/OC ratio was observed in Cleveland, OH compared to Dearborn, MI in 2011.

Elsewhere, concentrations of many of these organic species have been measured in PM (Table 4). Minimum concentration in our short-duration samples tended to be lower compared to PM samples from China, India, Poland, Czech Republic and Thailand (Wang et al. 2016; Giri et al. 2013; Górka et al. 2014; Kmal et al. 2013; Wiriya et al. 2013). Maximum concentration measured in Dearborn were also lower with the exception of benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[e]fluoranthene and Dibenz[a,h]anthracene which were higher compared to concentrations reported for PM in Raipur, India (Giri et al. 2013).

Daily Variation in Organic Compound Concentrations

Figure 1a is a stacked plot showing how organic compound concentrations in atmospheric samples vary over the four weeks of this study. The three highest organic concentrations (15 compounds) in samples occurred during weeks 1 (2824 pg m⁻³, 1590 pg m⁻³) and 3 (1836 pg m⁻³). While day-to-day variability was observed for individual compounds, maximum concentrations for some including 3-methyl chrysene, perylene, dibenz[a,h]anthracene, and picene were below 50 pg m⁻³. Maximum concentrations above 300 pg m⁻³ were observed for benzo[b]fluoranthene, benzo[e]pyrene, 17α(H),21β(H)-Hopane, and benzo[g,h,i]perylene.

Ratios of individual compound concentrations to total compound concentrations (15 compounds), for 3-methyl chrysene, perylene, dibenz[a,h]anthracene, and picene revealed little daily variation (~2%) as seen in Figure 1b. In contrast, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, benzo[g,h,i]perylene, and coronene ratios exhibited larger daily variation ranging from 4 to 17%. The largest daily variation was observed for 17α(H),21β(H)-Hopane (11–28%) and 17α(H),21β(H)-30-Norhopane (8–20%) ratios.

Using aerosol samples collected from gas and diesel-powered vehicle exhausts Rogge et al. quantified PAHs and Hopanes as fossil petroleum markers and identified them as suitable tracer compounds for vehicular sources to the atmosphere (Rogge et al. 1993). Mobile emissions from gasoline and diesel engines have slightly different fingerprints, e.g. fluoranthene, pyrene, and chrysenes are markers of diesel combustion (Landis et al. 2007; Vette et al. 2013). Low molecular weight PAHs (4–7 rings) have also been attributed to urban primary sources such as cooking emissions, mobile source exhaust, and some combustion sources whereas Hopanes were attributed to vehicle exhausts (Olson et al. 2009) and coal combustion sources (He et al. 2008; Kmal et al. 2013; Wang et al. 2016). Studies on distributions of organic constituents in coal smoke particulate matter have identified picene as a molecular marker for coal smoke emissions (Oros et al. 2000). Picene has also been found in emissions from uncontrolled combustion of shredded tires in a landfill (Downard et al. 2015).

Possible Sources of Organic Compounds in Dearborn, MI

Previous source apportionment analyses using data from 24-hour integrated PM_{2.5} samples collected in southwest Detroit (Hammond et al. 2008) and the Dearborn CSN site (Gildemeister et al. 2007) identified both regional and local source impacts. Secondary

sulfate and secondary nitrate were ascribed to regional sources, while local sources impacts were attributed to point (coal/oil combustion, iron and steel production) and mobile source emissions (gasoline, diesel combustion). A later study collected hourly PM_{2.5} chemical composition data at the Dearborn CSN site which were used in Positive Matrix Factorization (PMF) and Unmix models to apportion sources of inorganic PM_{2.5}. Both regional (sulfate and nitrate) and local (iron and steel production, coal and oil combustion, oil refining, motor vehicles road dust, incineration) source impacts to the receptor site were identified (Pancras et al. 2013). Organic species were not measured at the Dearborn CSN site in these previous studies, this study is the first to do so, but due to the overarching animal exposure study design, the number of samples collected was not sufficient to facilitate source apportionment analysis. We use meteorology, PM_{2.5} mass concentrations, emissions data, and PAH ratios to rationalize the probable sources of the organic source markers observed in our short duration samples.

Figure 2 is a pollution rose plot of hourly PM_{2.5} mass concentrations at the Dearborn site during this study. The highest PM_{2.5} mass concentrations ($\sim 30 \mu\text{g m}^{-3}$) occurred predominantly in the 180 – 230° wind sector, while PM_{2.5} mass concentrations $\sim 25 \mu\text{g m}^{-3}$ were observed over a wider wind sector range (70 – 270 °C). The 2011 NEI, (U.S. EPA 2011) report shows that the two largest sources of PM_{2.5} emissions (321,143 and 201,395 Kg year⁻¹, respectively) in Wayne County where the Dearborn site is located, were from two integrated iron and steel production facilities. These largest emissions are from facilities approximately 4 km southeast, and 0.6 km southwest of the monitoring site. Other large point sources of PM_{2.5} emissions in the inventory were from oil refining (65,318 Kg year⁻¹) and fossil fuel combustion electricity generation (56,246 Kg year⁻¹). Those facilities are located 3 km south and 0.6 km southwest of the monitoring site. Thus, based on the frequency of the wind directions during the study and documented PM_{2.5} point source emissions inventories, local PM_{2.5} emissions would be transported to the Dearborn site.

Mobile and fugitive source impacts would also be expected given the location of the Dearborn site, approximately 4 km north of the Fisher Freeway (Interstate 75) and approximately 2 km south east of the Edsel Ford Freeway (Interstate 94). The Michigan Department of Transportation, Traffic Monitoring Information System estimates that in 2011, annual average daily traffic volumes (AADT) were ~95,000 vehicles and 90,000, respectively, on those sections of I-75 and I-94 that are in the vicinity of the monitoring site (Michigan DOT, 2011). For both I-75 and I-94 Commercial Annual Average Daily Traffic (CAADT) was reported to be ~10,500 vehicles, each, on the same sections. Furthermore, the Ambassador Bridge, the busiest U.S./Canadian border crossing (~10,000 trucks and 4,000 cars daily) is located 6 km east of the site. Border crossings are notorious for congestion causing idling of truck and automobile engines and the potential for considerable mobile emissions and resultant air pollution hot spots (Morishita et al. 2015). The pollution rose shows some minor contributions to PM_{2.5} mass concentration in the 0 to 90° wind sectors and may be indicative of mobile source emissions from the Ambassador Bridge that are transported to the site with easterly flow.

The origins of PAHs found in environmental samples can be evaluated through a comparison of PAH concentration ratios calculated from well-identified contributions (parent PAHs) and

the same concentration ratios in samples. Previously, ratios of PAH concentrations in aerosols have been utilized for qualitative and quantitative characterization of sources (Gogou et al. 1996; Yunker et al. 2002; Vasilakos et al. 2007; Kmal et al. 2013; Wiriya et al. 2013; Górka et al. 2014; Wang et al. 2015; Wang et al. 2016).

In particular, the ratio of indeno[1,2,3-cd]pyrene, (IP), to indeno[1,2,3-cd]pyrene plus benzo[g,h,i] perylene, (BP), has been identified as definitive in distinguishing among petroleum fractions, single-source combustion products (gasoline, diesel, wood, wood soot, grasses), and environmental samples (Yunker et al., 2002, Gogou et al., 1996, Vasilakos et al., 2007, Kmal et al. 2013; Górka et al. 2014; Wang et al. 2015; Wang et al. 2016). Reported literature values for this ratio show that on average, a value < 0.2 implies an unburned petroleum source, while liquid fossil fuel (gasoline, diesel, and crude oil) combustion products are > 0.2 and < 0.5 and wood and coal combustion products have values > 0.5 (Gogou et al. 1996; Yunker et al. 2002; Vasilakos et al. 2007; Kmal et al. 2013; Górka et al. 2014; Wang et al. 2015; Wang et al. 2016). The [IP]/[IP+BP] ratio in daily Dearborn PM_{2.5} samples, (Figure 3), shows little daily variation among samples with the average ratio 0.40 and the range of ratios 0.30 – 0.45. Urban aerosol samples collected during the warm season in Greece had mean values of 0.46 and 0.41 at two different suburban monitoring locations (Vasilakos et al. 2007). Others have reported average summer values for this ratio in aerosol samples to be 0.48 in Sanya, China, (Wang et al. 2015), 0.58 in Guangzhou, China (Wang et al. 2016), 0.51 and 0.63 in Brno, Czech Republic, (Kmal et al. 2013), 0.52 and 0.67 in Šlapanice, Czech Republic, (Kmal et al. 2013) and 0.41 in Wrocław, Poland (Górka et al. 2014), (Table 5). NIST urban particulate matter standard reference material (SRM #1648) and urban dust (SRM #1649a) had similar ratios (Wise et al. 1988). The [IP]/[IP+BP] ratio for trucks and gasoline vehicle emissions has been reported to be in the range of 0.2 – 0.4 (Miguel et al. 1998; Marr et al., 1999). The [IP]/[IP+BP] ratios observed in our samples reflect that source impacts most likely from combustion of petroleum (gasoline and diesel) are dominant at this urban site.

Benzo[a]pyrene (BaP) and benzo[e]pyrene (BeP) are usually present in the same amounts in fresh exhaust emissions but benzo[a]pyrene is more reactive and can react with oxidants or undergo photolysis (Bi et al. 2003). The [BaP]/[BaP+BeP] ratio has been used as an indicator of ageing of particles (Oliveira et al. 2011), with values less than 0.5 indicative of ageing in particles. The variation of the [BaP]/[BaP+BeP] in our samples is shown in Figure 3, the average value was 0.37, suggesting ageing of particles sampled at Dearborn. Wang has reported a summertime [BaP]/[BaP+BeP] aerosol ratio of 0.5 in Sanya, China (Wang et al. 2015) (Table 5). Others have reported summertime [BeP]/[BeP+BaP] ratios of 0.51, 0.54 in Brno, Czech Republic, (Kmal et al. 2013), 0.50, 0.54, in Stepanice, Czech Republic, (Kmal et al. 2013) and 0.62 in Wrocław, Poland (Górka et al. 2014) (Table 5). Ratios in our samples indicate the presence of secondary particles formed from primary traffic exhaust emissions.

The Benzo[a]pyrene to Benzo[ghi]perylene, [BaP]/[BP], ratio has been proposed to be an indicator of traffic emissions (Katsoyiannis et al. 2011) where a ratio of 0.6 or above indicates traffic emissions and below indicates non traffic emissions. In our study the ratio varied from 0.41 to 0.82 and the average ratio in our samples was 0.61. Average summertime

ratios reported for aerosols reported collected at other locations were above 0.6, e.g. 1.1 in Guangzhou, China (Wang et al. 2016), 0.85 and 1.80 in Brno, Czech Republic, (Kmal et al. 2013), 0.84 and 2.58 in Stepanice, Czech Republic, (Kmal et al. 2013) (Table 5). In our samples this ratio exhibited the greatest variability suggesting that on certain days e.g. July 27th and August 16th, 2011 when the ratios were 0.82 and 0.84, respectively, traffic emissions sources were more dominant in our samples compared to other days. A (Benzo[b]fluoranthene /Benzo[k]fluoranthene), [Bb]/[Bk] , ratio > 0.5 has been reported to be diagnostic for diesel emissions (Ravindra et al. 2008). The average ratio in samples collected in this study was 2.63 whereas it was reported to be 0.84 for aerosols sampled in Guizhou, China (Wang et al. 2016) suggesting the importance of impacts from vehicle emission sources in our samples.

Contribution of this Study to Further Characterization of Organic Carbon in the Urban Environment

The results of the present study provide confirmation regarding the quantification of atmospheric levels of organic carbon that are comparable to previous observations in numerous urban airsheds (Schauer et al. 1996; Vasilakos et al. 2007; Gildemeister et al. 2007; Lewandowski et al. 2008; Olson et al. 2009; Heo et al. 2013; Pancras et al. 2013; Vette et al. 2013; Piletcic et al. 2013; Morishita et al. 2015). However, these previous studies were of a longer sample duration (typically 24 hours), or no quantification of organic speciation during health exposure studies was reported. Since results obtained from 24-hour integrated samples may not be accurate representations of ambient air during the shorter timescales of some animal and human exposure studies (Morishita et al. 2015), our results improve previous knowledge by reporting new temporally-relevant exposure information on organic speciation in short-duration PM_{2.5} samples, and can be used to further understand source-to-receptor pathways in near-source urban environments. Analysis using this speciated data in combination with meteorology, emissions data from the NEI, and diagnostic PAH concentration ratios ([IP]/[IP+BP], [BaP]/[BaP+BeP], [BaP]/[BP]) corroborates evidence for combustion impacts especially from traffic-related sources during the study at a near-source urban location.

Conclusions

Results from this 4-week study of short duration (8-hr) PM_{2.5} samples collected at an urban receptor site have identified and quantified two molecular classes of combustion-related organic compounds (12 PAHs and 3 Hopanes) that were above the detection limit in all samples. The Hopane compounds found in these short-duration samples are tracers for POAs and provide evidence that during the 8-hr sampling period (7:30am – 3:30 pm) there is a significant impact from petroleum combustion in the urban environment where many people live. The additional knowledge provided by organic speciation measurements over exposure-relevant time scales may enhance and assist with the design of future source apportionment, as well as exposure and health studies carried out within near-source urban environments.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1a.

Daily variation in organic source marker compound concentrations at the Dearborn, MI CSN site, July 26-August 25, 2011. Norhopane, Hopane and Homohopane refer to 17 α (H), 21 β (H)-30-Norhopane (C29), 17 α (H),21 β (H)-Hopane (C30) and 17 α (H),21 β (H)-22S-Homohopane (C31), respectively. **1b** Concentration ratios, individual/ Σ 15 compounds, in percentages, in short-duration PM_{2.5} samples collected in Dearborn, MI July 26 - August 25, 2011. Norhopane, Hopane and Homohopane refer to 17 α (H),21 β (H)-30-Norhopane (C29), 17 α (H),21 β (H)-Hopane (C30) and 17 α (H),21 β (H)-22S-Homohopane (C31), respectively

Fig. 2.
PM_{2.5} pollution rose at the CSN site in Dearborn, Michigan during sampling for organic source markers in short-duration samples, July 26 - August 25, 2011

Fig. 3.

PAH ratios in samples collected in Dearborn, MI, July 26-Aug 25, 2011. BaP = Benzo[a]pyrene, BeP = Benzo[e]pyrene, IP = Indeno[1,2,3-cd]pyrene, BP = Benzo[g,h,i]perylene, Bb = Benzo[b]fluoranthene, Bk = Benzo[k]fluoranthene

Table 1

Method Detection Limit, MDL, (pg m^{-3}), percent of samples above the MDL and sample to blank concentration ratio in short duration $\text{PM}_{2.5}$ samples collected in Dearborn, MI July 26-August 25, 2011

Organic Compound	Method Detection Limit, MDL	% Samples above MDL	[Sample]/[Blank]
Chrysene	0.50	100	68–456
3-Methyl Chrysene	0.31	100	-
Benzo[b]fluoranthene	0.69	100	41–380
Benzo[k]fluoranthene	1.0	100	-
Benzo[e]pyrene	0.76	100	32–291
Benzo[a]pyrene	0.66	100	-
Perylene	0.82	100	-
17 α (H),21 β (H)-30-Norhopane	5.1	100	-
17 α (H),21 β (H)-Hopane	4.5	100	28–138
17 α (H),21 β (H)-22S-Homohopane	9.6	100	24–127
Indeno[1,2,3-cd]pyrene	2.0	100	9–103
Benzo[g,h,i]perylene	0.47	100	39–461
Dibenz[a,h]anthracene	1.1	100	-
Picene	1.2	100	-
Coronene	0.72	100	-

Table 2

Summary statistics for PAH and Hopane concentrations (pg m^{-3}) in short duration $\text{PM}_{2.5}$ samples collected in Dearborn, MI July 26 - August 25, 2011

PAH(# of Carbons)	Mean	Std. Dev.	Median	Min	Max	Rings
Chrysene (C18)	91	47	83	34	227	4
3-Methyl Chrysene (C19)	9.1	3.4	8.0	5.5	18	4
Benzo[b]fluoranthene (C20)	169	88	150	49	447	5
Benzo[k]fluoranthene (C20)	72	38	63	21	188	5
Benzo[a]pyrene (C20)	73	43	65	20	193	5
Benzo[e]pyrene (C20)	118	59	104	33	303	5
Perylene (C20)	17	10	15	4.9	48	5
Indeno[1,2,3-cd]pyrene (C22)	82	50	77	22	245	6
Benzo[g,h,i]perylene (C22)	124	79	103	31	373	6
Dibenz[a,h]anthracene (C22)	17	10	16	4.7	48	5
Picene (C22)	12	7.1	11	3.4	35	5
Coronene (C24)	43	32	35	12	141	7
HOPANES						
17 α (H),21 β (H)-30-Norhopane (C29)	145	52	137	69	256	5
17 α (H),21 β (H)-Hopane (C30)	189	90	183	88	452	5
17 α (H),21 β (H)-22S-Homohopane (C31)	117	61	104	53	286	5

Table 3

Comparison of average PAH and Hopane concentrations (pg m^{-3}) in $\text{PM}_{2.5}$ samples collected in Dearborn, MI, July 26 – August 25th, 2011 (this study) and Cleveland, OH (data from Piletic et al., 2013)

Study Site	Average PAH Concentration (pg m^{-3})	Average Hopane Concentration (pg m^{-3})	Average OC Concentration ($\mu\text{g m}^{-3}$)	Sample Duration	Study Dates
Dearborn, MI (N = 17)	830	450	4.40 ^a	8 hours	July – August, 2011
Cleveland, OH (urban site) (N = 31)	240	240	2.26 ^b	24 hours	July – August, 2009
Cleveland, OH (rural site) (N = 31)	100	80	1.49 ^b	24 hours	July – August, 2009

^a data from the Michigan Department of Environmental Quality, Sun et al., 2013.

^b Piletic et al. 2013.

Table 4Comparison of PAH and Hopane concentrations (pg m^{-3}) in PM samples

PAH(# of Carbons)	This study	Guangzhou, China ^a PM _{2.5}	Raipur, India ^b PM ₁₀	Wroclaw, Poland ^c PM ₁₀	Brno, Czech Republic ^d PM ₁	Chiang Mai, Thailand ^e PM ₁₀
Chrysene (C18)	34–227	40–2810	400		300–420	80
3-Methyl Chrysene (C19)	6–18					
Benzo.b.fluoranthene(C20)	49–447		220	2520		830
Benzo.k.fluoranthene (C20)	21–188		70			410
Benzo.a.pyrene (C20)	20–193	560–2250	120	1020	330–390	590
Benzo.e.pyrene (C20)	33–303	400–1070	110	1690	330–390	
Perylene (C20)	5–48	600–2150			320–370	
Indeno.1.2.3.cd.pyrene (C22)	22–245	810–1117	900	790	370–500	1050
Benzo.g.h.i.perylene (C22)	31–373	LOD - 1000	820	1111	380–460	840
Dibenz.a.h.anthracene (C22)	5–48	200–2310	16		ND-590	110
Picene (C22)	3–35					
Coronene (C24)	12–141	140–2090				
HOPANES						
17 α (H),21 β (H)-30-Norhopane (C29)	69–256	320–630			310–480	
17 α (H),21 β (H)-Hopane (C30)	88–452	480–1140				
17 α (H),21 β (H)-22S-Homohopane (C31)	5–29				380–510	

LOD = limit of detection, ND = non detect.

^aWang et al. 2016^bGiri et al. 2013^cGórka et al. 2014^dKmal et al. 2013^eWiriya et al. 2013.

Table 5

Selected diagnostic PAH ratios in PM samples

PAH Ratio (Average)	This Study	Suburban Greecea	Sanya, Chinab	Guangzhou, Chinac	Brno, Czech Republicd	Slapanice, Czech Republicd	Wroclaw, Polande
[BaP]/[BaP+BeP]	0.37	-	0.5	-	-	-	-
BeP/[BaP+BeP]	0.63	-	-		0.51, 0.54	0.50, 0.54	0.62
[BaP]/[BP]	0.61	-	-	1.1	0.85, 1.80	0.84, 2.58.	-
[BP]/[BaP]	1.69	-	-	-	1.17, 0.56	1.19, 0.39	-
[Bb]/[Bk]	2.63	-	-	0.84	-	-	-
[IP]/[IP + BP]	0.41	0.46, 0.41	0.48	0.58	0.51, 0.63	0.52, 0.67	0.41

^aVasilakos et al. 2007^bWang et al. 2015^cWang et al. 2016a^dKamal et al. 2013^eGórka et al. 2014.

BaP = Benzo[a]pyrene, BeP = Benzo[e]pyrene, IP = Indeno[1,2,3-cd]pyrene, BP = Benzo[g,h,i]perylene, Bb = Benzo[b]fluoranthene, Bk = Benzo[k]fluoranthene, BP = Benzo[g,h,i]perylene, - = not reported.