



Review

A review on polycyclic aromatic hydrocarbons distribution in freshwater ecosystems and their toxicity to benthic fauna



Fátima Jesus ^{a,*}, Joana L. Pereira ^b, Isabel Campos ^a, Martha Santos ^a, Ana Ré ^b, Jacob Keizer ^a, António Nogueira ^b, Fernando J.M. Gonçalves ^b, Nelson Abrantes ^a, Dalila Serpa ^a

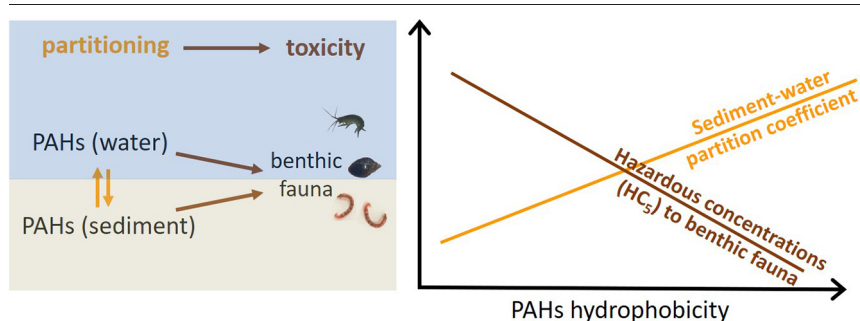
^a CESAM - Centre for Environmental and Marine Studies, Department of Environment and Planning, University of Aveiro, 3810-193 Aveiro, Portugal

^b CESAM - Centre for Environmental and Marine Studies, Department of Biology, University of Aveiro, 3810-193 Aveiro, Portugal

HIGHLIGHTS

- PAHs concentrations were 2–4 orders of magnitude higher in sediments than in water.
- PAHs sediment-water partitioning coefficients increased along with hydrophobicity.
- Hazardous concentrations decreased with increasing hydrophobicity.
- HC₅ values for benthic communities were ranked as NAP > PHE > PYR > FLT > ANT.
- These findings are pertinent for ecological risk assessment of PAHs.

GRAPHICAL ABSTRACT



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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds, found ubiquitously in all environmental compartments. PAHs are considered hazardous pollutants, being of concern to both the environmental and human health. In the aquatic environment, PAHs tend to accumulate in the sediment due to their high hydrophobicity, and thus sediments can be considered their ultimate sink. Concurrently, sediments comprise important habitats for benthic species. This raises concern over the toxic effects of PAHs to benthic communities. Despite PAHs have been the subject of several reviews, their toxicity to freshwater benthic species has not been comprehensively discussed. This review aimed to provide an overview on PAHs distribution in freshwater environments and on their toxicity to benthic fauna species. The distribution of PAHs between sediments and the overlying water column, given by the sediment-water partition coefficient, revealed that PAHs concentrations were 2 to 4 orders of magnitude higher in sediments than in water. The sediment-water partition coefficient was positively correlated to PAHs hydrophobicity. Toxicity of PAHs to benthic fauna was addressed through Species Sensitivity Distributions. The derived hazardous concentration for 5% of the species (HC₅) decreased as follows: NAP (376 $\mu\text{g L}^{-1}$) > PHE > PYR > FLT > ANT (0.854 $\mu\text{g L}^{-1}$), varying by 3 orders of magnitude. The hazardous concentrations (HC₅) to benthic species were inversely correlated to the hydrophobicity of the individual PAHs. These findings are pertinent for environmental risk assessment of these compounds. This review also identified future challenges regarding the environmental toxicity of PAHs to

Abbreviations: ACE, acenaphthene; ACY, acenaphthylene; ANT, anthracene; BaA, benzo(a)anthracene; BaP, benzo(a)pyrene; BbF, benzo[b]fluoranthene; BghiP, benzo[g,h,i]perylene; BkF, benzo[k]fluoranthene; CHR, chrysene; DahA, dibenzo[a,h]anthracene; dw, dry weight; EC₅₀, median effective concentration; FLT, fluoranthene; FLU, fluorene; HC₅, hazardous concentration, 5th percentile; HC₅₀, hazardous concentration, 50th percentile; HMW, high molecular weight; IcdP, indeno[1,2,3-c,d]pyrene; K_{oc}, organic carbon–water partition coefficient; K_{ow}, octanol–water partition coefficient; K_{sw}, sediment–water partition coefficient; LC₅₀, median lethal concentration; LMW, low molecular weight; NAP, naphthalene; OC, organic carbon; PHE, phenanthrene; PAH, polycyclic aromatic hydrocarbon; PYR, pyrene; SSD, species sensitivity distribution; TOC, total organic carbon; USEPA, United States Environmental Protection Agency.

* Corresponding author.

E-mail address: fatima.jesus@ua.pt (F. Jesus).

freshwater benthic communities, namely the need for updating the PAHs priority list and the importance of comprehensively and more realistically assess the toxicity of PAHs in combination with other stressors, both chemical and climate-related.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds that are ubiquitous hazardous contaminants, being found in air, soil, sediments, water and biota, commonly as mixtures. These compounds consist of only carbon and hydrogen atoms arranged in the form of two or more benzene rings bonded in linear, angular or cluster arrangements. PAHs include both unsubstituted parent PAHs (e.g. naphthalene) and their alkyl-substituted derivatives, also designated alkylated PAHs (e.g. 1,8-dimethylnaphthalene). In general, PAHs are characterized by low vapor pressure and very low aqueous solubility (Sverdrup et al., 2002).

PAHs raise widespread concerns about their deleterious effects on the environment and human health (Sun et al., 2021) due to several factors. First, they are continuously released to the environment as they are used and produced during daily routines in modern society (e.g. by using fossil fuels), which may ultimately lead to an increased environmental burden over time (Lima et al., 2005). Second, they exhibit very high persistence in the environment, which is related to their chemically stable structure and high resistance to biodegradation (Haritash and Kaushik, 2009). Third, their biological impacts comprise genotoxicity, carcinogenicity and teratogenicity (Baird et al., 2005; Sun et al., 2021).

In the 1970s the US Environmental Protection Agency (USEPA) listed 16 unsubstituted PAHs as priority pollutants, due to their adverse impacts on environment and human health and the existence of analytical methods (Andersson and Achten, 2015; Keith, 2015). In 2005, also the European Community (EC) created a list of 15 + 1 priority PAHs, especially in response to food-contamination problems, which included 8 of the PAHs on the USEPA list (Wenzl et al., 2006). Since the USEPA's priority list is more widely used to study the environmental effects of PAHs than the EC's list, the former list was selected as the focus of the present review. The main physicochemical properties of USEPA's 16 priority PAHs are presented in Table 1.

PAHs are classified according to their molecular structure and weight in two classes (Du and Jing, 2018; Yang et al., 2019; Liu et al., 2021): low molecular weight (LMW) and high molecular weight (HMW), as shown in Table 1. LMW PAHs have two to three benzene rings, whereas HMW PAHs contain four or more benzene rings.

PAHs can also be classified according to processes that lead to their formation. Pyrogenic PAHs are formed by pyrolysis, a process that occurs when organic materials are exposed to high temperatures under low or no oxygen conditions (Abdel-Shafy and Mansour, 2016). The most important sources of pyrogenic PAHs include industrial processes, combustion of wood and fossil fuels, wildfires and volcanic activity (Du and Jing, 2018; Abdel-Shafy and Mansour, 2016). Pyrogenic PAHs are the most prominent and ubiquitous PAHs in the environment, in particular in freshwater systems (Du and Jing, 2018; Y. Li et al., 2019).

Petrogenic PAHs are produced spontaneously during crude oil maturation being typically released into the environment as crude oil and petroleum products during off-shore exploitation of petroleum hydrocarbons as well as during the transport, storage and use of crude oil and respective sub-products (Abdel-Shafy and Mansour, 2016).

















Diagenetic PAHs are formed spontaneously during the decomposition of organic matter and derive from biogenic precursors such as plant terpenes, a process that commonly occurs in sedimentary environments (Wakeham et al., 1980; Brändli et al., 2007; Ravindra et al., 2008).

Some authors (e.g. Dhar et al., 2020; Honda and Suzuki, 2020) have identified a fourth type of PAHs, biogenic PAHs, that are synthesized exclusively by microorganisms (bacteria, fungi), plants and phytoplankton, without the involvement of diagenetic processes (USEPA, 2003).

PAHs can be transferred among environmental compartments (Fig. 1). They reach aquatic ecosystems mainly through dry and wet atmospheric deposition as well as through transport by water, in particular as discharges from sewage systems, industrial and urban effluents, and runoff from agricultural lands and burnt areas (Gevao et al., 2000; Guo et al., 2009; Campos et al., 2012; Sharma et al., 2018; Carvalho et al., 2019; Huang et al., 2019; R. Li et al., 2019). Once reaching the aquatic environment, PAHs may remain in the water (either in the free dissolved phase or bounded to dissolved organic matter) or adsorb to the suspended particulate matter or to the sediment (Akkanen et al., 2012; Qin et al., 2014a,b). PAHs exchange between the water and the sediment plays a key role in their environmental fate and potential effects to the aquatic biota. This distribution, given by the sediment-water partition coefficient (Yang et al., 2019), is highly dynamic and depends on several factors (cf. Section 3.1). PAHs bound to the

Table 1

Main physicochemical properties of the 16 priority PAHs. Data obtained from ATSDR (1995), except CAS number and molecular structure obtained from www.sigmaaldrich.com.

	PAHs	Abbreviation	CAS number	Molecular structure	n. of rings	Molecular weight (g mol ⁻¹)	Solubility at 25 °C (mg L ⁻¹)	Log K _{ow}	Log K _{oc}	Vapor pressure (Pa)
LMW	Naphthalene	NAP	91-20-3		2	128.12	31	3.37	3.11	–
	Acenaphthylene	ACY	208-96-8		3	152.20	16.1	4	3.64	3.87
	Acenaphthene	ACE	83-32-9		3	154.21	3.8	3.92	4.02	5.96 × 10 ⁻¹
	Fluorene	FLU	86-73-7		3	166.2	1.9	4.18	4.35	4.27 × 10 ⁻²
	Phenanthrene	PHE	85-01-8		3	178.2	1.1	4.57	4.31	9.07 × 10 ⁻²
	Anthracene	ANT	120-12-7		3	178.2	0.045	4.54	4.39	2.27 × 10 ⁻³
HMW	Fluoranthene	FLT	206-44-0		4	202.26	0.26	5.22	5.04	6.67 × 10 ⁻⁴
	Pyrene	PYR	129-00-0		4	202.3	0.132	5.18	4.86	3.33 × 10 ⁻⁴
	Benzo[<i>a</i>]anthracene	BaA	56-55-3		4	228.29	0.011	5.91	5.33	2.93 × 10 ⁻⁶
	Chrysene	CHR	218-01-9		4	228.3	0.0019	5.86	5.14	8.40 × 10 ⁻⁵
	Benzo[<i>b</i>]fluoranthene	BbF	205-99-2		5	252.3	0.0015	5.8	5.72	0.0012
	Benzo[<i>k</i>]fluoranthene	BkF	207-08-9		5	252.3	0.0008	6	5.73	7.6 × 10 ⁻⁴
	Benzo[<i>a</i>]pyrene	BaP	50-32-8		5	252.3	0.0038	6.04	6.24	2.3 × 10 ⁻³
	Benzo[<i>g,h,i</i>]perylene	BghiP	191-24-2		6	276.3	0.00026	6.5	6.23	2.6 × 10 ⁻⁴
	Indeno[1,2,3- <i>c,d</i>]pyrene	IcdP	193-39-5		6	276.3	0.00019	6.7	6.20	0.062
	Dibenzo[<i>a,h</i>]anthracene	DahA	53-70-3		5	278.35	0.0006	6.75	5.96	5.0 × 10 ⁻⁴

sediments can be transferred to the water column by resuspension, which is more likely to occur for lower molecular weight PAHs (Yang et al., 2008; Dong et al., 2016). Resuspension is a ubiquitous natural process that occurs

when the shear stress in the bottom disrupts the cohesion of the sediments, either due to the water flow or bioturbation. The effects of resuspension depend mainly on the composition of the sediments (e.g. type of sediment,

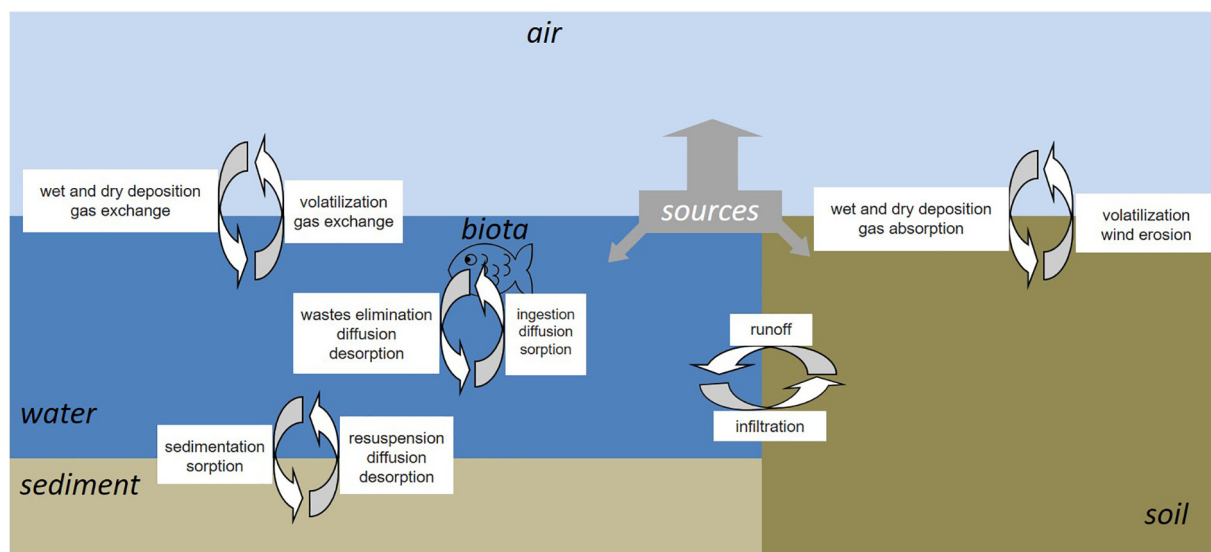


Fig. 1. Main pathways of PAHs transport in the environment.

granulometry, organic content), being also affected by the shear stress and duration of the event (Yang et al., 2008), as well as by the frequency of resuspension (Dong et al., 2016). Bioturbation can also play an important role in PAHs resuspension, except under anoxic conditions owing to the absence of animal species (Gevaio et al., 2000). Increasing resuspension translates into an increased risk for organisms, especially those living in the sediment-water interface (Dong et al., 2016).

Within the sediment, PAHs can be found in the porewater or adsorbed to sediment particles. Polycyclic aromatic hydrocarbons concentrations in the sediment porewater tend to be higher than those observed in overlying water (Zhang et al., 2011), which implies a potential flux of PAHs from porewater to overlying water (Lei et al., 2016).

In the aquatic ecosystems, PAHs are subject to transformation and degradation by photo-oxidation processes. This is especially the case for PAHs in top layers of the water column as photo oxidation is promoted by higher light intensity, higher temperature and greater oxygen availability (Fasnacht and Blough, 2003; Xiao and Shao, 2017). As a consequence of the reduced photo-oxidation in the sediments coupled with high hydrophobicity and low solubility, PAH concentrations are higher in sediments than in the water column, which underpins that sediments act as a sink of PAHs (Li et al., 2010; Kim et al., 2016; Huang et al., 2019; Maletić et al., 2019; Yang et al., 2019). As such, PAHs are likely to represent a high risk to benthic species.

Benthic communities include a panoply of organisms that live in close association to the sediment, ranging from microorganisms to plants and animals and covering a wide range of trophic levels. This review, however, is limited to benthic animal species given the reduced information available for other freshwater benthic groups. Benthic fauna species are broadly divided in two groups, i.e. the epibenthic or epifaunal species, living at the surface of the sediments or attached to rocks, and the endobenthic or infaunal species, living within the sediments. Both epi- and endobenthic fauna species have been reported to be affected by PAHs, concerning development, growth, reproduction and even survival (e.g. Meier et al., 2000; Paumen et al., 2008; Paumen et al., 2009; Ha et al., 2019). There are, however, no reviews of the effects of PAHs on freshwater benthic fauna. A previous review by Honda and Suzuki (2020) addressed the toxicity of PAHs to aquatic animals, but focused mainly in fish, mentioning only briefly benthic invertebrates. Herein we address this research gap by systematically tackling three specific objectives: (i) to estimate the partitioning of PAHs between the water column and sediments in lotic (streams and rivers) and lentic (lakes and ponds) systems; (ii) to review the acute ecotoxicity of PAHs to benthic fauna species; (iii) to identify and discuss needs for further research into the toxicity effects of PAHs.

2. Methodological approach

2.1. PAHs distribution in freshwater systems

A literature search was performed on the SciVerse Scopus (Elsevier Properties SA, USA) database for assessing the distribution of each of the 16 USEPA's priority PAHs in freshwater (lotic and lentic) ecosystems, addressing papers published between January 2000 and July 2021. No restrictions were imposed regarding geography or expected PAH levels since the goal was to achieve a comprehensive dataset, reflecting the sediment-water partition coefficients in diverse areas.

The following search thread was used: "TITLE-ABS-KEY (concentration* AND PAH* AND water AND sediment AND PUBYEAR > 1999)". The obtained papers were thoroughly checked and their compliance with the following criteria was assessed: (i) studies in freshwater systems, including lakes, reservoirs, streams, and the headwaters of estuaries; (ii) papers written in English; (iii) papers providing numeric values (i.e. not graphical) of the PAHs determined for paired sets of sediment and corresponding overlying water samples; (iv) papers with sufficient description of the methods used to collect the samples and quantifying PAHs; (v) papers retrieving the concentration of PAHs in the water considering total (dissolved plus suspended) PAHs (i.e., unfiltered water samples) and, simultaneously, the

concentration of PAHs in the sediment expressed as dry weight, thus allowing a comparison of results from different papers. In the case of papers reporting mean values of each PAH or the sum of PAHs in several sites, the corresponding author(s) of the most relevant papers were contacted by e-mail requesting further information on the concentration of each PAH in each site for both the water and sediment fractions.

The information regarding the chemical species, their concentrations in water and sediments as well as the sampling location was extracted (Table S1).

For each sediment – water data pair, the sediment-water partition coefficient (K_{sw} , $\mu\text{g kg}^{-1}/\mu\text{g L}^{-1}$) was calculated using the following equation (Zhang et al., 2011):

$$K_{sw} = \frac{C_s}{C_w}$$

where C_s and C_w represent respectively, the PAHs concentration in sediment ($\mu\text{g kg}^{-1}$ dw) and in the overlying water ($\mu\text{g L}^{-1}$).

Despite some studies reported that total organic carbon (TOC) content influences the partition of PAHs between the water and sediment (Feng et al., 2007; Zhang et al., 2017), the partition coefficient (K_{sw}) was calculated herein without TOC-normalized concentration correction (Yang et al., 2019) for two reasons. First, several papers have reported no significant relationships between either PAHs concentrations or K_{sw} values and TOC contents (e.g. Chen et al., 2004, Liu et al., 2016, Yang et al., 2019, Mohammed et al., 2021; cf. Section 3.1). Second, the TOC content is not reported in several scientific papers, as is the case of many of the ones obtained following the literature search (Zhu et al., 2004; Barbee et al., 2008; Edokpayi et al., 2016; Akan et al., 2018; Adekunle et al., 2020; Ambade and Sethi, 2021; Ambade et al., 2021; Jazza and Khwadem, 2021).

2.2. Toxicity to benthic species

Aiming to provide an overview of PAHs toxicity to benthic fauna, a literature search was performed, addressing the effects of the 16 USEPA's priority PAHs to benthic freshwater species, considering both epifauna and endofauna species. This research was performed on the USEPA ECOTOX (<http://cfpub.epa.gov/ecotox/>) and SciVerse Scopus databases, addressing studies published before August 2021.

The search in the aquatic part of the ECOTOX database was constrained to concentration-based endpoints for individual effects of the 16 USEPA's priority PAHs (CAS numbers given as entry) in freshwater animal species (crustaceans, insects/spiders, molluscs, worms, other invertebrates) regarding growth, mortality, physiology and reproduction. Results for all PAHs were merged and a filtering/screening operation was performed to exclude non-benthic species, and limit the endpoints to EC_{50} and LC_{50} values. All results were checked in the source documents. Whenever these were unavailable (e.g. old reports not available online), the corresponding data were excluded.

The Scopus bibliographic search was performed using the following search thread: TITLE-ABS-KEY (PAH* AND toxicity), where PAH* stands for each one of the 16 USEPA's priority PAHs, i.e., PAHs were searched individually.

Documents that simultaneously verified the following criteria were included: (a) studies assessing the toxicity of one or more of the 16 interest PAHs to freshwater and benthic species; (b) studies reporting LC_{50} or EC_{50} values (concerning the endpoints growth/development, reproduction, immobilization, hatching); (c) studies reporting values concerning porewater (or interstitial water), overlying water or sediment. The following exclusion criteria were used: (a) unavailable source online, or impossibility to check the data; (b) studies not reporting original data; (c) documents not written in English.

2.2.1. Species sensitivity distributions

Data concerning PAHs acute toxicity to benthic species (Table S2) were further used to build Species Sensitivity Distribution (SSD) curves. These

curves represent an integrated evaluation of the communities' sensitivity to chemicals. The rationale behind SSDs is that chemicals can affect the whole community and not only some species, thus likely affecting species with different sensitivity to the chemicals (Carr and Belanger, 2019). Commonly, SSDs are used to determine the HC_5 (hazardous concentration, 5th percentile), which represents the hazardous concentration of a chemical to 5% of the species i.e., the concentration threshold under which 95% of the species are protected from toxic effects due to a chemical. This value has been adopted as criterion to protect aquatic life. Moreover, the HC_{50} (hazardous concentration, 50th percentile) is also commonly determined as, compared to the HC_5 , it is less sensitive to new data points and is associated with lower statistical uncertainty due to its position in the middle of the SSD curve (Carr and Belanger, 2019).

Based on data availability (Table S2), SSDs were built for acute toxicity (mortality, expressed as LC_{50} or its immobilization surrogate, expressed as EC_{50}) using the SSD generator from the United States Environmental Protection Agency (USEPA, 2016). This tool fits a log-probit distribution to data on concentrations at which different species exhibit a standard response to a stressor. The outcome is a curve relating the concentration of the stressor to the proportion of species expected to be affected at given concentrations. There is no consensus concerning the minimum number of aquatic species/taxonomic groups required to build SSDs (Belanger et al., 2017; Carr and Belanger, 2019), but most regulatory frameworks for the purpose of environmental risk assessment of chemicals and for the definition of water quality criteria consider 10, despite some regulations refer that lower values can be used (see references in Belanger et al., 2017). A minimum of 7 species was considered acceptable under the scope of the present work given that we do not intend to develop water quality criteria, but rather comparatively appraise the hazardous potential of different PAHs to benthic species. Due to the lack of available data, SSD curves were developed only for naphthalene, phenanthrene, pyrene, fluoranthene and anthracene, with data from 8, 12, 8, 15 and 7 species, respectively (see Fig. 6 and Table S2).

2.3. Statistical analysis

The relationship between the sediment-water (K_{sw}) and octanol-water (K_{ow}), as well as the relationship between $\log K_{ow}$ and $\log HC_5$ partition coefficients were assessed through Pearson's correlation. Statistical analyses were performed at a significance level of 0.05.

3. Sediment-water partitioning of PAHs

3.1. Factors affecting the sediment-water partitioning

The sediment-water partitioning depends on the physical-chemical properties of the individual compounds, including solubility, molecular weight, molecular structure, octanol/water partitioning coefficient (Narbonne et al., 1999) as well as on the environmental conditions, e.g. nature and concentration of suspended particles, and sediment properties (Aryal et al., 2005; Wu et al., 2012). For instance, as LMW PAHs are more soluble than HMW PAHs, they are usually the dominant PAHs in water (e.g. Li et al., 2010; Zhang et al., 2011; Huang et al., 2019; Yang et al., 2019; Jia et al., 2021). By contrast, HMW PAHs are typically the main PAHs in sediments, due to their strong hydrophobicity and low solubility, rendering a higher tendency to adsorb strongly to organic matter and sediment particles (Li et al., 2010; Zhang et al., 2011; Zhang et al., 2017; Yang et al., 2019; Lee et al., 2021).

In sediments, TOC content has been reported as a major variable controlling the distribution and fate of PAHs (e.g. Yang et al., 2008; Guo et al., 2009; Qin et al., 2014a,b). The distribution of PAHs is expected to follow equilibrium partitioning to sediment organic carbon (e.g. Fernández et al., 1999; Feng et al., 2007; Xu et al., 2007; Froehner et al., 2009; Wu et al., 2012), expressed by the sediment organic carbon-water partitioning coefficients (K_{oc}). However, K_{oc} values per se might not be appropriate to predict the environmental behavior of PAHs in field sediments (e.g.

Cornelissen et al., 2005; Hawthorne et al., 2006) because of the presence of multiple organic carbon types in sediments and their different sorption affinities for PAHs, leading to differential partitioning behavior between sediment and water (Hawthorne et al., 2006). For instance, sediments containing more carbonaceous materials such as black carbon (or soot), coke, pitch and kerogen can exhibit K_{oc} values 1–3 orders of magnitude higher than commonly established K_{oc} values for the same PAH (Hawthorne et al., 2006 and references cited therein). Therefore, sediments enriched in these organic carbon types exhibit higher PAHs concentrations than predicted solely based on the TOC content (Han et al., 2015; Y. Li et al., 2019), highlighting the crucial role of the organic carbon type on PAHs sorption to particles and, thus, on their distribution between sediment and water. This can explain the findings of some studies reporting no correlation between TOC content and PAHs concentrations in the sediments, as mentioned above (e.g. Chen et al., 2004; Liu et al., 2016; Yang et al., 2019; Mohammed et al., 2021). Other factors have been reported to influence PAHs concentrations in sediments and, thus, the sediment-water partitioning of PAHs, namely particle size (Razak et al., 1996; Froehner et al., 2009; He et al., 2016; Y. Li et al., 2019). Indeed, higher content of fine particles (silt and clay) increases the sediment's surface area, which may allow the accumulation of organic matter and, therefore, of adsorbed PAHs (Razak et al., 1996; Froehner et al., 2009; Yu et al., 2009). Sandy sediments, by contrast, commonly present low concentrations of PAHs (Froehner et al., 2009; Yu et al., 2009). However, grain size is not always a good predictor per se in this context (e.g. Guo et al., 2009; Tao et al., 2010). In addition, porosity (Razak et al., 1996; Guo et al., 2007) and cation exchange capacity (Guo et al., 2007) have been positively correlated to PAHs concentrations in sediments, thus affecting PAHs distribution in freshwater systems.

The determination of partition coefficients contributes to better understand the fate and distribution of PAHs between different matrices, as well as their environmental risks in affected aquatic systems (Yu et al., 2009; Yang et al., 2019). Decreased partition of PAHs to the sediment and the consequent increased partition to the water is associated with increased toxicity to aquatic benthic species (cf. Section 4.1).

3.2. Sediment-water partition coefficients

The bibliographic research on the distribution of PAHs between sediment and the overlying water retrieved 9 scientific papers (Table S1), which resulted in a number of pairs of PAHs concentration in the water and in the sediment between 41 (DahA) and 119 (FLU). As expected, PAH concentrations were much higher in the sediments than in the water (Fig. 2), with median values between these compartments varying by 2–4 orders of magnitude (Table S1). The high variability, particularly concerning the concentration in sediments, is not surprising as input data were not selected considering pollution levels. Also, despite some exceptions, there is a trend for increased concentration in the sediment with increasing molecular weight, which corroborates the general assumption that HMW PAHs are more common in the sediment than LMW PAHs (Li et al., 2010; Zhang et al., 2011; Zhang et al., 2017; Yang et al., 2019). This dominance of HMW PAHs in the sediment is due not only to their tight binding to organic particles and further sedimentation, but also to their reduced resuspension, as described above. The $\log K_{sw}$ values (Table 2) support this inference: PAHs with the highest molecular weight and hydrophobicity ($\log K_{ow}$) were confirmed to exhibit the highest $\log K_{sw}$ values (Table 2; Fig. 3), corroborating that these PAHs will be preferentially adsorbed to the sediments. Concordantly, Maletić et al. (2019) stated that “as a rule of thumb, compounds with a $\log K_{ow} > 5$ should preferably be measured in sediments, while compounds with a $\log K_{ow} < 3$ should preferably be measured in water; for compounds with a $\log K_{ow}$ between 3 and 5, the sediment matrix is optional and will depend on the degree of contamination”.

The $\log K_{sw}$ was positively and linearly correlated with $\log K_{ow}$ and $\log K_{oc}$ (Fig. 3, Pearson correlation: $\rho = 0.920$ and $\rho = 0.919$, respectively; $p < 1 \times 10^{-5}$). A good correlation between $\log K_{sw}$ and $\log K_{ow}$ was also observed previously (Yang et al., 2019). It is worth to refer that the organic

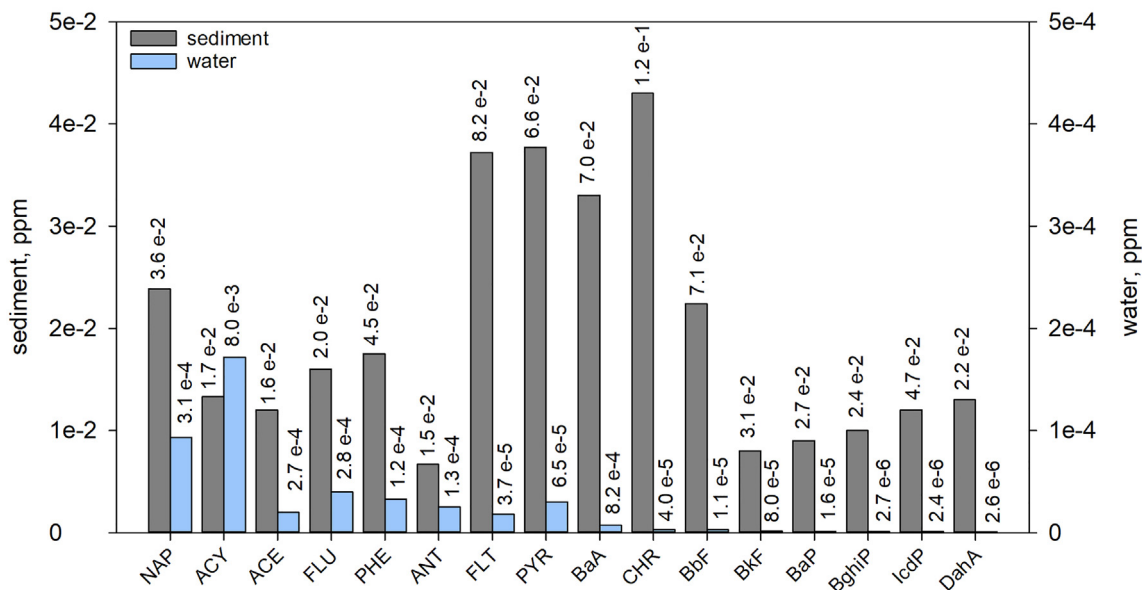


Fig. 2. Concentration (median values) of individual PAHs in sediments ($\text{mg kg}^{-1} \text{ dw}$) and in overlying water columns (mg L^{-1}) of freshwater ecosystems (detailed data in Table S1). The interquartile difference is presented above each bar, its magnitude being related with the wideness of raw data distribution and overall PAH levels. The number of water and sediment data pairs varied between 41 (DahA) and 119 (FLU). Raw data were obtained from references summarized in Table S1.

carbon-normalized partition coefficients for PAHs also positively correlates with $\log K_{ow}$ (e.g. Qiao et al., 2007; Zhang et al., 2011; Zhang et al., 2017).

The finding that $\log K_{sw}$ values were lower than the $\log K_{oc}$ values (comparing Tables 1 and 2), was also observed in previous studies (Zhang et al., 2011; Sun et al., 2017; Zhang et al., 2017; Yang et al., 2019). It suggests that the use of $\log K_{oc}$ as indicator of sediment-water partitioning of PAHs under field conditions might not be adequate to predict the environmental behavior of PAHs in field sediments (e.g. Cornelissen et al., 2005; Hawthorne et al., 2006).

In summary, these analyses show that PAHs concentrations will be markedly higher in the sediment than in water. This is especially the case for the PAHs with higher hydrophobicity.

Given that the transfer of PAHs between sediment and overlying water is dynamic, it would be advisable to determine PAHs concentrations in both compartments to have an overview of the environmental risk that PAHs pose at a specific site. Still, analysing PAH concentrations in water is most relevant near pollution sources (Guo et al., 2007; Meng et al., 2019), before water concentrations come into equilibrium with sediment concentrations.

Table 2

Estimated PAH partition coefficients between sediment and water ($\log K_{sw}$), expressed as $\mu\text{g kg}^{-1} \text{ dw} / \mu\text{g L}^{-1}$ (mean values \pm standard deviation) and number of data pairs used to determine $\log K_{sw}$ values (n). Raw data for the calculations were obtained from references summarized in Table S1.

PAH	$\log K_{sw} \pm \text{SD}$	n
NAP	2.601 \pm 1.127	104
ACY	1.985 \pm 1.949	78
ACE	2.638 \pm 1.080	104
FLU	2.655 \pm 1.160	119
PHE	2.86 \pm 1.037	106
ANT	2.745 \pm 1.337	113
FLT	3.585 \pm 1.018	84
PYR	3.322 \pm 1.076	92
BaA	3.132 \pm 1.784	101
CHR	3.854 \pm 1.300	89
BbF	3.883 \pm 1.300	76
BkF	3.635 \pm 1.572	83
BaP	4.131 \pm 1.415	63
BghiP	4.097 \pm 1.146	56
IcdP	4.284 \pm 1.336	59
DahA	4.415 \pm 1.338	41

4. Toxicity of PAHs

4.1. Bioavailability and uptake

As other chemicals, PAHs will only be toxic if they are bioavailable. The most bioavailable PAHs are those in dissolved forms as they easily cross biological membranes. PAHs adsorbed to the sediment particles might not be bioavailable, as supported by studies reporting no correlation between PAHs concentration in sediments and biological effects (Hawthorne et al., 2007; Kreitinger et al., 2007; Endo et al., 2020). By contrast, PAHs dissolved in porewater are bioavailable and, hence, may exert toxic effects on benthic species (Hawthorne et al., 2007; Kreitinger et al., 2007; Wang et al., 2011; Tuikka et al., 2016). Indeed, porewater concentrations were found to control the uptake, toxicity and bioaccumulation of PAHs in benthic species (Lu et al., 2003; Lu et al., 2004a, 2006; Hawthorne et al., 2007; Tuikka et al., 2016), regardless of the PAH uptake route and

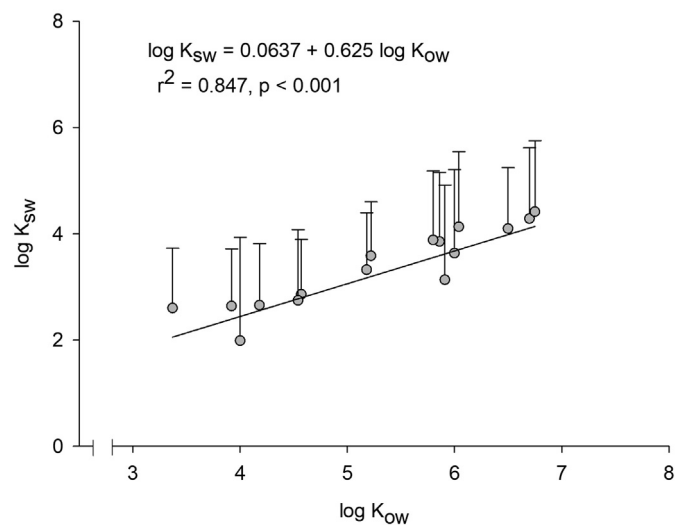


Fig. 3. Relationship between the log octanol-water partition coefficient ($\log K_{ow}$) and the log sediment-water partition coefficient ($\log K_{sw}$) of the 16 USEPA's priority PAHs. Error bars represent the standard deviation of the $\log K_{sw}$ values.

assimilation efficiency (Lu et al., 2003; Lu et al., 2004a, 2006). For this reason, the prevalent pathway for PAHs toxicity to benthic fauna is the onset by uptake from freely dissolved porewater fractions (Kreitinger et al., 2007; Wang et al., 2011).

PAHs concentrations in porewater are dependent on the sediment-porewater partition coefficients. As for the partitioning of PAHs between the sediment and the overlying water, also the partitioning between sediment and porewater is mostly affected by the amount and type of organic carbon in the sediment (Wang et al., 2011; Han et al., 2015; Endo et al., 2020). Indeed, sediments enriched in TOC or carbon types exhibiting high binding capacity, such as soot, will show decreased PAHs partition to the porewater and, consequently, reduced toxicity to benthic species (e.g. see review by Cornelissen et al., 2005; Kreitinger et al., 2007). For this reason, sediment-porewater partition coefficients have been suggested as predictors of PAHs bioavailability (Lu et al., 2006) and of biota-sediment accumulation factors (Lu et al., 2003; Lu et al., 2006). Therefore, the assessment of PAH concentrations in porewater is of major relevance to understand the mobility and bioavailability of PAHs in sediments (Lu et al., 2006; Yu et al., 2009) and, ultimately, it contributes to a more realistic assessment of the hazardous potential of PAHs to benthic species (Arp et al., 2009; Tuikka et al., 2016; Endo et al., 2020). Moreover, PAHs in porewater may also diffuse into the overlying water column (Dong et al., 2016; Liu et al., 2021), increasing the risk of deleterious effects to epibenthic and pelagic organisms (Pang et al., 2012).

The main route of uptake of bioavailable PAHs is through passive diffusion across cellular membranes, given their non-polar character and shared high lipophilicity (Gauthier et al., 2014). Uptake by benthic species can occur via two main routes: (i) through contact with water (porewater or overlying water), either directly by the skin or across respiratory surfaces; (ii) through dietary ingestion of sediment or food contaminated with PAHs, with absorption occurring mainly through the gut wall (Weston et al., 2000; Lu et al., 2004b; Wang et al., 2011), as summarized in Fig. 4. Therefore, ingestion of sediment or suspended particles can be an important additional mechanism for PAH intake, especially for deposit-feeding invertebrates (Lu et al., 2003; Wang et al., 2011). However, for these organisms, previous studies have showed that PAHs toxicity and bioaccumulation were independent of the uptake route (Lu et al., 2004a; Akkanen et al., 2012), which is supported by the fact that the solid and water phases are expected to be in approximate equilibrium.

Uptake of PAHs is controlled not only by the sediment-porewater partitioning, but also by other factors, namely the water physicochemical properties including the content and type (dissolved vs. particulate) of organic matter (Akkanen et al., 2012), the route of uptake (water, sediment or food) and the uptake efficiency from each route (Weston et al., 2000).

Upon uptake, PAHs are distributed among tissues, being the preferential organs for accumulation PAH-specific (e.g. Hellou and Leonard, 2004; Advaiti et al., 2013). Given the differential tissue distribution, the toxicity of PAHs will necessarily depend on the ability of these tissues to metabolize and detoxify PAHs (Gauthier et al., 2014).

4.2. Mechanisms of toxic action

Following Incardona et al. (2006), the underlying mechanisms of toxic action in the aquatic biota are various and can be grouped as: (1) “dioxin-like” toxicity, mediated by activation of the aryl hydrocarbon receptor (AHR), which controls a group of genes involved in PAHs metabolism, and (2) “nonpolar narcosis”, mediated by partitioning into lipid membranes, which is dependent only on hydrophobicity.

PAHs are relatively non-reactive compounds towards biological macromolecules, requiring metabolic activation in order to be converted to carcinogenic, genotoxic, and reactive oxygenated metabolites (see reviews by Baird et al., 2005, Ha et al., 2019). Such metabolization is mediated by the cytochrome P450 (CYP) enzyme super family, which is a large family of membrane-bound heme proteins. These proteins are involved in phase I reactions as they “functionalize” PAHs (e.g. through oxidation), which are further modified by other phase I and II enzymes into more soluble and readily excretable metabolites (see reviews by Baird et al., 2005, Nebert and Dalton, 2006 for further details on carcinogenicity). PAHs also have the capacity to change the metabolic pathway of the CYP1 family upstream of CYP1 induction, which is mediated by AHR transcription factors. Most PAHs are known to induce the AHR pathway (AHR-agonists), promoting the transcription of CYP1A1, thus stimulating PAH metabolism (Conney, 1982). More details in the mechanisms of action of PAHs through AHR pathway have been addressed in several reviews (Baird et al., 2005; Billiard et al., 2007; Zhou et al., 2010; Gauthier et al., 2014; Franco and Lavado, 2019). Some of the PAHs-derivatives can bound covalently to DNA and proteins, forming DNA and protein adducts, which may be responsible for mutagenesis, teratogenesis and carcinogenesis, the latter being a recognized flagship for PAHs toxicity (Baird et al., 2005; Santana et al., 2018).

Other recognized mechanism of PAHs toxicity is the onset of oxidative stress caused by derivatives of the metabolic pathways of parent compounds (Crowe et al., 2014; Santana et al., 2018) or by photoreaction (photoactivation) of parent compounds by UV light (see reviews by Yu et al., 2006, Fu et al., 2012). PAHs in a photo-excited state react with coexisting chemicals to produce reactive intermediates, such as reactive oxygen species (ROS), oxygenated PAHs and free radicals, which induce oxidative stress (Fu et al., 2012). Oxidative stress is evidenced through enzymatic disruption, affecting several antioxidant enzymes (e.g. superoxide dismutase, glutathione-S-transferase and catalase) and molecules like vitamins, urate and glutathione (GSH), ultimately translating into actual lipid peroxidative damage (Nogueira et al., 2011; Yazdani, 2020), as widely studied in fish (e.g. Santana et al., 2018).

Moreover, PAHs can act as immunosuppressors, by reducing the immunity of exposed organisms (Wootton et al., 2003), a mechanism linked to the induction of programmed cell death (apoptosis) of lymphocytes and phagocytes (Logan, 2007), and they have also been reported to act as endocrine disruptors (see review by Zhang et al., 2016).

Apart from these specific targets, PAHs are essentially nonpolar narcotics (Ha et al., 2019). Toxicity by narcosis occurs under acute exposure

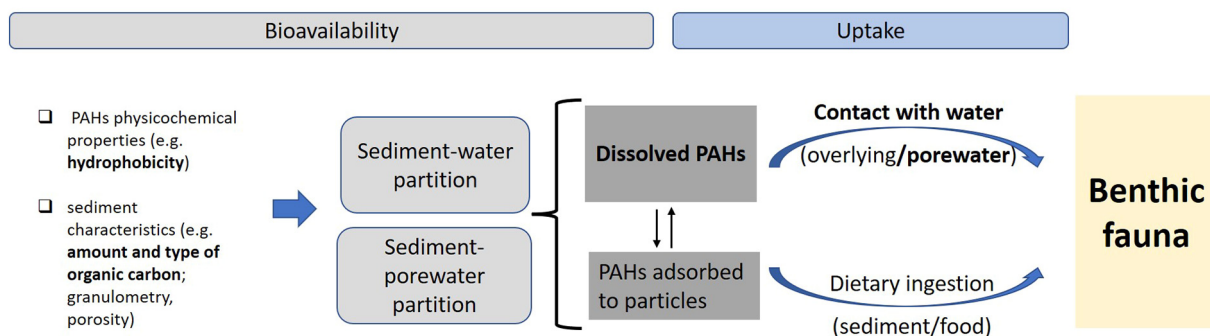


Fig. 4. Schematic representation of the most relevant aspects regarding bioavailability and uptake of PAHs by benthic fauna.

(Di Toro et al., 2000) but also under chronic exposure (Paumen et al., 2009). Narcosis is a non-specific mode of action common to all organic chemicals in general (Paumen et al., 2009) comprising a reversible anesthetic effect that is related to the partitioning into cell membranes and nervous tissues, thus strongly related to the lipophilicity of the compound - log K_{ow} (Di Toro and McGrath, 2000; Paumen et al., 2009). PAHs cause structural, compositional and functional modifications of the membrane (Hąc-Wydro et al., 2019), altering ionoregulation and, thus, homeostasis, as well as the disruption of the central nervous system function, ultimately causing cell death if intoxication persists (Bradbury and Lipnick, 1990; Gauthier et al., 2014; Hąc-Wydro et al., 2019).

PAHs toxicity can be enhanced by UV light (see Table S2), depending on their molecular structure (see reviews by Fu et al., 2012, Finch et al., 2017, Sun et al., 2021). Indeed, the incidence of UV light in phototoxic PAHs promotes electrons to photo-excited states and the reaction with coexisting chemicals, increasing toxicity. However, within phototoxic representatives, the increment in toxicity seems to be PAH-dependent. Newsted and Giesy (1987) classified PAHs according to their phototoxicity to the crustacean *Daphnia magna* in class 1 (extremely toxic: NAP, ANT, FLT, PYR, BaA, BkF, BaP, BghiP, DahA), class 2 (moderately toxic: CHR) and class 3 (non-toxic: PHE, FLU). Several studies reported phototoxicity of PAHs to benthic species (e.g. Kagan et al., 1987, Erickson et al., 1999, Bleeker et al., 2002, Bell et al., 2004 and references cited therein) hence highlighting that PAHs phototoxicity is also species-dependent. For instance, despite NAP was extremely phototoxic to *D. magna* (Newsted and Giesy, 1987), it was considered non-phototoxic to the freshwater endobenthic species *C. riparius* (Bleeker et al., 2002).

4.3. Toxicity to freshwater benthic fauna

4.3.1. Species sensitivity distributions

Following the literature search, a total of 298 toxicity records were obtained, reported in 48 documents (Table S2). Among the 298 values, 280 refer to acute toxicity (mortality or immobility), whereas 18 values presented in 5 studies concerned chronic effects (reproduction, emergence, hatching and development). Few studies reported concentrations in the porewater (12 data values) or sediment (57 data values), with 229 data values for PAHs concentrations in the overlying water. Among the 298 data values, 206 results referred to LC_{50} values determined in water exposures (overlying water, Fig. 5). The most commonly studied species was the epibenthic amphipod *Hyalella azteca* (120 results) followed by the endobenthic midge *Chironomus riparius* (33 results). No data was found for some of the 16 PAHs, especially for HMW PAHs (Table S2).

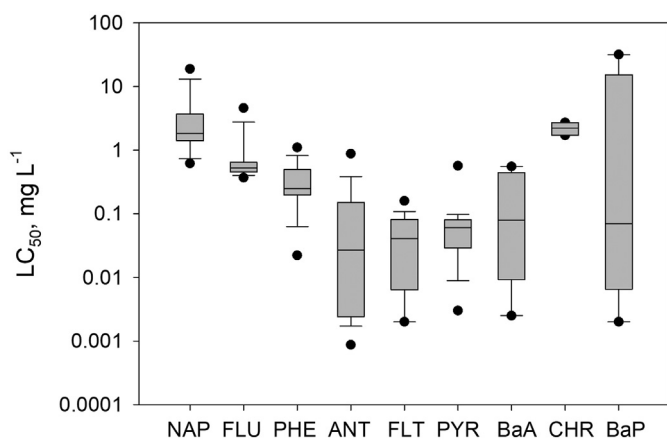


Fig. 5. Distribution (median and 25th–75th percentile) of lethal concentrations (LC_{50}) values for benthic freshwater species exposed to PAHs (overlying water). Error bars represent the 10th and 90th percentiles; dots represent the 5th and 95th percentiles. The LC_{50} values are presented in a logarithmic scale. Raw data were obtained from references summarized in Table S2.

The medians of LC_{50} values are below 1.0 mg L^{-1} , except for NAP and CHR (Fig. 5; Table S2). Note, however, that the median LC_{50} values found for BaA, CHR and BaP are above their water solubility limit at $25 \text{ }^\circ\text{C}$ (0.011 , 0.0019 and 0.0038 mg L^{-1} , respectively, see Table 1). Such high LC_{50} values are likely the result of laboratorial tests carried out under specific experimental conditions, e.g. involving the use of solvents, and thus, will unlikely occur in natural ecosystems. This suggests that in the environment, these PAHs will show reduced acute lethal toxicity to benthic species, unless some agents, such as surfactants (e.g. as highlighted in the review by Haritash and Kaushik (2009)) or microplastics (Zhang and Goss, 2020; Sun et al., 2021) co-occur in the aquatic environment, increasing their solubility and/or uptake likelihood. For HMW PAHs (the most hydrophilic), LC_{50} values have been found to exceed water solubility limits (Lee et al., 2001), which supports the claim for their reduced environmental risk under acute exposure conditions. However, when integrating these data considering the species-specific sensitivity to these PAHs, the risks as determined by SSD-based benchmark derivation do not provide such an optimistic picture.

The SSD curves (Fig. 6), built based on the LC_{50} toxicity values presented in Table S2, reveal a wide variation in the acute toxicity of each PAH, more pronounced for ANT and PYR (3 orders of magnitude). As expected, photoactivated PAHs (ANT, FLT and PYR) showed higher toxicity when tested under UV light conditions, which translates into reduced HC_5 values. The derived HC_5 values (Table 3) varied by 3 orders of magnitude (440-fold), whereas the HC_{50} values varied by 2 orders of magnitude (101-fold), with the photoactivated PAHs exhibiting HC_{50} values lower than non-photoactivated PAHs (NAP and PHE).

The estimated HC_5 values decrease as follows: NAP > PHE > PYR > FLT > ANT. The fact that the maximum concentration reported in the overlying water (regarding data presented in Table S1) exceeds the toxicity values for several species concerning FLT suggests that, among the studied PAHs, this is likely the one representing higher risk to aquatic benthic fauna, in particular under UV light conditions.

Note, however, that this analysis is constrained by the use of acute toxicity data (lethality and immobilization) to derive HC_5 values. Thus, one should not discard the hypothesis that higher risks are found if chronic and long-term toxicity to benthic species is considered. Also, several other aspects should be taken in consideration regarding the extrapolation of these results to field conditions. Although the body of literature used to compile our database refers mainly to laboratory studies, as field studies are unlikely to assess the effects of a single PAH, it is worth remarking that these two types of studies may have different outcomes. For instance, it was shown that biomarker responses in fish exposed to PAHs were stronger in laboratory than field studies (Santana et al., 2018). Under field conditions, one has to account for the occurrence of complex mixtures of PAHs and substituted-derivatives or degradation metabolites, as well as for microbial degradation processes which translate into decreased concentration of parent compounds but increased concentrations of derivatives. Also, as previously mentioned, UV light can increase PAHs toxicity (Bleeker et al., 2002; Fu et al., 2012; Baldwin et al., 2017). Indeed, despite toxicity of PAHs in the laboratory is usually tested under no UV radiation, this influence cannot be excluded in the field (Monson et al., 1995), exacerbated by the fact that UV radiation at the Earth's surface has been increasing (McKenzie et al., 2003). These factors may translate in decreased representativeness of the laboratorial tests for field conditions.

Several studies have determined the ecological risk of PAHs in aquatic systems (e.g. Guo et al., 2012; Qin et al., 2014a,b; Meng et al., 2019; Qiao et al., 2020). Guo et al. (2012) reported that the risk of individual PAHs to a lake (China) varied as follows: FLT > BaP > PYR > ANT > PHE > FLU > ACE > CHR. Another study reported a higher contribution of 4-ring PAHs (FLT, PYR, BaA and CHR) to acute risk to aquatic biota of several rivers (Qiao et al., 2020). The PAHs PYR, ANT and FLT were considered to exhibit the greatest ecological risk probability in a large lake (Qin et al., 2014a,b). Anthracene was considered the most hazardous PAH in the surface water from the Tianjin rivers according to Yang et al. (2006). A recent review showed that BaA and PHE were the PAHs exhibiting the highest risk

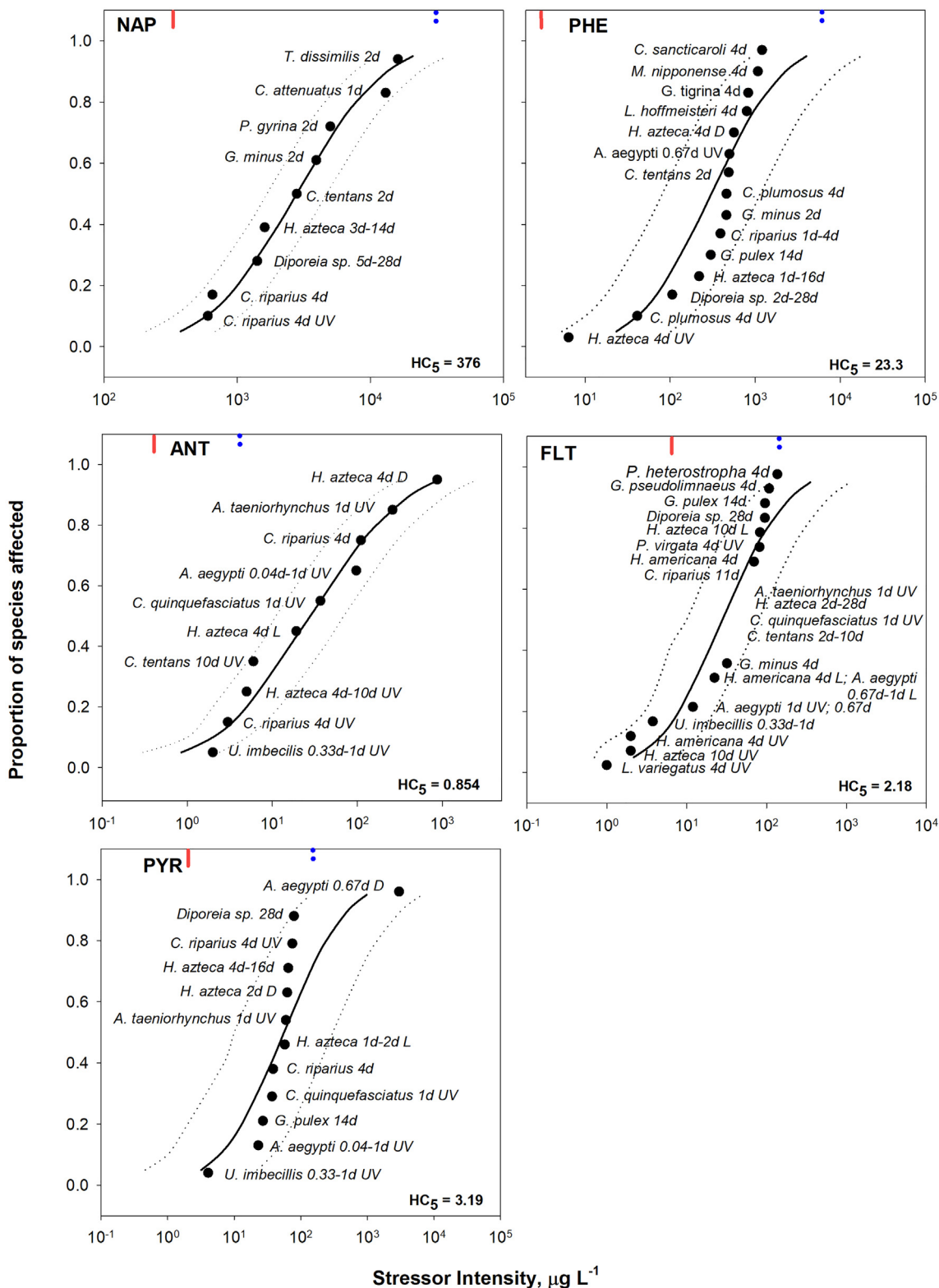


Fig. 6. Species sensitivity distribution (SSD) curves for acute endpoints (mortality and immobility) considering exposure of benthic freshwater fauna to naphthalene (NAP), phenanthrene (PHE), pyrene (PYR), fluoranthene (FLT) and anthracene (ANT). The dotted lines along each curve represent the 95% confidence intervals. For each data point, the species name is followed by the exposure period (or its range) and the light conditions: D – dark; UV - exposure to UV or solar radiation; L – specific light conditions (e.g. gold light; or different intensities of fluorescent light); the absence of a letter stands for fluorescent light or unspecified light conditions. The estimated HC₅ benchmarks are given for each PAH. The red continuous line at the top of each figure represents the maximum concentration reported in the overlying (unfiltered) water corresponding to data presented in Fig. 2/Table S1. The dotted blue line represents the solubility at 25 °C (ATSDR, 1995). Raw data were obtained from data presented in Table S2.

Table 3

Estimated HC₅ and HC₅₀ benchmarks for PAHs ($\mu\text{g L}^{-1}$) and the corresponding 95% confidence intervals within parenthesis, coefficient of determination (r^2) and number of data points (n) used to build the respective SSD curves.

	HC ₅	HC ₅₀	r^2	n
Naphthalene	376 (20.7–68.2)	2.80×10^3 (1.67×10^3 – 4.69×10^3)	0.960	9
Phenanthrene	23.3 (5.33–102)	305 (80.7 – 1.15×10^3)	0.796	15
Anthracene	0.854 (0.305–2.39)	28.1 (11.3–69.5)	0.754	12
Fluoranthene	2.18 (0.699–6.77)	27.7 (9.60–80.0)	0.858	21
Pyrene	3.19 (0.463–22.0)	55.7 (10.3–302)	0.956	10

to aquatic biota in Chinese lakes (Meng et al., 2019). Being the ecological risk of PAHs dependent on environmental concentrations and, thus, specific for each aquatic system, it is not surprising that the PAHs exhibiting the highest ecological risk differ among sites. Note, however, that if chronic toxicity data was considered instead of acute toxicity data, it would be expectable to find more PAHs bearing a hazardous potential to aquatic species.

Both the HC₅ and HC₅₀ values were negatively correlated to $\log K_{oc}$ ($\rho = -0.925$ and $\rho = -0.933$, respectively) and $\log K_{ow}$ ($\rho = -0.912$ and $\rho = -0.919$, respectively). In particular, the correlation between $\log K_{ow}$ and HC₅₀ (Fig. 7A) illustrates the high dependency of PAHs toxicity on their hydrophobicity. This agrees with the results obtained for the benthic freshwater species *H. azteca* exposed to 8 PAHs, evidencing increased toxicity with increased hydrophobicity (Ha et al., 2019). A similar correlation was found for *C. riparius* exposed to several PAHs in the presence or absence of UV light (Bleeker et al., 2002). Concordantly, a general trend for increased risk (lower HC₅) with increased hydrophobicity was found for aquatic biota concerning chronic toxicity (Chen et al., 2020). Also, HMW PAHs were indicated as posing higher risk than LMW PAHs based on multiple indicators (Qin et al., 2014a,b; Xu et al., 2015). The increased toxicity of PAHs with increased hydrophobicity is not surprising, as it is in line with the narcotic mode of action of PAHs and has also been reported for soil organisms (Sverdrup et al., 2002) and other organic chemicals (Di Toro et al., 2000). In addition, our results suggest that this correlation is also valid at the community level and generalized for other freshwater species (not only benthic fauna), which might be pertinent for addressing PAHs-related water pollution problems at a global scale.

The determined acute HC₅ values are similar to values reported in previous studies (Table S3). The literature values follow the same trend as the HC₅ values determined in the present work: decreased acute HC₅ values with increased hydrophobicity (Fig. 7B). These HC₅ values, within the micrograms range, suggest that PAHs can be highly toxic to aquatic organisms

under specific conditions. However, the SSD approach has two main limitations: HC_x values are derived from data based on laboratorial studies, which might not be representative of field conditions. Gthat PAHs occur mainly as mixtures, it is unlikely that exposure to a single PAH exists under natural field conditions. For sediments, a community HC₅ for total PAHs of 0.183 mg kg^{-1} was reported (Kwok et al., 2008). This value is lower than the total concentration of the USEPA-priority PAHs reported in Table S2, which supports the concerns on the potential environmental effects of PAHs to benthic species.

Summarizing, for benthic fauna, as for aquatic fauna in general, there is a trend for decreased HC₅ values with increasing hydrophobicity, i.e., PAHs with higher $\log K_{ow}$ values exhibit higher risk for aquatic communities, despite their lower aqueous solubility.

4.4. Sediment quality guidelines for PAHs

Aiming to protect aquatic benthic communities, sediment quality guidelines have been defined as reference for risk assessment to benthic species. These guidelines represent maximum concentrations of PAHs in sediments that should not be exceeded to protect sediment-dwelling organisms. A broad review of the numerous sediment quality guidelines was performed by McGrath et al. (2019), but see also Kane Driscoll and Burgess (2007). However, defining maximum concentrations in the sediment does not agree with the evidence that PAHs concentrations in the porewater, rather than in the sediment particles, relate to toxicity to benthic species (Hawthorne et al., 2007; Tuikka et al., 2016). Following this, it is desirable that porewater concentrations are determined to improve risk assessment of PAHs to benthic fauna. Still, the determination of PAHs concentrations in sediments is recommended in many countries and often mandatory (Crane et al., 2021) as they act as a sink for these compounds.

5. Conclusions and future challenges

This review highlighted that hydrophobicity is a key variable constraining PAHs distribution in freshwater systems and toxicity to freshwater benthic fauna. Increased hydrophobicity translates into increased partition to the sediment, as given by the sediment-water partition coefficients, and also into enhanced toxicity to benthic fauna communities, as given by HC₅ and HC₅₀ benchmarks. Allied, these factors indicate that the more hydrophobic PAHs are those who raise more concern to benthic species. However, given that toxicity to benthic species relates mostly to porewater concentrations, further studies concerning toxicity to benthic species regarding PAHs concentrations in the porewater are needed to fulfill this knowledge gap.

Research on PAHs distribution and ecological risk assessment to aquatic species will have to overcome major challenges. The first, and probably the most emergent, regards update of the PAHs priority list, as reviewed and

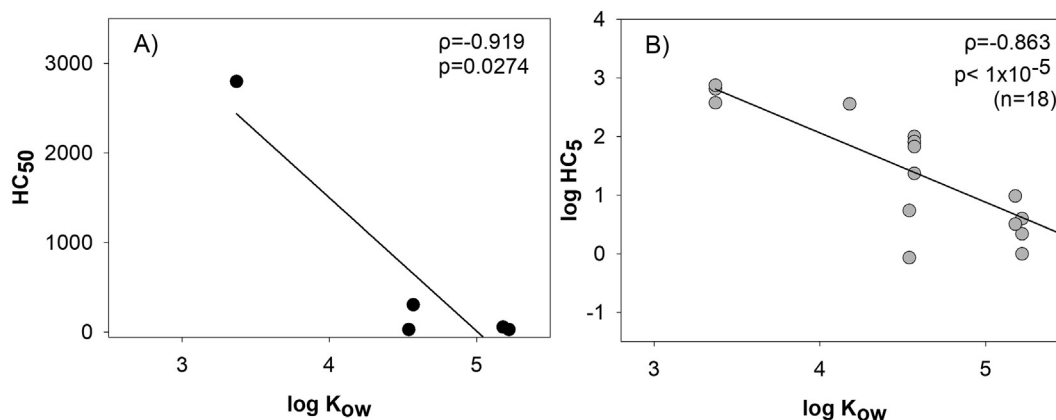


Fig. 7. Correlation between HC_x and $\log K_{ow}$: A) Correlation between the derived HC₅₀ ($\mu\text{g L}^{-1}$) in the present study and $\log K_{ow}$; B) Correlation between $\log HC_5$ for freshwater species (HC₅ values from Table S3 and from the present study; $\mu\text{g L}^{-1}$) and $\log K_{ow}$.

discussed by [Andersson and Achten \(2015\)](#). This list has been widely used in ecological risk assessment, but recent works have pointed out that non-included PAHs can be more toxic than the current USEPA priority PAHs (e.g. [Richter-Brockmann and Achten, 2018](#)) which, allied to their wide distribution and high chemical stability, raises concern about their environmental effects. Among these disregarded PAHs are the alkylated PAHs and higher molecular weight PAHs ([Andersson and Achten, 2015](#)). For instance, alkylated PAHs tend to be both more stable and resistant to weathering ([Liu et al., 2012](#)) and can be more toxic ([Lin et al., 2015](#)) and more abundant ([Mohammed et al., 2021](#)) than their respective unsubstituted PAHs. Similarly, higher molecular weight PAHs have also been found in the environment and are highly toxic ([Andersson and Achten, 2015](#)).

The second challenge entails the evidence that PAHs toxicity to aquatic organisms should not be evaluated independently from other (chemical or climate-related) stressors. The presence of other chemicals, such as metals, has been shown to influence PAHs toxicity ([Gauthier et al., 2014](#)). In addition, microplastics, in particular nanoplastics, can promote the uptake of PAHs thereby increasing their potential toxicity to aquatic fauna ([Zhang and Goss, 2020](#); [Sun et al., 2021](#)). Stressors associated with climatic change have been reported to exacerbate PAHs effects, namely increased temperature ([Vieira and Guilhermino, 2012](#)), increased UV radiation intensity ([Finch et al., 2017](#)) and reduced oxygen concentrations ([Cypher et al., 2017](#)). Thus, the environmental risk assessment of PAHs should incorporate these scenarios, in particular the phototoxicity of PAHs and their mixtures ([Fu et al., 2012](#)), which was found relevant not only under laboratorial ([Sun et al., 2021](#)) but also under field conditions ([Monson et al., 1995](#)).

A third challenge regards the definition of environmental quality guidelines for protection of aquatic life. The combined rather than the individual toxicity of PAHs should be considered for the purpose, as PAHs commonly occur as complex mixtures. This can indeed be challenging given their wide diversity and variability, expressed both temporally and spatially. However, efforts have been made in this respect (e.g. [Swartz et al., 1995](#); [Di Toro et al., 2000](#); [USEPA, 2003](#)), with some sediment quality guidelines being defined for total PAHs ([McGrath et al., 2019](#)). Moreover, given that PAHs toxicity to benthic species is better correlated to the concentrations in porewater rather than in sediment, it is recommended that sediment quality guidelines are defined considering porewater concentrations. Concordantly, it is desirable that PAHs concentrations in freshwater systems are preferably determined in the porewater, aiming at better predicting ecological risks to benthic species.

At last, the assessment of PAHs toxicity should address long-term effects and chronic toxicity, rather than just the acute and short-term effects, for an environmentally relevant evaluation of the ecological risks posed by these compounds. This is in line with the recognized mutagenic, teratogenic and carcinogenic effects of PAHs ([Baird et al., 2005](#); [Santana et al., 2018](#)).

Considering the development of cleaner technologies and environmental protection measures, namely increased use of alternative energy sources and the consequent reduced use of fossil fuels, future emissions of PAHs to the environment will likely tend to slowly decrease, concerning both pyrogenic and petrogenic PAHs ([Li et al., 2020](#)). A decline of PAHs loadings in some areas has already been observed ([Du and Jing, 2018](#)). Still, given that these compounds are accumulated in the sediments, dealing with PAHs effects to aquatic biota, in particular benthic species, will continue to be a major environmental problem in the next decades.

CRediT authorship contribution statement

Fátima Jesus: Conceptualization, Methodology, Investigation, Visualization, Writing - Original draft. **Joana Pereira:** Methodology, Visualization, Writing - Review & Editing. **Isabel Campos:** Methodology, Writing - Review & Editing. **Martha Santos:** Investigation, Writing - Review & Editing. **Ana Ré:** Writing - Review & Editing. **Jacob Keizer:** Writing - Review & Editing. **António Nogueira:** Methodology, Writing - Review & Editing. **Fernando JM Gonçalves:** Writing - Review & Editing. **Nelson Abrantes:** Methodology, Resources, Funding acquisition, Writing - Review

& Editing. **Dalila Serpa:** Conceptualization, Methodology, Resources, Writing - Review & Editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2022.153282>.

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