



Occurrence, distribution and composition of aliphatic and polycyclic aromatic hydrocarbons in sediment cores from the Lower Fox River, Wisconsin, US

Chase S. Brewster^{1,2} · Virender K. Sharma¹ · Leslie Cizmas¹ · Thomas J. McDonald¹

Received: 31 May 2017 / Accepted: 21 November 2017 / Published online: 5 December 2017
© Springer-Verlag GmbH Germany, part of Springer Nature 2017

Abstract

The Lower Fox River is a 39 mile section which supports approximately 270,000 rural inhabitants across 18 counties, 303,000 metropolitan residents in Green Bay and Appleton, Wisconsin, and several large industrial complexes such as paper mills and power plants. This paper presents the distribution and concentrations of aliphatic (*n*-alkanes) and aromatic hydrocarbons (polycyclic aromatic hydrocarbons [PAHs]) as well as total organic carbon (TOC) in the Lower Fox River to identify the sources of hydrocarbon contamination. Excluding one outlier, percent TOC values were between 0.73 and 19.9% with an average value of 6.74%. Total *n*-alkanes ranged from 3.51 µg/g to 117 µg/g and showed a strong presence of odd carbon-numbered *n*-alkane ratios (range of C25 to C35), suggesting source input from terrestrial biomass. The mean polycyclic aromatic hydrocarbon (PAH) concentration was 24,800 ng/g. High molecular weight PAH concentrations dominated the distribution of hydrocarbon contaminants. Cross-plots of PAHs were used to compare diagnostic source ratios of benz[a]anthracene (BaA), chrysene (Chr), fluoanthene (Flu), pyrene (Pyr), anthracene (Ant), phenanthrene (Phe), indeno[1,2,3-cd]pyrene (InP), and benzo[g,h,i]perylene (BghiP) by depth and area. PAH ratios varied slightly with the core depth. Deeper core sections indicated the presence of biomass combustion while the upper core sections indicated combustion of both petroleum and biomass. The PAH toxicity of one core was estimated using toxicity equivalency factors, and the benzo[a]pyrene toxic equivalence quotient totaled 2,293 ng/g-dry wt. Levels of PAHs in sediments are compared with established regulatory values and recommendations are made.

Keywords Lower Fox River · Polycyclic aromatic hydrocarbons · *n*-alkanes · Diagnostic source ratios

Introduction

Polycyclic aromatic hydrocarbons (PAHs), which are the result of incomplete combustion of organic materials (Olofade et al. 2017; Zhang et al. 2017a, b), are also classified as persistent organic pollutants. PAHs are a group of ubiquitous

environmental compounds with persistent toxic abilities known to bioaccumulate in the environment due to slow decomposition (Joyce et al. 2016; Li et al. 2017). The toxic effects of PAHs on human health are known to include mutagenicity, teratogenicity, immunogenicity, and carcinogenicity. PAHs such as benzo[a]pyrene can increase the risk of skin, lung, bladder, liver, and stomach cancers (Costa et al. 2016; Cucak et al. 2017; Leitão et al. 2017; Lou et al. 2016; Yuan et al. 2016). Additionally, PAHs have been known to cross the placental boundary suggesting that a fetus is 10 times more vulnerable to PAH-induced DNA damage than the offspring's mother (Herbstman et al. 2012; Lee et al. 2017a). Despite the associated dangers, several industrial processes produce PAHs and other hydrocarbons as byproducts during manufacturing processes (Gonçalves et al. 2016; Kim et al. 2016; Ranjbar Jafarabadi et al. 2017b).

PAHs are not found in the environment as individual compounds, but rather as mixtures consisting of at least two fused

Responsible editor: Philippe Garrigues

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s11356-017-0819-z>) contains supplementary material, which is available to authorized users.

✉ Thomas J. McDonald
tmcDonald@tamhsc.edu

¹ Department of Environmental and Occupational Health, School of Public Health, Texas A&M University, 1266 TAMU, College Station, TX 77843-1266, USA

² TDI-Brooks International, 10060 N Dowling Road, College Station, TX 77845, USA

carbon-carbon rings with alternating double and single bonds (i.e., benzene rings) (Stout et al. 2015). The understanding of formation parameters and degradation patterns of PAH compounds allows the analyst to chemically fingerprint potential sources based on their distinct compound signatures (Huang et al. 2017a; Stout et al. 2015; Stout and Wang 2016). Diagnostic ratios of parent components can be used to interpret the characteristics of specific PAH isomers based on their stability and the temperature at which the analyte was created. The relative stability of isomers and their associated alkylated compounds provide a basis for high versus low heat ratio comparisons, which further provide an indication of formation based on their variation (Katsoyiannis and Breivik 2014; Yunker et al. 2012; Yunker et al. 2015).

The Lower Fox River is a 39 mile section located in east Wisconsin. Starting at the Menasha and Neenah channels, the Lower Fox River flows northeast where it discharges into the Green Bay and Lake Michigan basin. The watershed of the Lower Fox River supports approximately 270,000 rural inhabitants in 18 counties, 303,000 metropolitan residents, and several large industrial complexes within the urban cities of Green Bay and Appleton. Despite the high probability of hydrocarbon contamination, limited literature can be found on the distribution of hydrocarbons within the Lower Fox River (Su et al. 2000). The present paper assesses the hydrocarbon contamination in sediments of the Lower Fox River, Wisconsin, to characterize the aliphatic and aromatic hydrocarbon distribution and concentration in the Lower Fox River in order to identify the sources of hydrocarbon contamination through forensic fingerprinting of chemical constituents.

The main objectives of the current paper were to (i) determine the distribution and concentration of 88 PAH analytes with respect to core location and section depth; (ii) determine hydrocarbon source through forensic fingerprinting of the chemicals within the sediment in the Lower Fox River; and (iii) assess the toxicity of hydrocarbon analytes within sediment cores (i.e., parent and alkylated constituents), including seven PAHs categorized as class B2 human carcinogens (Ares et al. 2000) (benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenzo[a,h]anthracene, and indeno[1,2,3-c,d]pyrene (ATSDR 1995).

Experimental

Sediment samples were provided by a third party group from Wisconsin, Natural Resource Technologies (NRT). These samples were collected upstream from the US Paper and Georgia-Pacific paper mills within the metropolitan area of Green Bay, Wisconsin. To ensure good representation of hydrocarbon input, sample sites were selected in areas that had not been influenced by discharge zones. In the lower quadrant,

sampling areas such as US Paper Mills and Georgia-Pacific were avoided due to the potentially high concentrations of hydrocarbon refuse. From 2009 through 2012, dredging was conducted in the lower river quadrant to remove high concentrations of polychlorinated biphenyls (PCBs) in order to fulfill the Fox River remedial action (RA) requirements set by the U.S. Environmental Protection Agency (USEPA 2013). Viable sampling locations were selected in areas that had not been dredged.

Sampling

Cores were obtained from a sampling zone below the DePere Dam and consisted of three different sampling areas, labeled area 1, area 2, and area 3 (Fig. 1). Three cores were collected from each area of interest using a vibracore system. Each core collected had a minimum length of three feet four inches. If the core length was not satisfactory, the sample was discarded and the disposable core liner was replaced. The core liner was then rinsed with river water prior to relocation and further sample acquisition. Cores were divided into three, one-foot sections and labeled "Fox River Department of Justice (FRDJ) - Matrix (SED) - "area#"-"core#"-"section starting inch mark" (i.e., area 1, core 1 top section = ID: FRDJ-SED-1-01-01). If the collected core was longer than three feet and four inches the remainder was labeled '3 T'. Each section was placed into a gallon Ziploc bag, and labeled by: core identifier, section number, site location, and collection date. Samples were frozen and shipped via FedEx. Samples were received by the laboratory on 26 July 2012. Custody seals were present and intact upon receipt, and chain of custody records accompanied each cooler. The coolers did not contain a temperature blank; however, the internal temperatures of the coolers ranged from -0.2 to 0.0 °C, well within the acceptable range for sediments of 4 °C \pm 2 °C. Samples were stored in a -20 °C freezer prior to analysis.

Sample processing and dry weight determination

The sample extract parameters are shown in Table SM-1. Samples were homogenized prior to subsampling. Pre-cleaned 16 ounce clear jars were used for the 'wet' sample aliquot and pre-cleaned 8 ounce clear jars were used for the 'dry' aliquot. The original sample and 'wet' aliquot were then stored at -20 °C. Wet weight determination was obtained by pre-weighing a 57 mm aluminum pan, and weighing approximately 1 g of sample into the pan. Samples were then dried at 105 °C and checked twice over the next 2 days. After the percent moisture was determined, a subsample of each sample was placed in a 40 °C forced-air oven until dry. Due to the polar nature of the extraction solvent, dichloromethane, water within the samples was removed prior to extraction. Samples were then pulverized using a mortar and pestle.

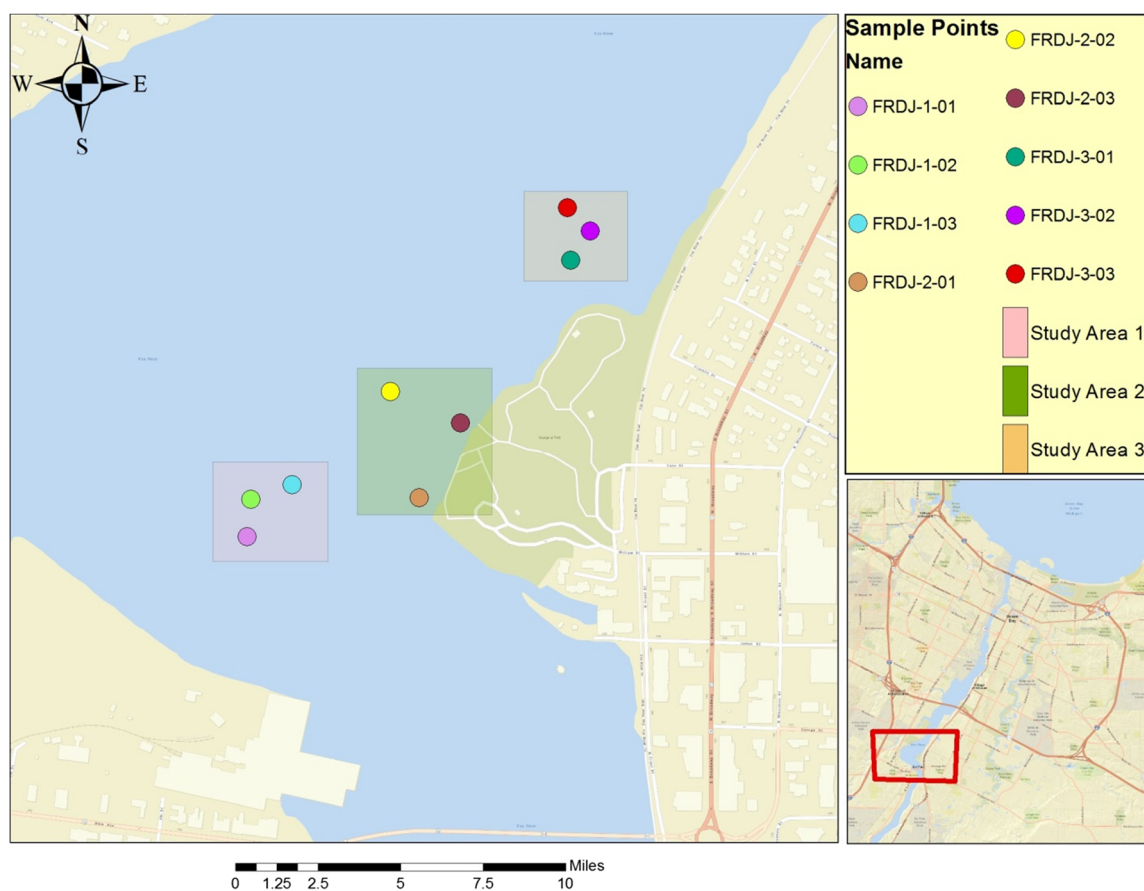


Fig. 1 Lower Fox River sampling areas and core sites. (Google Maps 2015)

Extraction process

Using a top loading balance, 15 g of dry sediment was weighed into a stainless steel extraction cell. A total of 100 μl of PAH and aliphatic surrogates were added to each sample prior to extraction. The PAH-saturated biomarker surrogate contained naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, perylene-d12, and 5 β (H)-cholane. The aliphatic surrogate contained n-dodecane-d26, n-icosane-d42, and n-triacontane-d62. Quality control samples (method blank, matrix spike, matrix spike duplicate, and laboratory duplicate sample) and National Institute of Standards and Technologies (NIST) SRM 1941b were also prepared with the appropriate surrogate and spike volumes. Using an Automated Solvent Extractor (Automated Solvent Extractor 200, Thermo Scientific Dionex, CA), samples were extracted using 100% dichloromethane (>99.8% purity chromatography grade, ECD Millipore Corporation, Darmstadt, Germany) at 100 $^{\circ}\text{C}$ and 1500 PSI into pre-cleaned 60 mL collection vials. Extracts were concentrated to 3–5 mL using a hot water concentration bath. Copper was used to remove sulfur. Extracts were then transferred into Kuderna-Danish (K-D) concentration tubes and the copper and vial were rinsed with dichloromethane a minimum of three times to remove

any residual extract. K-D tubes were returned to a water bath to reduce the extract volume to 3 mL.

Extracted organic material determination

Extracted organic material (EOM) determination was obtained by verifying each sample at a volume of 3 mL. VWR 2.4 cm glass microfiber filters were placed in a 40 $^{\circ}\text{C}$ oven on solvent cleaned stainless steel screens. Accuracy and range were verified by checking a dichloromethane solvent blank. A filter was pre-weighed on a microbalance, with sensitivity to approximately 0.001 mg and the initial weight was recorded. The filter was placed in a 40 $^{\circ}\text{C}$ oven and 100 μl of dichloromethane was applied to the filter. The filter remained in the oven for 2 min after which the filter was then weighed a second time, verifying a weight equal to 0.000 mg. An EOM standard was used to check high range by pre-weighing a filter. The initial weight was recorded. The filter was placed in the 40 $^{\circ}\text{C}$ oven and 100 μl of oil solution was applied to the filter. The filter remained in the oven for 2 min and the filter was weighed a second time, verifying a weight equal to 10.000 mg \pm 0.500. Each extracted sample was processed accordingly. The method blank was verified with required criteria of 0.000 mg + 0.003. EOMs were calculated

using Eq. 1. Duplicate relative percent difference (RPD) was recorded to within 25%.

$$EOM (\mu\text{g/g}) = [(We \times Vf)/(Ws \times Va)] \times (1000\mu\text{g}/1\text{mg}) \quad (1)$$

where

We was the residual weight of EOM aliquot (mg),
Ws was sample weight (g), and
Vf was volume of sample extract (3000 μL), and
Va was volume of aliquot (100 μL).

Sample cleanup and final concentration

To remove interferences such as pigments, sulfur oxide residuals, and large non-polar residues, samples were passed through silica gel, alumina, copper, and sodium sulfate. Extracts were run through a 6-mL solid phase extractor column (Resprep Normal Phase SPE Cartridge 6 mL 1000 mg silica, Restek, Bellefonte, PA) layered with 1 g of alumina, 1 g of silica gel, 1 cm of sodium sulfate, and 1 cm of copper. Using a vacuum pump system, the extract was processed through the cleanup column followed by 40–50 mL of dichloromethane. Extracts were collected in pre-cleaned 60 mL collection vials. Filtered extracts were concentrated to 3–5 mL using a hot water concentration bath and transferred to K-D tubes. K-D tubes were returned to the water bath to reduce the extract volume to 800 μL . Internal standards were added to each sample. PAH-saturated biomarker internal standards were fluorene-d10, pyrene-d10, and benzo[a]pyrene-d12. The aliphatic internal standards were n-hexadecane-d34 and 5 α -androstane. Extracts were adjusted to a final volume of 1 mL and then transferred to graduated 2 mL amber vials. Extracts that contained high EOM concentrations were adjusted by dilution using dichloromethane before gas chromatography/mass spectrometry (GC/MS) analysis. Additional surrogates and internal standards were added based on dilution factors.

Total organic carbon analysis

TOC analysis was used to evaluate the percent of organic carbon in sediment samples. Organic carbon input is generated by several sources: hydrocarbons, coals, vegetation (humic acid), microorganisms, and anthropogenic input. The sediment samples were dried at 105 $^{\circ}\text{C}$ to remove interstitial water. Dry sediment was then weighed at 350 mg into carbon-free, tared ceramic crucibles. A diluted phosphoric acid solution (50% by volume ratio) was added to remove any inorganic carbon within the material, such as calcium carbonate

(CaCO_3). Samples were then returned to the oven for a minimum of 16 h to remove the excess water. TOC was determined using a carbon analyzer (CR-412 Total Carbon Analyzer, Leco, St. Joseph, MI). Following quality assurance (QA) and quality control (QC) criteria, method blanks, SRMs, duplicates and continuous calibration checks (CCC) were used to ensure quality and accuracy. Each sample was individually analyzed at 1350 $^{\circ}\text{C}$ for a maximum duration of 180 s. The Leco CR-412 produced results in percent carbon (%C) based on sample weight and response (area times peak). Data was converted into an Excel report file calculating milligrams of carbon based on percent carbon and sample mass.

Gas chromatography/mass spectrometry

After the final concentration was attained, extracts were analyzed for PAH and aliphatic hydrocarbon concentrations using a HP5890 gas chromatograph (HP5890, Hewlett Packard Company, Wilmington, DE) coupled with an Agilent 5972 mass spectrometer (Agilent 5972, Agilent Technologies, Santa Clara, CA). A HP-5MS capillary column (Agilent HP-5MS, 60 m long with an interior diameter of 0.25 mm and 0.25 μm film thickness, Agilent Technologies, Santa Clara, CA) was used to chromatographically separate PAHs and *n*-alkanes analytes. The initial temperature of the injection port was held at 285 $^{\circ}\text{C}$, vaporizing the injected extract prior to entering the capillary column. The oven was initially set to 60 $^{\circ}\text{C}$. After injection, the oven was programmed to increase in temperature at a rate of 7 $^{\circ}\text{C}/\text{min}$ until it reached the final holding temperature of 310 $^{\circ}\text{C}$ with a final holding time of 22 min. Aliphatic hydrocarbons were determined using full scan mode. Full scan utilizes computer libraries to compare unknown analyte spectrums within the entire range of ions generated, providing information to resolve or confirm peaks qualitatively, pattern recognition, and structural elucidation (Wang et al. 2007). Full scan was used to identify aliphatic concentrations such as n-C9 through n-C44 (including isoprenoids: i-C13, i-C14, i-C15, and i-C18), and determine total resolved hydrocarbons (TRH), total petroleum hydrocarbons (TPH), and unresolved complex mixture (UCM). Selected ion monitoring mode (SIM) was used to identify and quantify PAH components. The use of SIM enables the determination of analytes of interest and improves the ability to measure highly specific compounds that occur at lower concentrations within the extract. Data generated by GC/MS was quantified using the ChemStation program (ChemStation software, Agilent Technologies, Santa Clara, California).

Quality assurance and quality control

Quality assurance (QA) and quality controls (QC) were in place to verify and determine recovery losses, potential contamination carry-over, and sample adjustments during the

extraction and instrumentation process. To establish retention times, NIST SRM 1941b, Organics in Marine Sediment was used. To ensure data reliability and integrity, quality control measures were followed. The GC/MS quality control measures included a system tune, six-level initial calibration (ICal), independent calibration verification solution (ICV), continuing calibration checks (CCC), reference oils (SRM 1582, and SRM1779), method blank, matrix spike (MS) and matrix spike duplicate (MSD), and duplicate sample (Dupl.). Extract concentration (C_e) was calculated based on:

$$C_e = ((AA) \times (CeIS)) / ((A_{IS}) \times (RRF_I)) \quad (2)$$

where,

Aa analyte area
 $CeIS$ concentration of internal standard added to the extract ($\mu\text{g/mL}$)
 A_{IS} area of internal standard, and
 RRF_I relative response factor of initial calibration.

Actual concentration (C) of extract is then calculated as

$$C = C_e \times (Ve/W) \times DF \quad (3)$$

where:

Ve final volume of the extract (mL),
 W original dry weight of the extract (g), and
 DF dilution factor.

QA and QC are important during the quantification stage; however, it is important to note the limitations of QA and QC in this study. The ICal analytes were quantified to within 25% of actual analyte values for PAH and aliphatic analysis. CCC values provided a periodic check amid the instrument analysis for consistency. It also provided a range of 50–200% of internal standard response for individual samples to be compared. Analyte concentrations were based on internal and surrogate recoveries and were adjusted based on these recovery percentages.

MS and MSD samples exceeded the 50 times known recovery values due to dilutions and high hydrocarbon concentrations for both analyses. Adjustments did not account for spiking solutions, which caused diluted MS and MSD responses to be unreliable. However, due to the high concentrations of hydrocarbon analytes within the samples, the ability to extract analytes of interest with efficiency was not impacted. Duplicates were quantified to within 20% relative difference; however, seven analytes were outside the 20% relative difference and above the minimum detection limit.

SRM1941b was quantified only for PAH analysis providing retention times for analytes not contained within the ICal and CCC solutions. Four analytes were outside the 50% recovery

window for PAH extractions. SRM1941b does not contain certified aliphatic reference values, thus SRM1941b was not quantified for aliphatic hydrocarbons. For SRM2779, all aliphatic analytes were within 50% of known value, with the exception of six analytes (n-C9, n-C10, n-C11, n-C12, n-C13, i-C12, and i-C13). For PAH analysis, three analytes were outside 50% recovery and above the minimum detection limit for both PAH extraction sets. SRM2779 was used to define analytic retention times for aliphatics and assess the quantification process for both analyses. The limited recoveries of the more volatile analytes did not impede the quality of the data due to the limited presence of the six outlying analytes within the sample extracts. SRM1582 was quantified for only the PAH analysis. All analytes were within 50% of known values above the minimum detection limit. Method blanks were monitored for potential contamination that occurred during the extraction process. GC/MS analyses determined that the method blank contained analyte concentrations exceeding three times the minimal detection limit within the second extraction set (NRT0017 through NRT0032). In contrast to the concentration levels in the samples, the contamination levels seen in the method blank would not impact the sample data concentrations.

Toxicological evaluation

PAHs are generated by both natural and anthropogenic processes and are not found in the environment as individual compounds, but rather as mixtures (ATSDR 1995). Humans and wildlife are rarely exposed to individual analytes, but rather to the potentially harmful mixtures which generate acute, chronic, individual, synergistic, and antagonistic responses (USEPA 2003b). As a result of human activities, PAH mixtures are released into the environment and pose potential toxicological risks (Ranjbar Jafarabadi et al. 2017a, b). These risks can be assessed by using toxic equivalency factors (TEFs) and the benzo[a]pyrene toxic equivalence quotient (TEQ) to better understand the hazardous levels posed by mixtures within an area of concern (USEPA 2003a).

A Toxic Equivalency Factor (TEF) approach was used to assess the toxicity of seven carcinogenic and ten non-carcinogenic analytes in the river sediment. TEF values are conservative estimates of toxicity for individual compounds, relative to the toxicity of an index chemical (Reeves et al. 2001; USEPA 2003a). PAHs are evaluated based on their relative potency with respect to benzo[a]pyrene, the index chemical for PAHs. PAH analytes that are classified as carcinogens typically are assigned higher TEF values than non-carcinogenic PAHs (i.e., 1.0, 0.1, or 0.01) (Nisbet and LaGoy 1992).

The TEF values and analyte concentrations (ng/g) can be used to evaluate the toxicity of the sediments (Egubbe et al. 2014; Nisbet and LaGoy 1992, Wickliffe et al. 2014). The

concentrations of the individual PAHs (C) were multiplied by the respective TEF for each compound to normalize the toxicity of each analyte in terms of benzo[a]pyrene equivalents, and the benzo[a]pyrene toxic equivalence quotient (TEQ) for the mixture was calculated as shown in Eq. 4.

$$TEQ = \sum_{n=1}^n (C \times TEF) \quad (4)$$

Diagnostic comparisons

After extraction and quantification, histograms, single ratio, and cross-plots were used to identify potential sources of hydrocarbon contamination. Chromatography profiles with m/z responses provided an understanding of these sources (i.e., m/z 178, m/z 191, and m/z 202). Fingerprint profiles of the suspected sources in the samples were examined graphically by reviewing PAH concentrations of parent and alkylation abundance to display their relative slope (decrease, increase, or bell-shaped). Diagnostic ratios were used to identify a probable match (Ma et al. 2017; Ranjbar Jafarabadi et al. 2017a). The diagnostic PAH ratios (Table SM-2) were used to determine petrogenic or pyrogenic sources and potential input sources (Short et al. 1998 and Crane 2014). Diagnostic ratios of n -alkanes (Table SM-3) were used to determine potential environmental and anthropogenic sources. Other diagnostic ratios (Table SM-4) were used to determine the total contribution of hydrocarbons within the extracts with respect to other organic materials and degradation.

TOC provides an indication of nonspecific organic influx by a weight/weight (mg/g) ratio and a percent carbon value. PAH/TOC or n -alkane/TOC ratios can be used to determine the input of PAHs or n -alkanes with respect to the total organic concentration. Low ratio values are an indication of low PAH or n -alkane contribution to the total organic carbon.

To calculate UCM, total petroleum hydrocarbon (TPH) and total resolved hydrocarbon (TRH) concentration values are needed. TRH concentration should always be higher than the total n -alkane concentration because TRH includes all peak values, which are individualized, not solely the selected n -alkane analytes. TPH is the sum of all peak area above the baseline of the chromatograph. TPH concentrations should always be less than EOM concentrations because of sample clean-up. TPH concentration includes the TRH and UCM, which are the bioresistant compounds of the organic mixture, and thus, UCM equals the difference between TPH and TRH.

Results and discussion

Total organic carbon

TOC analysis provides an indication of nonspecific organic influx based on a sum concentration of all organic carbon

molecules within a given sample (i.e., milligrams of carbon detected within grams of the sample). High TOC ratios and percentages are typically an indication of large organic influx such as biomass, petrochemicals, coal, or other hydrocarbon-based constituents (i.e., PAHs, n -alkanes, etc.). As shown in Table SM-5, the total organic carbon data averaged 6.7% TOC (excluding FRDJ-SED-2-03A-01U). The graphite-like material removed from core section FRDJ-SED-2-03A-01 (denoted as FRDJ-SED-2-03A-01U) was 85.2% TOC. Core sections ranged from 0.7% TOC (FRDJ-SED-3-01-23) to 19.9% TOC (FRDJ-SED-2-03A-23). FRDJ-SED-2-03A-23 contained significant amounts of the graphite-like material which may explain the high carbon values found in this sample. Core sections were averaged to obtain a TOC measurement for each core. Total organic carbon data per core ranged from 10.9% TOC (FRDJ-1-03) to 2.0% TOC (FRDJ-3-01).

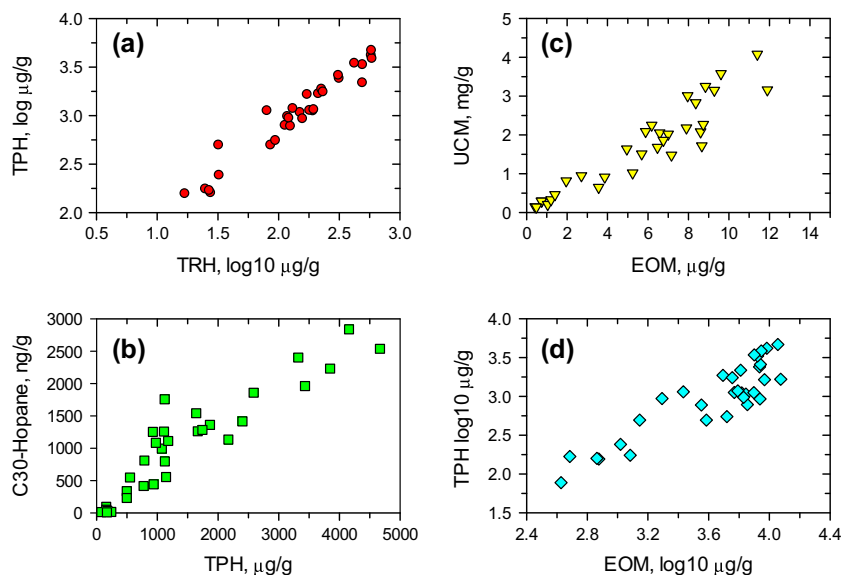
Extracted organic material

Extracted organic material (EOM) determination is the concentration of measurable organic matter extracted from a known weight of material. EOM analysis provides a $\mu\text{g/g}$ concentration value which can be used to prepare adjustments preventing column overload for better peak resolution. EOMs also provide an understanding of chromatography responses of unknown sample contamination such as EOM versus hydrocarbon contribution. Finally, EOMs can justify results of low or high UCM, TPH, TRH, and PAH concentrations versus unknown sample contamination levels. EOM results are unfiltered extract values, whereas final extracts are filtered and potentially diluted. EOM determination of core data averaged 5502 $\mu\text{g/dry g}$, as shown in Table SM-5. The graphite-like material removed from core section FRDJ-SED-2-03A-01U was 286 $\mu\text{g/dry g}$. Sample extracts were less than 0.08% organic by weight.

Saturated hydrocarbons

Core sediments were analyzed using GC/MS. Aliphatic hydrocarbon (n -alkanes and isoprenoids) data were adjusted according to dilution factors and surrogate corrected to 100% recovery. As shown in Table SM-5, total n -alkanes ranged from 3.51 $\mu\text{g/g}$ (FRDJ-SED-3-01-23) to 117 $\mu\text{g/g}$ (FRDJ-SED-1-03-01). The predominant aliphatic hydrocarbons in the samples were pristane, phytane, n -C27 and n -C29. The aliphatic odd:even ratio depicted a strong presence of odd carbon-numbered n -alkanes ratios (range of C25 to C35), with one exception, FRDJ-SED-2-03A-3T (data not shown). The strong presence of odd carbon-numbered n -alkanes within the range of C25 to C35 is an indication of terrestrial plant waxes and microalgae (Lichtfouse et al. 1994). However, FRDJ-SED-2-03A-3T contained an elevated concentration of n -C24 contributed by an unknown source. If n -C24 were excluded from the FRDJ-SED-2-03A-3T data, the

Fig. 2 Total petroleum hydrocarbon (TPH) cross-plots, depicting petroleum hydrocarbon abundance versus distribution and degradation. **a** Total resolved hydrocarbon (TRH) versus total petroleum hydrocarbon (TPH). **b** C30-hopane versus TPH. **c** Unresolved complex mixture (UCM) versus extracted organic material (EOM). **d** TPH versus EOM. Cross-plots depict degradation, abundance, and trends, assisting in deciphering hydrocarbon influx source(s)



ratio value would increase from 0.78 to 1.92, more closely resembling the other extract ratios.

Pristane/phytane ratios varied from 0.88 to 1.50, with an outlier at 6.67 (FRDJ-SED-2-03A-12), and a mean of 1.30. With the pristane/phytane ratios close to 1.0, pristane (Pr) and phytane (Ph) contributions may be a result of microbial activities in the

river (Peters and Walters 2005, Powell 1988, Shimeshan et al. 2017, Ten Haven et al. 1988). However, the abrupt changes in concentrations of pristane and phytane with an equivocal ratio may also indicate the presence of diffused residual petroleum in limited or degraded form, such as those contained in surface runoff (Hamilton and Cline 1981). The n-C17/Pr ratios ranged

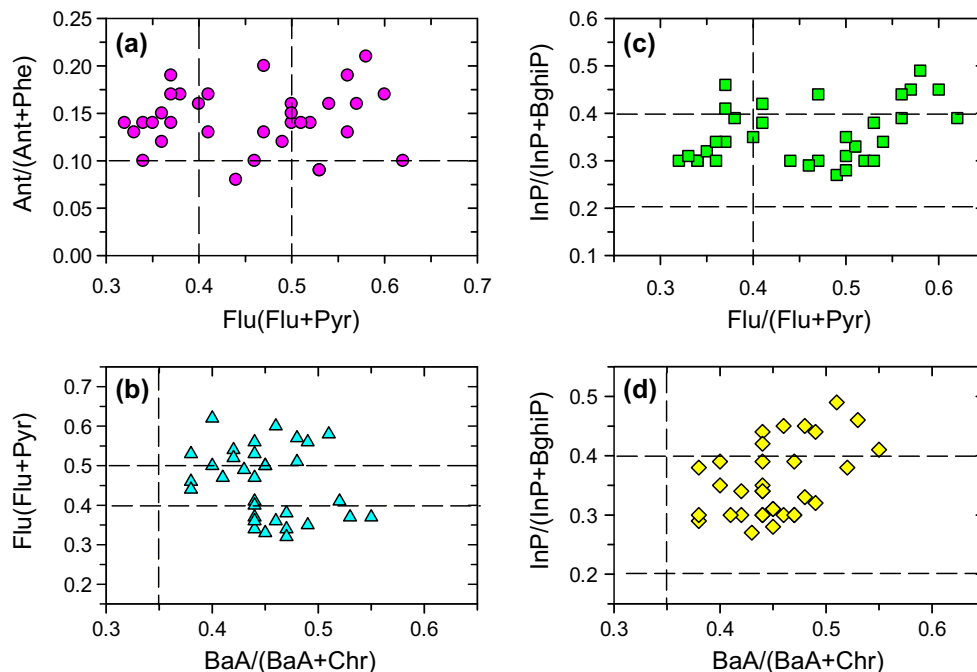


Fig. 3 PAH cross-plots based on diagnostic ratios of **(a)** [Ant/(Ant + Phe)] versus [Flu/(Flu + Pyr)], **(b)** [Flu/(Flu + Pyr)] versus [BaA/(BaA + Chr)]; **(c)** [InP/(InP + BghiP)] versus [Flu/(Flu + Pyr)]; **(d)** [InP/(InP + BghiP)] versus [BaA/(BaA + Chr)] for source appointment in the sediment cores from the Lower Fox River, Wisconsin. Indications of PAH source. Ant/(Ant + Phe) ratio < 0.1 petrogenic or > 0.1 pyrogenic. Flu/(Flu + Pyr) ratio < 0.4 petrogenic; 0.4–0.5 petroleum combustion (e.g., combustion engines, and furnaces); > 0.5 biomass combustion (e.g.,

grasses, wood, or coal combustion). BaA/(BaA + Chr) ratio < 0.2 petrogenic or > 0.35 pyrogenic. InP/(InP + BghiP) ratio < 0.2 petrogenic; 0.4–0.5 petroleum combustion; and > 0.5 biomass combustion. Abbreviations: Ant, anthracene; Phe, phenanthrene; InP, indeno[1,2,3-c,d]pyrene; BghiP, benzo[g,h,i]perylene; Flu, fluoranthene; Pyr, pyrene; BaA, benz[a]anthracene; Chr, chrysene; PAH, polycyclic aromatic hydrocarbon

from 0.29 to 2.33 with a mean of 0.88. The n-C18/Ph ratios ranged from 0.11 to 4.20 with a mean of 0.65. Both n-C17/Pr and n-C18/Ph indicate biodegradation of the hydrocarbon substrate with ratios less than 1.

TPH and TRH were compared by normalizing the large range of response values using a logarithmic scale (log10). This comparison provided an indication of weathered versus non-weathered saturated hydrocarbon influx. Because the concentration of TRH, with respect to TPH, showed linearity, hydrocarbon degradation was consistent throughout (Fig. 2a). The large variation in TPH and TRH concentrations indicates that low concentrations of resolved hydrocarbons are present within the more bioresistant organic substrate (i.e., limited biodegradation). Similarly, C30-hopane concentration versus TPH can be used to interpret degradation of hydrocarbons (Fig. 2b). A detectable linear trend provides an understanding of the current distribution and concentrations, or status, of hydrocarbon contamination with respect to C30-hopane. To determine organic influx, particularly petroleum incursion, EOM was compared to the UCM concentration (Fig. 2c). When the UCM concentrations were cross-plotted with EOM concentrations, the plot showed a linear correlation.

UCM versus EOM depicted a relatively low percentage of hydrocarbon-based material present in comparison to the total extracted material (Fig. 2c). UCM concentrations accounted for approximately 33% of total EOM extracted, indicating a large deposition of non-specific, non-petroleum based organic material within the sampling areas.

EOM concentrations were also cross-plotted with TPH to compare total extractable material versus degraded and non-degraded hydrocarbons within the extractable range (Fig. 2d). After EOM and TPH were normalized using a log10 base comparison, the plot provided an observation of a potential contribution of hydrocarbon-based contamination within the overall organic substrate. Log10 EOM versus log10 TPH shows all core sections had almost identical contributions of hydrocarbon-based composition with limited petroleum influx.

Total n-alkanes and identified TRH analytes provided a specialized tool in source identification. Although n-alkanes are subjected to weathering, the retained concentrations of identifiable n-alkanes provide an understanding of influx source. As shown in Fig. 2a, total n-alkane concentrations within the core sections varied with TPH concentration. The linearity of the total n-alkanes versus TPH depicts limited degradation of the n-alkanes.

Polycyclic aromatic hydrocarbons

The PAH data was adjusted according to dilution factors and surrogate corrected to 100% recovery. The predominant PAH analytes were chrysenes, pyrene, fluoranthene, and C4-phenanthrenes/anthracenes. The mean total PAH concentration was 24,800 ng/g with FRDJ-SED-1-03-12 and FRDJ-SED-

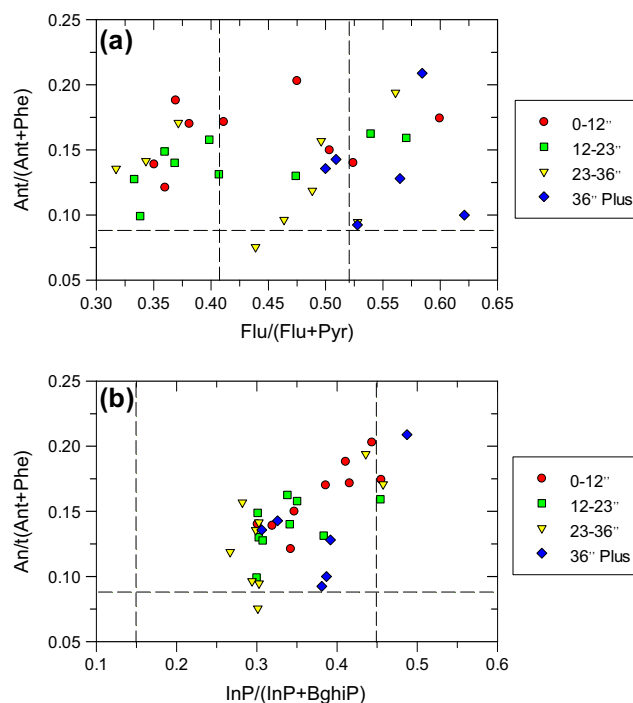


Fig. 4 PAH cross-plots based on diagnostic ratios of (a) $[Ant / (Ant + Phe)]$ versus $[Flu / (Flu + Pyr)]$ and (b) $[Ant / (Ant + Phe)]$ versus $[InP / (InP + BghiP)]$ based on depth (0–12", 12–23", 23–36", and >36") for source appointment in the sediment cores from the Lower Fox River, Wisconsin. Ant/(Ant + Phe) ratio <0.1 petrogenic or >0.1 pyrogenic. Flu/(Flu + Pyr) ratio <0.4 petrogenic; 0.4–0.5 petroleum combustion (e.g., combustion engines, and furnaces); >0.5 biomass combustion (e.g., grasses, wood, or coal combustion). InP/(InP + BghiP) ratio <0.2 petrogenic; 0.4–0.5 petroleum combustion; and >0.5 biomass combustion. Abbreviations: Ant, anthracene; Phe, phenanthrene; InP, indeno[1,2,3-c,d]pyrene; BghiP, benzo[g,h,i]perylene; Flu, fluoranthene; Pyr, pyrene; BaA, benz[a]anthracene

1-03-01 sections showing the highest concentrations at 63,600 ng/g and 56,700 ng/g, respectively. Both sections represent core FRDJ-SED-1-03 in the upper 23 in. Core FRDJ-SED-3-01 subsections had the lowest values with a range of 519.3 ng/g to 5802 ng/g. The mean values for the seven PAHs classified as B2 carcinogens present in the river sediment were benzo[a]anthracene (540 ng/g), benzo[a]pyrene (426 ng/g), benzo[b]fluoranthene (484 ng/g), benzo[k]fluoranthene (157 ng/g), chrysene (660 ng/g), dibenzo[a,h]anthracene (107 ng/g), and indeno[1,2,3-c,d]pyrene (249 ng/g), which equaled 10% of the total PAH concentration. Cores FRDJ-SED-1-03, FRDJ-SED-2-03A, and FRDJ-SED-2-02 contained the highest concentration of PAHs with respect to the upper three sections (see Table SM-5). FRDJ-SED-1-03, FRDJ-SED-2-03A, and FRDJ-SED-2-02 collection areas were located closest to the DePere Dam, upstream from the US Paper Mills and Georgia Pacific. Subsequently, the lowest PAH concentrations were located furthest downstream of the DePere Dam at FRDJ-SED-3-01 and FRDJ-SED-3-02. PAH concentrations were highest closest to the center of the river and lowest towards the shore.

Core sections showed an uneven distribution of low molecular weight (LMW) PAHs to high molecular weight (HMW) PAHs (Table SM-5, and Fig. 3). HMW PAHs were predominant over LMW PAHs with high concentrations of C0, C1, and C2 alkylated analytes indicating pyrogenic activities. LMW PAH and HMW PAH analytes are both depicted as a downward slope to bell-shape curve with C2 as the predominant alkylation (e.g., C2-Fluoranthenes/Pyrenes). The elevated presence of parent PAH analytes is an indication of recent deposition of pyrogenic PAH contamination. The high concentration of HMW PAHs such as 4-ring, 5-ring and 6-ring PAHs is typical of an urban region. C2 abundance, with respect to other alkylation levels, is an indication of combustion of both petroleum (LMW) and biomass (HMW) (Wagener et al. 2010). C2- and C3-anthracene/phenanthrene concentrations suggest an incursion of petrogenic residues in addition to pyrogenic PAH, typical of urban runoff (Uhler et al. 2005).

The presence and abundance of 2-methylanthracene (m/z 192) in comparison with methylphenanthrenes can indicate refined petrochemicals (e.g., combustion or byproducts) (Wilhelms et al. 1998). This presence of 2-methylanthracene in the cores is

an indication of a pyrogenic PAH source (Fig. SM-3 and Table SM-6). Further, the presence of both stable and unstable methylphenanthrenes is another example of pyrogenic activities. Generally, 3- and 2-methylphenanthrene isomers are more stable than 9-, 4-, and 1-methylphenanthrene. Therefore, the higher concentration of less stable methylphenanthrene isomers is an indication of pyrogenesis. The sample extracts contained significant concentrations of 2-methylanthracene and 9-, 4-, and 1-methylphenanthrenes, with respect to 3- and 2-methylphenanthrene.

Perylene is a constituent of PAH mixtures which can assist in the differentiation between natural and anthropogenic PAH sources. The abundance of Σ 5-ring PAHs with respect to perylene concentration indicates pyrogenesis. When perylene is compared to total PAHs, the provenance of perylene within sediments is identified as diagenetic when the ratio is larger than 0.1 (Readman et al. 2002). Perylene concentration within sampling area 3, with respect to total PAHs, exceeds 0.1. This indicates that the perylene source for area 3 is predominantly biogenic. The abundance of perylene elsewhere, less than 0.1, is an indication of pyrolytic contribution of PAHs.

Fig. 5 (a–c) Diagnostic cross-plots of Ant/(Ant+Phe) versus Flu/(Flu+Pyr) by area; and (d–f) diagnostic cross-plots of InP/(InP+BghiP) versus Ant/(Ant+Phe) by area. This figure displays PAH sources based on regional input. Ant/(Ant + Phe) ratio <0.1 petrogenic or >0.1 pyrogenic. Flu/(Flu + Pyr) ratio <0.4 petrogenic; 0.4 - 0.5 petroleum combustion (e.g., combustion engines, and furnaces); >0.5 biomass combustion (e.g., grasses, wood, or coal combustion). InP / (InP + BghiP) ratio <0.2 petrogenic; 0.4 - 0.5 petroleum combustion; and > 0.5 biomass combustion. Abbreviations: Ant, anthracene; Phe, phenanthrene; Flu, fluoranthene; Pyr, pyrene; InP, indeno[1,2,3-c,d]pyrene; BghiP, benzo[g,h,i]perylene; PAH, polycyclic aromatic hydrocarbon

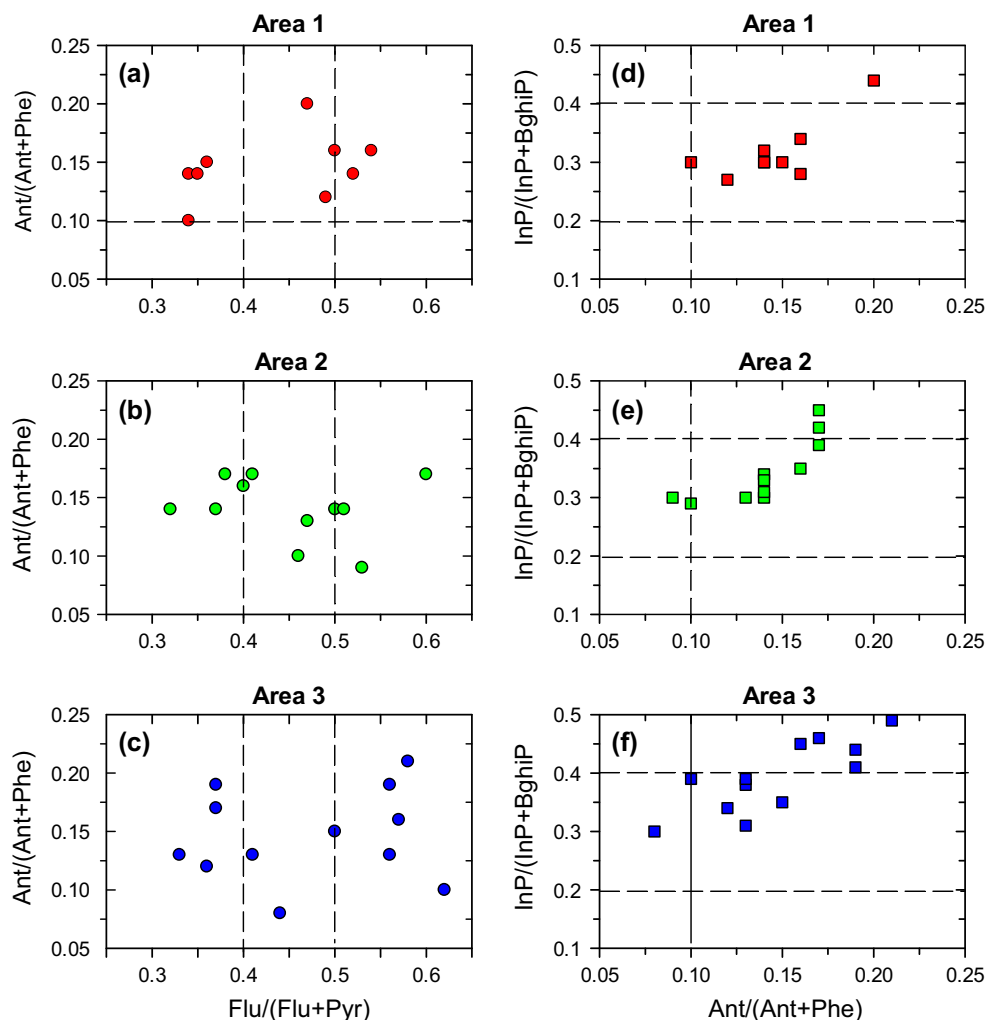


Table 1 Toxic equivalency factors for Lower Fox River core section FRDJ-SED-3-03-12 (area 3)

PAHs of interest	Sediment Conc. (ng/g dry)	Toxic equivalency factors (TEFs)	Calculated benzo(a)pyrene toxic equivalence quotient (ng/g dry wt.)	Sediment concentration at 1% TOC (ng/g dry wt.) [TOC = 8.6%]
Dibenzo(a,h)anthracene	213.8	5.0	1069	24.86
Benzo(a)pyrene	904.9	1.0	904.9	105.2
Benz(a)anthracene	1279	0.1	127.9	148.8
Benzo(b)fluoranthene	802.6	0.1	80.26	93.32
Benzo(k)fluoranthene	317.8	0.1	31.78	36.96
Chrysene/triphenylene	1575	0.01	15.75	183.2
Indeno(1,2,3-c,d)pyrene	447.2	0.1	44.72	51.99
Anthracene	225.5	0.01	2.255	26.22
Benzo[g,h,i]perylene	1008	0.01	10.08	117.2
Acenaphthene	87.36	0.001	0.0874	10.16
Acenaphthylene	140.5	0.001	0.1405	16.34
Fluoranthene	1020	0.001	1.020	118.6
Fluorene	207.5	0.001	0.2075	24.13
2-Methylnaphthalene	630.4	0.001	0.6304	73.30
Naphthalene	627.3	0.001	0.6273	72.95
Phenanthrene	1541	0.001	1.541	179.2
Pyrene	2044	0.001	2.044	237.7
Sum of 17 PAHs	13,072		2293	1520

The Ant/(Ant + Phe) ratio is used to distinguish between petrogenic (less than 0.1) or pyrogenic origin (greater than 0.1) (Yunker et al. 2002 and Bastami et al. 2014). The majority of sections contained a ratio greater than 0.1 indicating a pyrogenic source (Table SM-7). The Flu/(Flu + Pyr) ratio provides an indication of source (Table SM-7). Sample extracts contained a Flu/(Flu + Pyr) ratio with a range of 0.32–0.62 and a mean of 0.46. Many of the sample ratios fell between 0.4 and 0.5, indicating a mixture of combusted and non-combusted petrol fuels in conjunction with biomass combustion and degradation (Yunker et al. 2002 and Bastami et al. 2014).

The BaA/(BaA + Chr) ratio can also be used to indicate a petrogenic or a pyrogenic source (Table SM-7). The BaA/(BaA + Chr) ratios range from 0.38 to 0.55 with a mean of 0.45 indicating pyrogenic sources (greater than 0.35) (Dvorská et al. 2011). This range could indicate pyrogenic combustions of coals, biomass, and petrol fuels with a potential mixture of lubricants and road runoff. InP/(InP + BghiP) ratios provide an indication of source (Table SM-7). The InP/(InP + BghiP) ratio has a range of 0.27–0.49 with a mean 0.35, which indicates pyrogenic combustion, automotive residues, and road runoff (Yunker et al. 2002 and Bastami et al. 2014). However, similar to BaA/(BaA + Chr) ratio, the InP/(InP + BghiP) ratio range can include multiple potential sources.

To identify potential PAH sources, PAH analyte ratios were plotted using a typical oil geochemistry correlation cross-plot.

By comparing Ant/(Ant + Phe) versus Flu/(Flu + Pyr), a better understanding of primary and secondary PAH sources is achieved (Fig. 3). This cross-plot indicates a complexity of parameters with multiple PAH contributions from the surrounding environment. The core sections are comprised of organic sediments mixed with different PAH constituents from different sources. These disparate sources can be identified as pyrogenic with values representing the combustion of petroleum and combustion of biomass.

Flu/(Flu + Pyr) versus BaA/(BaA + Chr) were compared (Fig. 3) to differentiate combustion of different biomass materials (Bastami et al. 2014). This contrast provided an indication of the type of biomass that was combusted (e.g., coal, wood, or grasses). However, despite an attempt to isolate the primary source of PAHs through combustion, distribution indicates some petroleum combustion. Biomass and coal ranges (0.35–0.77) for Flu/(Flu + Pyr) and BaA/(BaA + Chr) overlap: gasoline (0.44) and diesel (0.20–0.58) combustion, roadway runoff and automotive/diesel oils (0.30–0.37), and roadway tunnel exhaust (0.41–0.49) (Yunker et al. 2002). This overlap limits the ability to identify a single source influx.

InP/(InP + BghiP) versus Flu/(Flu + Pyr) compares potential source PAHs with similar ranges (Agah et al. 2017; Rahmanpoor et al. 2014). Figure 4 shows InP/(InP + BghiP) ratio and Flu/(Flu + Pyr) ratio indicate multiple sources of PAH influx. However, both ratios identify petroleum

Table 2 Concentrations of hydrocarbons in different parts of the world

Location	Number of PAHs (ng/g)	Mean (ng/g)	References
Lower Fox River, Wisconsin, USA	16	5875	This study
Nakdong River Estuary, South Korea	16	65.22	(Lee et al. 2017b)
Huai River, China	16	7955	(Zhang et al. 2017a, b)
Yellow River Estuary, China	16	97.2–204.8	(Hu et al. 2014)
Estuaries in Haihe river basin, China	16	92–15,866	(Liu et al. 2014)
Huangpu River, Shanghai, China	16	7708.41; dry season	(Huang et al. 2017b)
Huangpu River, Shanghai, China	16	1109.62; wet season	(Huang et al. 2017b)
Yangtze River Estuary, China	16	193–7588	(Yu et al. 2015)
Luan River Estuary, China	16	5–545	(Zhang et al. 2016)
Kaohsiung Harbor, Taiwan	16	34–16,700	(Chen et al. 2013)
Tai Lake Basin, Jiangsu, China	16	349	Zhonghua Zhao et al.
Chitrapuzha River, India	16	5046–33,087	(Sanil Kumar et al. 2016)
Cochin estuary, India	16	194–14,149	(Ramzi et al. 2017).
Hormuz strait, Persian Gulf	16	195	(Bastami et al. 2013)
Selangor River estuary, Malaysia	16	203–964	(Masood et al. 2016)
Iko River estuary mangrove system, Nigeria	16	6100–35,270	(Essien et al. 2011)
Klip and Jukskei Rivers, South Africa	16	1060–1130	(Rimayi et al. 2017)
Marano and Grado Lagoon, Italy	16	50–1026	(Acquavita et al. 2014) 2014
Danube River, Hungary	16	8.3–1202	(Nagy et al. 2014)
Durance River, France	16	57–1528	(Kanzari et al. 2015)
Ammer River, Germany	16	112–22,900	(Liu et al. 2013)
Gulf of Trieste, Italy	16	214–4416	(Bajt 2014)
Huveaune River, France	16	572–4235	(Kanzari et al. 2014)
Porto Atlantic coast, Portugal	16	52,000	(Rocha et al. 2017)
Ría Arousa, Spain	16	3335	(Pérez-Fernández et al. 2015)
Rio de Arousa, NW Spain	16	44–7901	(Pérez-Fernández et al. 2015)
Bahía Blanca Estuary, Argentina	16	19–30,054	(Romero-Oliva et al. 2015)
Mundaú and Manguaba estuarine-lagoon system, Brazil	16	29–222	(Silva et al. 2013)
Patos Lagoon Estuary, Brazil	16	89–10,451	(Garcia et al. 2010)
Esterode Urias estuary, Mexico	16	27–418	(Jaward et al. 2012)

combustion and biomass combustion as main contributors. InP/(InP + BghiP) versus BaA/(BaA + Chr) was used to compare fossil fuel types. The cross-plots provide an understanding of coal grades and fuel variations. The cross-plot of InP/(InP + BghiP) versus BaA/(BaA + Chr), as with Ant/(Ant + Phe) versus Flu/(Flu + Pyr), indicates a complexity of sediments containing various PAH constituents from different pyrogenic sources, including the combustion of higher ranking coals and petroleum.

To understand the distribution and concentration of hydrocarbon sources, core sections were grouped by depth and

location. PAH analytes were cross-plotted based on depth. Ant/(Ant + Phe) versus Flu/(Flu + Pyr) and Ant/(Ant + Phe) versus InP/(InP + BghiP) display a deposition of PAH residues within the Lower Fox River sediments (Fig. 4a, b). These cross-plots visually indicate that over a period of time, changes in PAH source input occurred, with a shift from biomass combustion in the lower core sections to more petroleum combustion and automotive discharge in the upper two core sections.

PAH analytes were cross-plotted based on sampling area. Ant/(Ant + Phe) versus Flu/(Flu + Pyr) and Ant/(Ant + Phe)

versus $\text{InP}/(\text{InP} + \text{BghiP})$ show differences in PAH source (Fig. 5 and Table SM-8). Area 1 and area 2 display lower ratio groupings with a higher density of points in the petroleum combustion zone. However, in area 2, some presence of biomass combustion is observed. Area 3 displays more source diversity, with $\text{Flu}/(\text{Flu} + \text{Pyr})$ and $\text{InP}/(\text{InP} + \text{BghiP})$ ratios between 0.2 and 0.4 and some distributions greater than 0.4. All areas contain outliers below the $\text{Flu}/(\text{Flu} + \text{Pyr})$ 0.4 intercept; however, this does not indicate petroleum incursion. The residual PAHs are more consistent with diesel combustion (0.20–0.58) from automotive sources in the metropolitan area with respect to $\text{InP}/(\text{InP} + \text{BghiP})$ ratios. This area comparison indicates that over the course of the river, changes in PAH source input occur with a shift from upstream petroleum combustion and automotive discharge to an even distribution of both petroleum combustion and biomass combustion downstream.

Toxicological evaluation

A toxicity evaluation using toxicity equivalency factors (TEFs) was conducted for seven carcinogenic and ten non-carcinogenic analytes for core section FRDJ-SED-3-03-12 (Table 1). The benzo[a]pyrene toxic equivalence quotient (TEQ) was calculated for these 17 analytes, and totaled 2293 ng/g-dry wt. Based on this calculation, dibenzo[a,h]anthracene and benzo[a]pyrene accounted for 46.6 and 39.5%, respectively, of the toxicity within core section FRDJ-SED-3-03-12.

In accordance with the Wisconsin governmental standards issued by the Wisconsin Department of Natural Resources, the PAH concentrations were also normalized to 1% TOC for the PAHs of interest (WDNR 2003). After normalization, the new PAH value was 1520 ng/g-dry wt. at 1% TOC.

Comparison of total hydrocarbons with some regions of world

Table 2 presents a comparison of average ΣPAH_{16} concentrations in some regions of world, performed in recent years. The concentrations of hydrocarbons in sediments of different estuaries and rivers were found to be in the range from 5 to 52,000 ng/g (Table 2). Local anthropogenic sources determined the concentration in a particular region. The present study found an average ΣPAH_{16} of 5875 ng/g in sediment cores from the Lower Fox River, Wisconsin, US. This level of PAH concentrations was similar to the concentrations determined in sediments of the Huangpu River, China in the dry season (i.e., 7708 ng/g) (see Table 2). However, some regions have much higher levels of average ΣPAH_{16} than were found in our study. For example, concentrations of average ΣPAH_{16} in sediments of Porto Atlantic coast, Portugal, were determined as 52,000 ng/g (Table 2). It should be pointed out that Table 2 represents an

example of comparison of levels of ΣPAH_{16} . Table 2 does not include all the studies reported in the literature.

Conclusions

Extracts of the sediment core sections contained signatures of parent and alkylated PAHs. The sources of PAH influx were primarily pyrogenic with a complex mixture of coal, biomass, and petroleum combustion residuals. PAH ratios suggested a correlated high influx of petroleum combustion and biomass combustion sources. The presence of C0, C1, and C2 alkylated analytes are a strong indication of combustion with a limited degree of degradation. Total carbon, EOM, and saturated hydrocarbon data support the PAH data indicating high inputs of organic substrate with odd-numbered *n*-alkanes suggesting terrestrial or aquatic plant origin. Runoff from urban and rural roadways, diesel and gasoline combustion engines, household heating, and commercial-industrial byproducts accumulate within Lower Fox River sediments.

The benzo[a]pyrene toxic equivalence quotient (TEQ) of PAH concentrations within the river sediments of area 3 exceeded the CERCLA Method B levels of 137 ng/g due to high influxes of carcinogenic PAHs, particularly dibenzo[a,h]anthracene and benzo[a]pyrene. However, based on normalization to 1% TOC the core does not exceed the WDNR threshold effect concentration (TEC) for PAHs. To prevent concentrations from exceeding the TEC, continual monitoring and further studies may include biomarker fingerprinting, source identification, and toxicological evaluation tools to investigate hydrocarbon concentrations within the Lower Fox River sediments.

Acknowledgments We thank the anonymous reviewers for their comments, which improved the paper greatly.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflicts of interests.

References

- Acquavita A, Falomo J, Predonzani S, Tamberlich F, Bettoso N, Mattassi G (2014) The PAH level, distribution and composition in surface sediments from a Mediterranean lagoon: the Marano and Grado lagoon (northern Adriatic Sea, Italy). *Mar Pollut Bull* 81(1):234–241. <https://doi.org/10.1016/j.marpolbul.2014.01.041>
- Agah H, Mehdinia A, Bastami KD, Rahmanpour S (2017) Polycyclic aromatic hydrocarbon pollution in the surface water and sediments of Chabahar Bay. *Oman Sea Mar Pollut Bull* doi 115(1-2):515–524. <https://doi.org/10.1016/j.marpolbul.2016.12.032>
- Agency for Toxic Substances and Disease Registry (1995) Toxicological Profile for Polycyclic Aromatic Hydrocarbons (PAHs). U.S. Department of Health and Human Services, Public Health Service

- (Web access: <https://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=122&tid=25>)
- Ares J, Eckl PM, Raffelsberger I (2000) Genotoxicity at low level dose of inspirable urban ambient air particulate in a semiarid regime. *Environ Monit Assess* 63(3):389–408
- Bajt O (2014) Aliphatic and polycyclic aromatic hydrocarbons in gulf of trieste sediments (northern adriatic): potential impacts of maritime traffic. *Bull Environ Contam Toxicol* 93(3):299–305. <https://doi.org/10.1007/s00128-014-1321-7>
- Bastami KD, Afkhami M, Ehsanpour M, Kazaali A, Mohammadzadeh M, Haghparast S, Soltani F, Zanjani SA, Ghorghani NF, Pourzare R (2013) Polycyclic aromatic hydrocarbons in the coastal water, surface sediment and mullet *Liza klunzingeri* from northern part of Hormuz strait (Persian Gulf). *Mar Pollut Bull* 76(1-2):411–416. <https://doi.org/10.1016/j.marpolbul.2013.08.018>
- Bastami KD, Afkhami M, Ehsanpour M, Mohammadzadeh M, Haghparast S, Soltani F, Zanjani SA, Ghorghani NF, Pourzare R (2014) Polycyclic aromatic hydrocarbons in the coastal water, surface sediment and mullet *Liza Klunzingeri* from northern part of Hormuz Strait (Persian gulf). *Mar Pollut Bull* 76:411–416
- Chen C, Chen C, Dong C, Kao C (2013) Assessment of toxicity of polycyclic aromatic hydrocarbons in sediments of Kaohsiung Harbor. *Taiwan Sci Total Environ* 463-464:1174–1181. <https://doi.org/10.1016/j.scitotenv.2012.06.101>
- Costa E, Piazza V, Gambardella C, Moresco R, Prato E, Biandolino F, Cassin D, Botter M, Maurizio D, D'Adamo R, Fabbrocini A, Faimali M, Garaventa F (2016) Ecotoxicological effects of sediments from Mar Piccolo, South Italy: toxicity testing with organisms from different trophic levels. *Environ Sci Pollut Res* 23(13):12755–12769. <https://doi.org/10.1007/s11356-015-5471-x>
- Crane J (2014) Source apportionment and distribution of polycyclic aromatic hydrocarbons, risk considerations, and management implications for urban storm water pond sediments in Minnesota. *USA Arch Environ Contam Toxicol* 66:176–200
- Cucak DI, Spasojevic JM, Babic OB, Maletic SP, Simeunovic JB, Roncevic SD, Dalmacija BD, Tamaš I, Radnovic DV (2017) A chemical and microbiological characterization and toxicity assessment of the Pancevo industrial complex wastewater canal sediments, Serbia. *Environ Sci Pollut Res* 24(9):8458–8468. <https://doi.org/10.1007/s11356-017-8513-8>
- Dvorská A, Lammel G, Klánová J (2011) Use of diagnostic ratios for studying source apportionment and reactivity of ambient polycyclic aromatic hydrocarbons over Central Europe. *Atmos Environ* 45(2):420–427. <https://doi.org/10.1016/j.atmosenv.2010.09.063>
- Egubue PM, Iwegbue CMA, Ogala JE, Nwajei GE, Egboh SHO (2014) Distribution of polycyclic aromatic hydrocarbons (PAHs) in sediment cores of selected creeks in delta state. *Nigeria Environ Forensics* 15(2):121–133. <https://doi.org/10.1080/15275922.2014.890147>
- Essien JP, Eduok SI, Olajire AA (2011) Distribution and ecotoxicological significance of polycyclic aromatic hydrocarbons in sediments from Iko River estuary mangrove ecosystem. *Environ Monit Assess* 176(1-4):99–107. <https://doi.org/10.1007/s10661-010-1569-2>
- Garcia MR, Mirlean N, Baisch PR, Caramão EB (2010) Assessment of polycyclic aromatic hydrocarbon influx and sediment contamination in an urbanized estuary. *Environ Monit Assess* 168(1-4):269–276. <https://doi.org/10.1007/s10661-009-1110-7>
- Gonçalves C, Teixeira C, Basto MCP, Almeida CMR (2016) PAHs levels in Portuguese estuaries and lagoons: salt marsh plants as potential agents for the containment of PAHs contamination in sediments. *Reg Stud Mar Sci* 7:211–221. <https://doi.org/10.1016/j.rsma.2016.05.004>
- Hamilton S, Cline J (1981) Hydrocarbons Associated with Suspended Matter in the Green River, Washington. NOAA Technical Memorandum ERL PMEL-30, Boulder, Colorado: U.S. Dept. of Commerce, National Oceanic and Atmospheric Administration, Environmental Research Laboratories
- Herbstman JB, Tang D, Zhu D, Qu L, Sjödin A, Li Z, Camann D, Perera FP (2012) Prenatal exposure to polycyclic aromatic hydrocarbons, benzo[a]pyrene-DNA adducts, and genomic DNA methylation in cord blood. *Environ Health Perspect*
- Hu N, Huang P, Liu J, Ma D, Shi X, Mao J, Liu Y (2014) Characterization and source apportionment of polycyclic aromatic hydrocarbons (PAHs) in sediments in the Yellow River Estuary, China. *Environ Earth Sci* 71(2):873–883. <https://doi.org/10.1007/s12665-013-2490-0>
- Huang X, Chen S, Zeng Z, Pu X, Hou Q (2017a) Characteristics of hydrocarbons in sediment core samples from the northern Okinawa trough. *Mar Pollut Bull* 115(1-2):507–514. <https://doi.org/10.1016/j.marpolbul.2016.12.034>
- Huang Y, Liu M, Wang R, Khan SK, Gao D, Zhang Y (2017b) Characterization and source apportionment of PAHs from a highly urbanized river sediments based on land use analysis. *Chemosphere* 184:1334–1345. <https://doi.org/10.1016/j.chemosphere.2017.06.117>
- Jaward FM, Alegria HA, Reyes JGG, Hoare A (2012) Levels of PAHs in the waters, sediments, and shrimps of estero de Urias, an estuary in Mexico, and their toxicological effects. *Sci World J* 2012:1–9. <https://doi.org/10.1100/2012/687034>
- Joyce AS, Portis LM, Parks AN, Burgess RM (2016) Evaluating the relationship between equilibrium passive sampler uptake and aquatic organism bioaccumulation. *Environ Sci Technol* 50(21):11437–11451. <https://doi.org/10.1021/acs.est.6b03273>
- Kanzari F, Asia L, Syakti AD, Piram A, Malleret L, Mille G, Doumenq P (2015) Distribution and risk assessment of hydrocarbons (aliphatic and PAHs), polychlorinated biphenyls (PCBs), and pesticides in surface sediments from an agricultural river (durance) and an industrialized urban lagoon (Berre lagoon), France. *Environ Monit Assess* 187(9):591. <https://doi.org/10.1007/s10661-015-4823-9>
- Kanzari F, Syakti AD, Asia L, Malleret L, Piram A, Mille G, Doumenq P (2014) Distributions and sources of persistent organic pollutants (aliphatic hydrocarbons, PAHs, PCBs and pesticides) in surface sediments of an industrialized urban river (Huveaune), France. *Sci Total Environ* 478:141–151. <https://doi.org/10.1016/j.scitotenv.2014.01.065>
- Katsoyiannis A, Breivik K (2014) Model-based evaluation of the use of polycyclic aromatic hydrocarbons molecular diagnostic ratios as a source identification tool. *Environ Pollut* 184:488–494. <https://doi.org/10.1016/j.envpol.2013.09.028>
- Kim S, Sohn JH, Ha SY, Kang H, Yim UH, Shim WJ, Khim JS, Jung D, Choi K (2016) Thyroid hormone disruption by water-accommodated fractions of crude oil and sediments affected by the Hebei Spirit oil spill in zebrafish and GH3 cells. *Environ Sci Technol* 50(11):5972–5980. <https://doi.org/10.1021/acs.est.6b00751>
- Lee J, Kalia V, Perera F, Herbstman J, Li T, Nie J, Qu LR, Yu J, Tang D (2017a) Prenatal airborne polycyclic aromatic hydrocarbon exposure, LINE1 methylation and child development in a Chinese cohort. *Environ Int* 99:315–320. <https://doi.org/10.1016/j.envint.2016.12.009>
- Lee JH, Woo HJ, Jeong KS, Kang JW, Choi JU, Jeong EJ, Park KS, Lee DH (2017b) Spatial distribution of polycyclic aromatic hydrocarbon and polychlorinated biphenyl sources in the Nakdong River estuary. *South Korea J Environ Sci Health Part A Toxic Hazard Subst Environ Eng* doi 52(12):1173–1183. <https://doi.org/10.1080/10934529.2017.1356207>
- Leitão A, Al-Shaikh I, Hassan H, Ben Hamadou R, Bach S (2017) First genotoxicity assessment of marine environment in Qatar using the local pearl oyster *Pinctada Radiata*. *Reg Stud Mar Sci* 11:23–31. <https://doi.org/10.1016/j.rsma.2017.02.001>

- Li C, Huo S, Yu Z, Xi B, Yeager KM, He Z, Ma C, Zhang J, Wu F (2017) National investigation of semi-volatile organic compounds (PAHs, OCPs, and PCBs) in lake sediments of China: occurrence, spatial variation and risk assessment. *Sci Total Environ* 579:325–336. <https://doi.org/10.1016/j.scitotenv.2016.11.097>
- Lichtfouse É, Derenne S, Mariotti A, Largeau C (1994) Possible algal origin of long chain odd n-alkanes in immature sediments as revealed by distributions and carbon isotope ratios. *Org Geochem* 22(6):1023–1027. [https://doi.org/10.1016/0146-6380\(94\)90035-3](https://doi.org/10.1016/0146-6380(94)90035-3)
- Liu JL, Zhang J, Liu F, Zhang LL (2014) Polycyclic aromatic hydrocarbons in surface sediment of typical estuaries and the spatial distribution in Haihe river basin. *Ecotoxicology* 23(4):486–494. <https://doi.org/10.1007/s10646-014-1233-7>
- Liu Y, Beckingham B, Ruegner H, Li Z, Ma L, Schwientek M, Xie H, Zhao J, Grathwohl P (2013) Comparison of sedimentary PAHs in the rivers of ammer (Germany) and liangtan (China): differences between early-and newly-industrialized countries. *Environ Sci Technol* 47(2):701–709. <https://doi.org/10.1021/es3031566>
- Lou S, Lei B, Feng C, Xu J, Peng W, Wang Y (2016) In vitro toxicity assessment of sediment samples from Huangpu River and Suzhou River, Shanghai, China. *Environ Sci Pollut Res* 23(15):15183–15192. <https://doi.org/10.1007/s11356-016-6683-4>
- Ma J, Liu H, Tong L, Wang Y, Liu S, Zhao L, Hou L (2017) Source apportionment of polycyclic aromatic hydrocarbons and n-alkanes in the soil-sediment profile of Jiangnan oil field, China. *Environ Sci Pollut Res* 24(15):13344–13351. <https://doi.org/10.1007/s11356-017-8913-9>
- Masood N, Zakaria MP, Halimoon N, Aris AZ, Magam SM, Kannan N, Mustafa S, Ali MM, Keshavarzifard M, Vaezzadeh V, Alkhadher SAA, Al-Odaini NA (2016) Anthropogenic waste indicators (AWIs), particularly PAHs and LABs, in Malaysian sediments: application of aquatic environment for identifying anthropogenic pollution. *Mar Pollut Bull* 102(1):160–175. <https://doi.org/10.1016/j.marpolbul.2015.11.032>
- Nagy AS, Szabó J, Vass I (2014) Occurrence and distribution of polycyclic aromatic hydrocarbons in surface water and sediments of the Danube River and its tributaries. *Hungary J Environ Sci Health Part A Toxic Hazard Subst Environ Eng* doi 49(10):1134–1141. <https://doi.org/10.1080/10934529.2014.897155>
- Nisbet ICT, LaGoy PK (1992) Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). *Regul Toxicol Pharmacol* 16(3):290–300. [https://doi.org/10.1016/0273-2300\(92\)90009-X](https://doi.org/10.1016/0273-2300(92)90009-X)
- Ololade IA, Adetiba BO, Oloye FF, Ololade OO, Oladoja NA, Obadawo SB, Anifowose MM, Akinnifesi TA, Akerele D, Alabi AB, Adeola AO (2017) Bioavailability of polycyclic aromatic hydrocarbons (PAHs) and environmental risk (ER) assessment: the case of the Ogbese river. *Nigeria Reg Stud Mar Sci* 9:9–16. <https://doi.org/10.1016/j.rsma.2016.11.004>
- Pérez-Fernández B, Viñas L, Franco MT, Bargiela J (2015) PAHs in the Ría de Arousa (NW Spain): a consideration of PAHs sources and abundance. *Mar Pollut Bull* 95(1):155–165. <https://doi.org/10.1016/j.marpolbul.2015.04.028>
- Peters K, and Walters C (2005) Non-biomarker maturity parameters. In: *The Biomarker Guide*. . In: 2nd ed. (ed) . Cambridge University Press, Cambridge, UK, pp 290–300
- Powell TG (1988) Pristane/phytane ratio as environmental indicator. *Nature*
- Rahmanpoor S, Ghafourian H, Hashtroudi SM, Bastami KD (2014) Distribution and sources of polycyclic aromatic hydrocarbons in surface sediments of the Hormuz strait. *Persian Gulf Mar Pollut Bull* 78(1-2):224–229. <https://doi.org/10.1016/j.marpolbul.2013.10.032>
- Ramzi A, Habeeb Rahman K, Gireeshkumar TR, Balachandran KK, Jacob C, Chandramohanakumar N (2017) Dynamics of polycyclic aromatic hydrocarbons (PAHs) in surface sediments of cochin estuary. *India Mar Pollut Bull* 114(2):1081–1087. <https://doi.org/10.1016/j.marpolbul.2016.10.015>
- Ranjbar Jafarabadi A, Riyahi Bakhtiari A, Aliabadian M, Shadmehri Toosi A (2017a) Spatial distribution and composition of aliphatic hydrocarbons, polycyclic aromatic hydrocarbons and hopanes in superficial sediments of the coral reefs of the Persian Gulf. *Iran Environ Pollut* 224:195–223. <https://doi.org/10.1016/j.envpol.2017.01.080>
- Ranjbar Jafarabadi A, Riyahi Bakhtiari A, Shadmehri Toosi A (2017b) Comprehensive and comparative ecotoxicological and human risk assessment of polycyclic aromatic hydrocarbons (PAHs) in reef surface sediments and coastal seawaters of Iranian Coral Islands. *Persian Gulf Ecotoxicol Environ Saf* 145:640–652. <https://doi.org/10.1016/j.ecoenv.2017.08.016>
- Readman J, Fillman G, Tolosa I, Bartocci J, Villeneuve J, Catinni C, Mee L (2002) Petroleum and PAH contamination in the Black Sea. *Mar Pollut Bull* 44:48–62
- Reeves WR, Barhoumi R, Burghardt RC, Lemke SL, Matura K, McDonald TJ, Phillips TD, Donnelly KC (2001) Evaluation of methods for predicting the toxicity of polycyclic aromatic hydrocarbon mixtures. *Environ Sci Technol* 35(8):1630–1636. <https://doi.org/10.1021/es001689a>
- Rimayi C, Chimuka L, Odusanya D, de Boer J, Weiss JM (2017) Source characterisation and distribution of selected PCBs, PAHs and alkyl PAHs in sediments from the Klip and Jukskei rivers, South Africa. *Environ Monit Assess* 189(7):327. <https://doi.org/10.1007/s10661-017-6043-y>
- Rocha MJ, Dores-Sousa JL, Cruzeiro C, Rocha E (2017) PAHs in water and surface sediments from Douro River estuary and Porto Atlantic coast (Portugal)—impacts on human health. *Environ Monit Assess* 189(8):425. <https://doi.org/10.1007/s10661-017-6137-6>
- Romero-Oliva CS, Contardo-Jara V, Pflugmacher S (2015) Time dependent uptake, bioaccumulation and biotransformation of cell free crude extract microcystins from Lake Amatitlán, Guatemala by *Ceratophyllum demersum*. *Egeria densa* and *Hydrilla verticillata* *Toxicol* 105:62–73. <https://doi.org/10.1016/j.toxicol.2015.08.017>
- Sanil Kumar KS, Nair SM, Salas PM, Prashob Peter KJ, Ratheesh Kumar CS (2016) Aliphatic and polycyclic aromatic hydrocarbon contamination in surface sediment of the Chitrapuzha River. *South West India Chem Ecol* 32(2):117–135. <https://doi.org/10.1080/02757540.2015.1125890>
- Shirmeshan G, Bakhtiari AR, Memariani M (2017) Identifying the source of petroleum pollution in sediment cores of southwest of the Caspian Sea using chemical fingerprinting of aliphatic and alicyclic hydrocarbons. *Mar Pollut Bull* 115(1-2):383–390. <https://doi.org/10.1016/j.marpolbul.2016.12.022>
- Short J, Kvenvolden K, Carlson P, Hostettler F, Rosenbauer R, Wright B (1998) Natural hydrocarbon background in benthic sediments of Prince William sound, Alaska: oil vs coal. *Environ Sci Technol* 33:34–42
- Silva TR, Lopes SRP, Spörl G, Knoppers BA, Azevedo DA (2013) Evaluation of anthropogenic inputs of hydrocarbons in sediment cores from a tropical Brazilian estuarine system. *Microchem J* 109:178–188. <https://doi.org/10.1016/j.microc.2012.02.012>
- Stout SA, Wang Z (2016) Chemical fingerprinting methods and factors affecting petroleum fingerprints in the environment. In: *Standard handbook oil spill environmental forensics: fingerprinting and source identification: second edition*, pp 61–129. <https://doi.org/10.1016/B978-0-12-803832-1.00003-9>
- Stout SA, Emsbo-Mattingly SD, Douglas GS, Uhler AD, McCarthy KJ (2015) Beyond 16 priority pollutant PAHs: a review of PACs used in environmental forensic chemistry. *Polycycl Aromat Compd* 35(2-4):285–315. <https://doi.org/10.1080/10406638.2014.891144>
- Su M, Christensen ER, Karls JF, Kosuru S, Imamoglu I (2000) Apportionment of polycyclic aromatic hydrocarbon sources in

- lower Fox River, USA, sediments by a chemical mass balance model. *Environ Toxicol Chem*
- Ten Haven HL, Rullkötter J, De Leeuw JW, Damsté JSS (1988) Pristane/phytane ratio as environmental indicator. *Nature*
- Uhler AD, Emsbo-Mattingly S, Liu B, Hall LW Jr, Burton DT (2005) An integrated case study for evaluating the impacts of an oil refinery effluent on aquatic biota in the Delaware River: advanced chemical fingerprinting of PAHs. *Hum Ecol Risk Assess* 11(4):771–836. <https://doi.org/10.1080/10807030591008945>
- USEPA (U.S. Environmental Protection Agency) (2003a). Implementation. In *Procedures for the derivation of equilibrium partitioning sediment benchmarks (ESBs) for the protection of benthic organisms: PAH mixtures*. By David J. Hansen et al. EPA-600-R-02-013, Washington D.C.: Office of Research and Development, National Health and Environmental Effects Research Laboratory, Atlantic Ecology Division
- USEPA (U.S. Environmental Protection Agency) (2003b) Recommended toxicity equivalence factors (TEFs) for human health risk assessments of 2,3,7,8-Tetrachlorodibenzo-p-dioxin and dioxin-like compounds. In: EPA-600-R-10-005. Risk Assessment Forum, Washington D.C.
- USEPA (U.S. Environmental Protection Agency) (2013) implementation. In *Procedures for the derivation of equilibrium partitioning sediment benchmarks (ESBs) for the protection of benthic organisms: PAH mixtures*. By David J. Hansen et al. EPA-600-R-02-013, Washington D.C.: Office of Research and Development, National Health and environmental effects research laboratory, Atlantic Ecology Division
- Wagener A, Hamacher C, Farias C, Godoy J, Scofield A (2010) Evaluation of tools to identify hydrocarbon sources in recent and historical sediments of a Tropical Bay. *Mar Chem* 121:67–79
- Wang Z, Yang C, Fingas M, Hollebone B, Yim U, Oh J (2007) Petroleum biomarker fingerprinting for oil spill characterization and source identification. *Oil spill environmental forensics: fingerprinting and source identification*, 73–146. Elsevier/Academic Press, Amsterdam
- Wickliffe J, Overton E, Frickel S, Howard J, Wilson M, Simon B, Echsner S, Nguyen D, Gauthier D, Blake D, Miller C, Elferink C, Ansari S, Fernando H, Trapido E, Kane A (2014) Evaluation of polycyclic aromatic hydrocarbons using analytical methods, toxicology, and risk assessment research: seafood safety after a petroleum spill as an example. *Environ Health Perspect* 122(1):6–9. <https://doi.org/10.1289/ehp.1306724>
- Wilhelms A, Telnæs N, Steen A, Augustson J (1998) A quantitative study of aromatic hydrocarbons in a natural maturity shale sequence—the 3-methylphenanthrene/retene ratio, a pragmatic maturity parameter. *Org Geochem* 29(1-3):97–105. [https://doi.org/10.1016/S0146-6380\(98\)00112-0](https://doi.org/10.1016/S0146-6380(98)00112-0)
- Yu W, Liu R, Xu F, Shen Z (2015) Environmental risk assessments and spatial variations of polycyclic aromatic hydrocarbons in surface sediments in Yangtze River estuary. *China Mar Pollut Bull* 100(1):507–515. <https://doi.org/10.1016/j.marpolbul.2015.09.004>
- Yuan Y, Song D, Wu W, Liang S, Wang Y, Ren Z (2016) The impact of anthropogenic activities on marine environment in Jiaozhou Bay, Qingdao, China: A review and a case study *Reg Stud Mar Sci* 8: 287–296. <https://doi.org/10.1016/j.rsma.2016.01.004>
- Yunker M, Macdonald R, Vingarzanc R, Mitchell R, Goyette D, Sylvestre S (2002) PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Org Geochem* 33:489–515
- Yunker MB, Macdonald RW, Ross PS, Johannessen SC, Dangerfield N (2015) Alkane and PAH provenance and potential bioavailability in coastal marine sediments subject to a gradient of anthropogenic sources in British Columbia. *Canada Org Geochem* 89-90:80–116. <https://doi.org/10.1016/j.orggeochem.2015.10.002>
- Yunker MB, Perreault A, Lowe CJ (2012) Source apportionment of elevated PAH concentrations in sediments near deep marine outfalls in Esquimalt and Victoria, BC, Canada: is coal from an 1891 shipwreck the source? *Org Geochem* 46:12–37. <https://doi.org/10.1016/j.orggeochem.2012.01.006>
- Zhang D, Wang J, Ni H, Zeng H (2017a) Spatial-temporal and multimedia variations of polycyclic aromatic hydrocarbons in a highly urbanized river from South China. *Sci Total Environ* 581-582:621–628. <https://doi.org/10.1016/j.scitotenv.2016.12.171>
- Zhang D, Liu J, Jiang X, Cao K, Yin P, Zhang X (2016) Distribution, sources and ecological risk assessment of PAHs in surface sediments from the Luan River estuary. *China Mar Pollut Bull* 102(1):223–229. <https://doi.org/10.1016/j.marpolbul.2015.10.043>
- Zhang J, Liu G, Wang R, Huang H (2017b) Polycyclic aromatic hydrocarbons in the water-SPM-sediment system from the middle reaches of Huai River, China: distribution, partitioning, origin tracing and ecological risk assessment. *Environ Pollut* 230:61–71. <https://doi.org/10.1016/j.envpol.2017.06.012>