



Determination of oxygen, nitrogen, and sulfur-containing polycyclic aromatic hydrocarbons (PAHs) in urban stream sediments



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ABSTRACT

Recent studies indicate that PAH transformation products such as ketone or quinone-substituted PAHs (OPAHs) are potent aryl hydrocarbon receptor (AhR) activators that elicit toxicological effects independent of those observed for PAHs. Here, we measured eight OPAHs, two sulfur-containing (SPA), one oxygen-containing (DBF), and one nitrogen-containing (CARB) heterocyclic PAHs (i.e. Σ ONS-PAHs = OPAH₈ + SPAH + DBF + CARB) in 35 stream sediments collected from a small (~1303 km²) urban watershed located in south-central Pennsylvania, USA. Combined Σ ONS-PAH concentrations ranged from 59 to 1897 $\mu\text{g kg}^{-1}$ (mean = 568 $\mu\text{g kg}^{-1}$; median = 425 $\mu\text{g kg}^{-1}$) and were 2.4 times higher in urban versus rural areas, suggesting that activities taking place on urban land serve as a source of Σ ONS-PAHs to sediments. To evaluate urban land use metrics that might explain these data, Spearman rank correlation analyses was used to evaluate the degree of association between Σ ONS-PAH concentrations and urban land-use/land-cover metrics along an urban-rural transect at two spatial scales (500-m and 1000-m upstream). Combined Σ ONS-PAH concentrations showed highly significant ($p < 0.0001$) correlations with Σ PAH₁₉, residential and commercial/industrial land use (RESCI), and combined state and local road miles (MILES), suggesting that Σ ONS-PAHs originate from similar sources as PAHs. To evaluate OPAH sources, a subset of Σ ONS-PAHs for which reference assemblages exist, an average OPAH fractional assemblage for urban sediments was derived using agglomerative hierarchical cluster (AHC) analysis, and compared to published OPAH source profiles. Urban sediments from the Condoquinet Creek ($n = 21$) showed highly significant correlations with urban particulate matter ($X^2 = 0.05$, $r = 0.91$, $p = 0.0047$), suggesting that urban particulate matter is an important OPAH source to sediments in this watershed. Results suggest the inclusion of Σ ONS-PAH measurements adds value to traditional PAH analyses, and may help elucidate and refine pollutant source identification in urban watersheds.

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1. Introduction

Substituted polycyclic aromatic hydrocarbons containing oxygen, nitrogen, or sulfur heteroatoms, or ketone or quinone functional groups are common PAH co-contaminants because they derive from similar petrogenic and pyrogenic sources (Andersson et al., 2006). In urban areas, PAH sources include tires (Aatmeeyata, 2010), vehicle exhaust (Marr et al., 1999), atmospheric deposition (McVeety and Hites, 1988), leaking motor oil (Peake and Parker, 1979), roof runoff (Van Metre and Mahler, 2003),

and seal-coated pavements (Mahler et al., 2014). As urban areas grow, forests and undeveloped land are replaced by impervious surface cover such as commercial parking lots, residential driveways, and roads. Increased impervious surface cover increases surface runoff during rain and snow events (Arnold and Gibbons, 1996) and serves as an important transport pathway for substituted PAHs in addition to PAHs to urban streams.

Sediment risk assessment and source apportionment studies have traditionally focused on PAHs, with less attention paid to oxygen, nitrogen, or sulfur-containing derivatives that co-occur with these molecules. Although substituted PAH concentrations are often low (5–13%) relative to PAH concentrations (Meyer et al., 1999), recent evidence is accruing on their emerging role as potent environmental toxins independent of PAH toxicity (Lemieux et al., 2015). For example, sediment fractions collected from the river Elbe showed that mutagenic, estrogenic, and aryl hydrocarbon

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receptor (AhR) toxicity were dominated by polar organic compounds (Lubcke-von Varel et al., 2011). More recently, Knecht et al. (2013) exposed zebrafish embryos to a dilution series of 38 OPAHs and monitored 22 developmental endpoints to assess OPAH toxicity. Results showed that the most toxic OPAHs contained adjacent diones on 6-carbon moieties, or terminal para-diones on multi-ring structures. The OPAHs studied showed differential AhR dependencies, and oxidative stress was cited as an important mechanism for OPAH toxicity. In a similar study using authentic OPAH-containing soil extracts collected from a gasworks facility, a former wood preservation site, and a coke oven, Wincent et al. (2015) showed that OPAHs are potent AhR activators and developmental toxicants, and also cited oxidative stress as playing a role in OPAH toxicity. Heterocyclic nitrogen-containing PAHs including carbazole have been shown to induce estrogenic activity using the Estrogen Receptor mediated Chemical Activated Luciferase gene (ER-CALUX) assay, where relative equivalence factors were calculated to be of similar magnitude as other environmental xenoestrogens such as bisphenol A (Brinkmann et al., 2014).

Substituted PAHs are also important constituents of PAH-containing products intentionally applied in urban areas of the eastern U.S. such as coal-tar-based sealcoat (Mahler et al., 2005, 2014). In addition to high PAH concentrations, surface runoff from coal-tar sealcoated lots contains nitrogen-containing PAH heterocycles such as carbazole, quinoline and acridine, and sealcoat scrapings from the same lots contained anthraquinone (an OPAH) as well as the sulfur-containing PAH heterocycle dibenzothiophene (Mahler et al., 2014). In a recent study, fathead minnows and *Ceriodaphnia dubia* (a cladoceran) were exposed to runoff collected over 7 days from a coal-tar-sealed lot. The runoff was used undiluted and at 1/10 dilution and was shown to cause 100% mortality to both species after 24 h. If test organisms were additionally exposed to UVR light, 100% mortality was observed, even for runoff collected 111 days after application (Mahler et al., 2015). Coal-tar-sealed pavement runoff has also been shown to induce genotoxicity and impairment of DNA repair capacity in the RTL-W1 fish liver cell line (Kienzler et al., 2015).

In the present study, we measured oxygen, nitrogen, and sulfur-containing heterocycle concentrations and OPAH concentrations in sediments collected from the Conodoguinet Creek, a small river that traverses an urban-rural transect in south-central Pennsylvania, USA. We examined pairwise rank correlations between urban land-use metrics and substituted PAH concentrations at two spatial

scales. A second objective was to assess whether measuring substituted PAHs provides additional useful information on putative PAH sources. We hypothesized that if correlations emerged, they might help refine PAH sources associated with activities occurring on specific types of urban land. The twelve substituted PAHs evaluated in this study were selected because of their frequency of co-occurrence with PAHs reported in the literature. Also, with their newly emerging roles as potent environmental toxins in their own right, an assessment of their concentrations and distributions is warranted.

2. Materials and methods

2.1. Study location, sample collection, and land-use within the watershed

Thirty-five surface streambed sediments were collected from the Conodoguinet Creek watershed located southwest of Harrisburg, the state capital of Pennsylvania, USA in the Cumberland Valley between 39°95' and 40°27' N and 77°88' and 76°91' W during May 2010 (Supporting Information, Fig. S1). Land use in this basin is primarily agricultural (43%) and forested (42%), with smaller urban areas (11%) and transportation corridors (3%) located throughout the watershed. Land-use parameters including impervious surface area (%), residential land use (%), commercial & industrial land use (%), water (%), state road area (%) and combined state and local road miles (in km/km²) were measured at two spatial scales (500-m and 1000-m) upstream of the study sites. Detailed descriptions of geographic information system (GIS) data acquisition and sample collection procedures are described in Witter et al. (2014). Data used for land use correlation analyses are presented in the Supporting Information, Tables S1 and S2.

2.2. Chemicals

Standards for substituted PAHs quantified in this study (Table 1) were obtained from Alfa Aesar, Ward Hill, MA (9H-fluoren-9-one (FLUO), 7H-benz[de]anthracen-7-one (BEZO); Aldrich Chemical Co. Milwaukee, WI (carbazole (CARB), dibenzothiophene (DBT), benzo[b]naphtho[2,1-d]thiophene] (BNT), 5,12-naphthacene quinone (NAPQ), 11H-benzo[b]fluoren-11-one (BFLUO), 7,12-benz[a]anthraquinone (BaAQ)); Chem Service, West Chester, PA (9,10-anthraquinone (ANTQ)); and Santa Cruz Biotechnology, Dallas, TX

Table 1
List of target compounds and summary statistics for n = 35 sediments.

Group	Compound/class	Abbrev.	CAS#	MW (g/mol)	# of rings	MDL (ng/ml)	Mean Std Min Max				Detection freq. (%)
							(μg kg ⁻¹ sediment)				
<i>Ketone & Quinone PAHs</i>											
OPAH	9H-fluoren-9-one	FLUO	486-25-9	180.2	3	0.09	20.4	15.1	9.5	77.8	83
	9,10-anthracenedione	ANTQ	84-65-1	208.2	3	0.10	87.6	80.3	10.8	321.5	94
	4H-cyclopenta[def]phenanthren-4-one	PHEO	5737-13-3	204.2	4	0.09	44.4	38.8	9.8	178.4	94
	11H-benzo(b)fluorene-11-one	BFLUO	479-79-8	230.3	4	0.10	59.1	51.1	10.5	203.8	100
	7H-benz[de]anthracene-7-one	BEZO	82-05-3	230.3	4	0.12	73.9	69.8	17.6	383.3	94
	7,12-benz(a)anthraquinone	BaAQ	2498-66-0	258.3	4	0.12	103.3	90.2	19.6	402.3	94
	5,12-naphthacenequinone	NAPQ	1090-13-7	258.3	4	0.12	54.6	41.7	13.7	192.6	94
	6H-Benzo[cd]pyren-6-one	PYRO	3074-00-8	254.3	5	0.41	80.8	48.9	41.5	198.3	34
<i>Heterocyclic PAHs</i>											
OPAH	Dibenzofuran	DBF	132-64-9	168.2	3	0.08	19.2	8.1	10.8	45.7	100
NPAH	9H-Carbazole	CARB	86-74-8	167.2	3	0.08	25.2	14.5	10.5	82.1	100
SPA	Dibenzothiophene	DBT	132-65-0	184.3	3	0.08	17.2	8.9	8.6	48.5	100
	Benzo[b]naphtho[2,1-d]thiophene	BNT	205-43-6	234.3	4	0.08	64.9	53.8	15.3	237.9	97

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