POLYCYCLIC AROMATIC HYDROCARBON ACCUMULATION IN SOIL RECEIVING ROOFTOP RUNOFF

By

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Abstract: Polycyclic aromatic hydrocarbons (PAHs) are persistent organic pollutants that are ubiquitous in the environment and can potentially impact human health. The main objective of this study was to qualify and quantify PAH accumulation (especially the seven potentially carcinogenic PAHs (cPAHs)) throughout the Oklahoma City Metro Area and to investigate factors that could be related to higher accumulation. Factors included building use (residential, commercial, and school) and roofing type (asphalt, metal, and tar). To determine if cPAH concentrations were higher in soil receiving direct rooftop runoff, paired runoff receiving contact samples and reference samples (not receiving rooftop runoff) were evaluated from each site. In addition to determining the presence of certain PAHs, a digestive model was applied to give an indication as to what percent of the overall PAHs become bioavailable if contaminated soil is ingested.

Overall 77% of the locations analyzed had levels of cPAHs above the USEPA's soil screening level (SSL). Benzo[a]pyrene (BaP), a known carcinogenic PAH, appeared above SSL in 74% of the samples, with the 95th percentile of runoff contact samples at 880 ppb. Contact soil samples surrounding schools had the highest significant values of cPAHs contamination within building usage, with 95th percentile concentrations of cPAH for soil receiving rooftop runoff at 140,000 ppb. Schools and commercial contact soils had significantly elevated levels of cPAHs and BaP as compared to residential contact soils. Roof type did not vary in contributing to cPAH or BaP levels in contact samples. cPAHs and BaP concentrations in contact soils were significantly greater within each sampling subset compared to the paired reference sample.

The digestive model indicated that some of the soils with the highest concentrations of cPAHs and BaP had less than 3% bioavailability. Values of some samples were still more than 100 ppb bioavailable, but there was a great decrease in concentration of cPAHs within the bioavailable fraction. Because many high concentrated cPAH soils were found in school areas, school sites should be further investigated for contamination. While these sites may not show high potentials for bioavailability, the magnitude of cPAH concentrations in soil is still a cause for concern.

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INTRODUCTION

Pollution is a problem that human beings are faced with every day. Some forms of pollution are more obvious and can be directly observed, while others are more subtle: non-point source pollution, byproducts of point source pollution or simply pollution events not brought to the public's attention. One such pollutant that is common in the environment is a group of compounds known as polycyclic aromatic hydrocarbons (PAHs). This type of molecule consists of two or more benzene rings, with variations of low molecular weight (LMW) compounds having fewer than four rings and high molecular weight (HMW) PAHs having four or more ringed structures (Kim *et al*. 2013). Within these classifications there are alternant PAHs with six-carbon benzene rings, and non-alternant PAHs with both six-carbon rings and five-carbon rings (Huang and Penning 2014). There are upwards of 100 of PAHs found in the environment, and these compounds are almost always found as mixture (ATSDR 1995), and within a soil setting, these mixtures are likely to contain varying levels of both non-carcinogenic and carcinogenic PAH compounds (CCME 2010). Basic PAHs consist of benzene rings, but there are also substituted PAHs that include additional components such as added elements, methylsulfones, alkyl groups, hydroxy- and other groups (CCME 2010). These additional elements may increase or decrease the carcinogenic potential of the PAH molecule (CCME 2010). For example, the methylation of chrysene strongly increases its carcinogenic potential in rodents and the methylation of benz[*a*]anthracene can also increase carcinogenic activity depending on the site of the alkyl-substitution (CCME 2010).

PAHs arise in the environment from many different activities, both natural and man-created, but generally from impartial combustion events. According to the CDC, PAHs occur in gasoline and oil, as well as in coal (2009). They also occur in the environment as a result of combustion of these fuels, and from the burning of other items like garbage, wood, or tobacco (Zhang and Tao 2009). Dominguez et al. (2010) found that there is a correlation between 4-6 ringed PAHs and close proximity to industrialization as well as an elevated affinity of PAHs to soils with high soil organic carbon. In 2004, the atmospheric emissions of the 16 priority PAHs in the entire world were thought to be 520 Gg per year with North America being the fourth most PAH polluting world region, and the United States being the third most PAH polluting country overall with 32Gg per year PAH emissions (Zhang and Tao 2009). Globally, biofuel accounts for the highest release of PAHs and BaP into the environment with wild fires as a second, non-anthropogenic contributor, while in the United States, consumer products and traffic oil are the biggest contributors to atmospheric PAHs and waste incineration, biofuel, and traffic oil are the biggest contributors to BaP, in that order (Zhang and Tao 2009).

Among the PAHs widely distributed in the world, there are currently 16 priority PAHs that are more heavily studied and monitored by the EPA (Campro 2010, Keith and Telliard 1979). These priority PAHs include naphthalene, acenapthylene, acenapthene, fluorine, phenanthrene, anthracene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene (BaP), dibenz[*a,h*]anthracene benzo[*ghi*]perylene, and indeno[*1,2,3-cd*]pyrene (Zang and Tao 2009). These, along with other PAHs, can stem from quite specific sources and may be categorized as originating from one of three activities: petrogenic, pyrogenic, or biogenic (Wang *et al*. 2014). Petrogenic sources of PAHs include oil spills and fuel sources, while pyrogenic PAHs arise through high heat processes and combustion of fuels (Boehm 2010). Many petrogenic PAHs are differentiated because of added compounds resulting in alkylation or oxygenation (Huang and Penning 2014). The temperature at which these PAHs may form can be indicative of both the extent of alkylation as well as whether the products are petrogenic or pyrogenic. For example, when phenanthrene is petrogenic it is formed at lower temperatures (100-150ºC) and is also more heavily alkylated, but at higher temperatures (400ºC and higher) the alkylation decreases and it has been formed in a pyrogenic manner (Boehm 2010).

Urban areas are prone to higher levels of anthropogenic pollution as compared to surrounding rural areas because of concentrated traffic and industrialization.. Human exposure usually occurs with multiple PAHs at a time and not a single PAH because they are found in mixtures (ATSDR 1995). While PAHs occur in the environment through many vectors, Jongeneelen (1994) cited five main routes in which humans may be exposed through environmental means to PAHs: inhalation of tobacco smoke, inhalation of PAHs in outdoor air, exposure (dermal, ingestion, and inhalation) from polluted water, oral exposure through food contaminated with PAHs, exposure in urban areas with heavy industrial influences (dermal, ingestion, and inhalation). Within the United States, most PAH exposure is due to inhalation of smoke from tobacco or wood burning or contaminated air as well as eating contaminated foods (ATSDR 1995).

Out of the 16 priority PAHs there are seven noted carcinogenic PAHs , ranging from 4-6 rings: benz[a]anthracene, benzo[a]pyrene (BaP), benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenz[a,h]anthracene, and indeno[1,2,3-cd]pyrene (USEPA Regional Screening Levels 2015). Generally any of the common PAHs of four or more rings have a higher carcinogenic potential ((Huang and Penning 2014). Mumtaz and George (1995) reported that there were noted developmental and reproductive effects on animals that had been orally exposed to PAHs and minimum risk levels were adapted for a small percentage of PAHs. Of the carcinogenic PAHs, BaP is often used as comparative analyte (WHO 1984, Huang and Penning 2014) as this is a known, and well-studied animal and human carcinogen. One such study showcasing BaP showed that mice orally exposed to high dosages (100mg/kg/day) of BaP, were found to have a negative impact on reproductive tissues including fewer seminiferous tubular cells which lead to the production of testosterone as well as DNA damage (Jeng *et al.* 2015).

Oral exposure is a major route of exposure in humans. One route of oral exposure seen as a main-route for non-smokers is through food (Kim *et al*. 2013). Within the United States, estimates show that food is a major route of exposure for humans, accounting for 97% of intake when compared collectively with air and water (Hattermer-Frey and Travis 1991). In this same study, the general U.S. population was also estimated to have a daily intake of 2.2µg BaP (Hattermer-Frey and Travis 1991).

Food preparation accounts for a majority of this, but crops grown or fish living in contaminated environments also account for much of this potential exposure (Huang and Penning 2014). PAHs are unlikely to bioaccumulate within stock animals used for human consumption, even if grazing on contaminated vegetation occurs (CCME 2010), but because PAHs occur from combustion events, the acts of grilling, frying, or smoking meats leads to pyrolysis of fat which can contribute dietary PAHs (Huang and Penning 2014). Limiting the contact of food with flames and avoiding highly fatty meats decreases likelihood of increased PAH contamination (CCME 2010). A study in Catalonia, Spain, indicates that the mean dietary intake for an average man per day of cPAHs normalized for BaP equivalency is 0.248µg/day and BaP intake is about 0.128µg/day, leaving the risk of cancer from this intake at 1 in 20 million (Falco *et al*. 2003). Falco *et al*. (2003) also reported the main contributors to PAHs in diet were from cereals, meat, and oils and fats in order of greatest to least impact. These estimates are much lower than the estimate of 2.2µg/day by Hattermer-Frey and Travis (1991), but levels of PAHs do vary across countries and landscapes. Menzie *et al*. (1992) have predicted a range of oral exposure for carcinogenic PAHs in the U.S. to be from 1-5µg/day with an increased risk for individuals consuming larger quantities of meat.

Food exposure is one vector of PAH ingestion, but another less obvious exposure is through the ingestion of soil, which is potentially more problematic and frequent in children than adults, as children are likely to consume soil or practice hand-to-mouth behaviors before the age of 6 (Moya *et al*. 2004). Menzie *et al.* (1992) suggest that an individual consuming 50mg/day (a value that may be applied to soil consumption in children) may have the potential to ingest 0.003-0.3µg cPAHs per day with a median ingestion of 0.06µg/day. While Menzie *et al*. (1992) predicted the median ingestion of cPAHs to be 0.06µg/day, this was based off of soil in urban populations with a median soil concentration of 1.10 mg/kg dry weight. Levels of PAHs in soils, both carcinogenic, and non-carcinogenic, do vary across areas of land use, urbanization, and across countries. In a review of soils across varying landscapes, Nadal *et al*. (2004) show a potential variation from 0.05 mg/kg (dry weight)-300,000 mg/kg (dry weight). These sites varied based on use and included urban soils, rural soils, agricultural soils, and industrial soils across Europe and Asia. The estimation of ingestion of soil by Menzie *et al*. may be protective for adults in certain areas, but people living in areas with higher levels of soil contamination, who have the potential for greater soil-ingestion could be at a higher risk for contact with the carcinogenic PAHs.

CHAPTER II

POLYCYCLIC AROMATIC HYDROCARBON ACCUMULATION IN SOIL RECEIVING ROOFTOP RUNOFF

2.1 Abstract

Polycyclic aromatic hydrocarbons (PAHs) are persistent organic pollutants that are ubiquitous in the environment and can potentially impact human health. The main objective of this study was to qualify and quantify the degree of PAH accumulation (especially the seven potentially carcinogenic PAHs (cPAHs)) throughout the Oklahoma City Metro Area and to investigate factors that could be related to higher accumulation. Factors included building use (residential, commercial, and school) as well as roofing type (asphalt, metal, and tar). To determine if cPAH concentrations were higher in soil receiving direct rooftop runoff paired runoff receiving contact samples (samples directly under drip lines and downspouts, serving as a catchment for rooftop runoff) and reference samples (not receiving rooftop runoff) were evaluated from each site. In addition to determining the presence of certain PAHs, a digestive model was also applied to give an indication as to what percent of the overall PAHs become bioavailable if contaminated soil is ingested.

Overall 77% of the locations analyzed had levels of cPAHs above the USEPA's soil screening level (SSL). Benzo[a] pyrene (BaP), a known carcinogenic PAH, appeared above SSL in 74% of the samples, with the 95th percentile of runoff contact samples at 880 ppb. Contact soil samples surrounding schools had the highest significant values of cPAHs contamination within building usage, with 95th percentile concentrations of cPAH for soil receiving rooftop runoff at

140,000 ppb. Schools and commercial contact soils were found to have significantly elevated levels of cPAHs and BaP as compared to residential contact soils. Roof type did not vary in contributing to cPAH or BaP levels in contact samples. There was also a significantly greater concentration of cPAHs and BaP for contact soils within each sampling subset as compared to their paired reference samples.

A digestive model was used to provide an indication of bioavailability of cPAHs and BaP in select soils exhibiting levels of cPAHs greatly exceeding the USEPA SSL. This model indicated that some of the soils with the highest concentrations of cPAHs and BaP had less than 3% bioavailability. Values of some samples were still more than 100 ppb bioavailable, but there was a great decrease in concentration of cPAHs within the bioavailable fraction. Because many high concentrated cPAH soils were found in school areas, school sites should be further investigated for contamination. While these sites may not show high potentials for bioavailability, the magnitude of cPAH concentrations in soil is still a cause for concern in certain samples sites as the concentrations of bioavailable cPAHs found at these sites still exceed the SSL for whole soil. Further testing at school sites is recommended to explore the overall trend of highly concentrated cPAHs in both contact and reference soils, as well as to gain better knowledge about any trends in bioavailability of cPAHs in school areas. While small percentages of bioavailable cPAHs were found, there is still a risk for children who are most likely to be exposed to this group of compounds.

2.2 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are common environmental contaminants (World Health Organization 1987), and have been found to exist in the soil at higher concentrations at urban sites than rural sites (Mumtaz and George 1995). Accordingly, Dominguez et al. (2010) found that there is a correlation between 4-6 ringed PAHs and close proximity to industrialization as well as an elevated affinity of PAHs to soils with high soil organic carbon. PAHs can be released to the environment directly since they are present in motor oil and coal tar or they can be formed within the environment following impartial combustion events and released through vehicular exhaust and power plant emission (Baek et al. 1991, CDC 2009, National Research Council 1983, Hangebrauck et at. 1967). In a study conducted by Lorenzi et al. (2011) urban street dust was analyzed for PAH content and was found to contain a variety of PAHs. The concentrations correlated with the proximity to vehicle emissions, indicting a pattern where the most elevated concentrations of PAHs are near heavy vehicular traffic. PAHs have also ben found to be also present in tar used in both roofing and parking lot maintenance (Mumtaz and George 1995, Simon and Sobieraj 2006).

While there are upwards of 100 forms of PAHs, 54 have been found at various hazardous waste sites (Mumtaz and George 1995). Exposure to these PAHs in both animals and humans occurs via inhalation, ingestion, or dermal exposure, with degrees of oral absorption varying based on the type of PAHs present (Mumtaz and George 1995). When exposure to PAHs occurs it is nearly always to a mixture of PAHs and not a single compound (ATSDR 2015, CDC 2009, World Health Organization 1987). After exposure events, PAHs may be biodegraded by the body and potentially changed into substances that are more harmful than the original hydrocarbons causing mutagenesis (ASTDR 2015, National Research Council 1983). Seven PAHs have been identified as possibly or potentially carcinogenic PAHs or cPAHs (Mumtaz and George 1995). These PAHs have 4-6 rings including benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenz[a,h]anthracene, and indeno[1,2,3-cd]pyrene (USEPA 2016). cPAHs also fit into a group known as high molecular weight compounds and are often categorized as such for risk assessment purposes (USEPA 2016).

After occurrences of impartial combustion from industry or vehicular exhaust, gaseous PAHs are carried through the air where they may attach to dust particulates (Gobel et al. 2007, World Health Organization 1987). PAHs travel through the air in a continuous gaseous state or as attached to particulate matter where they may settle through dry atmospheric deposition and rainfall in locations such as soils or rooftops (Mumtaz and George 1995, Baek et al. 1991). PAHs in some soils have been found to persist for prolonged periods of time, with larger ringed (5- and 6-ringed) PAHs being less bioaccessible to microbes and therefore less easily degraded (Johnsen and Karlson 2007). Runoff from storms can greatly affect PAH deposition where PAHs have bound to particulates and can infiltrate soil (Gobel et al. 2007). In areas where PAHs have the potential to settle as dust on rooftops, rooftop runoff could contribute to concentrations of these organic compounds in the soil directly under gutters or drip lines; this is also supported by direct deposition as shown by higher levels of PAHs in soils based on proximity to vehicular traffic (Van Metre and Mahler 2003). Roofing material may also be found to play a role in PAH contribution as leaching of PAHs into rooftop runoff could result in contaminated receiving soil. Van Meter and Mahler (2003) found a very slightly higher, but not significant, contribution of lower molecular weight PAHs to rooftop runoff from asphalt roofs than from metal roofs, although the variation was not statistically different for all PAHs. Lay *et al*. (2014) found a significant difference in cPAH concentration in rooftop runoff itself, with metal roofs having a higher maximum cPAH concentration, and a higher initial concentration in water. Asphalt roofs also contributed to cPAHs but had a slower release, which was speculated to be from the difference in surface material and texture. BaP was also found in a higher percentage of runoff samples of asphalt-roofed buildings as opposed to metal or tar (Lay *et al*. 2014).

Exposure to PAHs could occur through dermal contact, inhalation, or ingestion or contaminated materials. While dermal contact can be a potential risk factor in areas of heavy cPAH pollution like toxic waste sites, inhalation and ingestion are more of a general concern for individuals in the United States (ATSDR 2015). Ingestion of soil containing high levels of cPAHs could be problematic for people of younger ages as children can ingest soil at an average rate of

208 mg/day at the 95th percentile for ages 1-4 (Stanek and Calabrese 1995). However, these estimates are not protective of all children. Children with pica are at risk of ingesting anywhere up to 60 g of soil in a day (Calabrese et al. 1997) and are at especially high risk for exposure if PAH contaminated soil is available. While certain quantities of PAHs are readily found in soils in the environment, these values do not give an accurate representation of exposure potentials based on bioavailability, which could be important in the case of direct exposure through soil ingestion (Menzie *et al*. 1992). To determine bioavailability, bioavailability assays and both *in vivo* and *in* vitro digestive models can be applied (Reid *et al.* 1999, Ramesh *et al.* 2004) to some of the highest cPAH-concentrated soils in order to better understand their overall bioavailable dynamics, as whole models (using full cPAH concentrations, not simply the bioavailable portion) generally overestimate exposure potentials (Alexander 2000).

Based on the wide distribution of PAHs in populated areas and potential occurrence in rooftop runoff, further identifying and quantifying these contaminants across different sites is important to potentially identify low risk versus high risk areas for PAH contamination. Because Oklahoma City is an urban environment, there are likely detectible levels of PAHs across the metro area. The main objective was to determine if cPAHs and benzo[*a*]pyrene (BaP) were higher in soils receiving rooftop runoff. In addition, soil surrounding buildings with different roof-types and building usage were assessed to see if contamination levels differed. Finally, in order to further qualify cPAH and BaP exposure potential in the soil, a digestive model was applied to ascertain more information about the bioavailability potentials of these compounds.

2.3 Methods and Materials

2.3.1 Materials

Solvents and reagents employed in soil preparation and compound examination were analytical grade. PAH and deuterated PAH mixes were obtained from Accustandard (New Haven, CT) and were used as internal standards.

2.3.2 Soil Contamination Survey

Ninety-two sites spread across Oklahoma City, OK and the metro area were sampled. (Fig. 1). Given the urbanization of the area, these sites were all within relatively close proximity to highways and industrialization, as well as located in the same precipitation gradient. The locations were haphazardly selected with variable characteristics of the buildings on site. These characteristics include building use type (commercial, residential, or school) as well as roofing material type (asphalt shingles, metal, or tar). In addition, other factors were noted for each site including building age, gutter presence, area of drainage, pitch, proximity to pavement, and latitude and longitude coordinates.

From each site, topsoil was collected with a metal spade within 5 cm of the downspout or drip line from a 6 cm x 6 cm square, 3 cm deep. These samples that were collected near rooflines were directly receiving rooftop runoff, or contacting the runoff, and shall be referred to as contact samples. A reference sample from an area with similar soil type, but at least 10 m from direct rooftop runoff sources, was also collected from each site. These reference samples were not receiving and drainage or runoff directly or indirectly from the roofs, nor were they downslope or receiving runoff from parking lots. The shovel was rinsed with filtered tap water between samples. Soil samples were thoroughly homogenized by hand mixing with stainless steel spatulas and rocks and vegetation were removed. Dry weight (105 °C for 16 hours) and total soil organic matter (360 °C for two hours) were determined by using the loss-on-ignition technique (Salehi et al. 2011).

To measure PAHs, soil samples were extracted using matrix dispersion followed by column extraction. Soil (1.5 g) was homogenized in a mortar with 0.5g magnesium sulfate, 0.75 g diatomaceous earth, 0.9 g Florisil, and 0.05 g PSA bonded silica. Homogenized material was funneled into a 12 mL column on a vacuum manifold that contains 0.5 g activated silica on the bottom of the column and 2 g sodium sulfate resulting in the soil matrix as the top layer. PAHs in the dispersed soil were recovered in solvent by passing 15 mL of 1:2 hexane: ethyl ether solution through the columns and into test tubes containing 300 μL isooctane. The extract was evaporated under a gentle stream of nitrogen, and rinsed three times with 100 μL isooctane. The final volume was 0.500 mL, which was transferred into amber GC vials. Extracts were analyzed by gas chromatography/mass spectrometry (GC-MS) on an Agilent 6850 GC with an Agilent 5975C inert XL EI MSD mass spectrometer. The GC operated with an initial oven temperature of 40 °C, held for 1 m, followed by a rate of 15 °C/min. to 100°C, 13.00 °C/min.to 240 °C, and 11.00 °C/min. to 300 °C. The GC inlet temperature was 250 °C and the column was a HP-5MS, 5% Phenyl Methyl Siloxane capillary column of 15.0 m with a helium flow rate of 1.1 mL/min. Analysis was conducted using selected ion monitoring. Deuterated PAH analogues were used as internal standards. Analytes and their respective ions that were monitored are listed in Table 1.

Chrysene D12 and perylene D12 were utilized in calibration as internal standards. The precision and accuracy of soil processing was monitored with spiking reagent mixes and blanks with a predeuterated PAH mix. Method detection limits were established based on background noise in blank samples (n=8 blanks).

2.3.3 Bioavailability of PAHs Using a Digestive Gastric and Gastrointestinal Model

Although soils contaminated with PAHs may have distinct concentration values, these are not necessarily representative of actual PAH bioavailability; therefore a digestive model was applied to a subset of soils exhibiting contamination above USEPA SSLs. The model used was adapted from Hack and Selenka (1996) and includes a simulated gastric and gastro-intestinal step to better mimic the human digestive process.

Soils were selected for this model based on levels of cPAH toxic equivalents (TEQs) exceeding the USEPA SSL for BaP (Table 2). These samples included the highest five concentrated samples for cPAHs as well as BaP. For each sample, 0.5 g of soil was added to water in a 100 mL laboratory bottle for a total volume of 50.5 mL and first run through a simulated gastric model. The pH was adjusted to 2.0 ± 0.1 with 1.85% HCl (w/v). Five milligrams of pepsin were added to samples as 2 mL of a 0.25% (w/v) solution in water. The soil solutions were placed in a 37 °C shaking incubator with a shaker setting of 185 RPM for 2 hours. The pH was check and adjusted as needed every 30 minutes. At 90 minutes, the salinity was adjusted to approximately 140 mmol Cl^- by adding 1.8% NaCl (w/v). After the 2 hours., the solutions were adjusted as follows for the gastrointestinal model.

To model the gastrointestinal digestion, samples were neutralized to a pH of 7 ± 0.1 with $NaHCO_3$. Five mg trypsin in 2 mL solution, 175 mg pancreatin in 5 mL solution, and 175 mg bile in 10 mL solution were added. Samples were again placed in the shaking incubator at the same settings for 6 hours. The pH was adjusted to neutral as needed every thirty minutes.

After incubation and shaking was complete, samples were first centrifuged for 10 minutes at 4000 RPM. Liquid fractions were pipetted into 500 mL separatory funnels. Soil was washed with 30 mL water and centrifuged for 10 minutes at 4000 RPM and the liquid fraction was once again added to the respective samples in separatory funnels. The water wash, centrifuge, and decanting was repeated once more ensuring that no particulate matter was transferred to funnels.

Five grams of NaCl were added to each isolated liquid fraction and shaken in the separatory funnel until dissolved. Next, 40 mL hexane was added to each sample, and the samples were shaken by hand for 2 min. Samples were allowed to separate for fifteen minutes before the lower, water layer was decanted into 100 mL flask. Emulsions containing the extraction solvent were decanted into centrifuge tubes and any separated hexane layers were funneled into flasks and set aside. Emulsions were centrifuged for 10 minutes at 4000 RPM. Hexane supernatants were added to previously separated hexane layers in their respective flask. Initially decanted water layers were once again added to separatory funnels and the process was repeated to obtain a second and third extraction.

Once the hexane supernatants were consolidated for each sample, 5 g Na_2SO_4 was added to each flask to ensure no additional water was present. Samples were then filtered into 200 mL glass Turbovap concentration tubes through Watman 125 mm filter paper. Each flask was rinsed with hexane three times, with rinses added to filtration. The filter papers were also then rinsed with hexane three times. Using a Turbovap, and 40 PSI streaming nitrogen at a temperature of 55 ºC, samples were evaporated to below 1 mL. When samples reached a point below 5 mL, 100 µL isooctane were added to solution. Samples were then quantitatively transferred to GC vials. Turbovap tubes were rinsed three times with 50 µL isooctane, which was added to samples. Further evaporation with nitrogen condensed the samples to 0.5 mL. Samples were then analyzed on a GC-MS with the same conditions as previously described.

2.3.4 Toxic Equivalents and Statistical Analysis

Toxic Equivalents (TEQs) were calculated for each sample by multiplying the concentration by the toxic equivalency factors (TEF) (Table 2) in order to determine the carcinogenic potential of all cPAHs. Using the soil screening level (SSL) established for BaP (USEPA 2007), whole cPAH TEQ values as well as levels of BaP were evaluated with respect to concentrations greater than 16 ppb.

A linear model was applied to determine correlations of concentration levels between reference and contact samples at all sites. Concentrations below detection limits were set to zero for statistical analyses. Nonparametric statistics were used due to left-censoring of data (13% and 23%, cPAH and BaP, respectively). Comparisons between reference and contact sites were determined using a Wilcoxon signed-rank test, as these samples were paired. Statistical analysis was performed with SPSS (IBM Version 20) using with $\alpha=0.05$. Comparisons between roof-type categories were determined using Kruskal-Wallis separately for each factor (asphalt, metal, and tar). Only contact samples were considered in the Kruskal-Wallis analysis. Mean separation was conducting using a Tukey analysis on ranked data. An *ex post facto* examination of building use (commercial, residential, and schools) was also performed using a Kruskal-Wallis test. This analysis also only examined contact samples, and mean separation was performed using a Tukey analysis for the ranked data. Soils receiving rooftop runoff were also reassigned values with paired reference concentrations subtracted and then evaluated statistically on ranked data for building use and roof type. Guttered area of roof for buildings with gutters only was also examined with Kruskal-Wallis for contact soils.

2.4 Results

Across all sites, the ages of the building characteristics varied. Overall, the buildings were on site an average of 46 ± 30 years (Site data is shown in Tables 4 and 5 for each sample). No data was collected for roof age itself. The roofs had on average a 35º slope (± 15º) and had a mean area of 730 m^2 (± 1,600 m^2). Fifty-four of the buildings had guttered roofs with an average of 17% (± 9%) of the surface area reaching the gutter catchment. The soil collected from each sample was made up of 5% (± 5%) soil organic matter. Additionally for analytical work, mean spike recoveries were within 5% of the expected concentration and blank recoveries were all below the method detection limits (Table 1).

2.4.1 PAH Contamination

Out of the total 92 sites and 184 total samples, 81 of the sites and 160 of the overall samples had cPAHs above method detection limits and thus had reportable TEQ values (Table 2). Of the individual PAHs measured, benzo[*b*]fluoranthene had the highest concentrations in both reference and contact samples. BaP had the third and fourth most concentrated cPAH in reference and in contact samples respectively; however, after adjusting for toxic equivalency factors, BaP was the most toxic contributor in a single sample, with a TEF of 1 (Table 2) and, therefore, accounted for a large percentage of the TEQ concentration for most samples.

Out of the 92 reference and 92 contact samples, 74 reference samples (80.4%) and 86 contact samples (93.5%) had a mixture of all seven cPAHs above the detection limit. Overall, 77% of samples (63 reference and 79 contact samples) had cPAH levels based on TEQs that were above the soil screening level of 16 ppb BaP set by the USEPA for resident soil (USEPA 2016). Collectively, 62% of all sites had paired cPAH TEQ reference and contact samples both above BaP SSL in values.

2.4.2. Comparison of Roof Contact and Reference Sites

Overall, cPAH TEQ and BaP values were significantly higher in each category for contact sites as compared to reference sites ($p<0.001$). As illustrated in Fig. 2, sixty-one of the sites (66.3%) had levels of cPAH TEQs that were higher in runoff contact samples than in reference samples. If groups were segregated by roof type or building usage, this comparison was still always significantly different within each category for cPAHs ($p<0.005$) and BaP ($p<0.005$).

2.4.3 Comparisons by Roof Type

There was not a significant difference found between samples of different roof types throughout the sites for cPAH or BaP concentration using Kruskal-Wallis nonparametric testing (p=0.111 and p=0.097); however, tar roofs tended to have higher levels of cPAHs and BaP as compared to asphalt and metal roofed buildings (Fig 3 and Fig. 4). The sample size for tar roofs was small (n=5).

2.4.4 Comparisons by Building Use

This analysis was an *ex post facto* examination based on observed trends in collected data as original sampling design focused on roof type and not building usage. Overall building use within contact samples found significance for both cPAHs (p=0.002) and BaP (p=0.001) (Fig. 5 and Fig. 6) in a comparison of all sites. A post hoc analysis revealed that cPAHs and BaP are significantly higher in concentration in schools (p=0.001 and p=0.001) and in commercial buildings (p=0.038 and p=0.031) than in residential areas within contact sites. There was not a significant difference between levels of cPAHs or BaP in school and commercial sites within contact samples (p=0.599 and p=0.493).

2.4.5 Comparisons of Other Characteristics

After adjusting soil concentration values of contact soils to reflect the subtraction of background cPAH TEQs from reference samples, the building age did not significantly contribute to the influence of cPAH TEQ concentration in soils receiving rooftop runoff. This is true for each roofing type and building use examined in terms of building age: age did not individually influence the accumulation of cPAHs in contact soils. Total area of roof was examined as a contributing factor to cPAH TEQ concentration with reference concentration subtracted. A multivariate ANOVA comparing slope of roof, age, and total area of roof within contact soils with subtracted paired-reference values, showed that area of roof was a significantly contributing factor (p=0.016, R^2=0.12) to cPAH concentrations in soil receiving rooftop runoff. Presence of gutters did not significantly affect cPAH TEQ concentrations in contact soil for either roof type or building usage. However, there was a significant effect (p=0.03, R^2=0.10) of area covered by gutters contributing to cPAH TEQ concentrations in contact soils within buildings having guttered roofs.

2.4.6 Bioavailability

Recoverable cPAHs based on the digestive model indicated a very low percentage of bioavailable PAHs for each sample analyzed (in a subset of the samples with the highest concentrations) relative to overall initial soil PAH concentrations (Fig. 7). The demographics of the samples tested for bioavailability are shown in Table 4 and Table 5. Only five cPAHs (benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, and BaP) were measured due to interferences in the chromatographic run from the components of the artificial digestion media. The bioavailability did not correlate with overall levels of soil contamination, and BaP was not above detection limits in six of the samples. The soil with the overall highest contamination for cPAHs and BaP, ranked third in percent bioavailability.

The sample with the greatest PAH contamination (sample 54- see Appendix (Table 4) for soil demographic data) was also shown to have the highest concentration of bioavailable 5cPAHs and BaP despite the low bioavailability (Fig. 8). Samples 52r and 79r were not the most concentrated overall PAH samples, but they had the highest percent bioavailability of 5cPAHs and BaP (Fig. 7). This resulted in the higher levels of concentration of bioavailable PAHs (Fig. 8). The samples shown in Fig. 8 with paired BaP values above detection limit have 5cPAH TEQ values that exceed USEPA SSL (USEPA 2007) for BaP, and all but sample 79r (15 ppb BaP) have BaP values that exceed this level as well.

2.5 Discussion

Soil PAH concentrations across the majority of the Oklahoma City Metro area were relatively high throughout the majority of sites. cPAHs and BaP in most samples exceeded the SSL of 16 ppb (USEPA 2007) in 77% and 74% of samples, respectively. PAHs have been found to be generally abundant in urban environments, and similarly this study showed high levels of PAHs in soils across urban areas in Oklahoma City. Nearly 89% of soil samples showed PAH concentrations in soil above detection limits. A previous study in the Oklahoma City area found that 84% of rooftop runoff water samples displayed concentrations of PAHs above detection limits (Lay *et al*. 2014). Lay's findings correspond with this study's findings of more than 80% of soil samples in the Oklahoma City region having PAH concentrations above the detection limit (Lay *et al.* 2014). The median values for cPAHs and BaP for contact and reference samples in this study collectively were 99 ppb and 69 ppb, as well as 160 ppb and 110 ppb for contact samples alone. The population for Oklahoma County, Oklahoma, which accounts for a large portion, but not all of the Oklahoma City Metro Area was nearly 800,000 as of 2015 (U.S. Census Bureau 2015). In a study by Mielke *et al*. (2004) median BaP concentrations across combined inner-city and suburban areas from building foundations in New Orleans, Louisiana were 163 ppb. This was lower than levels found for busy streets (255 ppb) but higher than residential streets and open areas. The population for the New Orleans Metro was approximately 1.3 million in 2005 (US Department of Housing and Urban Development 2008). These, as well as the levels of BaP, are comparable to what was found in Oklahoma City. Morillo *et al*.(2007) examined levels of PAHs in Glasgow, UK; Torino, Italy; and Ljubljana, Slovenia. Findings showed mean levels of BaP as 971 ppb, 229 ppb, and 76.8 ppb respectively. They attributed potential for variation between cities to organic carbon content differences and possible volatilization in warmer areas. Another study of Easter Europe showed that Tallinn, the capital of Estonia (with a population of about 421,000) had a mean BaP soil concentration of 106 ppb, but a much higher mean concentration of 398 ppb in the heavily trafficked city-center (Trapido 1999). The overall city mean BaP level is very similar to that found in the soils of Oklahoma City. While these cities have smaller overall populations than Oklahoma City, this does help to demonstrate that PAH deposition can be variable across cities, but PAHs and cPAHs are shown in elevated levels. Vane *et al.* (2014) also showed that even within a city there is a great potential for variation, with Greater London showing a range of 16 priority PAHs from 4,000 ppb to 67,000 ppb with mean and median values of 18,000 and 14,000 ppb. This is overall much higher for than the mean and median values found in Oklahoma City, but it was not adjusted for TEQ values and it includes non-carcinogenic PAHs. Although the PAH values for cites in London include more compounds in the overall evaluation, the variation across the city in 16 priority PAH levels helps to illustrate the change in PAH levels that are possible even within a single urban environment.

Sample differences in concentration between contact and reference soils across all sites show that concentrations were not equally distributed between sample types (contact vs. reference). PAHs are elevated in more of the corresponding contact samples than they were in the reference samples by about 65%. This is an indication that there was an influence in PAH accumulation in contact soils from concentrated PAHs because of rooftop runoff. This runoff factor could be affecting contribution to PAHs in soil from the wash of rainfall events of a large surface area (a roof) containing PAHs from atmospheric deposition. The runoff could also contribute PAHs in soil as a leachate from building materials or roofing materials, thereby concentrating accumulation directly under drip lines and gutters.

2.5.1 Roof Type

There was a distribution of soil receiving rooftop runoff from different roof types sampled across the city, but despite the finding that locations with roof contact were more highly contaminated than reference sites. Roof type did not significantly influence the cPAH or BaP contamination. Rocher *et al*. (2004) examined roof type as a potential contributor to PAH content in runoff, but found that metal roofing did not contribute PAHs; however, the sample size in the study was n=2. Mendez *et al*. (2011) also presented outcomes discrediting roof type for PAH contributing, finding no PAHs in rooftop runoff from either metal or asphalt roofs; but, their sample size was also very small, n=1 for both roof types. Hou *et al.* (2013) found that in a study comparing multiple roof surfaces, asphalt roof samples had a greater amount of PAHs than a ceramic subset; this was attributed to asphalt material leaching PAHs after being exposed to high heat from the sun.

Buildings with tar roofs had high levels of PAHs in the soil receiving rooftop runoff. The tar felt roof surface could be problematic in increasing PAHs in runoff as Forster (1999) stated that this type of roofing material not only can contribute directly to the release of PAHs, but as compared to metal roofs, it has a rougher surface which can trap PAHs easily and release greater quantities after a heavy rainfall event. This would explain the observationally high difference in tar roofs of contact sites being greater contributors to cPAHs and BaP in soil than the other roof types.

Another factor thought to potentially influence PAH deposition and concentration is age of building did not correlate with PAH concentration throughout this study. Only building age was available for consideration, age of the roof and time to last roof replacement would likely be better measures of the PAH content of the roofing material. While current roof type did not play a role in significantly contributing cPAHs in itself, buildings with larger surface area roofs did have significantly more cPAHs in the contact soil. This can be explained by a greater area collecting atmospheric deposition, as area and textures of roofs play a role in collection of particulate matter that could influence load in rooftop runoff from a rainfall event (Egodawatta *et al*. 2009). Guttering is also a factor that could influence the wash off of a large roof area to deposit in a singular location, but the presence of gutters did not influence the levels of contamination across sites. However, among roofs that had gutters, the contact soil for sites with gutters covering more surface area had higher concentrations of cPAHs in the soil as compared to those with gutters covering little surface area. This can be explained by more surface area collecting particulates contributing greater load of cPAHs in runoff to a single contact surface compared to a smaller area that may not be able to collect as much particulate matter.

2.5.2 Building Use

Buildings sampled were broken down into three categories (commercial, residential, and school), and an *ex post facto* examination of these building uses revealed that residential soils had overall significantly lower cPAH and BaP values than soils from commercial and school locations. While building use itself is unlikely to have a direct effect on PAH concentration in contact soils, there are potentially building-related factors that could contribute to this higher level of PAH accumulation in the contact soils of commercial and school buildings.

Twenty-one of the school and commercial buildings were in close proximity to parking lots and had greater than SSL cPAH TEQ concentrations; whereas, only one residential site was by a parking lot. Although none of the reference sites collected runoff from the parking lots, vehicular exhaust promotes atmospheric PAHs (Baek *et al*. 1991, CDC 2009). The higher concentration of daily traffic throughout these parking lots could be a contributing factor in excessive levels of cPAHs through atmospheric deposition.

The use of coal tar or roofing tar in buildings with older roofs could lead to elevated levels of PAHs in surrounding soils. PAH contributors, coal tar pitch and roofing tar have been used in roofing (Talaska *et al*. 1996). An example of this is from the 1960s where roofing material is found in sandwich roofing styles, where coal tar or petroleum oil was used as a primary component in an adhesive to hold roofing felt to a surface prior to the attachment of shingles (Chamberlain 1963). This type of tar adhesive has been shown to contain a variety of high molecular weight PAHs (Fetzer and Kershaw 1995) that could be responsible for runoff and partitioning in soils around these buildings. Because many of these buildings are aged, it is possible that coal tar was a component in the roofing in past years. However, without exact knowledge of roofing construction dates and earlier used materials, this is not directly testable in all sites.

Not only could additional construction material in buildings contribute to higher PAHs in certain areas, construction materials in parking lots surrounding these sites may also contribute PAHs. While there were 60 contact samples higher than their respective reference samples across all sites, 21 sites were found to have reference samples with higher cPAH TEQs than matching contact samples. Some of these locations were in close proximity to parking lots. This is a potential source of PAH contamination by means of blow off from coal tar sealants. Mahler *et al*. (2010) found elevated levels of cPAHs and BaP in dust samples stemming from surrounding parking lots that had been sealed with a coal-tar sealant as compared to sites with asphalt sealcoat or no sealant. Scoggins *et al*. (2007) also found a trend with PAHs and 6 cPAHs contributing to elevated levels in sediment of parking lot runoff downstream with lots coated with coal-tar sealant. This type of dust from parking lots with coal-tar sealant, could account for some of the reference samples near parking lots with higher than expected values of cPAH concentration.

2.5.3 Bioavailability

Our findings of bioavailability indicated that less than 3% of the PAHs in soils containing high levels of PAHs were actually bioavailable (Fig. 7). A number of factors could contribute to this. The total organic matter of the soils in question varied (6.8% average organic matter in soils used for digestive model) which could provide different surfaces for PAH binding strategies and affect the partitioning of PAHs to soil (Nam *et al*. 2008, Karickhoff 1981). This however, did not affect the overall partitioning of PAHs to soil throughout all of the sampling, as there was no correlation between soil organic matter levels and PAH contamination.

While Hack and Selenka (1996) found soil PAH bioavailability to be between 7-95% over twenty-two samples (soil, sewage sludge, and construction bi-products) in an *in vitro* model, the PAH mobilization we found was significantly lower. This could be due to differences in technique: we did not add powdered whole milk to our samples, which was shown by Hack and Selenka (1996) to increase mobility of PAHs. The addition of whole milk powder to their model increased the mobilization of PAHs from 5-14% to 23% in soil. This approach could be further tested for comparison with the inclusion of whole milk. Overall, *in vitro models* have not been shown to necessarily be representative of bioavailability as compared to *in vivo* models, and even with live models, bioavailability could have variation across species (Reid *et al*. 1999). Tang *et al*. (1998) found that microbial degradation and earthworm uptake of PAHs were different, meaning that the bioavailability was variable between these live models. This means that while, either type of model (*in vitro* or *in vivo*) could give predictions of PAH dissociation in terms of potential bioavailability, this does not give a definitive answer to the question of bioavailability, and potentially multiple models should be used in conjunction with one another for a more clear prediction (Alexander 2000, Ramesh *et al*. 2004). These methods should not be wholly discounted, however, as they do provide some insights into PAH binding under variable conditions. Despite these considerations, our initial analysis suggests markedly low bioavailability.

Further work must be completed to evaluate the bioavailability of PAHs in soil. There is a possibility of difference in bioavailability if PAHs arise in soil from atmospheric deposition versus from roofing material. Even if *in vitro* models are found to be not representative of determining whole bioavailability for humans, this model can be applied to focus on PAH dissociation for the soils in question. For future investigation, we predict that contact soils with less bioavailability or dissociation after digestion have PAHs that are more heavily influenced from roofing material, and that the more bioavailable fractions are from atmospheric deposition.

2.5.4 Conclusions

The levels and the variation in distribution of PAHs in Oklahoma City soil is comparable to other urban areas (Mielke *et al*. 2004, Vane *et al.* 2014). While there is a potential for great variance in PAHs in urban environments, mean levels of cPAHs and BaP in Oklahoma City were generally found to be present above detection limits and often above the US EPA SSL (Morillo *et al*. 2007, USEPA 2007). Concentrations tend to be especially high in soil containing rooftop runoff. This means that rooftop runoff is a probable contributing factor to PAH concentration in soils under downspouts and drip lines. While roof type did not significantly vary in PAH deposition in soil, area of roof and gutters receiving more rooftop area did contribute to cPAH concentrations. Further studies should be implemented to test these factors as well as other site characteristics like soil organic matter and roof age. The differences in building usage are suggestive that more detailed analysis of building factors might provide a better assessment of sites that are likely to be contaminated.

Building use did significantly influence PAH concentrations, and commercial buildings and especially schools have the potential to show general elevated levels of PAHs. Because of the elevated levels of cPAHs in soils around schools, there is potential for exposure to these compounds through ingestion in small children. While our bioavailability model did not show great bioavailability, there were samples that still showed bioavailability above the SSL. Bioavailability of cPAHs must be further examined in order to establish a better risk assessment of these overall areas. Additional factors should be examined to further determine what contributes cPAH concentrations in certain areas, and continual sampling of soils in the Metro Area school systems should be implemented to further evaluate exposure risk.

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Table 1. Selected analytes (seven carcinogenic polycyclic aromatic hydrocarbons) for screening with a GC/MS single quad instrument. Spike (n=12). Spike recovery was based on a target concentration of 200 ppb. MDL= method detection limits. SD %= relative standard deviation.

Analyte	**CAS#**	**MS Quant. Ion**	**MDL for Screening (ppb)**	**Spike Recovery**	
				Mean %	*SD%*
Benz[*a*]anthracene	56-55-3	228	6	82	16
Chrysene	218-01-9	228	5	85	11
Benzo[*b*]fluoranthene	205-99-2	252	6	89	17
Benzo[*k*]fluoranthene	207-08-9	252	3	90	8
Benzo[*a*]pyrene	50-32-8	252	4	97	16
Dibenz[*a,h*]anthracene	215-58-7	278	5	90	15
Indeno[*1,2,3-cd*]pyrene	193-39-5	276	1	99	8

Table 2. Toxic equivalency table for carcinogenic polycyclic aromatic hydrocarbons (cPAHs). By using benzo[*a*]pyrene (BaP) as a model compound for toxicity, toxicity equivalency factors (TEFs) are applied to the cPAHs in order to evaluate the toxic equivalency quotient or toxic equivalent (TEQ) for individual cPAHs as well as **Σ** cPAHs (Safe 1998, USEPA 2016). These TEF values can be used in reference to BaP screening levels to demonstrate relative toxicity of individual compounds or mixtures in conjunction or in relation to BaP (USEPA 2016).

cPAH	**TEF Value**
Benzo(a)pyrene	1
Benzo(a)anthracene	0.1
Benzo(b)fluoranthene	0.1
Benzo(k)fluoranthene	0.01
Dibenz(a,h)anthracene	1
Indeno(1,2,3-cd)pyrene	0.1
Chrysene	0.001

Table 3. Summary data for PAHs in soil in the Oklahoma City Metro area. Soil screening levels are in place for residential soils as set by the USEPA (2016). Toxic equivalent (TEQ) values were determined based on the toxic equivalency factors (TEFs) observed by the WHO; all values are set in reference to Benzo[*a*}pyrene (USEPA 2016). Reference samples refer to soils from each site that were not receiving rooftop runoff, while contact samples were in direct contact with rooftop runoff. Sites were broken down categorically by roof type (asphalt, metal, and tar) as well as by building use (commercial, residential, and school).

		Number of samples			**SSL (ppb)**	**Freq.> SSL, %**	**Max. Value, ng/g**	**Median, ng/g**	**Percentiles for all samples, ng/g**		
		Total	*Above MDL*	*Above SSL*					*75th*	*90th*	*95th*
cPAH TEQ	Reference	92	74	63	16	68.5	7700	38	100	530	960
	Contact	92	86	79	16	72.8	350000	160	260	1000	1300
	Asphalt	59	54	51	16	72.9	150000	120	220	640	980
	Metal	28	27	23	16	67.9	2200	180	530	1100	1300
	Tar	5	5	5	16	100.0	350000	410	1100	210000	280000
	Commercial	23	21	20	16	78.3	1100	190	410	920	1000
	Residential	46	42	36	16	63.0	1700	73	190	330	530
	School	23	23	23	16	87.0	350000	380	730	2000	140000
Benzo[a] pyrene	Reference	92	62	59	16	43.5	5400	27	70	360	600
	Contact	92	79	77	16	69.6	250000	110	170	670	880
	Asphalt	59	51	50	16	67.8	99000	85	150	440	680
	Metal	28	23	22	16	67.9	1500	130	350	730	880
	Tar	5	5	5	16	100.0	250000	280	720	150000	200000
	Commercial	23	20	20	16	78.3	770	120	250	640	730
	Residential	46	36	36	16	56.5	1000	49	120	220	350
	School	23	23	21	16	87.0	250000	260	520	1400	89000

Table 4. Comparison of soil demographics for each site and soil sample. Contact samples are soils directly under downspouts or drip lines that receive rooftop runoff. Reference samples are soils away from buildings and do no receive direct or indirect rooftop runoff. cPAH TEQ represents the sum concentrations of seven carcinogenic priority polycyclic aromatic hydrocarbons based on their toxic equivalents. Values above 16ppb are environmentally relevant as exceeding benzo[a]pyrene (BaP) reference soil screening level (USEPA 2007). Building usage for each site is represented by commercial, residential, or school usage. Roof type of each building is represented by asphalt, metal, or tar.

Site #	Sample	Building	Roof	cPAH TEQ	BaP
1	Contact	Residential	Asphalt	1733	1026
1r	Reference	Residential	Asphalt	156	95
2	Contact	Residential	Metal	63	37
2r	Reference	Residential	Metal	73	45
3	Contact	Commercial	Metal	322	184
3r	Reference	Commercial	Metal	141	89
4	Contact	Commercial	Metal	256	157
4r	Reference	Commercial	Metal	463	296
5	Contact	School	Metal	61	33
5r	Reference	School	Metal	115	70
6	Contact	School	Metal	1463	936
6r	Reference	School	Metal	791	499
7	Contact	Residential	Asphalt	76	48
7r	Reference	Residential	Asphalt	44	27
8	Contact	Residential	Asphalt	4	0
8r	Reference	Residential	Asphalt	27	17
9	Contact	Residential	Asphalt	247	155
9r	Reference	Residential	Asphalt	47	31
10	Contact	Residential	Asphalt	55	34

Site #	Sample	Building	Roof	cPAH TEQ	BaP
10r	Reference	Residential	Asphalt	0	0
11	Contact	Residential	Asphalt	34	22
11r	Reference	Residential	Asphalt	2	0
12	Contact	Residential	Asphalt	2	0
12r	Reference	Residential	Asphalt	2	0
13	Contact	Residential	Asphalt	46	30
13r	Reference	Residential	Asphalt	91	57
14	Contact	Residential	Asphalt	267	154
14r	Reference	Residential	Asphalt	67	43
15	Contact	Commercial	Asphalt	186	116
15r	Reference	Commercial	Asphalt	0	0
16	Contact	Residential	Asphalt	0	0
16r	Reference	Residential	Asphalt	0	0
18	Contact	School	Metal	1013	639
18r	Reference	School	Metal	139	90
19	Contact	School	Asphalt	379	245
19r	Reference	School	Asphalt	19	15
20	Contact	School	Asphalt	151358	98695
20r	Reference	School	Asphalt	1017	613
21	Contact	School	Metal	20	14
21r	Reference	School	Metal	906	587
22	Contact	Residential	Asphalt	2	0
22r	Reference	Residential	Asphalt	0	0
23	Contact	Residential	Metal	211	133
23c	Reference	Residential	Metal	0	0

Site #	Sample	Building	Roof	cPAH TEQ	BaP
24	Contact	Residential	Metal	2	0
24r	Reference	Residential	Metal	0	0
25	Contact	Residential	Asphalt	52	34
25r	Reference	Residential	Asphalt	22	17
26	Contact	Residential	Metal	31	25
26r	Reference	Residential	Metal	0	0
27	Contact	Residential	Asphalt	116	80
27r	Reference	Residential	Asphalt	0	0
28	Contact	Residential	Asphalt	40	29
28r	Reference	Residential	Asphalt	24	19
29	Contact	Residential	Asphalt	31	24
29r	Reference	Residential	Asphalt	19	14
30	Contact	Residential	Metal	2	0
30r	Reference	Residential	Metal	40	29
31	Contact	Residential	Asphalt	39	24
31r	Reference	Residential	Asphalt	3	0
32	Contact	Residential	Metal	1051	714
32r	Reference	Residential	Metal	2	0
33	Contact	Residential	Asphalt	202	130
33r	Reference	Residential	Asphalt	7	0
34	Contact	Residential	Metal	255	178
34r	Reference	Residential	Metal	0	0
35	Contact	Residential	Asphalt	0	0
35r	Reference	Residential	Asphalt	0	0
36	Contact	Residential	Asphalt	0	0

Site #	Sample	Building	Roof	cPAH TEQ	BaP
36r	Reference	Residential	Asphalt	17	15
37	Contact	Residential	Asphalt	122	87
37r	Reference	Residential	Asphalt	21	18
38	Contact	Residential	Asphalt	250	175
38r	Reference	Residential	Asphalt	0	0
39	Contact	Residential	Metal	2	0
39r	Reference	Residential	Metal	0	0
40	Contact	Residential	Asphalt	416	281
40r	Reference	Residential	Asphalt	386	252
41	Contact	Residential	Asphalt	187	118
41r	Reference	Residential	Asphalt	24	19
42	Contact	Residential	Asphalt	572	374
42r	Reference	Residential	Asphalt	0	0
43	Contact	Commercial	Metal	2	0
43r	Reference	Commercial	Metal	29	21
44	Contact	Residential	Asphalt	257	173
44r	Reference	Residential	Asphalt	256	181
45	Contact	Commercial	Asphalt	226	153
45r	Reference	Commercial	Asphalt	130	86
46	Contact	School	Metal	2166	1524
46r	Reference	School	Metal	485	337
47	Contact	School	Asphalt	701	496
47r	Reference	School	Asphalt	370	255
48	Contact	School	Metal	139	96
48r	Reference	School	Metal	256	178

Site #	Sample	Building	Roof	cPAH TEQ	BaP
49	Contact	School	Metal	551	377
49r	Reference	School	Metal	34	23
50	Contact	School	Asphalt	16	14
50r	Reference	School	Asphalt	16	0
51	Contact	School	Asphalt	194	135
51r	Reference	School	Asphalt	81	57
52	Contact	School	Tar	414	278
52r	Reference	School	Tar	3362	2450
53	Contact	School	Tar	54	40
53r	Reference	School	Tar	22	17
54	Contact	School	Tar	346803	245236
54r	Reference	School	Tar	1389	1007
55	Contact	School	Tar	1232	836
55r	Reference	School	Tar	595	409
56	Contact	School	Metal	179	126
56r	Reference	School	Metal	33	23
57	Contact	School	Asphalt	619	428
57r	Reference	School	Asphalt	2	0
58	Contact	School	Metal	184	149
58r	Reference	School	Metal	45	30
59	Contact	School	Asphalt	64	50
59r	Reference	School	Asphalt	20	17
60	Contact	School	Tar	376	259
60r	Reference	School	Tar	94	68
61	Contact	Commercial	Asphalt	166	117

Site #	Sample	Building	Roof	cPAH TEQ	BaP
61r	Reference	Commercial	Asphalt	76	53
62	Contact	Residential	Asphalt	215	153
62r	Reference	Residential	Asphalt	100	70
63	Contact	Residential	Asphalt	105	76
63r	Reference	Residential	Asphalt	75	54
64	Contact	Commercial	Metal	1106	773
64r	Reference	Commercial	Metal	7749	5429
65	Contact	Commercial	Asphalt	148	103
65r	Reference	Commercial	Asphalt	238	172
66	Contact	Commercial	Asphalt	0	0
66r	Reference	Commercial	Asphalt	32	25
67	Contact	Commercial	Asphalt	94	66
67r	Reference	Commercial	Asphalt	43	32
68	Contact	Commercial	Asphalt	39	29
68r	Reference	Commercial	Asphalt	2	0
69	Contact	Commercial	Asphalt	180	118
69r	Reference	Commercial	Asphalt	37	27
70	Contact	Commercial	Asphalt	169	116
70r	Reference	Commercial	Asphalt	2	0
71	Contact	School	Metal	772	547
71r	Reference	School	Metal	0	0
72	Contact	School	Metal	23	19
72r	Reference	School	Metal	2	0
73	Contact	Commercial	Metal	143	101
73r	Reference	Commercial	Metal	51	35

Site #	Sample	Building	Roof	cPAH TEQ	BaP
74	Contact	Commercial	Metal	19	17
74r	Reference	Commercial	Metal	0	0
75	Contact	Commercial	Metal	729	526
75r	Reference	Commercial	Metal	25	20
76	Contact	Commercial	Metal	0	0
76r	Reference	Commercial	Metal	0	0
77	Contact	Commercial	Metal	559	368
77r	Reference	Commercial	Metal	0	0
78	Contact	Commercial	Asphalt	244	171
78r	Reference	Commercial	Asphalt	470	318
79	Contact	Commercial	Asphalt	969	673
79r	Reference	Commercial	Asphalt	1309	907
80	Contact	Residential	Asphalt	120	85
80r	Reference	Residential	Asphalt	555	532
81	Contact	Residential	Asphalt	27	22
81r	Reference	Residential	Asphalt	0	0
82	Contact	Residential	Asphalt	77	53
82r	Reference	Residential	Asphalt	0	0
83	Contact	Commercial	Asphalt	708	493
83r	Reference	Commercial	Asphalt	95	67
84	Contact	Commercial	Asphalt	1041	741
84r	Reference	Commercial	Asphalt	394	269
85	Contact	Commercial	Asphalt	539	355
85r	Reference	Commercial	Asphalt	131	92
86	Contact	Residential	Asphalt	108	76

Site #	Sample	Building	Roof	cPAH TEQ	BaP
86r	Reference	Residential	Asphalt	85	58
87	Contact	Residential	Asphalt	183	130
87r	Reference	Residential	Asphalt	85	58
88	Contact	Residential	Asphalt	69	50
88r	Reference	Residential	Asphalt	85	58
89	Contact	Residential	Asphalt	66	48
89r	Reference	Residential	Asphalt	102	71
90	Contact	Residential	Asphalt	386	262
90r	Reference	Residential	Asphalt	532	364
91	Contact	Residential	Asphalt	0	0
91r	Reference	Residential	Asphalt	111	77
92	Contact	Residential	Asphalt	25	20
92r	Reference	Residential	Asphalt	0	0
93	Contact	Residential	Asphalt	98	64
93r	Reference	Residential	Asphalt	444	283

Table 5. Comparison of other site characteristics for each site within contact samples only. NG represents buildings with no gutters.

Site #	Age (years)	Roof Slope (º)	Total Roof Area (m^2)	Guttered Area of Roof (m^2)
1	59	30	190	28.5
2	59	30	14	NG
3	82	40	370	NG
4	104	45	408	NG
5	5	45	1007	100.7
6	50	45	417	NG
7	58	30	405	60.75
8	37	30	482	96.4
9	45	35	233	58.25
10	27	60	278	41.7
11	36	30	382	57.3
12	25	45	378	75.6
13	87	70	143	NG
14	49	45	317	31.7
15	112	50	105	21
16	49	45	350	70
18	111	15	615	92.25
19	80	45	888	NG
20	87	30	4442	444.2
21	29	60	715	NG
22	34	30	326	107.58
23	3	33	118	59

Site #	Age (years)	Roof Slope (º)	Total Roof Area (m^2)	Guttered Area of Roof (m^2)
24	34	10	100	25
25	62	25	153	NG
26	25+	45	10.5	NG
27	65	45	123	18.45
28	12	35	10.4	NG
29	36	35	366	73.2
30	25+	45	17	NG
31	60	45	213	NG
32	25+	30	41	NG
33	25+	30	11	2.2
34	25+	30	69	NG
35	2	75	628	62.8
36	21	45	378	56.7
37	100	30	115	34.5
38	25+	25	183	NG
39	25+	30	287	NG
40	68	45	114	11.4
41	68	40	155	NG
42	68	40	136	27.2
43	51	30	485	72.75
44	99	35	190	NG
45	85	35	365	NG
46	93	45	810	81

Site #	Age (years)	Roof Slope (º)	Total Roof Area (m^2)	Guttered Area of Roof (m^2)
47	25+	50	475	118.75
48	10	50	5752	NG
49	25+	45	2114	NG
50	25+	45	1586	158.6
51	84	50	560	56
52	25+	0	385	38.5
53	20	0	2411	241.1
54	25+	0	1023	102.3
55	25+	0	1089	217.8
56	25+	45	1362	136.2
57	10	40	905	90.5
58	25+	50	5363	268.15
59	25+	45	2267	113.35
60	49	0	2943	NG
61	25+	30	92	NG
62	53	50	320	32
63	65	35	100	15
64	25+	10	658	NG
65	25+	30	76	NG
66	25+	30	175	NG
67	25+	30	56	NG
68	25+	45	19	NG
69	25+	30	231	NG
70	25+	30	84	NG

Site #	Age (years)	Roof Slope (º)	Total Roof Area (m^2)	Guttered Area of Roof (m^2)
71	3	25	91	13.65
72	13	45	13062	NG
73	20	30	92	NG
74	20	30	97	NG
75	20	30	106	NG
76	13	45	334	NG
77	18	35	128	25.6
78	63	45	847	169.4
79	56	45	1131	113.1
80	40	30	68	NG
81	51	15	217	43.4
82	51	30	242	60.5
83	25+	15	101	20.2
84	25+	45	585	29.25
85	25+	20	177	NG
86	67	40	108	NG
87	67	40	104	52
88	71	40	95	0
89	31	40	595	NG
90	16	30	381	7.62
91	6	45	216	64.8
92	1	30	585	58.5
93	86	40	234	46.8

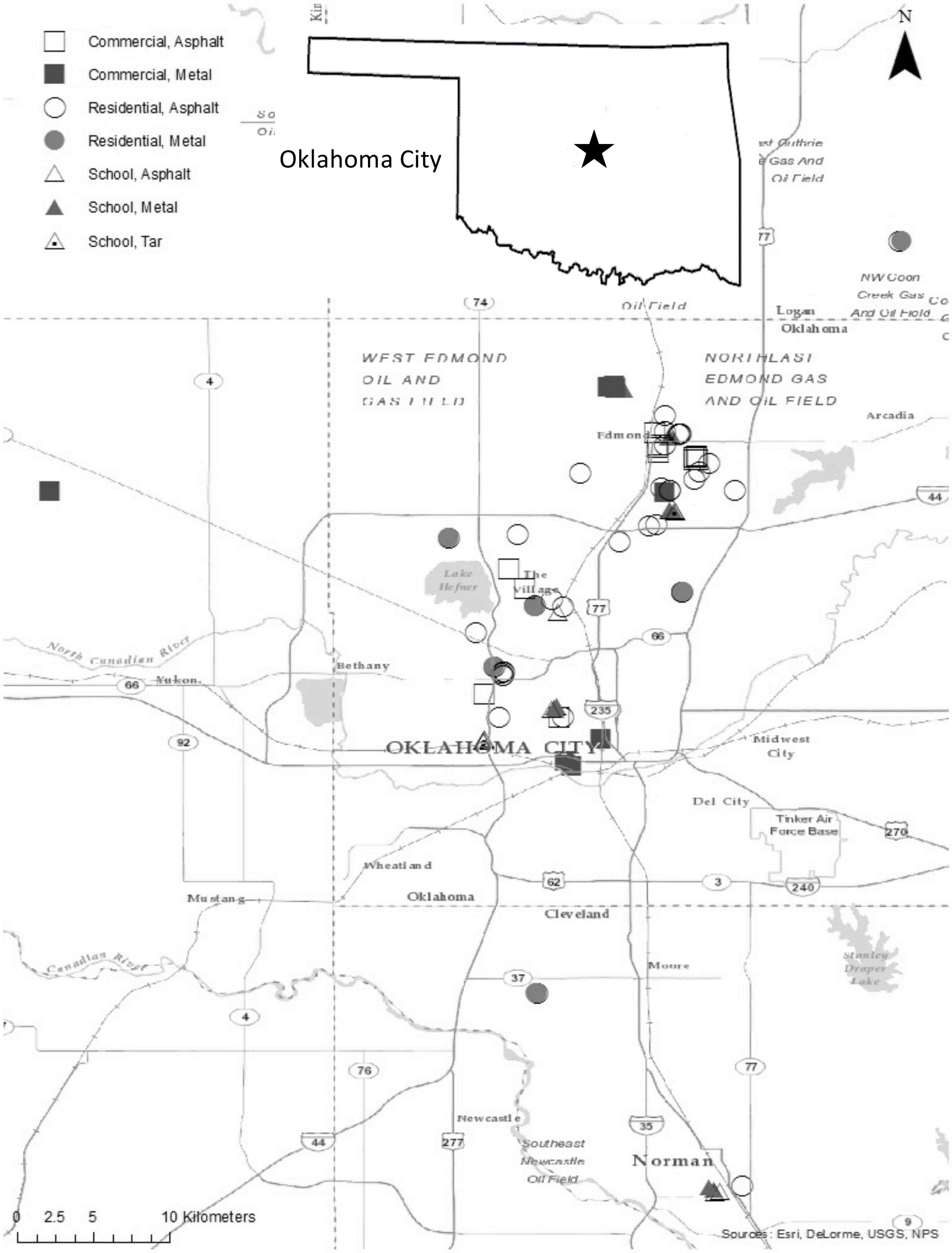

Figure 1. Soil sampling locations throughout the Oklahoma City Metro Area. A soil sample was taken from downspouts or drip lines as well as from a reference area not receiving rooftop runoff at each of the ninety-two sampling locations. Locations were chosen based on roof type and were later categorized according to building use.

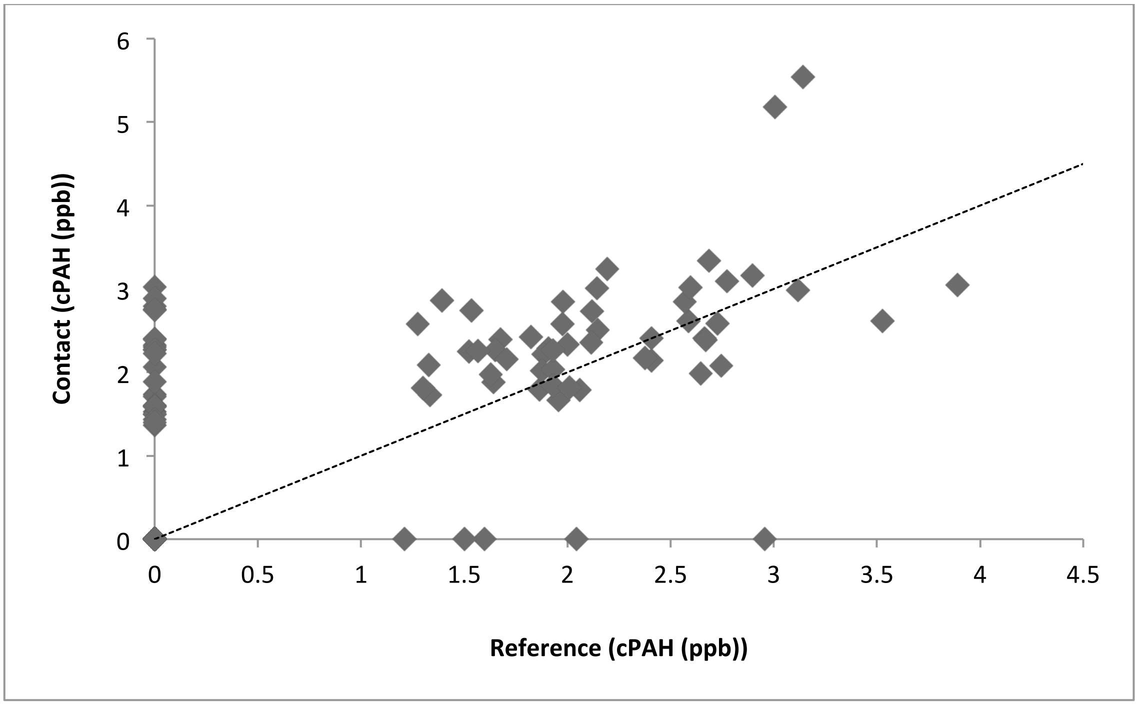

Figure 2. Log transformed relationship of overall seven carcinogenic polycyclic aromatic hydrocarbon (cPAH) values based on their toxic equivalencies for paired reference and rooftop runoff contact soil samples across 92 sample sites in the Oklahoma City Metro Area. The dotted trend line is indicative of a 1:1 trend, with 66.3% of all samples falling above this trend, showing that more frequently cPAH concentrations are greater in soil samples receiving rooftop runoff as compared to their paired reference sample.

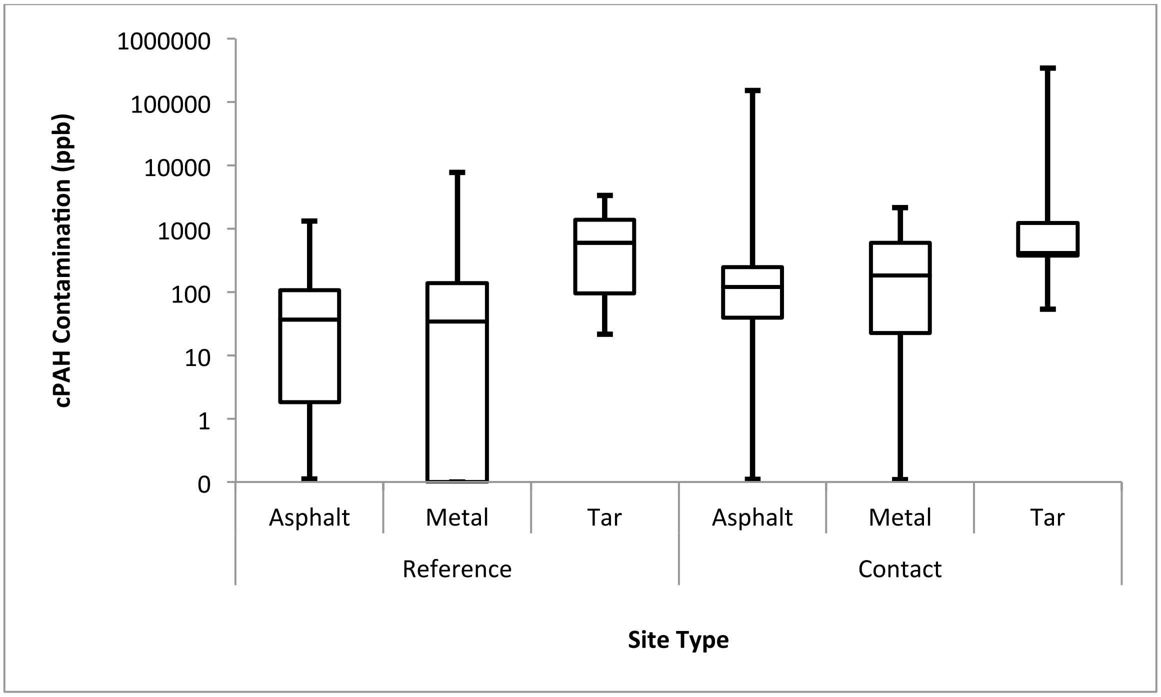

Figure 3. Carcinogenic polycyclic aromatic hydrocarbon (cPAH) concentrations in paired soils (based on toxic equivalencies) at sites as compared by roof type. Values above 16ppb are environmentally relevant as exceeding benzo[a]pyrene reference soil screening level (USEPA 2007). Upper and lower bars represent maximum and minimum values with corresponding whiskers displaying upper and lower quartiles. Boxes depict the middle 50% values of cPAH toxic equivalent soil concentrations with mean value displayed as a central bar. Reference (soils not receiving rooftop runoff): Asphalt (n=59), Metal (n=28), Tar (n=5); Contact (soils directly receiving rooftop runoff): Asphalt (n=59), Metal (n=28), Tar (n=5).

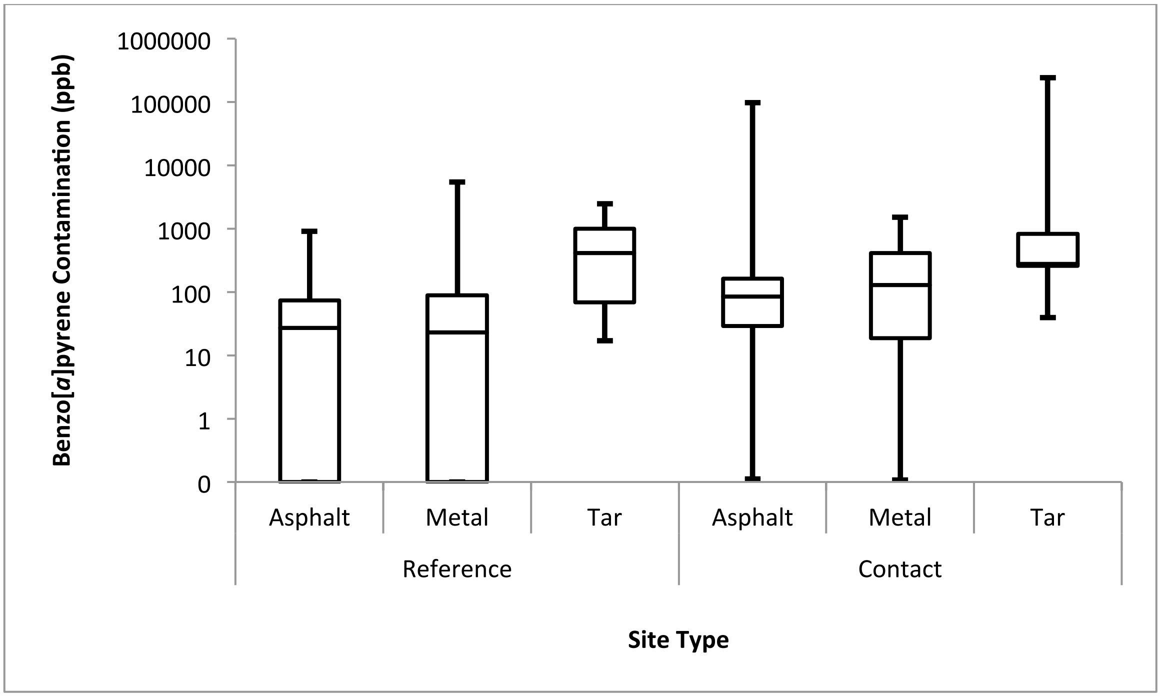

Figure 4. Benzo[*a*]pyrene (BaP) concentrations in paired soils at sites as compared by roof type. Values above 16ppb are environmentally relevant as exceeding BaP reference soil screening level (USEPA 2007). Upper and lower bars represent maximum and minimum values with corresponding whiskers displaying upper and lower quartiles. Boxes depict the middle 50% values of soil BaP concentrations with mean value displayed as a central bar. Reference (soils not receiving rooftop runoff): Asphalt (n=59), Metal (n=28), Tar (n=5); Contact (soils directly receiving rooftop runoff): Asphalt (n=59), Metal (n=28), Tar (n=5).

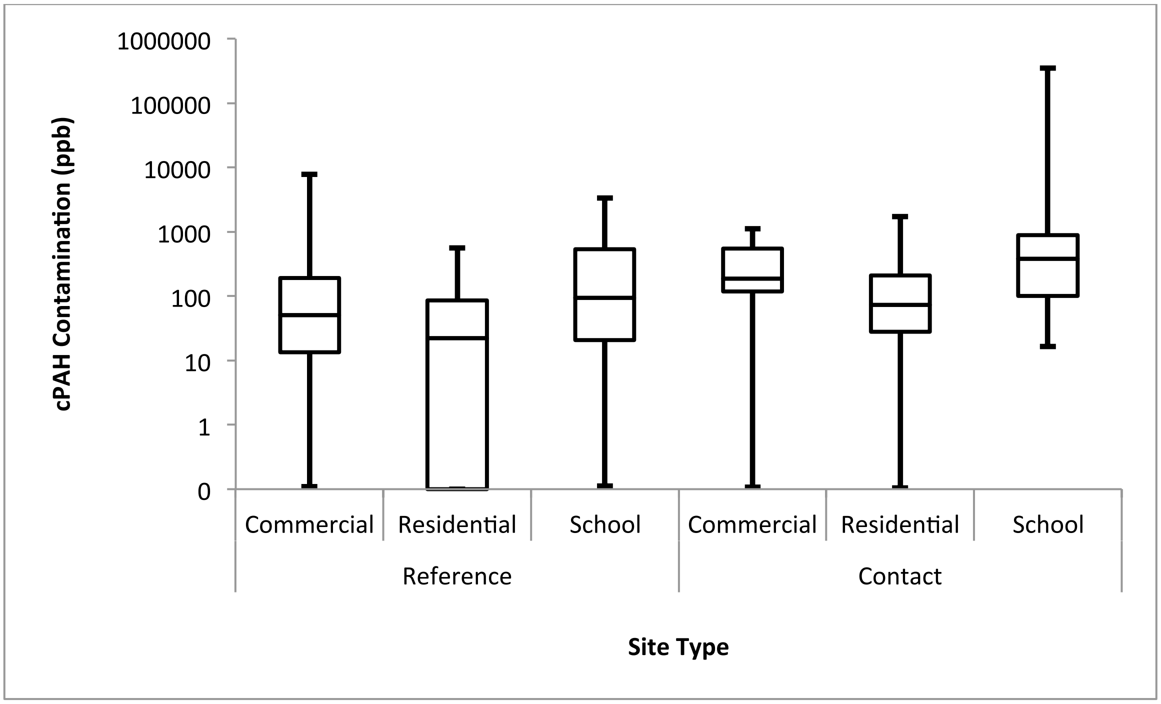

Figure 5. Carcinogenic polycyclic aromatic hydrocarbon (cPAH) concentrations in paired soils (based on toxic equivalencies) at sites as compared by building use. Values above 16ppb are environmentally relevant as exceeding benzo[a]pyrene reference soil screening level (USEPA 2007). Upper and lower bars represent maximum and minimum values with corresponding whiskers displaying upper and lower quartiles. Boxes depict the middle 50% values of cPAH toxic equivalent soil concentrations with mean value displayed as a central bar. Reference (soils not receiving rooftop runoff): Commercial (n=23), Residential (n=46), School (n=23); Contact (soils directly receiving rooftop runoff): Commercial (n=23), Residential (n=46), School (n=23).

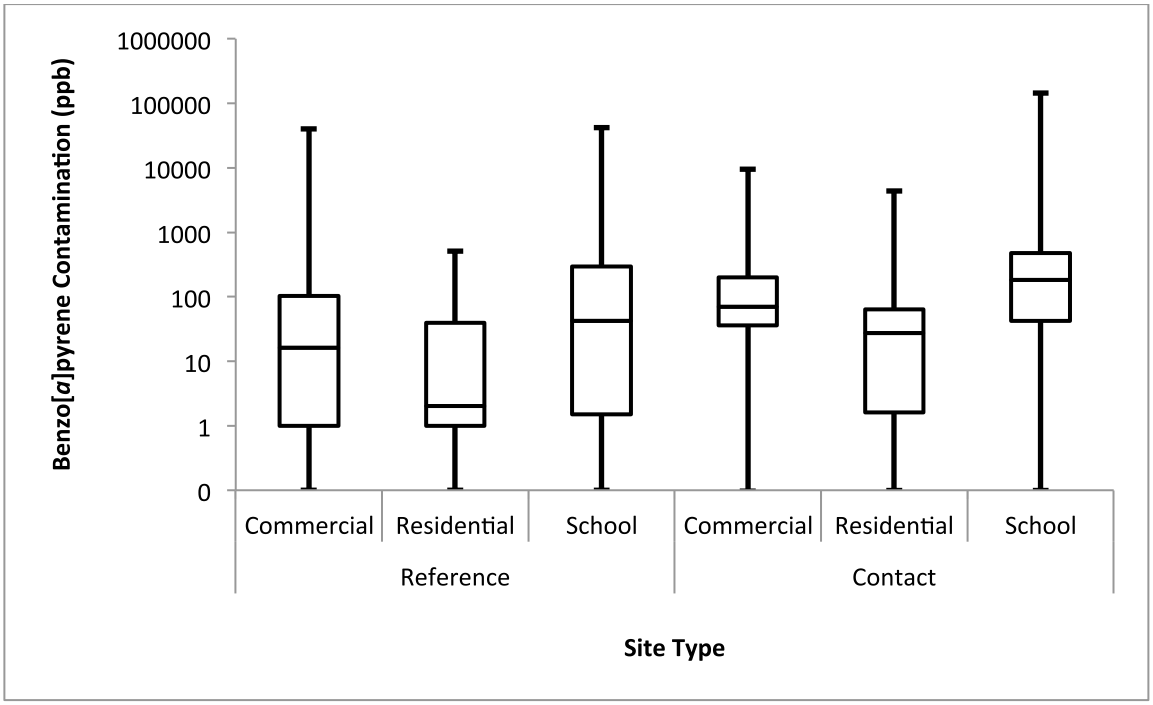

Figure 6. Benzo[*a*]pyrene (BaP) concentrations in paired soils at sites as compared by building use. Values above 16ppb are environmentally relevant as exceeding BaP reference soil screening level (USEPA 2007). Upper and lower bars represent maximum and minimum values with corresponding whiskers displaying upper and lower quartiles. Boxes depict the middle 50% values of soil BaP concentrations with mean value displayed as a central bar. Reference (soils not receiving rooftop runoff): Commercial (n=23), Residential (n=46), School (n=23); Contact (soils directly receiving rooftop runoff): Commercial (n=23), Residential (n=46), School (n=23).

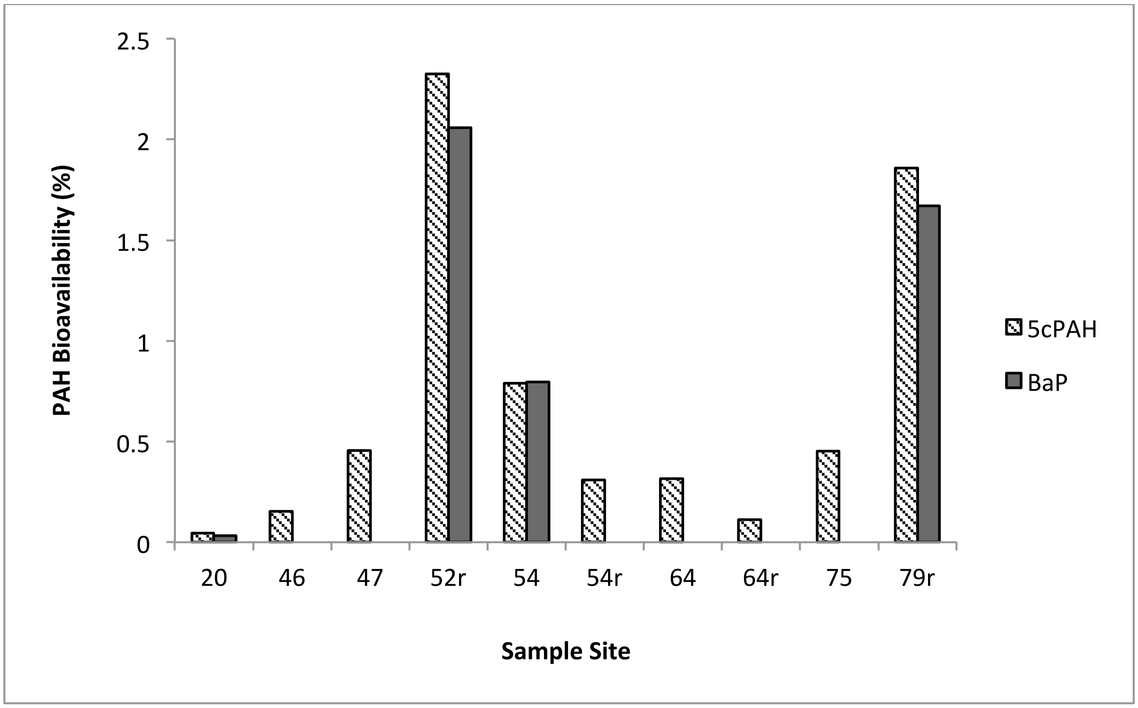

Figure 7. Percent bioavailability from digestion model of soils (both receiving rooftop runoff and reference) in the top 20% overall polycyclic aromatic hydrocarbon (PAH) recovery (including the top five most concentrated samples). Percentages of PAH bioavailability are based off of toxic equivalent values of five carcinogenic PAHs (5cPAHs) (benz[*a*]anthracene, benzo[*a*]pyrene (BaP) , benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, and chrysene) and BaP individually. Samples with an “r” indicate that the soil was a reference soil, while soils without a letter are rooftop receiving contact samples. Identical numbers are paired samples from the same site.

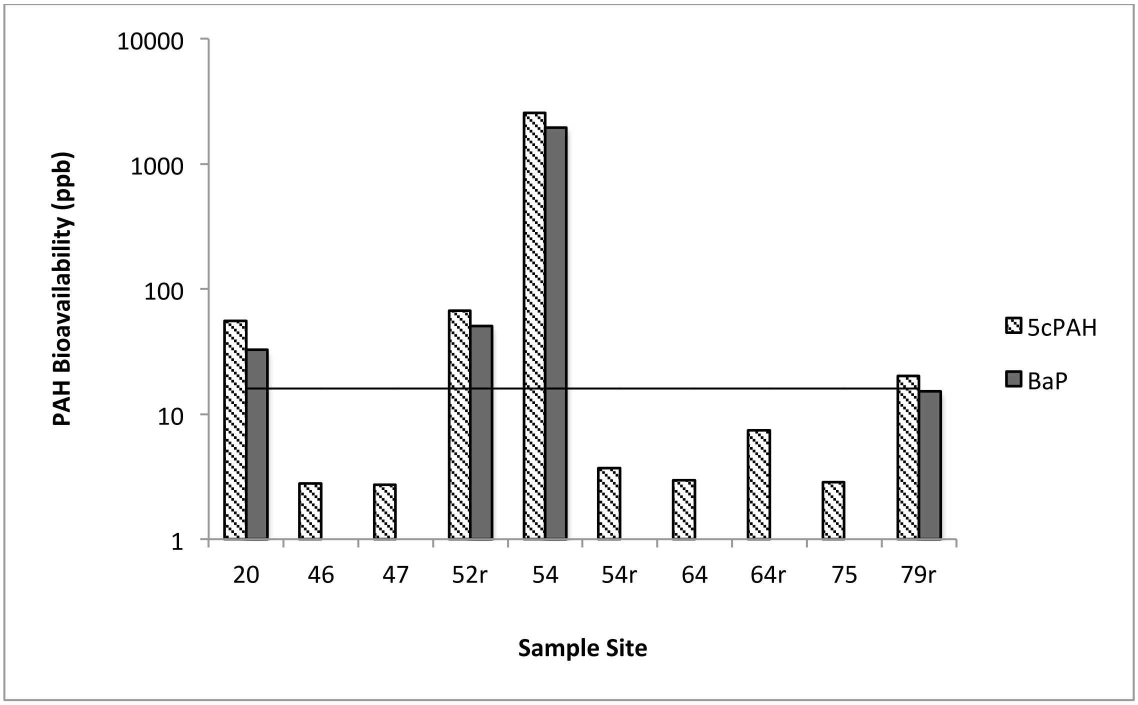

Figure 8. Quantity of recovery from digestion model of soils (both receiving rooftop runoff and reference) in the top 20% overall polycyclic aromatic hydrocarbon (PAH) recovery (including the top five most concentrated samples). PAH levels are represented by toxic equivalent values of five carcinogenic PAHs (5cPAHs) (benz[*a*]anthracene, benzo[*a*]pyrene (BaP) , benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, and chrysene) and BaP individually. Samples with an "r" indicate that the soil was a reference soil, while soils without a letter are rooftop receiving contact samples. Identical numbers are paired samples from the same site. All samples shown with paired BaP values exceed BaP reference soil screening level (USEPA 2007), as represented by the horizontal line at 16 ppb, except for BaP in sample 79r.

VITA

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