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Particulate emissions of tire combustion

Jared Matthew Downard
University of Iowa

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PARTICULATE EMISSIONS OF TIRE COMBUSTION

by

Jared Matthew Downard

A thesis submitted in partial fulfillment
of the requirements for the
Master of Science degree in Chemistry
in the Graduate College of
The University of Iowa

May 2014

Thesis Supervisor: Assistant Professor Elizabeth A. Stone

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Graduate College
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CERTIFICATE OF APPROVAL

MASTER'S THESIS

This is to certify that the Master's thesis of

Jared Matthew Downard

has been approved by the Examining Committee
for the thesis requirement for the Master of Science
degree in Chemistry at the May 2014 graduation.

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To my parents who have blessed me with so many opportunities in life and allowed me to grow up and become myself

And now that you don't have to be perfect, you can be good.

John Steinbeck
East of Eden

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ABSTRACT

The disposal of used tires represents an environmental and health hazard, especially when large stockpiles of tires start on fire. This study focuses on ambient particulate matter samples collected during the Iowa City landfill tire fire and laboratory emissions of tire combustion. Levels of elemental (EC) and organic carbon (OC), metals, polycyclic aromatic hydrocarbons (PAH), azaarenes and oxygenated PAH (oxy-PAH) were determined by thermo-optical analysis, high precision mass, inductively-coupled plasma mass spectrometry and gas chromatography mass spectrometry. Results demonstrate that tire combustion emissions are enriched in elemental carbon and PAH. Levels of hazardous metals, such as lead and zinc, are not enhanced in particulate emissions 4.2 km from the fire. In addition, fresh tire combustion emissions have increased amounts of lower molecular weight PAH in the particle phase when compared to diluted real world emissions. This is due to gas phase partitioning of lower molecular weight PAH in plume transport. To build on the prior, qualitative understanding of organic compounds in tire emissions, 15 total azaarenes and oxy-PAH were identified, including four azaarenes and three oxy-PAH that were identified in tire combustion emission for the first time. The combustion of tires has significant health implications, particularly when open burning occurs near populations. This study serves to characterize the major chemical components of tire smoke and to quantify emissions of select chemicals with known carcinogenic, mutagenic, and toxic effects.

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CHAPTER 1

INTRODUCTION

1.1 Waste Tires: Disposal, Reuse and Risk of Fire

The disposal of used automobile tires has become a significant environmental concern. In 2009, the U.S. generated 291.8 million scrap tires (U.S. RMA, 2011). With large amounts of waste tires created each year efforts for reuse are becoming more common. Some of these efforts include retreading tires or using shredded tires in various applications such as drainage layers in landfills and soft surfaces for playgrounds (Phaneuf and Glander, 2003; US RMA, 2011). Full scrap tires can be placed on embankments or under road ways for added stability (Turer, 2012). Rubber powder obtained from recycled tires can be used again in tire making or in coatings, sealants and plastics (Bomgardner, 2011). Tires have a complex configuration of rubber, metals and other chemicals. Tires are composed of natural or synthetic (styrene-butadiene, butadiene) rubber and carbon black. Evans and Evans (2006) reported the composition of a passenger tire by weight of 47% rubber, 21.5% carbon black, 16.5% metal (mostly steel in the belt), 5.5% textile (nylon and polyester threading), 1% zinc oxide, 1% sulfur and 7.5% additives. The large carbon content of tires results in a high heat value, 29-37 MJ/kg, making them an attractive energy source that finds use in industrial boilers (Giere et al., 2004). Despite reuse efforts many tires still end up in landfills. In the year 2009, this number was 653,000 tons of used tires, representing 22% of scrapped tires (U.S. RMA, 2011).

One of the major challenges with the storage of used tires is the risk of fire (Sherman et al., 1998). An estimated 8,300 landfill fires occur in the United States annually (U.S. Fire Adm, 2001). The presence of large stock piles of tires contributes to

the fire risk. Although difficult to ignite, once started tire fires are extremely challenging to extinguish.

Several major tire fires have occurred in recent U.S. history. The largest tire fire in the United States to date was the Rhinehart fire which occurred in 1983 in Winchester, Virginia. The Rhinehart fire blazed for over seven months, consumed seven million tires and deposited emissions in three surrounding states. An estimated five million whole tires burned in a 1999 tire fire in Westly, California causing health concerns in the surrounding community. Pyrolytic oil from this fire drained into a nearby creek, were it ignited and increased smoke emissions. Both instances lead to large, expensive cleanups in the immediate and surrounding area (U.S. EPA, 2008). While large-scale tire fires in the United States occur at a rate of one or fewer per year, smaller-scale events occur more frequently. In other parts of the world, such as Nepal, burning of tires occurs in political demonstrations and as a fuel source (Shakya et al., 2008).

1.2 Prior Laboratory and Ambient Emission Studies of Tire Combustion

Emissions from burning tires are a concern due to hazardous gases (i.e. CO and SO₂) polycyclic aromatic hydrocarbons (PAH) and particulate matter that are produced from carbon, sulfur and other components used in tire production (Lemieux and Ryan 1993). Emissions of CO, SO₂ and NO_x ranged 1800-60,000, 31,000-35,000 and 1300-3700 mg kg⁻¹ of tire burned, respectively during a controlled burn study (Levendis et al. 1996). Total particle emissions ranged from 64,500-149,000 mg kg⁻¹ of tire in an open burn simulation (Lemieux and Ryan 1993). This same study reported heavy metals lead and zinc at 0.10 and 24.4 mg kg⁻¹, respectively; however the presence of metals was deemed inconclusive due to analytical challenges (high background levels and limits of detection) cited by the authors (Lemieux and Ryan 1993).

Poly-cyclic aromatic compounds (PAH) are a major class of tire combustion products. A laboratory-determined emission factor for total (gaseous and particulate) PAH was 5330 mg kg⁻¹ of shredded tire in an open burn simulation and 11,450 mg kg⁻¹ of pulverized tire in a controlled burn study (Lemieux and Ryan 1993; Levendis et al. 1996). PAH are primary and secondary reaction products from tire combustion. At elevated temperatures in controlled environments light olefinic and aromatic compounds, arising from butadiene and styrene, are volatilized (Atal and Levendis 1995). As these light olefins and aromatics evolve from the heated tires, they combine to form PAH compounds via Diels-Alder type reactions (Williams and Taylor 1993). PAH produced from tire burning range from two to six rings in size and may contain methyl or other alkyl substituents (Lemieux and Ryan 1993; Levendis et al. 1996). Enriched in tire combustion emissions is benzo[a]pyrene (B[a]P), a five-ring PAH that has been extensively studied and is classified by the International Agency for Research on Cancer as a known human carcinogen (Siddens et al. 2012) and is used as a general indicator of carcinogenic PAH emissions (Bostrom et al. 2002).

PAH emissions increase in oxygen-limited combustion environments. A massed-based equivalence ratio of fuel to air can be used to describe different combustion conditions; a larger ratio signifies an oxygen-limited environment, whereas a small ratio relates to an oxygen rich environment. Variance of this equivalence ratio, in a controlled laboratory burn, from 0.1 to 5.0 resulted in total gas phase PAH emissions of 40 and 7170 mg kg⁻¹ of tire, respectively. Particle phase PAH emission were < 1 and 4280 mg kg⁻¹ of tire for the same two equivalence ratios. PAH emissions are drastically enhanced when the amount of fuel exceeds the stoichiometric amount of air (Levendis et al. 1996).

While PAH emissions from tires have been studied under controlled conditions, measurements of PAH emissions from large-scale open burning of tires are limited. Analysis of soot and water samples collected from a tire fire in Quebec revealed 165 individual PAH with two to seven aromatic rings and molecular weights ranging 216 to

302 Daltons (Da). Aromatic compounds containing sulfur, nitrogen and oxygen, including phenols, quinolines, thiophenes and carbazoles have also been identified as products of tire combustion (Demarini et al. 1994; Wang et al. 2007).

1.3 Significance and Impact of Research

Either in the form of a large-scale tire fire or small-scale burning, emissions of burning tires presents health and environmental hazards. While prior studies have characterized tire emissions in controlled settings, substantially less is known about ambient emissions under real-world burn conditions. The Iowa City landfill tire fire in the summer of 2012 provided a research opportunity to advance the understanding of tire burning emissions *in situ* and yielded the first measurement of elemental and organic carbon, PAH, heterocyclic PAH, and metals from open burning of tires. These results serve to clarify prior reports of metal emissions from tire combustion (Lemieux and Ryan 1993), which is important information when considering the environmental and human health impacts of airborne metals. This study also presents the first quantitative emission factors of select PAH, azaarenes, and oxygenated PAH in tire emissions, some of which had only been qualitatively identified in prior studies (Demarini et al. 1994; Wang et al. 2007). Moreover, this study identifies new organic compounds in tire burning emissions, building upon the qualitative analysis of Wang et al. (2007). Particular emphasis is placed upon characterizing unique organic compounds that may serve as tracers for this source to identify and quantify its presence in future atmospheric studies.

This study also provides the first side-by-side comparison of emissions from the open burning of tires *in situ* and in the laboratory. With parallel methods of sample collection and analysis, we can begin to understand the differences in combustion of tires across field and laboratory measurements, including the effects of dilution and chemical aging. Side-by-side comparisons provide information as to what effect these forces have on tire combustion emissions.

Understanding more about the composition and quantity of organic compounds emitted from tire burning is important to evaluating the extent of human population exposure. Emissions from tire fires have been measured to be 16 times more mutagenic than a typical wood fire in a home fireplace and 13,000 times more mutagenic than commercial coal fired emissions with pollution control technology in place (Demarini et al. 1994). In the study of 16 combustion sources, tire burning was found to be the most mutagenic combustion emission source, even surpassing the burning of polyethylene, toluene and open burning of plastic (Demarini et al. 1994). Improved ambient emission information could be used to improve response to large scale tire combustion events in the future.

CHAPTER 2

EXPERIMENTAL METHODS

2.1 Ambient Sample Collection at the University of Iowa Air

Monitoring Site

Samples of particulate matter (PM) were collected in Iowa City, IA before, during, and after the tire fire in the summer of 2012. The University of Iowa Air Monitoring Site (IA-AMS, 41.664527, -91.584735) is immediately surrounded by recreational fields, woodlands, and parking lots and is near to two major roadways; U.S. Highway-218 is located 1.7 km to the southwest and Interstate-80 is located 2.5 km to the north. The Iowa City landfill is located 4.2 km to the southwest of the sampling site.

PM_{2.5} samples were collected with a medium-volume PM_{2.5} sampler (URG Corp.). The sampler was equipped with a Teflon-coated aluminum cyclone operating at 90 liters per minute that selected particles of 2.5 microns or less. Samples were collected on quartz fiber filters (Whatman) that had been pre-cleaned by baking at 550 °C for eighteen hours. The filters were stored in petri dishes lined with aluminum foil that had also been prebaked at 550 °C for eighteen hours.

The samples discussed surrounding the tire fire were collected from May 24 to June 10, 2012. Time of collection of the 2012 samples was as follows. The May 24 sample was collected prior to the start of the fire from midnight to midnight local time. The May 27 sample was collected from midnight to 8:00 A.M. of the 28. On May 28 and the 29, samples were collected from morning to the following morning for total sample times of 24 hours respectively. The May 30 sample was collected from the morning of the 30 until midnight of the same day. Finally from May 31 to June 10 sampling was resumed from midnight to midnight for 24 hour sampling times, in parallel to PM₁₀ samples described below. One field blank was collected for every fire samples.

Several days after the fire had started, the State Hygienic Laboratory installed a PM₁₀ filter sampler at IA-AMS. PM₁₀ samples (particles 10 microns or less) were collected using a Thermo 2025 air sampler and Teflon filters (Whatman). Samples were collected on a 24 hour interval at midnight of each day. This sampler was operational from May 30 to June 26, 2012.

For comparison, data from samples collected in 2012 were compared to the prior summer of 2011. From May 24 to June 13, 2011, twenty-four hour sample was collected every three days from midnight to midnight, local time. From June 19 to July 3, twenty-four hour samples were collected from approximately 9:00 A.M. to 9:00 A.M. daily. For both periods, three days of samples were composited and analyzed together, except July 4, which was analyzed individually.

2.2 FLAME IV Emission Study Sample Collection

FLAME IV emissions samples were collected at the U.S. Forest Service's combustion facility at the Fire Services Laboratory in Missoula, Montana. A more detailed experimental set up of the burn facility is described by Hosseini et al. (2013). Briefly, material is burned on a fuel bed and emissions are collected into a funnel opening. The emissions traveled 17m up an exhaust stack. At this height, there was a platform around the stack with samplers, all at the same height, to collect the emissions.

Two PM_{2.5} samplers were employed. One sampler ran at 42 liters per minute and collected particulate on a prebaked quartz fiber filter (QFF). This was the front QFF. The other sampler operated at 30 liters per minute and had a Teflon filter, to collect particulate, followed by a QFF behind it. The secondary QFF was the back-up filter to correct for positive artifact sampling (Subramanian et al. 2004). Two burns of shredded tire were performed in the study. Burn #27 occurred on October 17, 2012 and consisted of 500 grams of shredded tire. Burn #45 occurred on October 18, 2012 and consisted of 50 grams of shredded tire. After sample collection, all filters were stored in petri dishes

lined with prebaked aluminum foil and frozen until analysis. One field blank was collected for the two tire burns.

2.3 Chemical Measurements

PM₁₀ mass was measured at the State Hygienic Laboratory (SHL) at the University of Iowa. The mass of PM collected was calculated as the difference between Teflon filter masses pre- and post-sample collection that were measured with a high-precision balance (Mettler Toledo XP6) (U.S. EPA, 1999). Metals analysis of PM₁₀ filters, including filter preparation, was performed by SHL following EPA method EQL-0710-192 (U.S. EPA, 2010). The procedure utilizes a nitric-acid digestion followed by analysis by inductively coupled plasma mass spectrometry (ICP/MS). The ICP/MS system used was an Agilent ICP-MS 7500.

Elemental and organic carbon were analyzed by the Wisconsin State Laboratory of Hygiene on PM_{2.5} quartz fiber filters following the ACE-Asia protocol using a thermal-optical technique (Schauer et al. 2003). The filter is heated under an inert atmosphere and vaporized organic carbon is oxidized to CO₂. The CO₂ is then reduced to methane and detected using flame-ionization. After organic carbon oxidation, the filter is again heated under an oxygen containing environment. In this step, elemental carbon is oxidized to CO₂ and detected in a similar manner as the organic carbon. Laser transmittance of the filter corrects for organic carbon that is pyrolytically converted to elemental carbon.

To quantify organic species from the Iowa City landfill tire fire, PM_{2.5} quartz fiber filters underwent solvent-extraction and extracts were analyzed by GCMS following a previously established method (Stone et al. 2012). Filters were first spiked with isotopically-labeled internal standards including pyrene-D₁₀ and benz[a]anthracene-D₁₂. Samples were extracted by sonication (Branson) with two 20 mL portions each of dichloromethane (99.9% Sigma-Aldrich) and methanol (99.9% Fisher). The combined

extract was concentrated under ultra-high pure (UHP) nitrogen (99.999% Praxair) in a conical vial using a Caliper Life Sciences Turbovap and gentle heating (50 °C). Samples were first concentrated to a volume of 1 mL, and then filtered through a 0.2 µm PTFE filter (Whatman). The filtered extracts were then concentrated to a final volume of 50µL or 100µL, depending on the organic carbon loadings on the filter (Thermo Scientific Reacti-Therm III). Quality control measures included analysis of laboratory and field blanks and spike recovery samples, to establish background levels and evaluate extraction efficiency, respectively.

The extraction procedure for the FLAME IV samples was altered to improve the recovery of the more volatile azaarene and oxygenated PAH compounds. Filters were spiked with isotopically-labeled phenanthrene-D₁₀ and benz[a]anthracene-D₁₂. Samples were extracted by sonication (Branson) with two 20 mL portions each of hexanes (99.9% Fisher) and acetone (99.9% Sigma-Aldrich). The combined extracts were concentrated using a rotary-evaporator (Heidolph) with a water bath temperature and pressure of 30 °C and 450 mbar, respectively, to a volume of five mL. The extracts were filtered through a 0.2 µm PTFE filter (Whatman) and further concentrated under gentle heating and UHP nitrogen in a mini-vap (Thermo Scientific Reacti-Therm III) to a final volume of 100µL. Quality control once again included laboratory and fields blanks as well as spike samples.

Aerosol extracts were analyzed using GCMS (Agilent Technologies 7890, 5975C Inert Electron Ionization [EI]/Chemical Ionization [CI] MSD). Separation was performed using an Agilent HP-5 MS column with dimensions 30m (length) x 0.250mm (diam) x 0.25 µm (film). The samples had a 3 µL injection volume, an inlet temperature of 300 °C, and a temperature program with a starting value of 65 °C held for ten minutes, followed by heating to 300 °C at 10 °C per minute and held for 26.5 minutes. The flow rate through the column was set at 1 mL/min and the carrier gas was UHP Helium (99.999% PraxAir). The mass spectrometer was in the EI mode and masses scanned from 50-550 Da with a source temperature of 230 °C. PAH were quantified using five-point calibration curves,

normalized to internal standards. A six point calibration curve was prepared for the two azaarene compounds and two oxygenated PAH. Both azaarenes were normalized to phenanthrene-D₁₀ and the oxygenated PAH were normalized to benz[a]anthracene-D₁₂. All data was analyzed with MSD Chemstation software (Agilent). Benzo[b]fluoranthene and benzo[k]fluoranthene were quantified together in the Iowa City landfill tire fire samples because they coeluted.

High-resolution mass data was obtained on a gas chromatography time of flight mass spectrometry system (Agilent 7890A, MicroMass MS Technologies GCT Premier) using electron ionization and the same column and temperature program of the previous analysis. The time of flight mass spectrometer was continuously calibrated with lock mass (perfluorotributylamine). Data was acquired in centroid mode and analyzed using MassLynx instrument software (Waters).

2.4 Calculation of Emission Factors

Ambient emission factors (EF) of PAH (mg species kg⁻¹ tire) from the Iowa City landfill tire fire were calculated using equation 1

$$EF_{PAH} = \frac{[PAH]_{plume} - [PAH]_{background}}{[EC]_{plume} - [EC]_{background}} EF_{EC} \quad \text{Eq. 1}$$

Where [PAH] refers to the ambient PAH concentration in the plume and background air, [EC] is the ambient concentration of elemental carbon in the plume and in background air, and EF_{EC} is a previously estimated elemental carbon emission factor (mass of EC per kg fuel burned) from the Iowa City landfill tire fire (Downard et al, 2014, *in preparation*). The concentrations of PAH and EC in the equation take into account a pre-landfill fire background subtraction.

PAH emission factors from the FLAME emissions study were calculated in a three-step process. First the mass of CO in the emission smoke is determined by measuring the mixing ratio of CO by Fourier transform infrared spectroscopy and using equation 2.

$$Mass_{CO} = X_{CO} \frac{M_{CO} * P}{R * T} \quad \text{Eq.2}$$

Where X_{CO} is the mixing ratio of CO, M_{CO} is the molar mass of CO and P, T and R are the ambient pressure, temperature and gas constant, respectively. Organic carbon (OC) mass in the emission smoke was then divided by the mass of CO to obtain a mass ratio. The mass ratio was converted to an emission factor for organic carbon (mass of OC per kg of tire burned) using equation 3.

$$EF_{OC} = \frac{Mass_{OC}}{Mass_{CO}} EF_{CO} \quad \text{Eq.3}$$

Where EF_{OC} is the emission factor of organic carbon, and EF_{CO} is the emission factor of CO (mass of CO per kg of tire burned). A detailed description of the CO emission factor calculation is described by Yokelson et al. (1996). To calculate the final emission factor of PAH species (mass of species per kg of tire burned) equation 4 was used.

$$EF_{PAH} = \frac{Mass_{PAH}}{Mass_{OC}} EF_{OC} \quad \text{Eq.4}$$

In this equation, EF_{OC} is the previously calculated OC emission factor and the masses of PAH and OC were determined through filter analysis. The mass of PAH in the equation takes into account a back-up filter subtraction. These experiments are measuring particulate species, however, positive artifacts (in increase in the expected amount) can arise due to gas phase adsorption to particulate matter on the QFF. The assumption in the

back-up filter subtraction is that the same amount of gas phase species has adsorbed to the front and back QFF filters. This back-up filter subtraction eliminates the positive artifacts (Subramanian et al. 2004).

2.5 Qualitative Identification of Organic Species Emitted from Tire Combustion

Qualitative analysis of organic compounds from tire burning emissions was performed by overlaying chromatograms of ambient aerosol samples from the strongest plume impact and a background day. Peaks that were unique to the plume impact day were identified by comparing its mass spectrum to the NIST mass spectral library (NIST, 2011). For further confirmation, aerosol samples were analyzed by GC followed by high-resolution (7,000) time of flight mass spectrometry. The monoisotopic mass of target compounds was extracted from the total ion chromatograms. Compounds were considered to be positively identified if the difference in the observed and theoretical mass was equal to or less than 3 mDa. Lee's retention index (Lee et al. 1979) was employed for further confirmation. This index utilizes four reference PAH compounds of increasing ring number (naphthalene, phenanthrene, chrysene, picene) and their retention times. An index of retention for unknown compounds can be calculated from its retention time and the two reference PAH that "bracket" the unknown compound according to equation 5

$$I_x = 100N + 100 \left[\frac{t_x - t_N}{t_{(N+1)} - t_N} \right] \quad \text{Eq.5}$$

Where N is the ring number of the reference PAH that elutes just before the unknown, t_x is the retention time of the unknown, t_N is the retention time of the reference PAH eluting just before the unknown and $t_{(N+1)}$ is the retention time of the reference PAH eluting right

after the unknown. The calculated retention indices of the unknown compounds were compared to referenced retention indices of standards.

Based on the high resolution data, 15 azaarene and oxygenated PAH compounds were identified. Standards were purchased for four of these compounds (2,4-dimethyl quinoline, acridine, 2-methyl-anthracenedione and benz[a]anthracene-7,12-dione) for emission factor quantitation and unequivocal identification of unknown peaks.

CHAPTER 3

EMISSIONS OF CARBON AND METALS

3.1 Elemental and Organic Carbon Emissions of Tire

Combustion

Combustion of carbon containing materials results in “soot” or elemental carbon particles that have been associated with adverse health effects (Janssen et al. 2011). The elemental (EC) and organic (OC) carbon concentrations observed at the IA-AMS during the Iowa City landfill tire fire are shown in Figure 3.1. EC concentrations ranged from 0.09 to 0.84 $\mu\text{g m}^{-3}$ from May 24 to June 10, with maximum concentrations occurring on May 28, June 1-3, 5 and 7, peaking on June 2. The wind directions were favorable for transport of the tire fire plume to the stationary IA-AMS site on these days. Visually, the plume was dark in color due to the light absorbing particulate. Around one fifth (21.5%) of a tire’s composition is carbon black, which can be considered EC (Evans and Evans, 2006). Consequently, days when the smoke plume impacted IA-AMS showed enriched levels of EC. The tire fire plume had characteristically high EC concentrations and low OC to EC ratios as well. On impact days, the OC to EC ratio ranged from 3.6 to 7.4, compared to non-impact days when it ranged 9 to 46. The OC concentrations were variable over the period with several days pre-fire having similar concentrations as impact days. The OC did not seem to be as influenced by the tire fire in the same way as the elemental carbon.

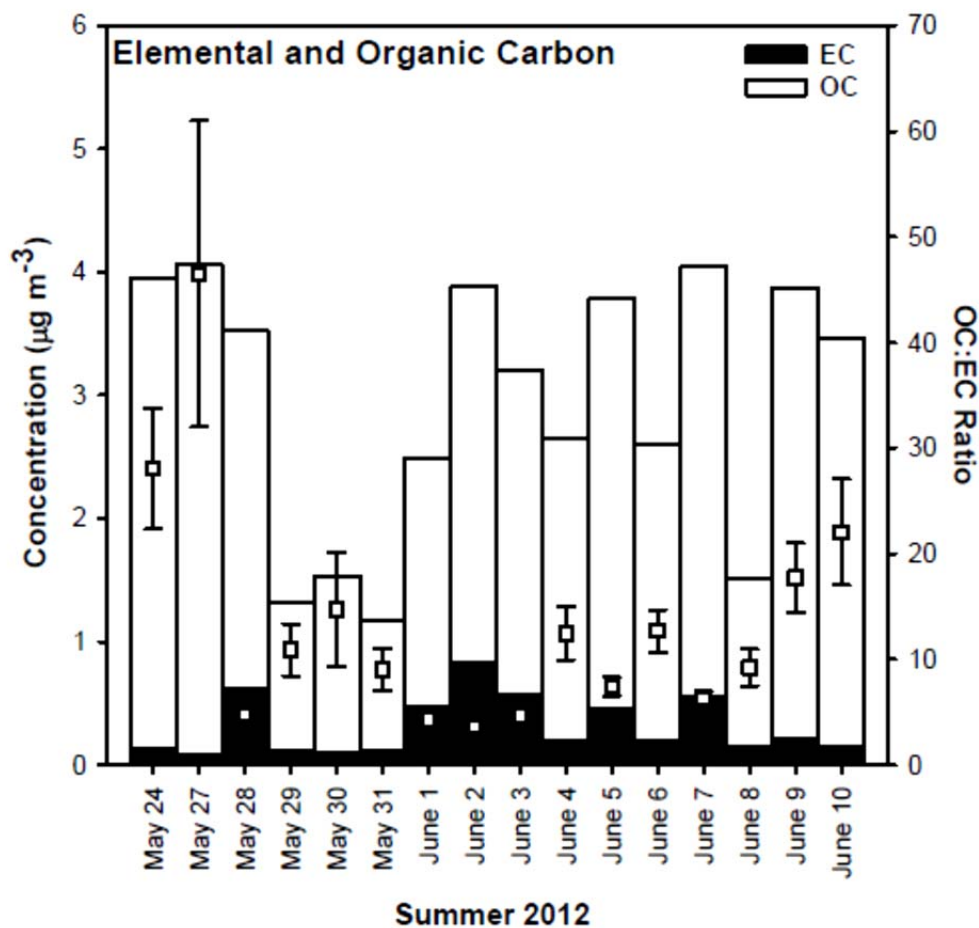


Figure 3.1 Ambient elemental and organic carbon concentrations (bars) and OC:EC ratio (boxes with error bars) during the Iowa City landfill tire fire.

Laboratory measurements of OC and EC corroborated the ambient measurements of high elemental carbon associated with the smoke plume. Figure 3.2 shows the mass fraction of EC and OC from two different laboratory burns of shredded tires. Nearly 80% of carbon in both samples was found to be elemental carbon. The large fraction of EC from the laboratory burn helps to explain the increased concentrations in ambient samples with smoke plume impact. Similarly, the organic carbon fraction is less than $22 \pm 6\%$ in both samples.

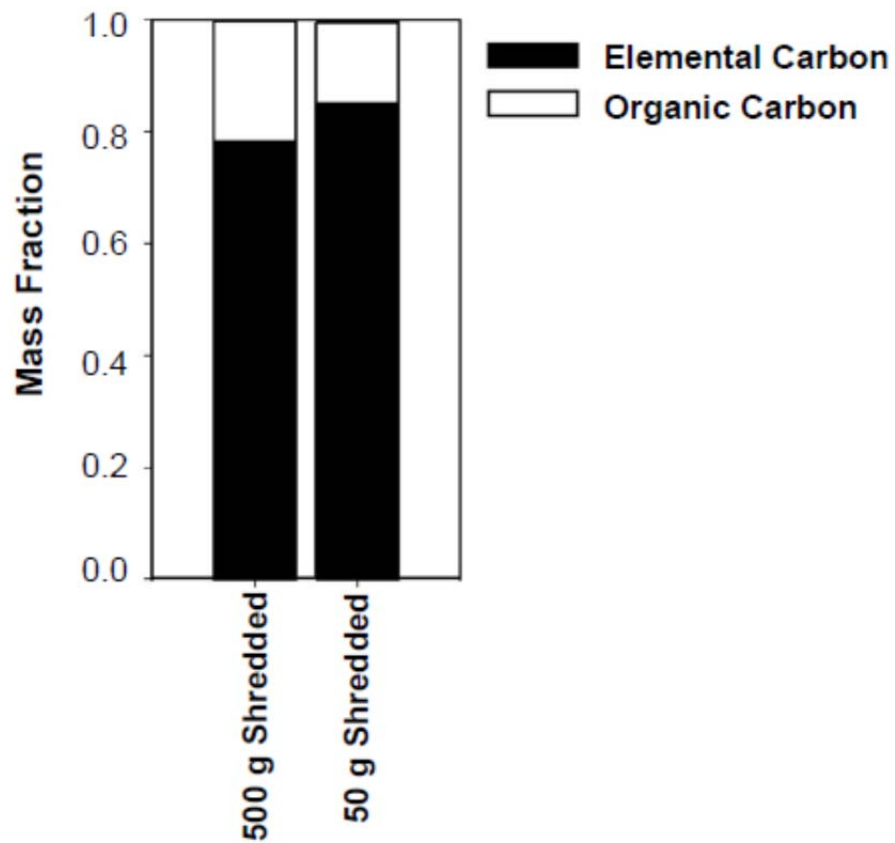


Figure 3.2 Mass fraction of elemental and organic carbon from laboratory tire combustion.

3.2 Metal Emissions of Tire Combustion

A prior study by Lemieux and Ryan (1993) raised concerns about emissions of toxic metals in tire burning emissions. Owing to the toxic nature of lead and the possibility of increased emissions, metal species were quantified in Iowa City during the tire fire.

Ambient concentrations of iron (Fe) at the IA-AMS site are shown in Figure 3.3 and did not show enhancement when the plume impacted the site. During the tire fire period (May 30 – June 12) Fe concentrations ranged from 80 to 311 ng m⁻³, (average \pm one standard deviation of 203 \pm 68 ng Fe m⁻³) On June 2, when the smoke plume from the fire was confirmed to have impacted IA-AMS, the Fe concentration was 105 ng m⁻³ which was near to the average for this period. After the fire was contained (June 13 – 26) the average concentration was 247 \pm 166 ng Fe m⁻³. The absolute concentration of Fe observed after fire containment was higher than during the tire fire, but this difference was not statistically significant at the 95% confidence interval. Fe's mass fraction of PM₁₀ is also shown in Figure 3.3 (right axis). This value ranged over the fire period from 7.3 to 13.1 mg Fe g⁻¹ of PM₁₀ with an average of 11.1 \pm 1.7 mg Fe g⁻¹ of PM₁₀. Once again the difference in mass fractions observed during the fire and after containment was not statistically significant at the 95% confidence interval.

Ambient concentrations of zinc (Zn) are also shown in Figure 3.3. During the fire period and on June 2 the range and absolute concentrations of Zn were 13 to 43 ng Zn m⁻³, (29 \pm 9 ng Zn m⁻³) and 31 ng m⁻³, respectively. After fire containment, the average concentration was 44 \pm 19 ng m⁻³. Additionally, during the fire period, Zn's mass fraction ranged from 0.56 to 5.3 mg Zn g⁻¹ PM₁₀ with an average of 2.0 \pm 1.3 mg Zn g⁻¹ PM₁₀. Similar to Fe, differences in absolute concentrations and mass fractions during the fire and after containment were not statistically significant at the 95% confidence interval.

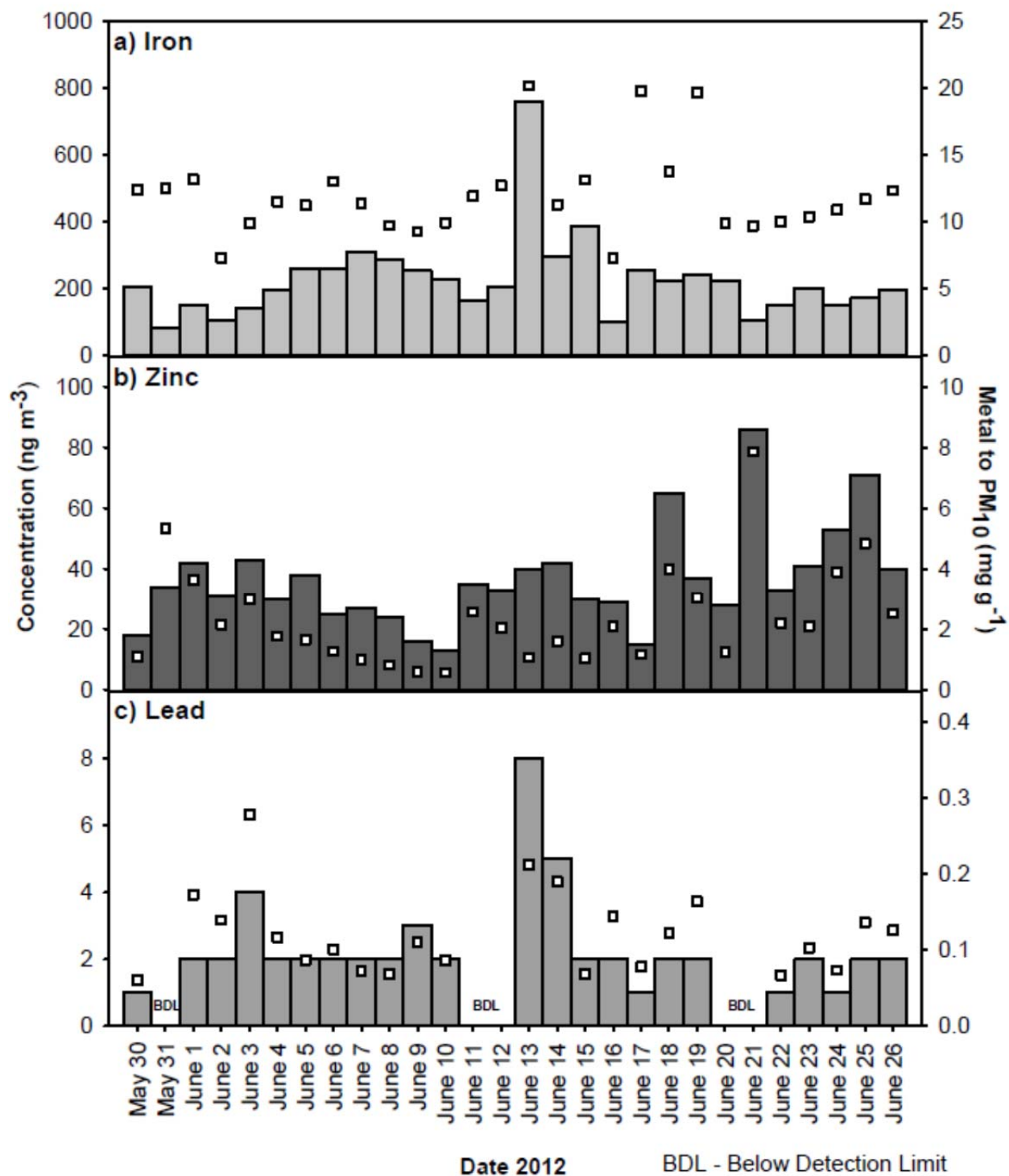


Figure 3.3 Ambient concentrations (bars) of a) iron, b) zinc, and c) lead and PM₁₀ mass fractions (squares) during the Iowa City landfill tire fire.

Lead (Pb) concentrations ranged from < 1 to 4 ng Pb m^{-3} ($2.0 \pm 0.8 \text{ ng Pb m}^{-3}$) and on the day with the strongest plume influence was 2 ng Pb m^{-3} , respectively. After containment, Pb concentrations averaged $3 \pm 2 \text{ ng Pb m}^{-3}$. Also, the mass fraction of Pb during the fire period ranged from 0.06 to $0.28 \text{ mg Pb g}^{-1} \text{ PM}_{10}$ with an average of $0.12 \pm 0.06 \text{ mg Pb g}^{-1}$ of PM_{10} . Differences between the fire and after containment period were again not statically significant at the 95% confidence level. The observed PM_{10} lead concentrations in Iowa City are consistent with $\text{PM}_{2.5}$ lead concentrations at rural and urban locations in Iowa, including EPA monitoring sites in Van Buren County and Cedar Rapids, respectively; from 2008 to 2010 the average Pb concentration was $2.2 \pm 0.6 \text{ ng m}^{-3}$ for Van Buren and $2.3 \pm 0.8 \text{ ng m}^{-3}$ for Cedar Rapids (AQS Data Mart). These data demonstrate that there was no enhancement in the absolute concentration and mass fraction of Pb during the tire fire compared to other periods in Iowa City and other urban and rural sites in Iowa.

There was a spike in absolute concentrations of Pb and Fe on June 13, after the fire had been covered and there was no longer visible emission of particulate matter to the atmosphere. No increase in Zn was observed on this day and based on the previous laboratory study; a tire combustion influenced sample would have elevated levels of Zn (Lemieux and Ryan 1993). Winds were southeasterly on June 13, which was not from the direction of the landfill (southwest) but rather, traveled over Iowa City. The Zn concentration and wind direction on June 13 indicate that the tire fire was not a plausible source. Also on June 13, total PM_{10} and aluminum (Al) concentrations were $37.6 \mu\text{g m}^{-3}$ and 680 ng m^{-3} , respectively, reaching levels that were twice as high as the days before and after. PM_{10} , Al and Fe are known components of soil (Yanai, Okada and Yamada 2012), suggesting June 13 was impacted by an episode of PM_{10} dust.

Overall, Fe, Zn, and Pb concentrations did not increase relative to background levels during plume impact like elemental carbon. Even during the fire period there was not a significant increase in absolute ambient metal concentration when compared to the

period when the fire had been covered. Additionally, the metals species mass fraction of PM_{10} also did not show increases during plume impact or during the fire period.

Together, these data clearly indicate that the Iowa City landfill tire fire was not a source of respirable metals in the atmosphere at a distance of 4.2 km from the fire. Although metals are used in the production of tires, the metal species from the tires were not transported through the air in PM_{10} mass at the distance of the sampling site. However, fence line measurements are needed to confirm if elevated levels of metals exist in closer proximity to the tire fire.

Laboratory data also support the result that tire burning is not a significant source of airborne metals. Two samples of $PM_{2.5}$ produced from the combustion of shredded tires emissions were collected during the FLAME IV emission study. Samples were analyzed by SHL using parallel standard EPA method EQL-0710-192. Calculated metals emissions from the FLAME IV study and the EPA study by Lemieux and Ryan (1993) can be seen in Table 3.1. Analysis from these filters showed that only Zn had an increase over the field blank levels. The combustion of 500 and 50 g of shredded tires resulted in 2.1 and 1.5 mg of Zn kg^{-1} of tire, respectively. The emission of Zn was reported by Lemieux and Ryan (1993) at 24.35 mg kg^{-1} of tire. Pb and Fe were below the detection limit of 0.81 mg kg^{-1} of tire in both FLAME IV samples. These two metals had emissions in the EPA study of 0.10 mg kg^{-1} of tire and below detection limits for Pb and Fe, respectively.

Table 3.1 Emissions of Iron, Zinc and Lead from Laboratory Tire Combustion

Reference	This Study	This Study	Lemieux and Ryan, 1993 ^a
Sample Type	PM _{2.5}	PM _{2.5}	TSP
Tire Mass	500 g	50 g	4.5-9.0 kg
Tire Type	Shredded	Shredded	Shredded
Emission Factor	(mg kg ⁻¹)		
Iron	<0.8	<0.8	BDL
Zinc	2.1	1.5	24.35
Lead	<0.8	<0.8	0.1

a) Lemieux, P.M. and Ryan, J.V., 1993.

BDL - Below Detection Limit

It is of importance that the study by Lemieux and Ryan (1993) observed a significant emission of Zn in total suspended particulate (TSP) while significant emissions of Zn were neither observed in PM₁₀ ambient samples during the Iowa City landfill fire nor PM_{2.5} FLAME IV samples of laboratory burning. The size of sampled PM may account the apparent discrepancy. The TSP sample may have included large pieces of particulate metal (greater than 10 microns) that were suspended by thermal convection or mechanical forces. The size selection of PM₁₀ and PM_{2.5} in the samples discussed in this study would have excluded these large particles. During the Iowa City landfill tire fire, similar large metal-containing particles may have become suspended through convection forces or mechanical forces, (i.e. strong winds or the stir-burn-and-

cover operation). In accordance with Stoke's Law, large particles have higher terminal settling velocities than fine particles and therefore deposit more readily from the atmosphere (Hinds 1999). Hence, larger particles from the Iowa City landfill would not have been transported 4.2 km to IA-AMS. However, elevated PM metal levels may have occurred near to the source. Thus, there remains a need for fence line sampling of metals close to a large tire combustion source to determine if metal exposure is of concern to fire fighters or other responding personnel.

Based on the result from FLAME IV, though, zinc appears to have a slight emission during tire combustion and comprised 0.04% of PM_{2.5} mass. This emission may depend on how much of the metal in the tire is exposed to burning and the extent of thermal convection that may lead to the suspension of metal-containing particles. Larger particles associated with metals may also be produced and become airborne through convective or mechanical forces. Depending on the size cut or distance of sampling, these particles may not be sampled.

CHAPTER 4

EMISSIONS OF POLYCYCLIC AROMATIC HYDROCARBONS

4.1 Ambient Concentrations of PAH during the Iowa City

Landfill Tire Fire

Polycyclic aromatic hydrocarbons are organic compounds that consist of two or more fused aromatic rings and are known to have mutagenic and carcinogenic effects (Nielsen et al. 1996). Their main source is the incomplete combustion of carbon containing materials including coal, biomass and gasoline and diesel fuels (Levendis et al. 1996; Fine, Cass and Simoneit 2001; Bergvall and Westerholm 2009). Their structures lead to many different ring arrangements, which give rise to a wide range of isomers. In soot from a fire involving whole tires at warehouse, Wang et al. (2006) identified 13 isomers of molecular weight 302 alone. Examples of PAH are shown in Figure 4.1.

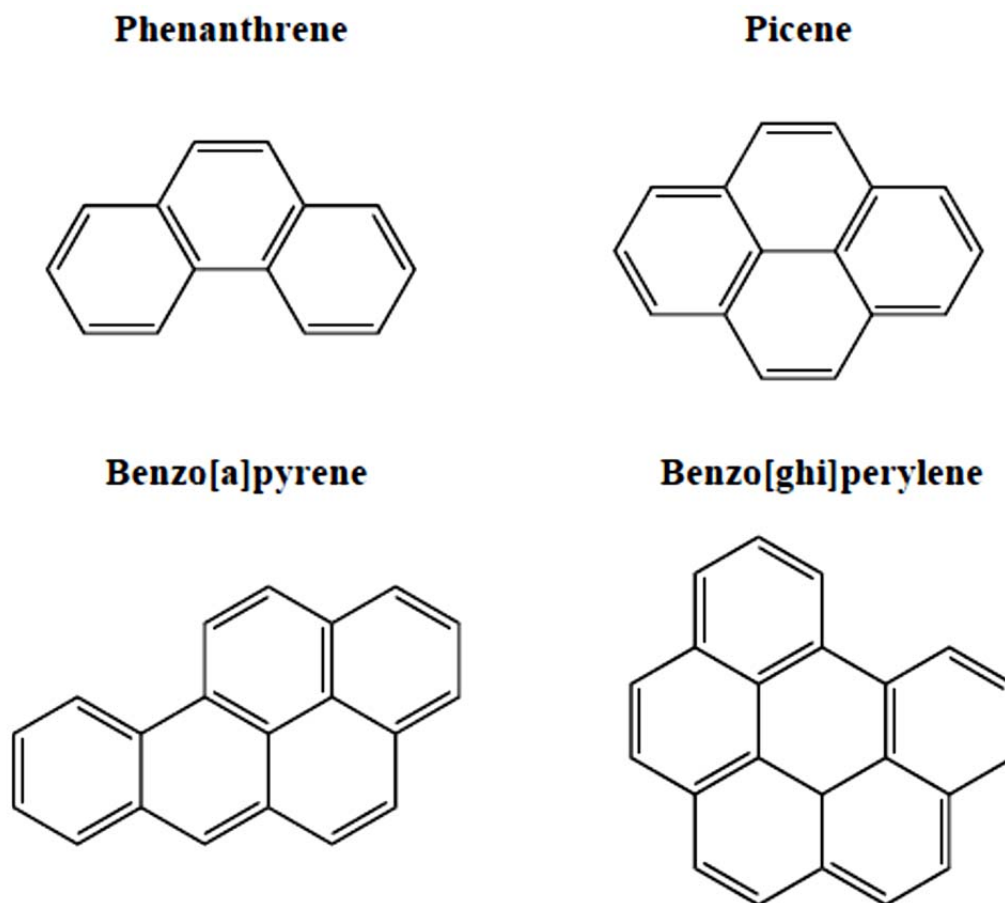


Figure 4.1 Examples of PAH structures

PAH have been previously identified in tire combustion and given the negative health impacts associated with them, their concentrations are of considerable interest. Twenty quantified PAH and benzo[a]pyrene levels in Iowa City between the summer of 2011 and the landfill fire period in 2012 are shown in Figure 4.2.

The sum of the measured PAH concentrations from 2011 ranged from 0.15 to 0.42 ng m⁻³ and had an average concentration over this period of 0.24 ng m⁻³, corresponding to a relatively low background concentration. July 4 was not included in the background calculation for 2011, due to interfering local activities, likely fireworks. During the tire fire, PAH concentrations increased more than 100 fold on days where the

tire fire plume was transported to the sampling site. On June 2, the 24 hour total PAH concentration was 138 times larger than the average concentration in 2011, reaching $33 \pm 7 \text{ ng m}^{-3}$.

Comparisons to other ambient concentrations of PAH highlight the drastic increases during the fire period. Sun et al. (2006) reported a daily average range of concentrations of 12 summed particulate PAH at five rural Lake Superior sites of 0.11 to 0.65 ng m^{-3} . This range is comparable to the background levels seen in Iowa City in 2011. In the same study, daily concentrations of 12 PAH at a semi-urban site near Buffalo, NY and an urban site in Chicago were 1.0 ± 0.1 and $10 \pm 1 \text{ ng m}^{-3}$, respectively. On June 2, 2012 the concentration of the same 12 PAH, reported in this study, reached a concentration of $29 \pm 6 \text{ ng m}^{-3}$ at the IA-AMS. This concentration is substantially larger than the semi-urban and urban sites, with enhancements of 28 and 19 ng m^{-3} , relative to the semi-urban and urban sites, respectively.

Ambient concentrations of B[a]P are of particular interest given its carcinogenicity. On June 2, during the landfill fire period, the concentration of B[a]P reached $1.6 \pm 0.3 \text{ ng m}^{-3}$. Sun et al. (2006) recorded particulate B[a]P concentrations of 0.05 ± 0.01 and $0.75 \pm 0.06 \text{ ng m}^{-3}$ at their semi-urban and urban sites, respectively. Also, Pedersen et al. (2005) observed concentrations of B[a]P at an urban site in Boston, Massachusetts of 0.21 ng m^{-3} . The June 2 concentration is nearly 8 times greater than summertime Boston and twice as large as an urban Chicago environment.

The four PAH with the largest concentrations seen during the landfill fire period were, benzo[b]fluoranthene, benzo[k]fluoranthene (five ring), benzo[e]pyrene (five ring) and chrysene (four ring). Chrysene is the lightest of the four with a molecular weight of 228 Da while the other three most abundant PAH have a molecular weight of 252 Da. The enhanced concentrations of PAH are largely in the higher molecular weight range. It has been seen in previous studies that two to four ring PAH are primarily found in the gaseous phase, while five to seven ring PAH are primarily found in the particle phase.

However, a unique observation was that chrysene, although a four ring species, had similar levels in the gaseous and particle phase (Mandalakis et al. 2002; Park, Wade and Sweet 2001; Kishida et al. 2008).

Besides the four most abundant PAH, on June 2 all other quantified PAH had lower, individual concentrations in the range 0.07 to 2 ng m⁻³. On all other days during the fire period the quantified PAH had individual concentrations of below detection limits to 2 ng m⁻³. Alkylated-PAH, such as methyl anthracene, was detected 9 out of 15 days during the fire period. Methyl chrysene and retene were detected 12 out of 15 days during the fire period. The Iowa City sampling site is not equipped to collect gaseous phase PAH. Lower molecular weight PAH are expected to primarily be in the gas phase. This accounts for the low concentrations of light PAH (three and four ring) observed during the tire fire.

The smoke plume from the Iowa City landfill tire fire was a significant source of PAH to the atmosphere, even at a distance of 4.2 km. However, it should be noted that when there was no smoke plume impact, PAH concentrations at IA-AMS were similar to background levels, indicating that the Iowa City tire fire only impacted local air sheds immediately downwind of the landfill. Consequently, the trajectory of the smoke plume is of more importance when determining population exposure than distance to the source.

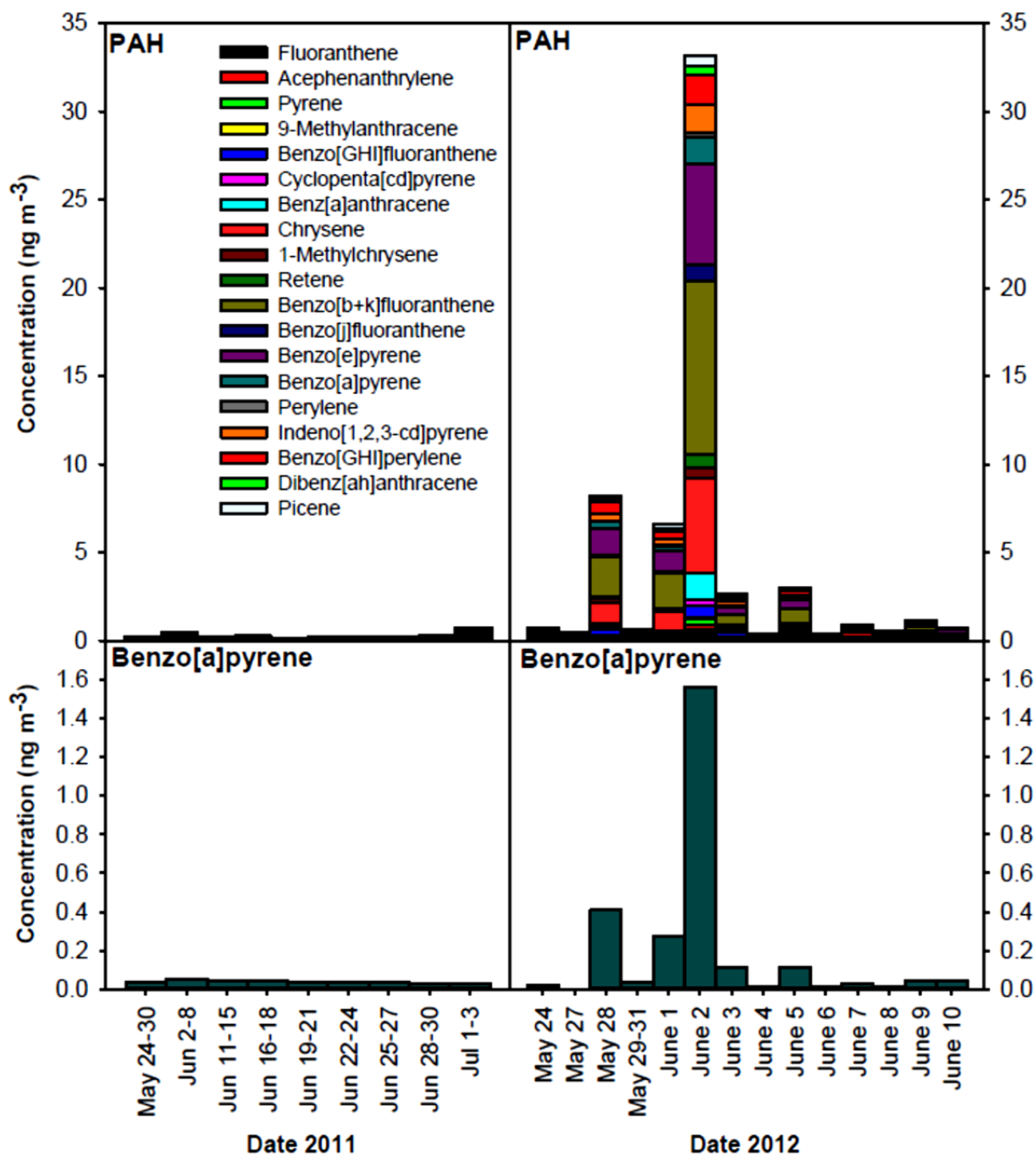


Figure 4.2 Ambient PAH concentrations measured at IA-AMS in Iowa City during summer of 2011 and the landfill fire period of 2012.

4.2 Relative Concentrations of PAH during the Iowa City

Landfill Tire Fire

The relative concentrations of each individual PAH to total PAH concentration did not vary significantly over the fire period. The four most abundant PAH, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene and chrysene, comprised 25-73% of the measured PAH. PAH with a molecular weight of 252 Da were the largest contributors to total PAH concentrations, in the range of 25-68% over the fire period. Four ringed PAH (benz[a]anthracene and chrysene) with a molecular weight 228 Da made up the second largest amount of total PAH concentration in the range of 9-24%.

4.3 Comparisons of PAH Profiles

Comparisons between laboratory and ambient studies of PAH highlight how sample collection and emission aging affects PAH distributions. Profiles of PAH emission factors from three studies are shown in figure 4.3. The PM_{2.5} sample collected on June 2, 2012 contained particle emissions on a quartz fiber filter. The open burn sample was collected during a simulation of chunk tire burning by Lemieux and Ryan (1993) who cooled tire fire smoke to ambient temperature prior to collection of particulate PAH on filters and gaseous PAH on XAD-2 resin. Thus, their measurements include gas and particle phase PAH. The FLAME IV sample was collected on a quartz fiber filter and includes only particle phase PAH after correction for positive artifacts arising from gas adsorption. All three studies used GCMS for PAH detection and authentic standards for quantification.

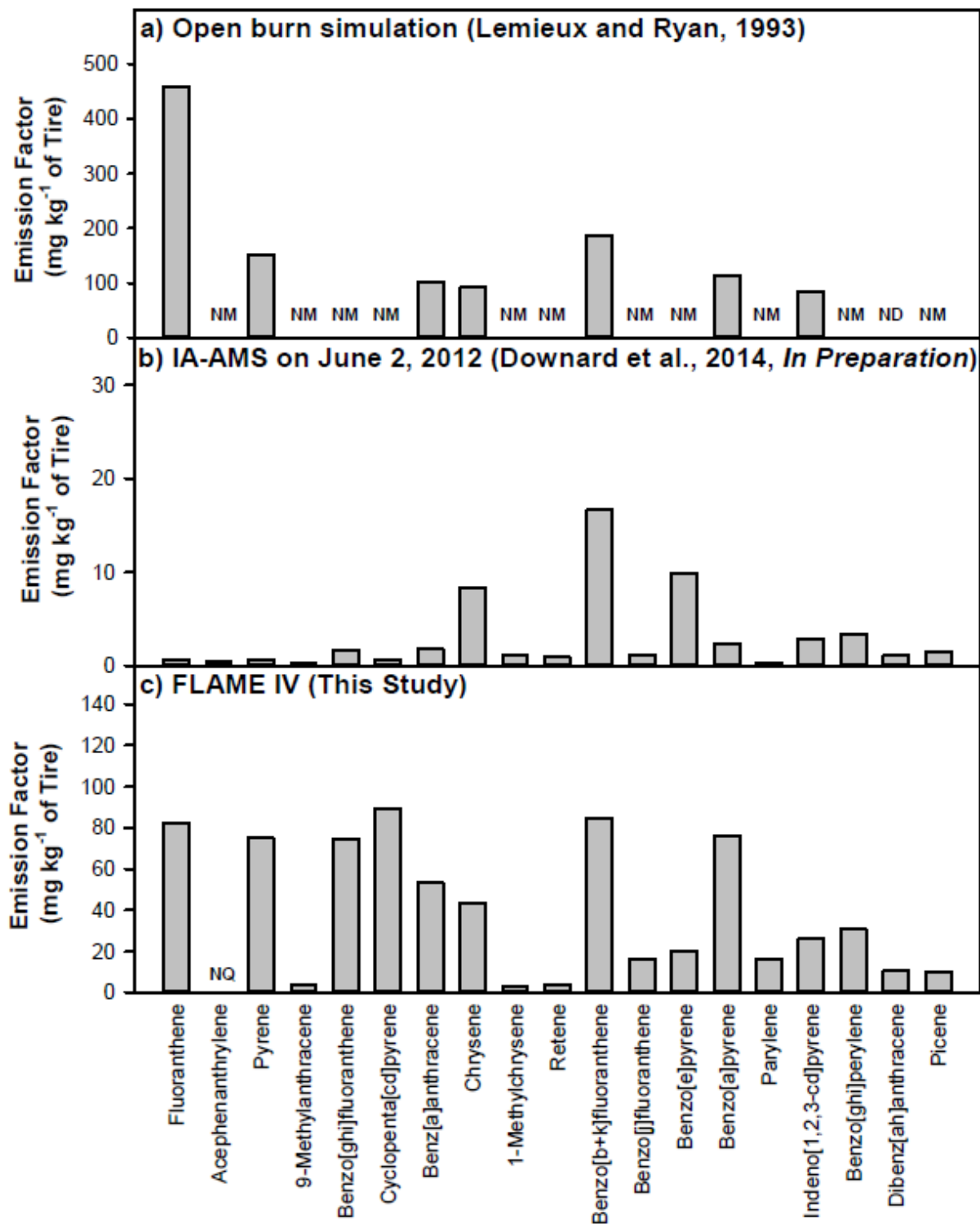


Figure 4.3 PAH profile comparisons of one ambient (Iowa City, Panel b) and two laboratory samples (Shredded Tires, Panels a and c).

There are several similarities and differences between these studies that help highlight the semi-volatile nature of PAH and reveal characteristics of real world tire combustion emissions. All three studies reported measurements of fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene and indeno[1,2,3-cd]pyrene. Low molecular weight PAH did not have large concentrations in the ambient sample from IA-AMS, which is agreeable with knowledge of the number of rings in a PAH molecule and whether it is in the gas or particle phase (Mandalakis et al. 2002; Park, Wade and Sweet 2001; Kishida et al. 2008). Lemieux and Ryan (1993) detected a considerable amount of fluoranthene and pyrene, both four ring PAH species. This is consistent with the inclusion of gas phase species on XAD resin.

Interestingly, the sample from the FLAME IV laboratory study had increased amounts of lower molecular weight PAH, when compared to the ambient sample. Fresh tire combustion emissions contain more lower molecular weight PAH in the particle phase that are apparently lost to volatilization prior to ambient sample collection. Based on this reasoning and data from Lemieux and Ryan (1993) there are expected to be significant emission of gas phase PAH from tire combustion, that were not detected during the Iowa City landfill tire fire 4.2 km downwind.

4.4 PAH Emission Factors and Soot Composition

Emission factors give a quantitative understanding of the magnitude of emissions from a particular source and are useful for risk assessment and comparison to other sources. Emission factors and soot composition for PAH from tire combustion are shown in Table 4.1. Emission factors were calculated in the two laboratory studies by burning shredded tires with similar dimensions. The tires present in the Iowa City landfill tire fire were also shredded. The soot sample was a surface wipe sample collected from the rear windshield of car parked near a building where a large scale tire fire took place (Wang et

al. 2007). Emission factors and soot composition were calculated for PAH across all studies in a size range of two to six rings.

Emission factors calculated from the FLAME IV study represent fresh particulate emissions from tire combustion. Analysis of two samples (500 g and 50 g of fuel) was performed. After normalizing to mass of fuel, the 500 g sample had a much larger total emission factor for quantified PAH of $770 \pm 180 \text{ mg kg}^{-1}$ in comparison to the 50 g sample that had a total emission factor of the same quantified PAH of $120 \pm 28 \text{ mg kg}^{-1}$. Levendis et al. (1996) determined in their study of controlled burning of pulverized tires that combustion in a fuel-rich (oxygen-limited) environment resulted in increased PAH emissions. This could help explain the emissions from the 500 g sample. If the larger mass of tire limited the oxygen available for combustion, the result would be increased emissions of PAH relative to an oxygen rich environment.

Another possibility is the adsorption efficiency of gas phase species on the 500 g QFF compared to the 50 g QFF. Lower molecular weight PAH would be most affected by the adsorption of the front filter. During the FLAME IV study, the 500 g sample filter became heavily loaded with particulate, more so than the 50 g filter. The EC loadings ($\mu\text{g EC cm}^{-2}$ of filter) of the 500 g and 50 g filters were 239 ± 15 and 41 ± 2 , respectively. Although the filters were corrected for positive artifact sampling, it is possible this correction was not enough in the 500 g sample to account for the increased loading of the filter. Roth, Goss and Schwarzenbach (2005) reported that organic vapor sorption was dominated by adsorption to EC in diesel soot particles comprised of 75% EC. Analysis of the 50 g back-up filter revealed concentrations of four ring PAH expected to have concentrations in the gas phase, such as chrysene and benz[a]anthracene. These species were not detected in the back-up filter of the 500 g sample, suggesting they were trapped in particles on the front filter. An increased amount of particulate would result in more adsorption sites for gas phase PAH compared to the 50 g filter and is another reasonable explanation for observation of greater emissions from the 500 g sample compared to the

50 g. This result also supports that tire burning emits significant amounts of gas phase PAH.

Hosseini et al. (2013) calculated laboratory emission factors for particulate PAH of several different biomass materials from the Southwestern United States. Emission factors for 15 PAH ranged from 1.3-11.7 mg kg⁻¹ of fuel for California sage and oak savanna, respectively. These values are an order of magnitude lower than what was observed in the laboratory emission of tire combustion. When only comparing similarly quantified PAH between both studies, the maximum total emission factors were 11 ± 7 and 462 ± 116 mg kg⁻¹ of fuel for biomass and tires, respectively. On an equal mass of fuel basis, open tire combustion emits much larger amounts of particle PAH than biomass burning.

The field derived emission factors from the Iowa City landfill tire fire are much lower in comparison to the laboratory derived emission factors. The total field derived emission factor was 56 ± 44 mg kg⁻¹. However, the equation used in the calculation takes into account the ambient concentrations observed at the IA-AMS sampling site. As noted previously, this site is 4.2 km away from the landfill. Observed ambient concentrations were generally low, due to transport and dilution, compared to concentrations that would be encountered during an emission study. As a result, the calculated emission factors are lower. In comparison, Miguel et al. (1998) calculated total (n=10) road side particulate PAH emission from gasoline vehicles to have a range of 0.09 ± 0.01 to 2.3 ± 0.1 mg kg⁻¹ of fuel. The same ten particulate PAH during the Iowa City tire fire had a total emission of 38 ± 31 mg kg⁻¹, which is significantly greater than the gasoline emissions.

The EPA open burn simulation emission factors comprise gas and particle phase PAH. Once again, emissions of lower molecular weight PAH were significant. This is especially true for acenaphthene, a three ring species, which had an emission of 2445.7 mg kg⁻¹ of tire which accounts for nearly half of the total emissions. The inclusion of gas phase PAH during sampling would account for these large values. The total emission of

PAH in the open burn simulation was 5146 mg kg^{-1} of tire, which was much larger than the 500 g sample from FLAME IV which only had a total emission of $770 \pm 180 \text{ mg kg}^{-1}$ of tire. Even when comparing only PAH that were quantified in both samples, the total emission factors are 1650 and $530 \pm 110 \text{ mg kg}^{-1}$ for the EPA and FLAME IV studies, respectively. Gas phase PAH are the likely cause for the high emission factor in the simulated open burn. This also depends on temperature, flow rates and collection efficiency. The researchers noted that the filter loadings were quite large and caused clogging in some cases. The collected particulate in the EPA study was also not size selected and represents TSP. A larger particle ($> 2.5 \mu\text{M}$) with adsorbed organic species would have been sampled in the open burn simulation and not in the FLAME IV study.

Field derived composition of soot gives a different perspective on PAH concentrations resulting from tire combustion. The collected sample had a composition of PAH at $1144.3 \text{ mg kg}^{-1}$ of soot. In comparison, the mass fractions from the FLAME IV emission study were 5960 and $2110 \text{ mg kg}^{-1} \text{ PM}_{2.5}$ for the 500 and 50 g samples, respectively. PAH composition arising from three ring PAH was not significant; however, the composition was consistent in four to six ring PAH. Compositions for pyrene (four ring), benzo[a]pyrene (five ring) and indeno[1,2,3-cd]pyrene (six ring) were 121, 154 and 160 mg kg^{-1} of soot, respectively.

Table 4.1 Comparison of emission factors and soot composition of tire combustion

Reference	Laboratory Derived Emission Factors			Field Derived Emission Factor	Field Derived Composition of Tire Fire Soot
	This Study	This Study	Lemieux and Ryan, 1993 ^a	Downard et al., 2014 ^b <i>In Preparation</i>	Wang et al., 2006 ^c
Sample Type	PM _{2.5}	PM _{2.5}	TSP and Gas Phase	PM _{2.5} ^d	Soot
Tire Mass/Amount	500 g	50 g	4.5-9.0 kg	1.3 million	4000-6000
Tire Type	Shredded	Shredded	Shredded	Shredded	Whole Tires
Emission Factor or Soot Composition	(mg kg ⁻¹)	(mg kg ⁻¹)	(mg kg ⁻¹)	(mg kg ⁻¹)	(mg kg ⁻¹ soot)
Naphthalene	NQ	NQ	486	NQ	NQ
Acenaphthylene	NQ	NQ	561.8	NQ	0.26
Acenaphthene	NQ	NQ	2445.7	NQ	0.01
Phenanthrene	36.7 ± 7.3	1.9 ± 0.4	252.5	NR	NQ
Anthracene	18.7 ± 4.0	1.0 ± 0.2	49.6	NR	2.59
Fluoranthene	82.0 ± 16.4	4.2 ± 0.8	458	0.67 ± 0.80	129
Pyrene	75.0 ± 15.0	4.0 ± 0.8	151.7	0.70 ± 0.34	121
9-Methylanthracene	3.7 ± 0.9	0.82 ± 0.20	NQ	0.35 ± 0.19	NQ
Benzo[GHI]fluoranthene	74.5 ± 14.9	15.1 ± 3.0	NQ	1.6 ± 0.5	NQ
Cyclopenta[cd]pyrene	89.5 ± 27.2	15.7 ± 4.8	NQ	0.65 ± 0.34	NQ
Benz[a]anthracene	53.4 ± 10.7	9.4 ± 1.9	102.4	1.8 ± 2.2	115
Chrysene	43.2 ± 8.6	8.7 ± 1.7	91.6	8.3 ± 8.0	NQ
1-Methylchrysene	3.3 ± 0.7	0.6 ± 0.1	NQ	1.2 ± 0.9	NQ
Retene	3.8 ± 0.8	4.1 ± 0.8	NQ	0.90 ± 0.96	NQ
Benzo[b]fluoranthene	37.7 ± 7.5	8.9 ± 1.8	88.4	17 ± 13	140
Benzo[k]fluoranthene	47.0 ± 9.4	8.6 ± 1.7	99.4	^e	67.4
Benzo[j]fluoranthene	16.3 ± 3.3	2.7 ± 0.5	NQ	1.1 ± 1.4	NQ
Benzo[e]pyrene	20.2 ± 4.0	4.3 ± 0.9	NQ	9.8 ± 7.6	61.5
Benzo[a]pyrene	76.2 ± 23.2	14.7 ± 4.5	113.9	2.3 ± 2.2	154
Perylene	16.4 ± 6.2	2.8 ± 1.1	NQ	0.35 ± 0.26	21.0

Table 4.1 Continued

Indeno[1,2,3-cd]pyrene	26.1 ± 5.2	5.0 ± 1.0	85.5	2.9 ± 2.1	160
Benzo[GHI]perylene	30.7 ± 6.1	5.6 ± 1.1	159.4	3.4 ± 2.1	83.0
Dibenz[ah]anthracene	10.6 ± 2.1	2.0 ± 0.4	ND	1.1 ± 0.65	28.0
Picene	10.0 ± 2.0	2.0 ± 0.4	NQ	1.6 ± 0.68	NQ
Total	770 ± 180	120 ± 28	5146	56 ± 44	1144

Values reported with ± represent analytical uncertainty, NR - Not Reported, NQ - Not Quantified, ND - Not Detected

a) Lemieux, P.M. and Ryan, J.V., 1993.

b) Downard, J., Singh, A., Bullard., Jayarathne, T., Rathnayake, C., Simmons, D.L., Wels, B.R., Spak, S.N., Stanier, C., Stone, E.A., 2014

c) Wang, Z., Li, K., Lambert, P., Yang, C., 2007.

d) Ambient PM_{2.5} emission factors calculated from June 2, 2012 data only

e) Benzo[b]fluoranthene and benzo[k]fluoranthene were quantified together in ambient PM_{2.5} sample

Ratios of specific PAH can be used diagnostically to identify combustion sources (Goncalves et al. 2011). The ratios of benzo[GHI]perylene/ benzo[a]pyrene for the 500 and 50 g samples were 0.40 ± 0.14 and 0.38 ± 0.14 , respectively. This is lower, in comparison, to the same ratio calculated for vehicle gasoline emissions with and without a catalytic converter and diesel truck emissions, which were 3.3, 2.5 and 1.2, respectively (Rogge et al. 1993). Additionally, the same ratio had a range of 0.19 to 0.35 in agricultural residue burning (Goncalves et al. 2011). The benzo[a]anthracene/ chrysene + benzo[a]anthracene ratio was 0.55 ± 0.13 and 0.52 ± 0.13 for the 500 and 50 g FLAME IV samples, respectively. These values are comparable to gasoline vehicle emission without a catalytic converter, for which this ratio was 0.57. Gasoline vehicle emission with a converter and diesel truck emissions had ratios of 0.33 and 0.27, respectively (Rogge et al. 1993). Furthermore, the ratio of fluoranthene/fluoranthene + pyrene had values of 0.52 ± 0.13 , 0.51 ± 0.12 and 0.67 ± 0.12 for the 500 g, 50 g and ambient sample, respectively. This ratio ranged from 0.46 to 0.63 for agriculture residues (Goncalves et al. 2011), 0.20 to 0.45 for biomass fuels (Hosseini et al. 2013) and 0.37 to 0.61 for gasoline and diesel automobiles (Rogge et al. 1993). The diagnostic ratios

calculated from the laboratory and field emission factors are not significantly different across tire, biomass, and fossil fuel burning. Consequently, they are not recommended to differentiate tire combustion emissions from other combustion sources.

The decrease of B[a]P relative to B[e]P (benzo[e]pyrene/ benz[e]pyrene + benzo[a]pyrene) is an indicator of emission aging by photolysis (Bi et al. 2003). In the FLAME IV study this ratio was 0.21 ± 0.07 and 0.23 ± 0.07 for the 500 and 50 g samples, respectively. This same ratio calculated from the ambient derived emission factors was 0.79 ± 0.16 . Consequently, plume aging had taken place in the ambient samples and this further justifies aging tire combustion studies to determine what other changes are occurring.

The PAH picene has previously been identified in coal combustion (Oros and Simoneit 2000) and is used as a tracer for coal burning in source apportionment modeling in ambient studies (Gao et al. 2013). Hence, the detection of high concentrations of picene in tire combustion emissions was surprising. The maximum ambient concentration observed was $0.58 \pm 0.10 \text{ ng m}^{-3}$ on June 2. Also, emissions from the FLAME IV 500 and 50 g samples were 10.0 ± 2.0 and $2.0 \pm 0.4 \text{ mg kg}^{-1}$ of tire, respectively. The high concentrations during the tire fire and from laboratory tire combustion indicated that picene is not unique to coal. This result demonstrates that picene is not a suitable tracer for coal combustion when tire burning may be present in the region.

Examined together, these emission factors and soot composition demonstrate that tire combustion results in enhanced emission of hazardous PAH compounds relative to background levels to the atmosphere. The magnitude of emissions is ten times larger when gas and particle phase PAH are considered. Quantified PAH were found to comprise 0.6% of $\text{PM}_{2.5}$ mass in laboratory combustion. Additionally, the fuel-to-oxygen ratio has a considerable effect on PAH emissions and hence the efficiency of the burning conditions should be considered when evaluating exposure during open combustion of tires (Levendis et al. 1996).

CHAPTER 5

EMISSIONS OF AZAARENES AND OXYGENATED PAH

5.1 Structures, Sources and Health Implications of Azaarenes and Oxygenated PAH

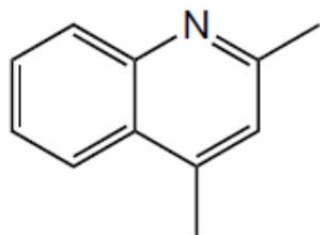
Combustion of tires generates analogs of PAH that contain heteroatoms (Wang et al. 2006). An azaarene is a PAH with one or more carbon atoms in the ring system replaced by a nitrogen. An oxygenated PAH (oxy-PAH) is a PAH with one or more carbonyl functional groups. Examples of azaarenes and oxy-PAH structures can be seen in Figure 5.1.

Azaarenes and oxy-PAH have been measured in ambient aerosols (Delhomme and Millet 2012; Chen and Preston 1998; Delgado-Saborit et al. 2013) and are detected in PM emitted by combustion sources such as waste incineration (Minomo et al. 2009), gasoline and diesel emissions (Jakober et al. 2007) bio-mass burning (Fine, Cass and Simoneit 2001), and tire combustion (Demarini et al. 1994; Wang et al. 2007). Oxy-PAH have also been shown to form in a secondary nature as a result of parent PAH reacting with atmospheric oxidants such as ozone and hydroxyl radicals (Wang, Atkinson and Arey 2007; Perraudin, Budzinski and Villenave 2007).

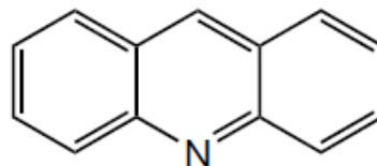
The presence of heteroatoms in these polycyclic compounds changes their interactions with biological tissues, giving them different health effects, when compared to PAH. Carbonyl functional groups on PAH do not increase mutagenic properties of these compounds; oxy-PAH are on average 50 times less mutagenic than benzo[a]pyrene (Durant et al. 1996). Contrary to carbonyl functionalities, nitrogen atoms in the PAH structure impart an enhancement of negative health impacts. Azaarenes have been shown to have higher toxic and genotoxic potentials than their parent PAH compounds (Bartos et al. 2006). During a large scale open tire combustion event, population exposure is of

concern. The negative health impact of azaarenes makes their identification and quantification in tire combustion emissions crucial.

2,4-Dimethylquinoline



Acridine



2-Methyl-9,10-anthracenedione **Benz[a]anthracene-7,12-dione**

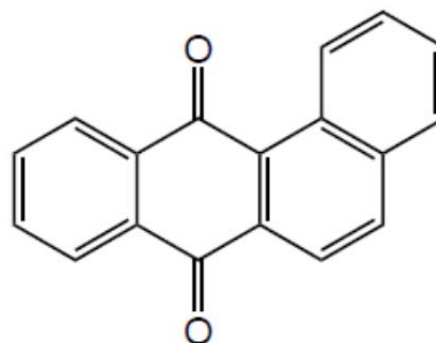
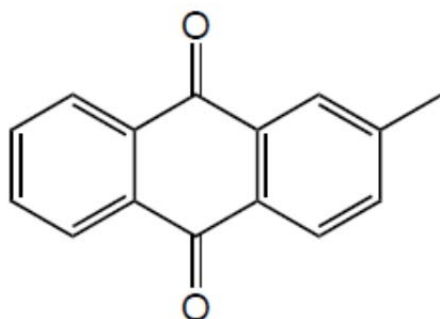


Figure 5.1 Azaarenes and oxy-PAH quantified in this study.

5.2 Qualitative Identification of Azaarenes and Oxygenated PAH in Laboratory and Real World Tire Combustion

Azaarenes were first qualitatively identified in ambient aerosol and laboratory combustion samples and select compounds quantified in laboratory emissions. The qualitative results are summarized in Table 5.1 and include accurate masses, mass error, retention times and calculated Lee's retention indices.

Azaarenes with two to four rings were identified, meanwhile PAH with up to six rings were detected in tire combustion emissions. Here, the size range of identified azaarenes was two to four rings with molecular weights of 129 Da (isoquinoline) to 217 Da (benzo[b]carbazole). Wang et al. (2006) identified three of the same azaarene species (2,4-dimethylquinoline, carbazole and benzo[b]carbazole) in their soot and water samples. Wang et al. (2006) also identified quinoline and benzo[h]quinoline. Similar to this study, the work of Demarini et al. (1994) revealed the presence of acridine in tire combustion emissions. An observation of notice is that no azaarene with a molecular weight greater than 217 Da was identified in this study or by Demarini et al. (1994). Wang et al. (2006) only identified one azaarene greater than this, with a molecular weight of 282 Da. Unlike PAH compounds, larger molecular weight azaarenes were not forming in tire combustion. All of the identified azaarenes have only one nitrogen in their ring structure. Wang et al. (2006) also identified mono-methylated carbazole and quinoline species. Here, only a di-methylated azaarene was found and that was 2,4-dimethylquinoline. Isoquinoline, phenanthridine, 2-azapyrene and 4-azapyrene are four azaarenes that were identified for the first time in tire combustion emissions in this study.

Oxy-PAH identified in laboratory and real world tire combustion are also summarized in Table 5.1. The identified oxy-PAH had similar characteristics to azaarenes. The size range in this class was three to four rings with a molecular weight range of 180 Da (9-fluorenone, 1H-Phenalen-1-one) to 258 Da (benz[a]anthracene-7,12-

dione) In comparison to previous studies, similarly identified oxy-PAH included 9-fluorenone, 1H-phenalen-1-one, anthraquinone and benzanthrone (De Marini et al. 1994; Wang et al. 2006). Similar to azaarenes, no identified oxy-PAH had a molecular weight greater than 258 Da across all three studies, suggesting again that larger molecular weight oxy-PAH were not forming. Mono and di-carbonyl functionalities existed in the identified oxy-PAH. Additionally, one mono-methylated oxy-PAH was observed and that was 2-methyl-9,10-anthracenedione. 2-Methyl-9,10-anthracenedione, benzo[b]fluorenone and benz[a]anthracene-7,12-dione are three oxy-PAH identified in tire combustion emissions for the first time.

Comparisons between laboratory and real world studies show no formation of larger molecular weight compounds in both classes. Unlike the laboratory and real world emissions of PAH from tire combustion, there was no preference for lower molecular weights in the identified azaarenes and oxy-PAH between sample types. Excluding 1-azapyrene, 4-azapyrene, and benzanthrone, all other azaarenes and oxy-PAH were found in the laboratory and ambient sample. None of these species were detected in the back-up filters from the laboratory study, indicating that fresh emissions are enriched in particle phase compounds of these classes similar to PAH. This is a curious finding since 2,4-dimethyl-quinoline and acridine have boiling points of 264 and 346 °C, respectively. These boiling points are lower than some four ring PAH expected to have concentrations in the gas phase.

Many of the same compounds were found between this study and previous studies of tire combustion, suggesting that azaarenes and oxy-PAH are common components in this emission source. However, these compounds are also common in atmospheric aerosols from alternative sources. The presence of azaarenes in tire combustion emissions and their known genotoxicity re-emphasize the health concerns associated with this source.

Table 5.1 Qualitative identification of azaarenes and oxy-PAH in laboratory and real world tire combustion

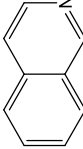
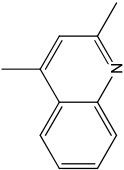
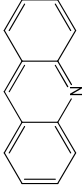
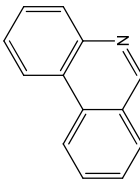
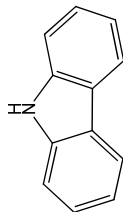
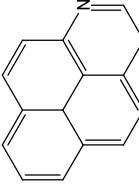
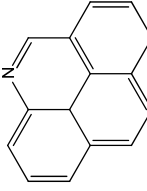
Azaarenes	Structure	Formula	Observed Mass (Da)	Actual Mass (Da)	Error (mDa)	Retention Time (mins)	Calculated Lee's Retention Index ^a	Reference Index	Observed in June 2, 2012 Ambient Sample	Confirmed with Standard
Isoquinoline		C ₉ H ₇ N	129.0591	129.0578	1.6	16.72	213.1	214.41 ^b	x	
2,4-Dimethyl-quinoline		C ₁₂ H ₉ N	157.0886	157.0891	-0.5	20.06	252.0	247.38 ^b	x	x
Acridine		C ₁₃ H ₉ N	179.0730	179.0756	-0.5	24.42	303.8	303.99 ^b	x	x
Phenanthridine		C ₁₃ H ₉ N	179.0756	179.0735	2.1	24.67	307.7	307.30 ^b	x	
Carbazole		C ₁₂ H ₉ N	167.0744	167.0735	0.9	24.76	309.1	309.8 ^c	x	
1-Azapyrene		C ₁₅ H ₉ N	203.0739	203.0735	0.4	27.80	356.7	357.73 ^d		
4-Azapyrene		C ₁₅ H ₉ N	203.0736	203.0735	0.1	27.94	358.9	357.94 ^d		

Table 5.1 Continued

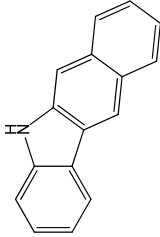
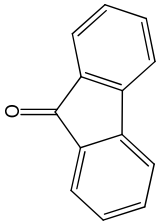
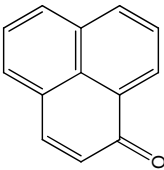
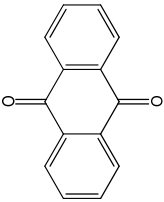
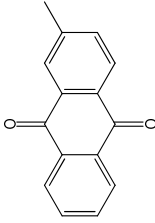
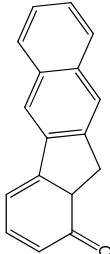
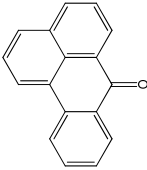
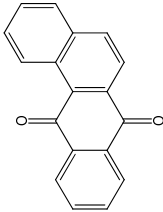
 Benzo[b]carbazole	$C_{16}H_{11}N$	217.0921	217.0891	2.9	31.11	409.3	409.31 ^c	x	
Oxygenated PAH									
 9-Fluorenone	$C_{13}H_8O$	180.0553	180.0575	-2.2	23.71	294.5	293.88 ^b	x	
 1H-Phenalen-1-one	$C_{13}H_8O$	180.0566	180.0575	-0.9	25.46	320.1	320.74 ^e	x	
 9,10-Anthraquinone	$C_{14}H_8O_2$	208.0535	208.0524	1.1	26.15	330.9	331.22 ^e	x	
 2-Methyl-9,10-anthracenedione	$C_{15}H_{10}O_2$	222.0695	222.0681	1.4	27.49	351.7	350.1 ^f	x	

Table 5.1 Continued

Benzo[b]fluorenone		$C_{17}H_{10}O$	230.0740	230.0732	0.8	30.15	393.6	393.84 ^e	x
Benzanthrone		$C_{17}H_{10}O$	230.0726	230.0732	-0.6	30.84	404.7	405.44 ^e	
Benz[a]anthracene-7,12-dione		$C_{18}H_{10}O_2$	258.0686	258.0681	0.5	31.60	417.5	419.09 ^e	x

Observed mass, mass error, retention time and calculated Lee's retention index data all from FLAME emission sample

- a) Lee, M. L., White, M. C., Novotny, M., 1979
- b) Pereira, W. E., Rostad C. E., 1986
- c) Wang, Z., Li, K., Lambert, P., Yang, C., 2006
- d) Vassilaros, D. L., Kong, R. C., Later D. W., Lee, M. L., 1982
- e) Pedersen, D.U., Durant, J.L., Taghizadeh, K., Hemond, H.F., Laffleur, A.L., Cass, G.R., 2005
- f) Lundstedt, S., Haglund, P., Oberg, L., 2002

5.3 Emissions of Azaarenes and Oxygenated PAH in Laboratory Tire Combustion

In this study, emission factors of azaarenes and oxy-PAH in laboratory tire combustion were determined for the first time; results are summarized in Table 5.2. Emissions of benz[a]anthracene-7,12-dione are the largest in both the 500 g and 50 g sample at 6.4 ± 1.3 and 4.1 ± 0.8 mg kg⁻¹ of tire, respectively. The emissions of two oxy-PAH were 17.2 ± 4.3 and 11.6 ± 2.8 mg kg⁻¹ for the 500 g and 50 g samples, respectively. Emissions of PAH with heteroatoms were on the same order of magnitude as non-substituted PAH for the 50 g sample. Unlike PAH emission, for which the total emission factor was seven times greater in the 500 g sample, azaarene and oxy-PAH emission factors were comparable across both samples. This observation implies that the formation processes of these compounds are different from PAH, and their emissions are comparable under certain conditions.

Using the ratio of azaarene to benzo[GHI]perylene from the FLAME IV emissions and applying this ratio to ambient samples, an estimation of ambient concentrations of azaarenes was calculated. On June 2, 2012 the estimated ambient concentrations of 2,4-dimethyl-quinoline and acridine had minimum and maximum values of 0.20 – 0.60 and 0.18 – 0.56 ng m⁻³, respectively. On a background day during the tire fire (May 24, 2012) the estimated minimum and maximum concentrations were 0.01 and 0.02 ng m⁻³ for 2,4-dimethyl-quinoline and acridine. Delhomme and Millet (2012) observed total mean azaarene concentrations (sum of two, three, four and five ring species, n=17, 2,4-dimethyl-quinoline and acridine included) at three urban sites in France of 2.8, 1.6 and 1.0 ng m⁻³. The maximum estimated concentration on June 2 of 2,4-dimethyl-quinoline and acridine represent a significant percentage of these totals in urban atmospheres in the range of 41% to greater than 100%.

Table 5.2 Emission factors of azaarenes and oxy-PAH from laboratory tire combustion

Compound	Emission Factor 500 g Shredded Tire (mg kg⁻¹)	Emission Factor 50 g Shredded Tire (mg kg⁻¹)
2,4-Dimethylquinoline	3.7 ± 1.0	2.0 ± 0.6
Acridine	3.3 ± 1.3	1.9 ± 0.7
2-Methyl-9,10-anthracendione	3.8 ± 0.8	3.6 ± 0.7
Benz[a]anthracene-7,12-dione	6.4 ± 1.3	4.1 ± 0.8
Total	17.2 ± 4.3	11.6 ± 2.8

CHAPTER 6

CONCLUSIONS AND HEALTH IMPLICATIONS

This research clarifies and expands what is known about the composition of tire combustion emissions. The $PM_{2.5}$ mass generated by laboratory combustion was found to contain elemental carbon at 80% mass. However, hazardous metals were found not to be enriched in ambient PM_{10} collected 4.2 km from the Iowa City tire fire. Laboratory measurements also support that tire burning is not a significant source of Pb or Fe, although may sporadically emit Zn. Zn was found to comprise 0.04% of $PM_{2.5}$ mass in laboratory combustion. To verify these results, metals should be measured near to an open emission site.

PAH were confirmed as major combustion products from tires, quantified PAH species represent 0.6% of $PM_{2.5}$ mass in laboratory combustion. Ambient concentrations of PAH in the smoke plume were enhanced by two orders of magnitude in tire combustion smoke compared to background levels. When considering just the particle phase, a larger mass of burned tires resulted in six times greater PAH emissions compared to a smaller mass. This result implies the combustion environment was affecting PAH emissions (Levendis et al. 1996). The nature of the sample (ambient v. laboratory) and the equipment used to collect it affects the absolute and relative amount of PAH measured. Lower-molecular weight PAH partition to the gas phase after cooling and dilution, whereas the larger PAH are adsorbed to particles when collected at the source. Consequently, ambient gas phase PAH concentrations are considered to have been significantly impacted by the Iowa City tire fire, and should be quantified in future studies.

Azaarenes and oxy-PAH have been shown to be significant components in tire combustion emissions. Four azaarenes and three oxy-PAH, however, were identified in

tire combustion emissions for the first time and these compounds extend the list of known azaarenes and oxy-PAH arising from this emission source. Emission factors of azaarene and oxy-PAH compounds have been quantitatively evaluated in tire combustion emissions for the first time. Their emissions are similar to PAH when low tire masses are combusted. Interestingly, their emissions are not increased when more tire mass is burned suggesting a difference in formation process between azaarenes, oxy-PAH and PAH.

In conclusion, a more comprehensive description of tire combustion emission was gained through this study. The presence of hazardous compounds in tire combustion emissions, such as PAH, azaarenes, oxy-PAH and a high fraction of elemental carbon make it apparent these emissions have serious health implications. The concern over hazardous metals, though, can be eliminated at distances 4.2 km and greater from large scale open combustion. Nevertheless, population exposure to the smoke should be avoided.

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