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ORIGINAL PAPER

Estimation of bioavailability of polycyclic aromatic hydrocarbons in river sediments

S. Froehner · L. F. Dombroski · K. S. Machado · C. Scapulatempo Fernandes · M. Bessa

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Abstract This study aimed to evaluate the total concentration of polycyclic aromatic hydrocarbons in sediments of Iguassu River in Southern Brazil. Alongside the concentration, the amount of such compounds bioavailable was also evaluated. This is accomplished by comparing its total amount present in sediments and the amount extracted by *n*-butanol. The results showed that the total concentration of polycyclic aromatic hydrocarbons presented in sediment ranged from 4.49 to 58.75 μg/g. The total amount of polycyclic aromatic hydrocarbons extracted by *n*-butanol ranged from 1.22 to 17.07 μg/g. The use of *n*-butanol represents the mimetic conditions that hydrocarbons, derived from oil, could be taken up by organisms. Most of the hydrocarbons extracted by *n*-butanol were those with lower octanol–water partition constant, usually those with three and four rings. Compounds with more than four rings were extracted in lower or insignificant amounts. Even the hydrocarbons with lower molecular weight available may be degraded or eliminated by organisms, when accumulated. Estimating bioavailability of hydrocarbons represents what specific hydrocarbons could be available to be taken up by organisms.

Keywords Accumulation · Estimating bioavailability · Hydrocarbons from oil · Toxicity

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widespread in the environment. Because of their carcinogenic and mutagenic properties (IARC 1991), these compounds have been intensively studied in various compartments of the environment such as soil, sediment and water (Froehner and Martins 2008). Due to their hydrophobic character, these neutral organic compounds tend to be rapidly adsorbed by sediment. Therefore, sediments can be considered as a pollution reservoir (Budzinski et al. 1997). In general, the toxicity of sediments is assessed by the presence of chemical substances in concentration higher than the limit established by toxicological tests (Wania and Mackay 1999; Doong and Lin 2004). Considering the sediment capacity to trap organic compounds, chemical markers can be used to monitor and assess the sediment quality and the presence of pollutants in water. Sediment and soil are the major sinks for organic contaminants such as PAHs as a result of their hydrophobicity (Wania and Mackay 1999). Organic matter, naturally presents in soil and sediments, can sorb organic compounds poorly water soluble (Gobas 1993). In general, most PAHs are considered toxic; however, the fate and toxic effects are largely governed by their bioavailability, which is strongly affected by organic carbon content in sediment and soil (Schwarzenbach et al. 2006). In fact, after accumulation in sediments, a small fraction is bioavailable, while a large fraction is unavailable due to the adsorption by organic matter content in sediment. The strong interaction between PAHs and organic matter in sediments has as a consequence pollutants that are difficult to be completely degraded by microorganisms (Barriuso et al. 2008). The toxic level of pollutants depends on their bioavailability to the organisms. However, to determine the amount available

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S. Froehner (✉)
Department of Environmental Engineering,
Federal University of Parana, Curitiba-PR 81531-980, Brazil
e-mail: froehner@ufpr.br

L. F. Dombroski · K. S. Machado ·
C. Scapulatempo Fernandes · M. Bessa
Department of Hydraulics and Sanitation,
Federal University of Paraná, Curitiba-PR 81531-980, Brazil

for microorganism is not a simple task. Recently, a number of chemical procedures have been developed to mimic the biological process for determination of the bioavailability instead of direct measurement of bioavailability which is not so simple. For example, Doick et al. (2005) suggested that a cyclodextrin can extract a good fraction of phenanthrene available to indigenous microorganisms that are able to transform them to lower toxic compounds. Also, the Tenas extraction was demonstrated by Cornelissen et al. (1998) as a good methodology to determine the availability of sediment-sorbed organic contaminants. Also, poly(dimethylsiloxane) coated glass fibers were applied to measure the freely dissolved PAHs in soil to assess the bioavailability of PAHs. Some chemical reagents were used for this purpose, *n*-butanol and cyclodextrine for example (Yang et al. 2010). Nam et al. (1998) observed changes in *n*-butanol extractabilities and microbiologic mineralization of phenanthrene during 200 days aging period.

The potential of applying *n*-butanol extraction to mimic bioavailable fractions of organic pollutants has also been validated. Research into the bioavailability of pollutants in soil is rapidly intensifying and the number of articles concerning the bioavailability of PAHs in soil is increasing each and every year (Bergknut et al. 2007). However, the concept of bioavailability lacks a formal definition and there is little agreement on what bioavailability means, how it should be measured, and how it should be calculated. Consequently, it is difficult to compare findings by different authors or proposed techniques for assessing the bioavailability of PAHs in soil or sediments, since different studies are often based on different concepts of bioavailability. The bioavailable fraction of PAHs in sediments is envisaged as the fraction of PAHs in the matrix that can be taken up by organisms. However, it should be noted that uptake rates differ between species and that the timescale considered will affect the amounts of accumulated PAHs. The most widely accepted theory concerning the uptake of chemicals by organisms in the soil and sediments is the equilibrium partitioning theory, that is the freely dissolved PAHs concentrations in soil pore waters and the amount adsorbed in soil or sediments (Cornelissen et al. 2001; Yang et al. 2010).

That is to say, the equilibrium partitioning between the compartments and organisms controls the bioavailability of PAHs, as the pollutants general speaking (Ditoro et al. 1991; Sijm et al. 2000). Some deviations from expected partitioning theory results have been observed, which are usually attributed to sequestration of pollutants in the sediments, the effects of feeding, and biotransformation (Cornelissen et al. 2001; Ditoro et al. 1991). In this paper, *n*-butanol (chemical reagent) was used to extract the PAHs in sediments and assumed as bioavailable. This research has been carried out in the School of Environmental Engineering, Federal University of Parana (Curitiba, Brazil), in July 2010.

Materials and methods

Study area

The selected area for this study was Upper Iguassu watershed and is located within the metropolitan region of Curitiba (Fig. 1). The Upper Iguassu watershed has its sources along the Serra do Mar, whose main river runs for about 90 km until reaching the limits of the metropolitan region of Curitiba, draining an area of around 2,800 km^2 (Froehner et al. 2010), with population of this area is approximately 3 millions in 14 municipalities. The area covered is heavily urbanized and has been submitted to a process of irregular occupation of flood plains and watershed areas, which has led to the clear degradation of rivers in the region. This work presents a collection campaign in urban rivers considered within the basin. Sediments samples were collected in rivers Irai, Barigui and Iguassu, although the Upper Iguassu watershed has 26 major tributaries.

Samples collection

Seven sampling stations were established in Upper Iguassu River (Fig. 1; Table 1). The sediments were collected in July 2010. Surface sediment samples were collected with a Van Veen Grab. Most of the sediments investigated were muddy, with a high amount of organic carbon. In the laboratory, the sediment samples were wrapped in aluminum foil and stored at −21 °C until the final analysis. Before the determination of organic carbon, the samples were decarbonated using 0.5 mol/L HCl solution. Then, the sediments samples were freeze dried to determine the organic carbon content. Aliquots were taken for elemental analysis using a Carlo Erba EA 1110 CHNS-O analyzer after being centrifuged, washed with deionized water, and gently dried at 60 °C.

Chemicals

Solvents used (Dichloromethane, hexane, and acetone) were HPLC grade, purchase from Honeywell Brand. *n*-Butanol was analytical grade (99.4 % pure), purchase from Merck. All chemicals solvents used in this study were HPLC grade, with exception of *n*-butanol which was analytical grade (99.4 % purity). A mixture of stock solution of PAHs was prepared by dilution of a commercial standard (Accustandard) with *n*-hexane. Furthermore, the working standard solution in *n*-hexane was prepared by diluting the stock standard. All glassware was cleaned in an ultrasonic cleaner (UltraCleaner 14000 Unique).

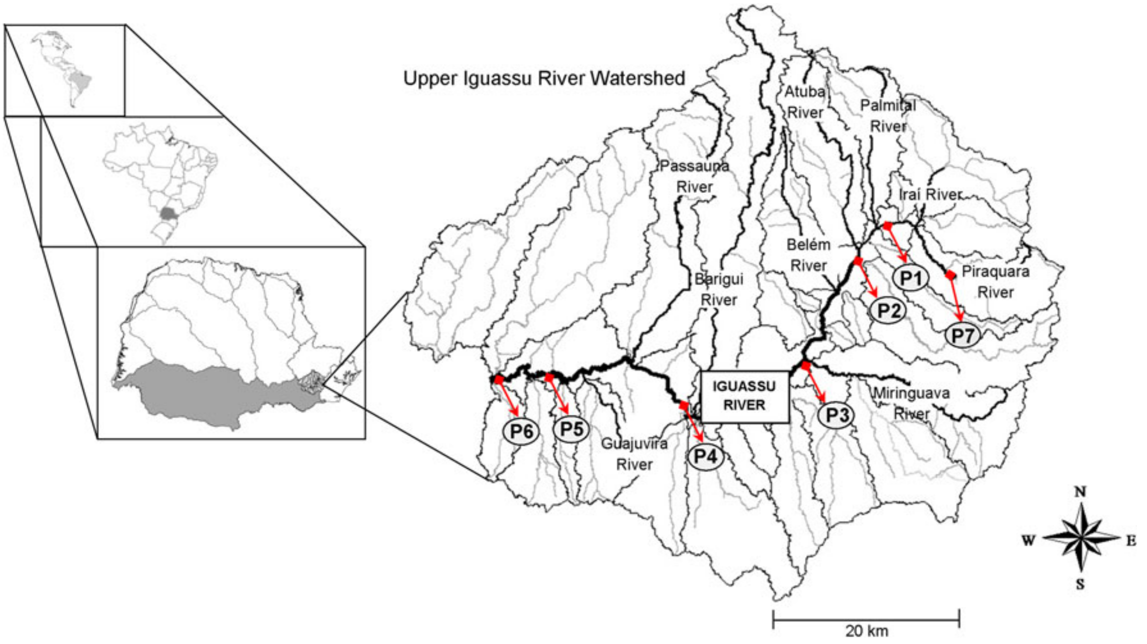

Fig. 1 Map with sampling station in metropolitan region of Curitiba. *P1* Irai river, *P2* Barigui river (Tingui Park), *P3* Iguassu river (North site), *P4* Barigui river (Barigui Park), *P5* Iguassu river (South site), *P6* Barigui river (Caximba), *P7* Piraquara

Table 1 Location of the sites for sediment samples collection in the Iguassu River

Site	Watershed area (km^2)	Latitude	Longitude	Altitude (m)
P1	282.88	25° 26′ 36″	49° 08′ 26″	875
P2	625.53	25° 29′ 00″	49° 11′ 21″	869
P3	1,283.65	25° 35′ 36″	49° 15′ 39″	865
P4	2,122.22	25° 36′ 01″	49° 23′ 52″	860
P5	2,577.76	25° 35′ 01″	49° 30′ 48″	858
P6	3,048.69	25° 35′ 14″	49° 37′ 54″	854
P7	182.00	25° 26′ 27″	49° 07′ 06″	876

Extraction of total PAHs

20 g of dried sample sediments was used for quantifying the 16 PAHs listed as priority by Environmental Protection Agency-USA. The sample extraction procedure was performed according to previously reported methods (Mai et al. 2002; Froehner et al. 2010). PAHs were extracted twice with 50 mL of dichloromethane for 15 min by ultrasonic agitation with frequency of 20 kHz. The extracts were combined and concentrated to 1 mL by rotatory evaporator (Buchi 210 V). As the final step, performed the clean up processes by passing the extract through a silica gel and alumina (silica and alumina were activated at 200 °C for 4 h and then partially deactivated with 5 % Milli-Q water). The extracts were filtered, concentrated, and solvent exchanged to hexane. The clean up and fractionation were performed on an alumina/silica gel chromatography column. The PAHs fraction were successively eluted with 15 mL hexane and 70 mL dichloromethane/hexane (3:7, v:v), respectively. The second fraction was concentrated under a gentle flow of high-purity nitrogen to volume of 200 uL.

Analysis of PAHs was performed on an Agilent 7890 gas chromatograph system equipped with flame ionization detector (FID). The GC-FID conditions were: injection temperature 270 °C; FID detector temperature 300 °C; carrier gas nitrogen with flow rate 1 mL/min. Temperature program: initially 45 °C, increasing at a rate of 13–150 °C/min, then at 5–200 °C/min.

n-Butanol extraction of PAHs

The procedure described by Northcott and Jones (2003) was followed. 20 g of dried sediment was extracted with 100 mL *n*-butanol in a 250 mL glass-flask (100 rpm) for 24 h on a horizontal shaker at room temperature. The samples were centrifuged at 3000 rpm for 20 min. The supernatant contained the PAHs extractable in *n*-butanol, while those in sediments stand for non-extractable fraction. The *n*-butanol phase was concentrated to 1 mL by rotatory evaporator at 80 °C and the solvent was then changed to hexane. The PAHs were finally quantified by GC-FID following the conditions described above (the same for total PAHs).

Organic carbon content analysis

Immediately prior to further analysis, the sediments were dried under vacuum crushed in dry mortar with a porcelain pestle and decarbonated using 0.5 mol/L HCl solution. Aliquots were taken for elemental analysis. Total organic carbon (TOC) were measured using a Carlo Erba EA1110 CHNS-O analyzer after being centrifuged, washed with deionized water and gently dried at 60 °C.

Results and discussion

Distribution of total PAHs in sediments

Table 2 shows the concentration of all PAHs found in sediments samples of Iguassu River. Lower molecular weight (LMW) PAHs dominated the distribution of such compounds. The total concentration of PAHs varied from 4.49 to 58.75 µg/g. The highest concentration was found in site P5. This high concentration could be associated with granulometric composition of sediments (Froehner and Martins 2008). In general, the sediments of Iguassu River presented high percentage of silt and clay, and minimal percentage of sand in their composition (less than 15 %). Exception is made for site P7, in which sand dominated the composition of sediment (63 %); consequently, the organic carbon content was also lower in comparison with other sites. The lower organic carbon content reflects in sediment capacity of organic compounds adsorption. The organic carbon content is shown in Table 2. The higher concentration of total PAHs was found in those sites with more organic carbon content (sites P4, P5 and P6).

Soil and sediments with high organic carbon content present higher capacity to retain PAHs, as well as other organic compounds that are poorly water soluble (Yang et al. 2010). For instance, the polychlorinated biphenyl (PCBs) in top soil revealed a positive correlation between soil PCBs and soil organic matter and a tenfold increase in the organic matter leads to a sixfold increase of total PCBs concentration in soils (Moermond et al. 2007).

The initial studies aimed at analyzing sediments from completely different scenarios regarding the amount of pollution. Sites P1, P2 and P3 are located in a region distant from pollution sources, while others are located in regions near anthropic activities (industrial activities, intense traffic, and oil refinery) (Froehner et al. 2010). Most of the sampled sites are closed to industrial areas and near highways with intense traffic of buses and trucks. The presence of PAHs has been identified as one of the most useful chemical markers for identifying anthropogenic inputs in lakes, rivers, estuarine areas, and oceans. For example, Liu et al. (2009) found PAHs concentration in river sediments from 0.11 to 1.70 µg/g. Fang et al. (2007) observed PAHs in marine sediments ranging from 0.023 to 45.10 µg/g.

The sources are defined by isomer ratios, according to the studies presented by Yunker et al. (1999, 2002) According to their findings, one isomer predominates over its pair due to thermodynamic processes such as pyrolysis or petroleum formation. The widely used analysis of molecular compound ratios has been applied to identify the source and origin of the PAHs. Some typical isomers ratios include: Naphthalene/Fluoranthene, Phenanthrene/Anthracene, Fluoranthene/Pyrene, Chrysene/Benzo(a)Anthracene, Fluoranthene/(Fluoranthene + Pyrene), Anthracene/(Anthracene + Phenanthrene), Pyrene/Benzo(a)Pyrene and Benzo(a)Pyrene/228 (Yunker et al. 2002). Those ratios have been developed for interpreting PAHs compositions and inferring the possible sources (Budzinski et al. 1997). Generally, thermodynamically more stable compounds such as naphthalene, fluorene, phenanthrene, and chrysene are abundant in petrogenic PAHs, while fluoranthene and pyrene are usually the most abundant compounds of pyrolytic PAHs.

PAHs of molecular mass 178 and 202 are commonly used to distinguish between combustion and petroleum sources (Soclo et al. 2000). The ratio of mass 178 (anthracene/anthracene + phenanthrene) ranged from 0.03 to 1.71. Usually ratios <0.10 indicate petroleum while a ratios >0.10 indicate dominance of combustion products (Budzinski et al. 1997). Here the results showed that PAHs come from both sources, pyrogenic and petrogenic. Episodes of leakage of petroleum compounds and also crude oil was reported in this region, justifying the presence of petrogenic compounds.

Ratios of mass 202, fluoranthene/(fluoranthene + pyrene) of 0.50 are usually defined as the petroleum/combustion transition point (Budzinski et al. 1997). According to this ratio only site P1 had PAHs from petrogenic source; for the rest of the sites, the source is predominantly pyrogenic, i.e., burning of gasoline, diesel and oil fuel emitted from cars and diesel trucks. Other commonly used ratio is fluoranthene/pyrene; values higher than 1 imply in pyrolytic origin, while values lower than 1 are attributed to petrogenic sources (Soclo et al. 2000; Budzinski et al. 1997). Except for site P1, in which the ratio value was 2.50, all the other sites presented values lower than 1. Such values imply that the presence of PAHs in sediments has its origin in pyrolytic sources, as the fluoranthene/(fluoranthene + pyrene) ratio pointed out.

Once entered into the environment, PAHs are widely dispersed through atmospheric and aquatic transport and deposited into the river sediments. Yang et al. (1999) analyzed the size distributions of PAHs for road dust and for engine exhausts of cars and found that road dust was the major contribution of dry deposition flux for a total of 21

Table 2 Distribution of total PAHs in sediments of Iguassu River, in ng/g

Compound	P1	P2	P3	P4	P5	P6	P7
Naphthalene	14.36	6.07	5.40	461.40	228.59	21.26	23.51
Acenaphthalene	202.96	360.67	39.92	20.85	47.60	98.40	62.80
Acenaphthene	78.04	3,214.30	2,399.72	259.81	3,663.65	4,430.20	13.72
Fluorene	11.50	143.06	50.19	55.06	60.04	70.36	26.00
Fenantrene	19.22	307.58	36.33	319.30	7,168.88	342.72	187.97
Antracene	27.05	10.00	277.29	59.97	533.60	35.41	24.59
Fluoranthene	60.22	103.77	9.12	376.91	330.03	18.97	16.57
Pyrene	28.66	383.19	342.57	5,208.48	1,565.85	516.36	114.59
Benzo(a)Anthracene	942.15	479.42	710.63	369.67	18,875.20	267.18	1,495.96
Crysene	13.01	25.59	18.32	85.16	35.18	31.43	4.66
Benzo(b)Fluoranthene	1,800.66	1,555.41	1,433.51	742.31	2,368.98	371.38	183.57
Benzo(k)Fluoranthene	120.81	314.86	134.45	573.93	336.45	434.81	48.57
Benzo(a)Pyrene	1,701.54	8.15	1,711.47	3,561.31	4,102.46	1,100.05	112.38
Indene	2,856.12	2,233.71	4,097.62	1,177.12	1,959.68	3,873.99	1,853.05
Dibenzo(a,h)anthracene	4,673.98	2,764.79	3,622.03	19,811.61	17,327.00	4,081.02	328.42
Benzo(ghi)Perilene	43.43	1.06	18.77	431.54	152.13	62.01	1.83
Total	12,593.73	11,911.62	14,907.34	33,514.42	58,755.32	15,755.56	4,498.19
TOC (% w/w)	2.30	2.47	2.74	4.71	4.65	2.55	1.73

SD <3.5 %

PAHs and all individual PAHs. These results show that the road dust associated with leaked gasoline or other compound derived from petroleum might contribute to LMW PAHs in the aquatic environment of Iguassu River (Yunker et al. 1999, 2002). Higher weight PAHs are usually found in a smaller percentage in refined petroleum products (Wang et al. 1998) and generally are present in significant amounts only in higher fractions such as asphalt, and possibly in bitumen or coal.

Distribution of PAH extracted by *n*-butanol

The presence of PAHs in sediments does not mean toxicity to ecosystems. The most acceptable theory concerning the uptake of chemicals by organisms in the soil is the equilibrium partitioning, i.e., the bioavailability of organic compounds is controlled by equilibrium partitioning between the sediment or soil, water and the organisms (Shea 1998; Bergknut et al. 2007). The toxicity is represented by the extractable fraction (Yang et al. 2010), in this study, by *n*-butanol extraction. Also, when assessing bioavailability it is important to bear in mind that the process is governed by three-way interactions between the pollutant, the matrix and the organism in the matrix (Madsen 2003). The reason to employ *n*-butanol for the extraction is that the reagent mimics the bioavailability of genotoxic organic compounds in soils to *P. putida* (Alexander and Alexander 2000). *n*-Butanol can extract PAHs from soil and sediments and the amount extractable depends on the organic carbon content whichever the affinities of PAHs to different fractions of organic matter (Pan et al. 2007).

Table 3 showed the total concentration of PAHs extracted by *n*-butanol. It is clear that most of LMW PAHs were extracted, while high molecular weight (HMW) PAHs were extracted in lower proportions. Naphthalene, acenaphthalene, acenaphthene and fluorene were the most common compounds in extraction. When organic compounds reach the soil or sediments, the most common consequence is the adsorption of those compartments. The interaction between PAHs and organic matter in such compartments is extremely important, e.g., the octanol–water partition constant (Kow) of individual PAHs. Generally, the transfer of PAHs between the compartments occurs rapidly (air, water, soil and sediment) (Froehner and Martins 2008). Due to the chemical characteristics of the sediments (organic carbon content), most part of PAHs are trapped by organic matter present in sediments. In this study, the adsorbed fraction of PAHs accounted for 37.2–84.3 %. Similar results were found by Yang et al. (2010), but by means of laboratory experiments. Bergknut et al. (2007) used different solvents to extract PAHs, the percentage of extraction using *n*-butanol was 14 %, but the studies were conducted in purposely contaminated soil and laboratory experiments. The extraction efficiency is related with the non-polar conditions of the solvent. Here, it was used pure *n*-butanol, thus, the amount extracted was high,

Table 3 Distribution of extracted PAHs by *n*-butanol from sediments, in ng/g

Compound	P1	P2	P3	P4	P5	P6	P7
Naphthalene	9.79	ND	ND	455.00	220.05	15.84	19.98
Acenaphthalene	176.75	334.06	32.61	2.26	16.01	72.01	39.66
Acenaphthene	36.82	3,190.60	2,366.97	11.37	3,589.10	4,413.23	ND
Fluorene	9.87	133.64	38.91	10.67	35.36	64.71	25.05
Fenantrene	ND	278.73	ND	ND	7091.63	317.27	185.35
Antracene	20.24	ND	267.14	25.28	526.62	28.72	21.77
Fluoranthene	40.37	103.73	9.12	0.07	329.39	15.43	14.52
Pyrene	ND	327.15	269.66	2,013.58	964.90	480.11	89.47
Benzo(a)Anthracene	ND	ND	ND	ND	1,339.97	ND	ND
Crysene	3.01	23.33	13.24	56.05	18.05	17.83	4.66
Benzo(b)Fluoranthene	ND	1,034.19	978.09	ND	1,399.17	147.55	ND
Benzo(k)Fluoranthene	ND	135.35	ND	98.20	ND	382.97	ND
Benzo(a)Pyrene	ND	ND	ND	69.51	ND	157.17	ND
Indene	598.31	1,191.90	814.48	ND	ND	1,192.48	827.03
Dibenzo(a,h)anthracene	1,061.50	725.39	170.67	2,214.19	1,536.64	78.62	ND
Benzo(ghi)Perilene	19.10	ND	ND	ND	ND	ND	ND
Total	1,975.74	7,498.08	4,960.90	4,956.17	17,066.88	7,383.95	1,227.48

SD <3.5 %

15 % for P1 (the lowest percentage) to 62 % (the highest percentage).

For instance, 1 % of *n*-butanol in water extracts only 0.16 % of total PAHs (Bergknut et al. 2007). The adsorption of organic compounds is not only dependent on organic carbon but also by longer contact times (Doick et al. 2005). The higher amount of LMW PAHs extracted by *n*-butanol shows the weak interaction of these compounds with organic matter in sediments. The highest extractable concentrations of LMW PAHs were observed in those sites with low organic carbon content. For example, in sites P4 and P5, the amount of PAHs extractable by *n*-butanol was only 14.8 and 29.0 %. It seems that the *n*-butanol extracted PAHs that had weak association with organic matter. Humic and fulvic substances contained in organic matter are referred to more or less bioavailable compartment. The *n*-butanol extracted fraction was already demonstrated to be more relevant to bioavailability of PAHs to microorganisms (Nam et al. 1998). Furthermore, the Kow is extremely important to define the final situation of organic compounds in the environment. PAHs with log Kow higher than 6 are probably adsorbed in sediments, while compounds with log Kow lower than 6 (between 4 and 6) can accumulate in organisms (Wania and Mackay 1999; Gobas 1993). Considering the log Kow, PAHs with low values were extracted in higher amounts in comparison with those with higher log Kow values. The main concern with the presence of PAHs in soil and sediments is due to the toxic power of such compounds, especially those with more than four rings. According to the literature, PAHs with lower log Kow are degraded by microorganisms or eliminated in feces (Alexander and Alexander 2000; Wania and Mackay 1999). However, the behavior of such compounds in soil or sediments is completely different in organisms. For instance, in experiments with earthworms, PAHs with lower log Kow were rapidly eliminated, while those with higher log Kow were accumulated and then degraded. Thus, the uptake rates also control the degradation and accumulation. Therefore, the uptake is very important in such processes. However, the uptake is dependent on the bioavailability of compounds. Here, the results showed that most of PAHs were not available for further uptake by microorganisms. In a general fashion, only low molecular weight PAHs were available. Such compounds are considered, according to USEPA, as less toxic. The sediments studied showed an equal distribution of PAHs. The carcinogenic/non-carcinogenic ratio is almost 1. Nonetheless, this ratio is lower than 1 when the distribution of PAHs is analyzed for PAHs extracted by *n*-butanol. Even the sediments that contain a significant amount of PAHs not at all poly aromatic compounds are available for uptake by organisms.

Conclusion

Polycyclic aromatic hydrocarbons were analyzed in sediments from Iguassu River in Southern Brazil. The results showed that PAHs were present and the total concentration ranged from 4.50 to 58.75 µg/g. Sites with higher organic carbon content presented the highest concentration. To perform the evaluation of the bioavailable amount of PAHs, the sediments were treated with *n*-butanol. PAHs with lower molecular weight were extracted in higher amounts than PAHs with high molecular weight. It seems that adsorption process is essential in trapping organic compounds such PAHs with higher molecular weights. LMW PAHs are readily degraded, while HMW PAHs were not due to stronger association with organic matter. Finally, even sediments showed the presence of PAHs, but only those considered as less toxic and less carcinogenic are available for uptake by organisms.

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