

Use of QSAR and SSD methods on deriving predicted no-effect concentrations in seawater and sediment for ten individual parent- and alkyl-PAHs and a case study on the assessment of their ecological risks from the Dalian Bay, China

Ying Wang^{1,2}, Xing Liu¹, Yi Cong¹, Jin Fei¹, Juying Wang^{1*}, Dian Zhang³, Liang Liu¹, Jingli Mu¹, Ziwei Yao¹

¹Key Laboratory for Ecological Environment in Coastal Areas of Ministry of Ecology and Environment, National Marine Environmental Monitoring Center, Dalian 116023, China

²State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

³Third Institute of Oceanography, Ministry of Natural Resources, Xiamen 361005, China

Received 21 August 2019; accepted 18 May 2020

© Chinese Society for Oceanography and Springer-Verlag GmbH Germany, part of Springer Nature 2020

Abstract

Parent and alkylated polycyclic aromatic hydrocarbons (alkyl-PAHs), which are a class of important toxic components of crude oil especially in the marine environment, exhibit adverse effects on aquatic life and potentially pose a human health risk. However, the lack of chronic toxicity data is one of the hindrances for alkyl-PAHs when assessing their ecological risks. In this study, predicted no-effect concentrations (PNECs) in seawater and marine sediment for ten parent- and alkyl-PAHs were derived by applying species sensitivity distributions (SSDs) and quantitative structure–activity relationships (QSARs). The local area, Dalian Bay, where an oil-spilled accident happened in 2010, was chosen as a case site to assess ecological risks for ten PAHs in surface seawaters and marine sediments. Their PNECs in seawater and sediment for protecting aquatic organisms in marine ecosystems were calculated and recommended in the range of 0.012–2.79 µg/L and 48.2–1 337 ng/g (dry weight), respectively. Overall, the derived PNECs for the studied PAHs in seawater and marine sediment were comparable to those obtained by classical methods. Risk quotient results indicate low ecological risks to ecosystems for ten parent- and alkyl-PAHs in surface seawaters and surface sediments from the Dalian Bay. These findings provide a first insight into the PNECs and ecological risks of alkyl-PAHs, emphasizing the role of the computational toxicology in ecological risk assessments. The use of QSARs has been identified as a valuable tool for preliminarily assessing ecological risks of emerging pollutants, being more predictable of real exposure scenarios for risk assessment purposes.

Key words: alkyl-PAHs, QSARs, PNECs, ecological risks, Dalian Bay

Citation: Wang Ying, Liu Xing, Cong Yi, Fei Jin, Wang Juying, Zhang Dian, Liu Liang, Mu Jingli, Yao Ziwei. 2020. Use of QSAR and SSD methods on deriving predicted no-effect concentrations in seawater and sediment for ten individual parent- and alkyl-PAHs and a case study on the assessment of their ecological risks from the Dalian Bay, China. *Acta Oceanologica Sinica*, 39(12): 95–105, doi: 10.1007/s13131-020-1693-y

1 Introduction

In recent decades, the marine pollution issue caused by oil spill accidents has drawn considerable public concerns. Parent and alkylated polycyclic aromatic hydrocarbons (PAHs) were identified as the most important components being responsible for the toxicities of crude oil to aquatic organisms (Liu et al., 2013; Kang et al., 2014; Yin et al., 2015); they have been detected in various marine environmental compartments, including seawaters, sediments, and organisms (Pie et al., 2015; Hong et al., 2016). This has promoted concerns about the potential impacts of parent and alkyl-PAHs on marine ecosystems and health risks associated with the consumption of contaminated seafood because of their toxicity and persistence (Wilson et al., 2015; Wang et al., 2019).

Predicted no-effect concentrations (PNECs) in ecological risk assessments of chemicals are one of the most useful and key parameters (Wang et al., 2014a; Sun et al., 2017). From a regulatory viewpoint, adverse effects on ecosystems are acceptable if the environmental concentrations of pollutants are below PNECs according to the European Commission Technical Guidance Document (European Commission, 2003). Thereafter, derived PNECs based on chronic toxicity data have usually been used to determine low-risk concentrations of chemicals in aquatic environments. A certain amount of toxicity data covering different species are needed for deriving PNECs of chemicals by applying species sensitivity distributions (SSDs) (del Signore et al., 2016; Brock et al., 2018; Jin et al., 2014).

To date, there have been a variety of studies on occurrence,

Foundation item: The National Key Research and Development Program of China under contract No. 2016YFC1402305; the Postdoctoral Research Foundation of China under contract No. 2016M601148; the Scientific Research Special Fund of Marine Public Welfare Industry under contract No. 201305002.

*Corresponding author, E-mail: jywang@nmemc.org.cn

distribution and ecological/health risks of 16 priority PAHs in China due to their bioaccumulation, teratogenic and carcinogenic properties (Meng et al., 2019). The sources, spatial and temporal distributions and risk levels have frequently been reported in different marine compartments including surface seawaters, surface sediments and marine organisms (Li et al., 2016, 2017; Tong et al., 2019). Ecological risks have always been assessed by Monte Carlo simulation or point estimation, respectively (Li et al., 2016; Tong et al., 2019). However, to our knowledge, scant research on risk assessments for PAH derivatives exist due to the lack of their toxicity data limited by the availability of standard emerging chemicals (Hong et al., 2016).

Alkyl-PAHs have demonstrated higher toxicities to fish compared with their parent PAHs and induce dioxin-like responses via the activation of aryl hydrocarbon receptors (Billiard et al., 1999; Turcotte et al., 2011; Lee et al., 2015). Alkyl-PAHs are known to exert effects and/or possess carcinogenic, mutagenic, or teratogenic properties as well as parent ones (Engraff et al., 2011; Baldwin et al., 2017). However, little experimental, chronic toxicity values for alkyl-PAHs are available to develop SSD curves. Therefore, it would be helpful for ecological risk assessments if we could involve some computational models to supplement the experimental chronic toxicity dataset of these PAHs.

Quantitative structure–activity relationship (QSAR) models relating molecular structure with toxicological activities are of great value to fill the toxicity data gap and meet the need of an ecological risk assessment (RIVM, 2001; Aldenberg and Rorije 2013; Rorije et al., 2013). QSAR models for existing chemicals can be developed by collecting measured data and using some regression methods like partial least squares (Wang et al., 2009; Ghosh et al., 2020). Moreover, they are available by directly using some software like ECOSAR (<https://www.epa.gov/tsca-screening-tools/ecological-structure-activity-relationships-ecosar-predictive-model>). In our previous study, the aquatic toxicities of 16 US EPA priority PAHs were predicted by the QSAR approach, and aquatic PNECs were subsequently derived using the SSD approach and the predicted data (Wang et al., 2016). Good agreement for the aquatic PNECs of eight PAHs based on predicted and experimental chronic toxicity values was observed (Wang et al., 2016). Additionally, ecological risks for individual parent PAHs and total alkyl-PAHs in Dalian coastal sediments were assessed in a previous study using sediment quality guidelines (Hong et al., 2016). However, as far as we know, the PNECs and ecological risks for the individual alkyl-PAHs in seawater and sediment have been rarely reported until now.

Dalian is a coastal city in northeastern China and is located in the southernmost tip of Liaodong Peninsula. The Dalian Bay is a semi-enclosed inland sea facing a high risk of spilled oil due to maritime transport (Liu et al., 2013; Wang et al., 2014b). Several oil spill accidents have happened here in recent years, one of the most severe ones being the Dalian pipeline explosion in 2010.

The purpose of this study is to derive PNECs for ten typical PAH components in seawater and sediment and to preliminarily assess ecological risks in surface waters and sediment from the Dalian Bay. Chronic toxicity experimental dataset and QSARs were combined to derive their PNECs using SSDs and equilibrium partitioning methods. Surface seawater and sediment samples in the Dalian Bay were collected, treated and analyzed by gas chromatograph–mass spectrometry (GC/MS). The Dalian Bay was selected as the case area to assess ecological risks of ten parent- and alkyl-PAHs in surface seawaters and sediments. Their ecological risks were assessed by a risk quotient (RQ) method based on the derived PNECs and the measured concentrations.

2 Materials and methods

2.1 Chemical selection

The studied chemicals were selected according to assessment on their detection frequency, environmental concentrations, persistence, bioaccumulation and toxicity (PBT) characteristics. The PBT properties were calculated by BioWin Version 4.10, BCFBAF Version 3.01, and ECOSAR Version 1.11 softwares, separately. The criteria for the identification of PBT substances are shown in Table A1. Accordingly, three parent PAHs and seven alkyl-PAHs including benzo(a)pyrene (BaP), dibenz(a,h)anthracene (DbA), chrysene (Chr), 2,3,6-trimethylnaphthalene (2,3,6-tmNaP), 2-methylantracene (2-mAnt), 1-methylphenanthrene (1-mPhe), 3-methylphenanthrene (3-mPhe), 9-methylphenanthrene (9-mPhe), 1,7-dimethylphenanthrene (1,7-dmPhe), and 7-isopropyl-1-methylphenanthrene or retene (Ret), were sorted out as the studied chemicals. The information about chemical structures, abbreviations, purities and some physical chemical properties are shown in Table A2.

2.2 Aquatic chronic toxicity datasets

In this study, the toxicity datasets employed for deriving PNECs were obtained from laboratory toxicity tests, ECOTOX (US EPA) databases, and a QSAR model. Toxicological model organisms living in Chinese coastal waters including artemia (*Artemia salina*), fish (*Oryzias melastigma*), and diatom (*Phaeodactylum tricornutum* Bohlin), were chosen to test three PAHs: BaP, 3-mPhe, and Ret. Standardized test guidelines and related public research papers were followed to investigate their toxicities (International Organization for Standardization, 2006; Sarabia et al., 2002; Mu et al., 2014). Toxicity data of BaP were also reported in our previous study (Wang et al., 2014a). Chronic toxicological data for the chemicals are shown in Table A3. Because of the lack of toxicological data for saltwater organisms, experimental data on freshwater organisms were also involved. All the toxicity data originating from laboratory toxicity tests were evaluated according to the method put forward by Klimisch et al. (1997), and the reliable data designated as Code 1 and Code 2 were used. In order to satisfy the test species requirement for deriving PNECs by using the SSD method, the toxicity dataset was supplemented by QSAR prediction if there were no enough experimental data ($n < 5$). The predicted chronic values of studied chemicals on aquatic species (fish, mysids, and algae) were obtained by ECOSAR, Ver 1.11 software, shown in Table A4.

2.3 Aquatic and sediment PNEC calculations

Aquatic chronic toxicity data were fitted by using log-normal statistical distributions. Goodness-of-fit was evaluated by the Anderson-Darling test with a statistical significance level of 0.01 by ETX 2.0 software. The experimental toxicity data mentioned above were preferentially used compared with QSAR data. Overall, the amount of dataset for fitting SSD curves needs to be greater than 5. Subsequently, hazard concentrations (HC_5 s), the concentration at which 5% of the target species in the aquatic system would be affected, were derived by fitting the SSD curves and using the calculation shown as

$$\log_{10}HC_5 = X_m - S_m \times K_m, \quad (1)$$

where m is the number of species, X_m is the logarithm mean of chronic toxicities for m species, K_m represents the one-side extrapolation constant for log-normal distribution (RIVM, 2001), and S_m is the standard deviation of logarithm chronic toxicities for m

species. Then the obtained median HC_{5s} were used to derive PNECs in seawater ($PNEC_{water}$) (Wang et al., 2016).

The equilibrium partitioning method can be used for compounds with logarithm values of the octanol/water partition coefficient (K_{OW}) greater than 3, in view of the absence of ecotoxicological data for sediment dwelling organisms (European Commission, 2003).

Then PNECs in marine sediment ($PNEC_{sed}$) were calculated as follows (European Commission, 2003):

$$PNEC_{sed} = \frac{K_{sed-water}}{RHO_{sed}} \times PNEC_{water} \times 1\,000, \quad (2)$$

$$K_{sed-water} = F_{water,sed} + F_{solid,sed} \cdot \frac{K_{p,sed}}{1\,000} \cdot RHO_{solid}, \quad (3)$$

$$RHO_{sed} = F_{solid,sed} \cdot RHO_{solid} + F_{water,sed} \cdot RHO_{water}, \quad (4)$$

$$K_{p,sed} = F_{oc,sed} \cdot K_{oc}, \quad (5)$$

where $K_{sed-water}$ is the sediment–water partitioning coefficient; RHO_{sed} is the bulk density of wet sediment (kg/m^3); $PNEC_{water}$ is the PNEC of chemicals in seawater (mg/L); $PNEC_{sed}$ is the PNEC of chemicals in sediment (mg/kg); $F_{water,sed}$ is volume fraction of water in sediment ($0.8, V_{water}/V_{sed}$); $F_{solid,sed}$ is volume fraction of solids in sediment ($0.2, V_{solid}/V_{sed}$); $K_{p,sed}$ is the partition coefficient of solid–water in sediment (L/kg); RHO_{solid} is density of the

solid phase ($2\,500\,kg/m^3$); RHO_{water} is density of the water phase ($1\,000\,kg/m^3$); $F_{oc,sed}$ is weight fraction organic carbon sediment solids ($0.05, m_{oc}/m_{solid}$); K_{oc} is organic carbon–water partition coefficient (L/kg).

2.4 Sample collection, extraction and analysis

On 16 July, 2010, an explosion of a fuel pipeline in the south-west of the Dayao Bay of Dalian resulted in the release of over 1 500 t of crude oil leakage (Zhang et al., 2013). The investigation region in this study is located at the Dalian Bay (Fig. 1). The surface seawater (about 0.5 m below the surface) samples (5 L for each sample) were collected using pre-cleaned glass bottles with polytetrafluoroethylene screw caps in July 2015. Samples were filtered under vacuum conditions through a Whatman GF/F filter ($0.7\,\mu m$, glass fiber) and were frozen at $-20^\circ C$ before treatment. Surface sediment (about 5 cm below the surface) samples were collected with a box corer, packed into pre-clean aluminum foils and were stored at $-20^\circ C$ until analysis.

The seawater and sediment samples were extracted with dichloromethane (DCM) for three times by liquid–liquid extraction and Soxhlet extraction, respectively (Wang et al., 2014a; Hong et al., 2016). Specifically, the water samples (1 L for each sample) were extracted with 50 mL of DCM in separatory funnels with agitation followed by a 1 h setting. The extraction process was repeated twice and the extracted solutions were combined. The extracted samples were then filtered through a glass wool and a layer of anhydrous sodium sulfate and concentrated with a rotary evaporator to 1 mL. Then the solvent for the eluates were ex-

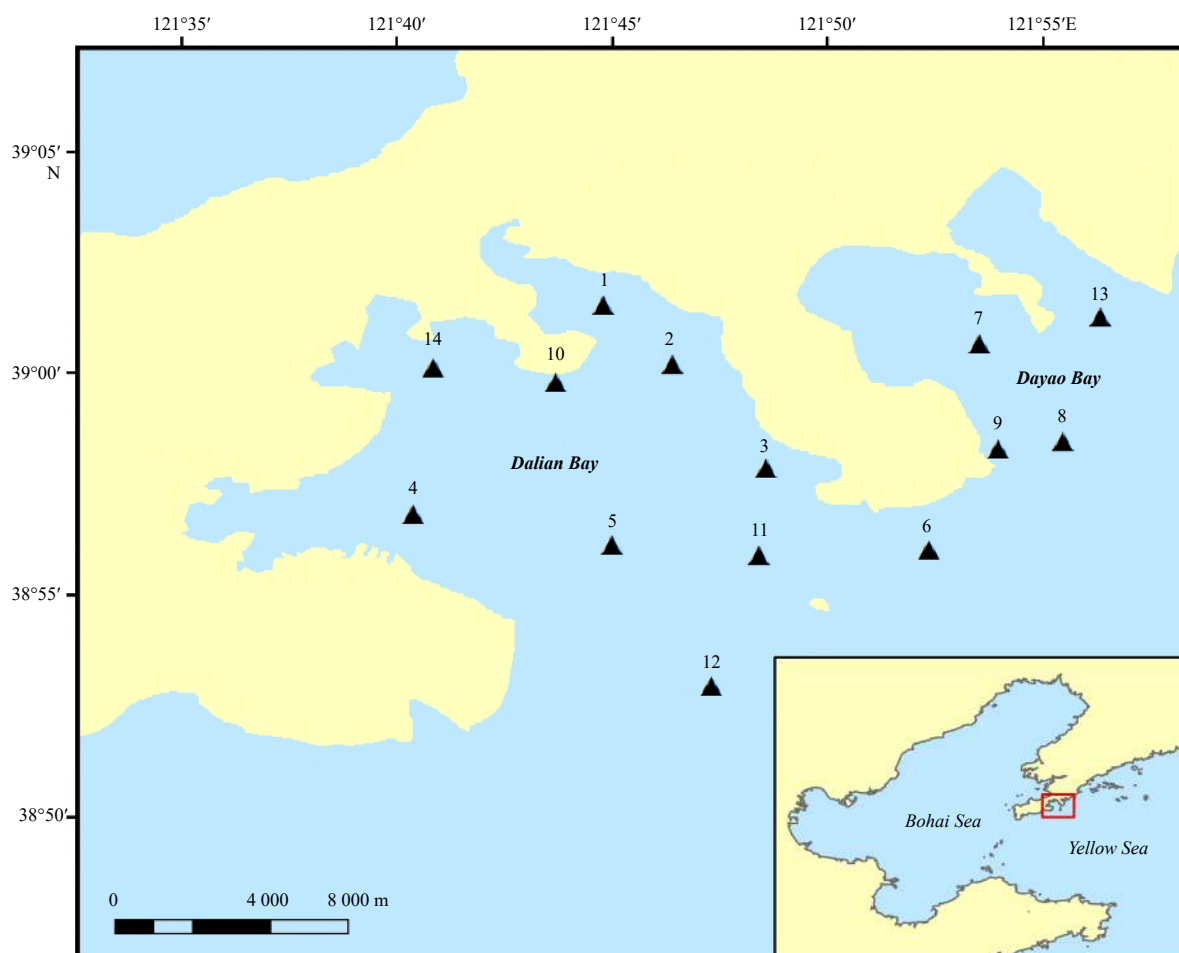


Fig. 1. Sampling sites in the Dalian Bay for seawater and sediment samples.

changed to hexane. A total of 5 g sediment and 2 g anhydrous sodium sulfate were mixed into an extraction thimble followed by Soxhlet extraction for 20 h with 100 mL mixed solvent (DCM/hexane, 1:1, v/v). The extracts were then transferred into rotary evaporator to 1 mL. The extracts were purified on a 4 g activated silica, 6 g neutral alumina and 1 g anhydrous Na_2SO_4 column with 80 mL of hexane/DCM (1:1) mixture. The eluates were further concentrated and the solvent were exchanged to hexane.

A known internal standard (p-terphenyl-d14) was added followed by GC-MS analysis (Agilent 6890N gas chromatograph-5975B mass spectrometry). A DB-5 (30 m×0.25 mm, 0.25 μm) GC capillary column was equipped for the determination of parent- and alkyl-PAHs. Helium was used as the carrier gas at a constant flow rate of 1.0 mL/min. A column temperature program was used as follows: an initial temperature of 50°C was held for 2 min followed by ramping to 300°C at 6°C/min with a final hold time of 16 min. The injection volume was 1.0 μL by splitless mode. The injector temperature was set to 290°C. Recoveries of test chemicals ranged from 81% to 115% ($n=6$). Surrogate standards including naphthalene-d8, acenaphthene-d10, phenanthrene-d10 and perylene-d12 were added to all samples prior to extraction. The limit of detection (LOD) was determined based on the signal-to-noise ratio of 3. The LODs for parent- and alkyl-PAHs in seawater and sediment were 0.2–1.0 ng/L and 0.1–1.0 ng/g, respectively.

2.5 Risk characterization

To better understand the site-specific risk, RQ was used to characterize potential risks of the studied chemicals to aquatic organisms both in water and sediment. RQ in this study is expressed as follows:

$$\text{RQ} = \frac{\text{EEC}}{\text{PNEC}}, \quad (6)$$

where EEC represents the environmental exposure concentration ($\mu\text{g/L}$ or ng/g); PNEC is $\text{PNEC}_{\text{water}}$ or PNEC_{sed} . Chemicals with $\text{RQ} \geq 0.3$ may pose a potential risk to the ecosystem (Parkhurst, 1996).

3 Results and discussion

3.1 Derivation of PNECs in seawater and marine sediment for the ten studied PAHs

SSD curves of the ten studied PAHs were fitted using com-

bined experimental and predicted chronic toxicity data (Fig. 2). The sensitivity variability for BaP, 2-mAnt, and Ret based on experimental toxicity data covered 5–7 orders of magnitude. The same species with the same effect responded differently to different PAHs. For instance, *Artemia salina* had the least and moderate sensitivity to BaP and 3-mPhe, respectively, while using mortality as the biological effect. Large differences in their sensitivity for the aquatic species may be explained by different response and their uptake/depuration rates in water (Wang et al., 2014a; Nagai and Taya, 2015).

Due to the limitation of the availability of standard emerging chemicals, for example, alkyl-PAHs in this study, little toxicity data especially chronic data are available (Martin et al., 2014; Lin et al., 2015; Sørensen et al., 2019); this resulted in difficulties in assessing their ecological risks. The computational toxicological techniques including QSAR models and interspecies correlation estimations have recently been recommended to derive PNECs or water quality criteria (RIVM, 2001; Feng et al., 2013). In our previous study, the QSAR method was used to predict the chronic toxicities of 16 PAHs to fish, aquatic invertebrates (daphnids and mysids), and algae. Good agreement for aquatic PNECs of the eight studied PAHs based on predicted and experimental chronic toxicity data was observed ($R^2=0.746$) (Wang et al., 2016). Moreover, QSAR tools were used to supplement the toxicity data of emerging chemicals such as methyl-triclosan and to derive their PNECs (Carlsen, 2006; Rüdell et al., 2013). In this study, ECOSAR software was used to obtain the predictive chronic aquatic toxicities of the ten studied PAHs, as shown in Table A4.

In this study, PNECs for individual PAHs in seawater were derived ($\text{PNEC}_{\text{water}}$) by employing the experimental and predicted chronic toxicity data, ranging from 0.012 $\mu\text{g/L}$ to 2.79 $\mu\text{g/L}$ (Table 1). For BaP, its $\text{PNEC}_{\text{water}}$ was 0.012 $\mu\text{g/L}$, close to that in our previous study (Wang et al., 2014a), in which it was 0.011 $\mu\text{g/L}$. While only using the QSAR data, 0.073 $\mu\text{g/L}$ was derived for the $\text{PNEC}_{\text{water}}$ of BaP (Wang et al., 2016). The $\text{PNEC}_{\text{water}}$ for Ret was 0.02 $\mu\text{g/L}$ with the use of combined experimental and QSAR data, slightly lower than that based on QSAR data, 0.07 $\mu\text{g/L}$. Overall, $\text{PNEC}_{\text{water}}$ s using the QSAR data as input were comparable with those based on experimental data or combined ones (Table 1). SSDs have been used to develop PNECs or HC_5 s, which typically require large datasets of measured toxicity values. However, there has been a considerable debate regarding the minimum requirements for establishing protective concentrations. Thus, further studies regarding how many taxa are needed to derive PNECs

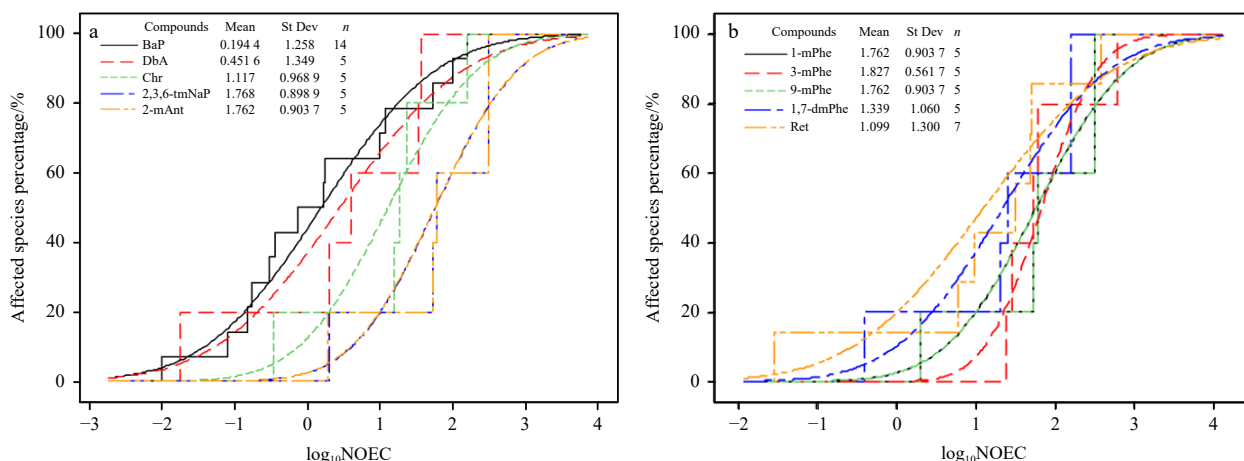


Fig. 2. Species sensitivity distribution of the ten studied PAHs based on experimental toxicity data and quantitative structure–activity relationship data. NOEC represents no observed effect concentrations ($\mu\text{g/L}$). Abbreviations of chemicals are shown in Section II.

Table 1. The derived seawater PNECs ($\text{PNEC}_{\text{water}}$) for ten PAHs based on combined experimental and quantitative structure-activity relationship (QSAR) data

Relationship (QoM) data							
	BaP		DbA	Chr	2,3,6-tmNaP	2-mAnt	
PNEC _{water} /μg·L ⁻¹	0.012 ¹⁾	0.073 ^{2), 3)}	0.029 ²⁾	0.49 ²⁾	2.79 ²⁾	2.7 ²⁾	1.43 ⁴⁾
<i>n</i>	14	5	5	5	5	5	5
	3-mPhe		1-mPhe	9-mPhe	1,7-dmPhe	Ret	
PNEC _{water} /μg·L ⁻¹	2.7 ²⁾	1.98 ⁴⁾	2.7 ²⁾	2.7 ²⁾	0.60 ²⁾	0.02 ²⁾	0.07 ⁴⁾
<i>n</i>	5	5	5	5	5	5	7

Note: 1) Based on only experimental data; 2) based on only QSAR data; 3) data from Wang et al. (2016); 4) based on both experimental and QSAR data. $\text{PNEC}_{\text{water}}$ values in bold were used to derive PNEC_{sed} . Abbreviations of chemicals are shown in Section 2.

and QSAR model application domain are needed.

Sediment PNECs (PNEC_{sed}) for the ten studied PAHs were calculated using $\text{PNEC}_{\text{water}}$ s based on experimental toxicity data as priority, ranging from 48.2 ng/g to 1 337 ng/g (dry weight) (Table 2). As for marine sediment, a biological effects database for sediments (BEDS) was generally employed to derive sediment quality guidelines (SQGs), specifically, threshold effects level (TEL), probable effects level (PEL), effects range-low (ERL), and effects range-median (ERM) (Long et al., 1995; Macdonald et al., 1996). TELs are chemical concentrations in sediment below which adverse biological effects rarely occur. In contrast, PELs are concentrations above which adverse biological effects frequently occur. Both TELs and PELs were considered to provide a higher and lower level of protection for aquatic organisms, respectively (Macdonald et al., 1996).

As shown in Table 3, the PNEC_{sed} for BaP (48.2 ng/g) was in the same order of magnitude when compared with its TEL (88.8 ng/g). In this study, the estimated HC_5 was adopted to calculate the $\text{PNEC}_{\text{water}}$. In comparison, its incidence of effects within the minimal range ($\leq \text{TEL}$) was 8.5%. This revealed that the derived PNEC_{sed} s using equilibrium partitioning were approximate with SQGs protecting organisms in sediment. However, the PNEC_{sed} s for DbA and Chr are close to their PELs instead of TELs, which may be caused by a toxicity underestimation of QSAR models. Nevertheless, their sediment PNECs could still be used to preliminarily assess ecological risks in relatively high PAH contaminated areas. For instance, the maximum concentrations for DbA in the Dalian coastal sediment reached 293 ng/g higher than PNEC_{sed} for DbA (266.9 ng/g) (Hong et al., 2016). In general, derived PNECs in sediment employing equilibrium partitioning method and QSAR models in this study were comparable to those obtained by the classical method, BEDS. Therefore, QSARs could be a beneficial supplement especially for emerging chemicals with limited toxicity data and further for their ecological risk assessments.

Additionally, interspecies correlation estimation (ICE) statistical models have been applied for PNEC derivation as an attractive additional approach (Dyer et al., 2006; Bejarano and Barron, 2016). Based on acute toxicity values from surrogate species, the ICE model can predict the toxicity of multiple species (Qi et al., 2011). Generally, there are three differences between ICEs and QSARs. First, ICEs are based on single known measured toxicity values to estimate other toxicity values. In comparison, QSARs predict toxicity values based on structural information of chemicals. Second, the amount of toxicity data acquired by ICE models is much higher than QSAR models in general. Third, QSAR models can predict both acute and chronic toxicity values. Therefore, we could select appropriated models in PNECs derivation of chemicals under specific circumstance.

There are no scientific methods to assess which PNECs derived from different data sources are more appropriate. Normally, experimental data especially with the consideration of indigenous species are preferred by using SSDs. If experimental data are not enough to develop SSD models, ICE or QSAR models could be beneficial to supplement datasets to derive PNECs (RIVM, 2001). Therefore, we recommend $\text{PNEC}_{\text{water}}$ s in bold in Table 1 and PNEC_{sed} s in Table 2 to be used in future research for the purpose of ecological risk assessments.

3.2 Exposure concentrations of ten PAHs in surface waters and sediments from the Dalian Bay

To preliminarily assess ecological risks for typical parent and alkyl-PAHs, we collected surface water and sediment samples near the oil accident area (Fig. 1) in this study. The statistical data of the ten individual PAH concentrations in seawaters and sediments of the Dalian Bay are presented in Fig. 3. Their average concentrations in seawaters and sediments were in the range of 0.87–8.48 ng/L and 0.89–13.53 ng/g, respectively (Tables A5 and A6). Among them, DbA and 3-mPhe were the least and most abundant compounds, respectively. Overall, the concentrations

Table 2. The derived sediment PNECs (PNEC_{sed}) for ten PAHs based on seawater PNECs and equilibrium partitioning method

	BaP	DbA	Chr	2,3,6-tmNaP	2-mAnt
$\text{PNEC}_{\text{sed}}/\text{ng}\cdot\text{g}^{-1}$	48.2	266.9	1 042	684.2	600
	3-mPhe	1-mPhe	9-mPhe	1,7-dmPhe	Ret
$\text{PNEC}_{\text{sed}}/\text{ng}\cdot\text{g}^{-1}$	629	1 337	914.6	61.25	436

Table 3. Comparison of sediment PNECs (PNEC_{sed}) for several studied PAHs with sediment quality guidelines

	This study	Sediment quality guidelines (Macdonald et al., 1996)				Sediment quality guidelines (Long et al., 1995)			
	$\text{PNEC}_{\text{sed}}/\text{ng}\cdot\text{g}^{-1}$	TEL /ng·g ⁻¹	Effects/% ($\leq \text{TEL}$)	PEL /ng·g ⁻¹	Effects/% ($\geq \text{PEL}$)	ERL	Effects/% ($< \text{ERL}$)	ERM	Effects/% ($\geq \text{ERM}$)
BaP	48.2	88.8	8.5	763	70.9	430	10.3	1 600	80
DbA	266.9	6.22	15.8	135	65.1	63.4	11.5	260	66.7
Chr	1 042	108	9.2	846	72.4	384	19.0	2 800	88.5

Note: TEL represents threshold effects level, PEL probable effect levels, ERL effect range-low, and ERM effects range-median.

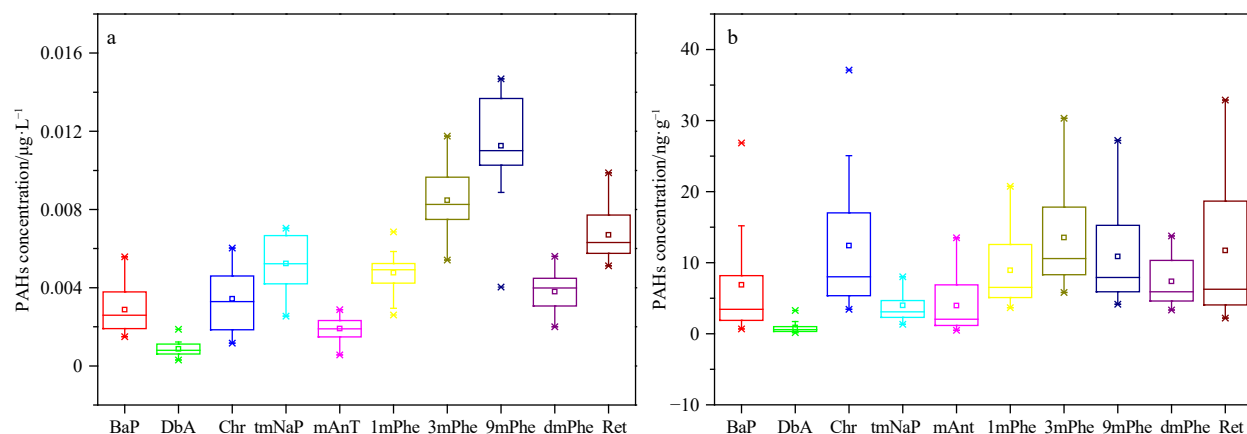


Fig. 3. Boxplot of exposure concentrations for ten PAHs in surface seawater (a) and sediment (b) of the Dalian Bay. Abbreviations of chemicals are shown in Section 2.

of alkyl-PAHs were at the same order or slightly higher than those of parent PAHs.

In contrast, three parent PAH concentrations in seawaters from the Dalian Bay were close to those in the northeast coastal area in China (Wang et al., 2011). However, they were slightly lower than those in the Liaodong Bay, but slightly higher than those in the Yangpu Bay, China and the Singapore's coastal waters (Lim et al., 2007; Li et al., 2015; Wang et al., 2016). Their levels in sediments were 1–2 orders of magnitude lower than that reported in the similar area (Hong et al., 2016). This might be caused by two reasons: their sampling sites covered a wider area than ours, and their sampling time was one month later after the oil accident. In general, parent PAH concentrations in this study were at a medium level on the global scale.

The total concentration of alkylated phenanthrenes including 1-, 3-, 9-methyl phenanthrene in this study was 78.28 ng/g, higher than the reported C1-phenanthrene (27.2 ng/g in winter and 58.6 ng/g in summer) in the Dalian coastal sediments and close to that (78.9 ng/g) in the southwest Caspian Sea (Varnosfaderany et al., 2015; Hong et al., 2016). There are no sufficient studies for us to compare with other studies because most studies reported alkylated PAH concentrations in the form of mixtures. In addition, the degree of alkylation increased rapidly with higher proportions for C3 and C4 PAHs after weathering (Lee et al., 2015).

3.3 Ecological risks of PAHs in surface seawaters and surface sediments from the Dalian Bay

Risk quotients of ten PAHs in seawaters and sediments of the Dalian Bay are listed in Tables A7 and A8. Among them, ecological risks in surface seawaters and surface sediments for BaP existed with $0.3 < RQs < 0.6$, at nearly one-third of the studied sampling sites. For other PAHs, they were at lower risks with RQs less than 0.3. In general, the remaining adverse impact of crude oil on aquatic organisms was limited. Otherwise, for biota in ecosystems, it is exposed to a complex mixture of chemicals, not the least considering the studied chemicals. Thus, the mixture toxicity caused by co-existence of PAHs and other chemicals should also pose potential risks to marine organisms.

In this study, ten PAHs in surface waters and sediments showed nearly no ecological risks. The present result is similar with that of Hong et al. (2016) obtained in sediment from coastal area of Dalian using the ERM/ERL and TEL/PEL method. However, only thresholds for C1-phenanthrene instead of their

individuals are available (Varnosfaderany et al., 2015; Hong et al., 2016). Research indicated that alkyl-PAHs, especially alkyl-phenanthrenes including 1,7-dmPhe, 1-mPhe and Ret were more toxic to early life stages of freshwater fish such as medaka (*Oryzias latipes*) and rainbow trout (*Oncorhynchus mykiss*), than unsubstituted phenanthrene (Billiard et al., 1999; Turcotte et al., 2011). Potencies of aryl hydrocarbon receptor-mediated processes were also greater when a chrysene group was substituted by alkylation (Lee et al., 2015). Due to their high detection frequencies and toxicities of alkyl-PAHs compared with parent PAHs, it would be helpful if we performed more research on their toxicities and risk assessment in the future.

To date, there have been a variety of studies on ecological risks of 16 priority PAHs in China (Meng et al., 2019). However, PNECs in seawater especially for alkyl-PAHs have not been reported yet. In this study, derived PNECs for ten parent- and alkyl-PAHs in seawater and sediment have a broad application in ecological risk assessments across China because we preferred to adopt marine organisms living in Chinese coastal waters. The local area, Dalian Bay, where there was an oil-spilled accident in 2010, was chosen as a site to assess the ecological risks for ten individual parent- and alkyl-PAHs. The developed method in this study could be beneficial for ecological risk assessments of emerging contaminants with less toxicity data across Chinese coastal areas.

It would be so helpful if we could develop more QSAR and ICE models to be further used in the PNECs or environmental quality criteria derivation. A mathematical model, based on QSAR and SSD was developed and then was used to predict water quality criteria by use of acute toxicities of six metals to eight marine species and accessory environmental conditions (Mu et al., 2018). Meanwhile, more validation on model data by use of experimental data species are needed in the future. Additionally, a certain amount of qualified experimental toxicity data especially based on indigenous are preferred for both thresholds and environmental quality criteria derivation in different countries or areas with current geographical and climatic conditions. Therefore, it is of great significance to perform more acute and chronic toxicity tests in high good quality. Now, the standard toxicity test methods are lack in China, especially in marine environment, so toxicity experiments for indigenous species are highly needed.

3.4 Uncertainty analysis

Uncertainty in ecological risk assessments is inevitable and its analysis can deliver a more comprehensive risk assessment (Jin

et al., 2014; Obiakor et al., 2017). In this study, sources of uncertainty included variability in exposure concentrations, experimental toxicity data, and use of QSAR, SSD and log-normal statistics. For exposure assessment, variability in measured PAH concentrations might be caused by locations of the sampling sites, errors in sampling and chemical analysis, inputs of sewage and atmospheric deposition. The uncertainty could be lowered by sampling more at larger spatial and temporal scales. For effect assessment, toxicity data amount, ecological relevance affected by the inclusive nontraditional endpoints and the use of QSARs are important factors. These factors may influence the accuracy of derived PNECs and subsequent risk assessment results. We should be cautious to use estimated aquatic toxicity values by QSARs to derive PNECs. In this study, experimental toxicity data for PNEC derivation were preferred to use compared with QSAR data requirement. The octanol/water partition coefficient ($\log_{10}K_{OW}$) cut-off for QSAR predicting chronic effects in this study is equal to 8.0. Actually, all the selected chemicals have $\log_{10}K_{OW}$ values less than 8.0 in this study, meeting the criteria of QSAR application domain. The uncertainty could be reduced by performing more qualified chronic toxicity tests to rich the measured toxicity dataset instead of using QSAR data. Moreover, the QSAR models we chose here are routine, with less consideration of the toxic mode of action. Further toxicological studies for chemicals based on adverse outcome pathways were also encouraged in ecological risk assessments (Wang et al., 2018). Additional limitation for the QSAR models were used is the low amount of the dataset. In general, five aquatic toxicity data obtained by this method is less, which would increase the variability of derived PNECs by SSD method. Otherwise, the statistical extrapolation method, limited by the presumption, would also introduce a certain degree of uncertainty to protect the whole aquatic ecosystems. Due to the limited number of the studied chemicals ($n=10$), combined ecological risks were not assessed in this study. However, it is important to address combined ecological risks of PAHs and alkyl-PAHs in the future research in view of their possible additive effects caused by their co-existence in the environments.

4 Conclusions

The PNECs of three parent-PAHs and seven alkyl-PAHs in a marine environment were derived by a combination of SSDs and QSARs. Their PNECs for individual (alkyl-)PAHs derived in seawater and sediment based on experimental and QSAR data were in the range of 0.012–2.79 $\mu\text{g/L}$ and 48.2–1 337 ng/g (dry weight), respectively. The ecological risks for individual PAHs in surface seawaters and marine sediments from the Dalian Bay near the oil accident region were low, except for benzo(a)pyrene. More research on toxicities and ecological/health risk assessments for parent and alkyl-PAHs is needed for scientists in the future.

References

- Aldenberg T, Rorije E. 2013. Species sensitivity distribution estimation from uncertain (QSAR-based) effects data. *Alternatives to Laboratory Animals*, 41(1): 19–31, doi: [10.1177/026119291304100105](https://doi.org/10.1177/026119291304100105)
- Baldwin A K, Corsi S R, Lutz M A, et al. 2017. Primary sources and toxicity of PAHs in Milwaukee-area streambed sediment. *Environmental Toxicology and Chemistry*, 36(6): 1622–1635, doi: [10.1002/etc.3694](https://doi.org/10.1002/etc.3694)
- Bejarano A C, Barron M G. 2016. Aqueous and tissue residue-based interspecies correlation estimation models provide conservative hazard estimates for aromatic compounds. *Environmental Toxicology and Chemistry*, 35(1): 56–64, doi: [10.1002/etc.3164](https://doi.org/10.1002/etc.3164)
- Billiard S M, Querbach K, Hodson P V. 1999. Toxicity of retene to early life stages of two freshwater fish species. *Environmental Toxicology and Chemistry*, 18(9): 2070–2077, doi: [10.1002/etc.5620180927](https://doi.org/10.1002/etc.5620180927)
- Brock T C M, Belgers J D M, Boerwinkel M C, et al. 2018. Toxicity of sediment-bound lufenuron to benthic arthropods in laboratory bioassays. *Aquatic Toxicology*, 198: 118–128, doi: [10.1016/j.aquatox.2018.03.005](https://doi.org/10.1016/j.aquatox.2018.03.005)
- Carlsen L. 2006. A combined QSAR and partial order ranking approach to risk assessment. *SAR and QSAR in Environmental Research*, 17(2): 133–146, doi: [10.1080/10659360600636196](https://doi.org/10.1080/10659360600636196)
- del Signore A, Hendriks A J, Lenders H J, et al. 2016. Development and application of the SSD approach in scientific case studies for ecological risk assessment. *Environmental Toxicology and Chemistry*, 35(9): 2149–2161
- Dyer S D, Versteeg D J, Belanger S E, et al. 2016. Interspecies correlation estimates predict protective environmental concentrations. *Environmental Science & Technology*, 40(9): 3102–3111
- Engraff M, Solere C, Smith K E C, et al. 2011. Aquatic toxicity of PAHs and PAH mixtures at saturation to benthic amphipods: linking toxic effects to chemical activity. *Aquatic Toxicology*, 102(3–4): 142–149, doi: [10.1016/j.aquatox.2011.01.009](https://doi.org/10.1016/j.aquatox.2011.01.009)
- European Commission. 2003. Technical guidance document in support of commission directive 93/67/EEC on risk assessment for new notified substances and commission regulation (EC) No. 1488/94 on risk assessment for existing substance: II. Luxembourg: Office for the Official Publications of the European Communities
- Feng Chengliang, Wu Fengchang, Mu Yunsong, et al. 2013. Interspecies correlation estimation-applications in water quality criteria and ecological risk assessment. *Environmental Science & Technology*, 47(20): 11382–11383
- Ghosh S, Ojha P K, Carnesecchi E, et al. 2020. Exploring QSAR modeling of toxicity of chemicals on earthworm. *Ecotoxicology and Environmental Safety*, 190: 110067, doi: [10.1016/j.ecoenv.2019.110067](https://doi.org/10.1016/j.ecoenv.2019.110067)
- Hong Wenjun, Jia Hongliang, Li Yifan, et al. 2016. Polycyclic aromatic hydrocarbons (PAHs) and alkyl-PAHs in the coastal seawater, surface sediment and oyster from Dalian, Northeast China. *Ecotoxicology and Environmental Safety*, 128: 11–20, doi: [10.1016/j.ecoenv.2016.02.003](https://doi.org/10.1016/j.ecoenv.2016.02.003)
- International Organization for Standardization. 2006. EN ISO 10253: 2006 Water Quality-Marine Algal Growth Inhibition Test with *Skeletonema costatum* and *Phaeodactylum tricornutum*. London, UK: European Committee for Standardization Comité Européen de Normalisation Europäisches Komitee für Normung
- Jin Xiaowei, Wang Yeyao, Jin Wei, et al. 2014. Ecological risk of nonylphenol in China surface waters based on reproductive fitness. *Environmental Science & Technology*, 48(2): 1256–1262
- Kang H J, Lee S Y, Roh J Y, et al. 2014. Prediction of ecotoxicity of heavy crude oil: contribution of measured components. *Environmental Science & Technology*, 48(5): 2962–2970
- Klimisch H J, Andreae M, Tillmann U. 1997. A systematic approach for evaluating the quality of experimental toxicological and ecotoxicological data. *Regulatory Toxicology and Pharmacology*, 25(1): 1–5, doi: [10.1006/rtp.1996.1076](https://doi.org/10.1006/rtp.1996.1076)
- Lee S, Shin W H, Hong S, et al. 2015. Measured and predicted affinities of binding and relative potencies to activate the AhR of PAHs and their alkylated analogues. *Chemosphere*, 139: 23–29, doi: [10.1016/j.chemosphere.2015.05.033](https://doi.org/10.1016/j.chemosphere.2015.05.033)
- Li Ping, Cao Jia, Diao Xiaoping, et al. 2015. Spatial distribution, sources and ecological risk assessment of polycyclic aromatic hydrocarbons in surface seawater from Yangpu Bay, China. *Marine Pollution Bulletin*, 93(1–2): 53–60, doi: [10.1016/j.marpolbul.2015.02.015](https://doi.org/10.1016/j.marpolbul.2015.02.015)
- Li Jiafu, Dong Han, Xu Xiang, et al. 2016. Prediction of the bioaccumulation of PAHs in surface sediments of Bohai Sea, China and quantitative assessment of the related toxicity and health risk to humans. *Marine Pollution Bulletin*, 104(1–2): 92–100, doi: [10.1016/j.marpolbul.2016.02.005](https://doi.org/10.1016/j.marpolbul.2016.02.005)
- Li Ye, Liu Xinran, Liu Min, et al. 2017. Distribution, sources and eco-

- logical risk of polycyclic aromatic hydrocarbons in the estuarine-coastal sediments in the East China Sea. *Environmental Science: Processes & Impacts*, 19(4): 561–569
- Lim L, Wurl O, Karuppiyah S, et al. 2007. Atmospheric wet deposition of PAHs to the sea-surface microlayer. *Marine Pollution Bulletin*, 54(8): 1212–1219, doi: [10.1016/j.marpolbul.2007.03.023](https://doi.org/10.1016/j.marpolbul.2007.03.023)
- Lin Hongkang, Morandi G D, Brown R S, et al. 2015. Quantitative structure-activity relationships for chronic toxicity of alkyl-chrysenes and alkyl-benz. *Aquatic Toxicology*, 159: 109–118, doi: [10.1016/j.aquatox.2014.11.027](https://doi.org/10.1016/j.aquatox.2014.11.027)
- Liu Xianjie, Jia Hongliang, Wang Luo, et al. 2013. Characterization of polycyclic aromatic hydrocarbons in concurrently monitored surface seawater and sediment along Dalian coast after oil spill. *Ecotoxicology and Environmental Safety*, 90: 151–156, doi: [10.1016/j.ecoenv.2012.12.024](https://doi.org/10.1016/j.ecoenv.2012.12.024)
- Long E R, Macdonald D D, Smith S L, et al. 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environmental Management*, 19(1): 81–97, doi: [10.1007/BF02472006](https://doi.org/10.1007/BF02472006)
- Macdonald D D, Carr R S, Calder F D, et al. 1996. Development and evaluation of sediment quality guidelines for Florida coastal waters. *Ecotoxicology*, 5(4): 253–278, doi: [10.1007/BF00118995](https://doi.org/10.1007/BF00118995)
- Martin J D, Adams J, Hollebone B, et al. 2014. Chronic toxicity of heavy fuel oils to fish embryos using multiple exposure scenarios. *Environmental Toxicology and Chemistry*, 33(3): 677–687, doi: [10.1002/etc.2486](https://doi.org/10.1002/etc.2486)
- Meng Yuan, Liu Xiaohui, Lu Shaoyong, et al. 2019. A review on occurrence and risk of polycyclic aromatic hydrocarbons (PAHs) in lakes of China. *Science of the Total Environment*, 651: 2497–2506, doi: [10.1016/j.scitotenv.2018.10.162](https://doi.org/10.1016/j.scitotenv.2018.10.162)
- Mu Jingli, Wang Juying, Jin Fei, et al. 2014. Comparative embryotoxicity of phenanthrene and alkyl-phenanthrene to marine medaka (*Oryzias latipes*). *Marine Pollution Bulletin*, 85(2): 505–515, doi: [10.1016/j.marpolbul.2014.01.040](https://doi.org/10.1016/j.marpolbul.2014.01.040)
- Mu Yunsong, Wang Zhen, Wu Fengchang, et al. 2018. Model for predicting toxicities of metals and metalloids in coastal marine environments worldwide. *Environmental Science & Technology*, 52(7): 4199–4206
- Nagai T, Taya K. 2015. Estimation of herbicide species sensitivity distribution using single-species algal toxicity data and information on the mode of action. *Environmental Toxicology and Chemistry*, 34(3): 677–684, doi: [10.1002/etc.2828](https://doi.org/10.1002/etc.2828)
- Obiakor M O, Tighe M, Wang Z, et al. 2017. The relative sensitivity of freshwater species to antimony (III): implications for water quality guidelines and ecological risk assessments. *Environmental Science and Pollution Research*, 24(32): 25276–25290, doi: [10.1007/s11356-017-0168-y](https://doi.org/10.1007/s11356-017-0168-y)
- Parkhurst B R. 1996. *Aquatic Ecological Risk Assessment: A Multi-Tiered Approach*. Alexandria, VA, USA: Water Environment Research Foundation
- Pie H V, Heyes A, Mitchelmore C L. 2015. Investigating the use of oil platform marine fouling invertebrates as monitors of oil exposure in the northern Gulf of Mexico. *Science of the Total Environment*, 508: 553–565, doi: [10.1016/j.scitotenv.2014.11.050](https://doi.org/10.1016/j.scitotenv.2014.11.050)
- Qi Ping, Wang Ying, Mu Jingli, et al. 2011. Aquatic predicted no-effect-concentration derivation for perfluorooctane sulfonic acid. *Environmental Toxicology and Chemistry*, 30(4): 836–842, doi: [10.1002/etc.460](https://doi.org/10.1002/etc.460)
- Rijksinstituut voor Volksgezondheid en Milieu. 2001. Guidance document on deriving environmental risk limits. Bilthoven, Netherlands: National Institute of Public Health and the Environment
- Rorije E, Aldenberg T, Peijnenburg W. 2013. Read-across estimates of aquatic toxicity for selected fragrances. *Alternatives to Laboratory Animals*, 41(1): 77–90, doi: [10.1177/026119291304100109](https://doi.org/10.1177/026119291304100109)
- Rüdel H, Böhmer W, Müller M, et al. 2013. Retrospective study of triclosan and methyl-triclosan residues in fish and suspended particulate matter: results from the German Environmental Specimen Bank. *Chemosphere*, 91(11): 1517–1524, doi: [10.1016/j.chemosphere.2012.12.030](https://doi.org/10.1016/j.chemosphere.2012.12.030)
- Sarabia R, del Ramo J, Varo I, et al. 2002. Comparing the acute response to cadmium toxicity of nauplii from different populations of *Artemia*. *Environmental Toxicology and Chemistry*, 21(2): 437–444, doi: [10.1002/etc.5620210229](https://doi.org/10.1002/etc.5620210229)
- Sørensen L, Hansen B H, Farkas J, et al. 2019. Accumulation and toxicity of monoaromatic petroleum hydrocarbons in early life stages of cod and haddock. *Environmental Pollution*, 251: 212–220, doi: [10.1016/j.envpol.2019.04.126](https://doi.org/10.1016/j.envpol.2019.04.126)
- Sun Hongwei, Giesy J P, Jin Xiaowei, et al. 2017. Tiered probabilistic assessment of organohalogen compounds in the Han River and Danjiangkou Reservoir, central China. *Science of the Total Environment*, 586: 163–173, doi: [10.1016/j.scitotenv.2017.01.194](https://doi.org/10.1016/j.scitotenv.2017.01.194)
- Tong Yifan, Chen Li, Liu Yan, et al. 2019. Distribution, sources and ecological risk assessment of PAHs in surface seawater from coastal Bohai Bay, China. *Marine Pollution Bulletin*, 142: 520–524, doi: [10.1016/j.marpolbul.2019.04.004](https://doi.org/10.1016/j.marpolbul.2019.04.004)
- Turcotte D, Akhtar P, Bowerman M, et al. 2011. Measuring the toxicity of alkyl-phenanthrenes to early life stages of medaka (*Oryzias latipes*) using partition-controlled delivery. *Environmental Toxicology and Chemistry*, 30(2): 487–495, doi: [10.1002/etc.404](https://doi.org/10.1002/etc.404)
- Varnosfaderany M N, Bakhtiari A R, Gu Zhaoyan, et al. 2015. Distribution and characteristic of PAHs in sediments from the southwest Caspian Sea, Guilan Province, Iran. *Water Science & Technology*, 71(11): 1587–1596
- Wang Degao, Alaei M, Byer J, et al. 2011. Fugacity approach to evaluate the sediment-water diffusion of polycyclic aromatic hydrocarbons. *Journal of Environmental Monitoring*, 13(6): 1589–1596, doi: [10.1039/c0em00731e](https://doi.org/10.1039/c0em00731e)
- Wang Ying, Chen Jingwen, Li Fei, et al. 2009. Modeling photoinduced toxicity of PAHs based on DFT-calculated descriptors. *Chemosphere*, 76(7): 999–1005, doi: [10.1016/j.chemosphere.2009.04.010](https://doi.org/10.1016/j.chemosphere.2009.04.010)
- Wang Ying, Na Guangshui, Zong Humin, et al. 2018. Applying adverse outcome pathways and species sensitivity-weighted distribution to predicted-no-effect concentration derivation and quantitative ecological risk assessment for bisphenol A and 4-nonylphenol in aquatic environments: a case study on Tianjin City, China. *Environmental Toxicology and Chemistry*, 37(2): 551–562, doi: [10.1002/etc.3994](https://doi.org/10.1002/etc.3994)
- Wang Qian, Peng Fei, Chen Yiqin, et al. 2019. Heavy metals and PAHs in an open fishing area of the East China Sea: multimedia distribution, source diagnosis, and dietary risk assessment. *Environmental Science and Pollution Research*, 26(21): 21140–21150, doi: [10.1007/s11356-019-05355-z](https://doi.org/10.1007/s11356-019-05355-z)
- Wang Ying, Wang Juying, Mu Jingli, et al. 2016. Aquatic predicted no-effect concentrations of 16 polycyclic aromatic hydrocarbons and their ecological risks in surface seawater of Liaodong Bay, China. *Environmental Toxicology and Chemistry*, 35(6): 1587–1593, doi: [10.1002/etc.3295](https://doi.org/10.1002/etc.3295)
- Wang Ying, Wang Juying, Mu Jingli, et al. 2014a. Aquatic predicted no-effect concentration for three polycyclic aromatic hydrocarbons and probabilistic ecological risk assessment in Liaodong Bay of the Bohai Sea, China. *Environmental Science and Pollution Research*, 21(1): 148–158, doi: [10.1007/s11356-013-1597-x](https://doi.org/10.1007/s11356-013-1597-x)
- Wang Wanpeng, Zhang Rongqiu, Shan Dapeng, et al. 2014b. Indigenous oil-degrading bacteria in crude oil-contaminated seawater of the Yellow sea, China. *Applied Microbiology and Biotechnology*, 98(16): 7253–7269, doi: [10.1007/s00253-014-5817-1](https://doi.org/10.1007/s00253-014-5817-1)
- Wilson M J, Frickel S, Nguyen D, et al. 2015. A targeted health risk assessment following the *Deepwater horizon* oil spill: polycyclic aromatic hydrocarbon exposure in Vietnamese-American shrimp consumers. *Environmental Health Perspectives*, 123(2): 152–159, doi: [10.1289/ehp.1408684](https://doi.org/10.1289/ehp.1408684)
- Yin Fang, John G F, Hayworth J S, et al. 2015. Long-term monitoring data to describe the fate of polycyclic aromatic hydrocarbons in Deepwater Horizon oil submerged off Alabama's beaches. *Science of the Total Environment*, 508: 46–56, doi: [10.1016/j.scitotenv.2014.10.105](https://doi.org/10.1016/j.scitotenv.2014.10.105)
- Zhang Dayi, Ding Aizhong, Cui Shuangchao, et al. 2013. Whole cell bioreporter application for rapid detection and evaluation of crude oil spill in seawater caused by Dalian oil tank explosion. *Water Research*, 47(3): 1191–1200, doi: [10.1016/j.watres.2012.11.038](https://doi.org/10.1016/j.watres.2012.11.038)

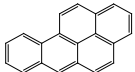
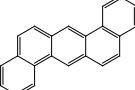
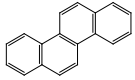
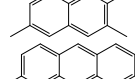
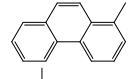
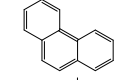
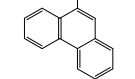
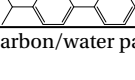
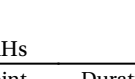
Appendix:

Table A1. Identification criteria for persistence, bioaccumulation and toxicity substances

	Description
Persistence	half-life >60 d in marine water or >40 d in freshwater, or half-life >180 d in marine sediment or >120 d in freshwater sediment
Bioaccumulation	BCF>2 000 L/kg
Toxicity	chronic NOEC <0.01 mg/L or CMR or endocrine disrupting effects

Note: BCF represents bioconcentration factor; NOEC no observed effect concentrations; CMR carcinogenic, mutagenic or toxic for reproduction.

Table A2. Information about their abbreviations, structures, physical chemical properties and purities for ten PAHs

No.	Chemical name	Abbreviation	Chemical structure	$\log_{10}K_{OW}$	$\log_{10}K_{OC}$ /L·kg ⁻¹	Chronic toxicity experiments	
						Company	Purity/%
1	benzo(a)pyrene	BaP		6.11	5.32	Sigma	96
2	dibenz(a,h)anthracene	DbA		6.7	5.67	-	-
3	chrysene	Chr		5.52	5.04	-	-
4	2,3,6-trimethylnaphthalene	2,3,6-tmNaP		4.81	4.1	-	-
5	2-methylanthracene	2-mAnt		4.89	4.34	-	-
6	1-methylphenanthrene	1-mPhe		4.89	4.41	-	-
7	3-methylphenanthrene	3-mPhe		4.89	4.21	TCI	99.5
8	9-methylphenanthrene	9-mPhe		4.89	4.24	-	-
9	1,7-dimethylphenanthrene	1,7-dmPhe		5.44	3.72	-	-
10	7-isopropyl-1-methylphenanthrene/retene	Ret		6.35	5.51	Chem Service	99.5

Note: K_{OW} is octanol/water partition coefficient and K_{OC} organic carbon/water partition coefficient.

Table A3. Chronic experimental aquatic toxicity data for some PAHs

Chemical	Scientific name	Phylum	Endpoint	Duration/d	Effect	Media	Value/ $\mu\text{g}\cdot\text{L}^{-1}$
BaP	<i>Artemia salina</i>	Arthropoda	EC ₁₀	11	mortality	SW	0.079
BaP	<i>Oryzias melastigma</i>	Chordata	NOEC	25	development	SW	1.7
Ret	<i>Oryzias melastigma</i>	Chordata	NOEC	25	development	SW	9.6
Ret	<i>Artemia salina</i>	Arthropoda	EC ₁₀	7	mortality	SW	376.62
Ret	<i>Oncorhynchus mykiss</i>	Chordata	NOEC	42	development	FW	32 ¹⁾
Ret	<i>Oncorhynchus mykiss</i>	Chordata	NOEC	42	mortality	FW	100 ¹⁾
Ret	<i>Oncorhynchus mykiss</i>	Chordata	NOEC	42	development	FW	100 ¹⁾
3-mPhe	<i>Artemia salina</i>	Arthropoda	EC ₁₀	14	mortality	SW	28.79
3-mPhe	<i>Phaeodactylum triconutum</i>	Bacillariophyta	EC ₁₀	3	growth	SW	607.5
3-mPhe	<i>Oryzias melastigma</i>	Chordata	NOEC	25	development	SW	24

Note: FW represents freshwater, SW seawater, EC₁₀ 10% effective concentrations, and NOEC no observed effect concentrations. 1) Data from Billiard et al. (2010).

Table A4. Chronic predictive aquatic toxicity data ($\mu\text{g/L}$) for ten PAHs

	BaP ¹⁾	DbA ¹⁾	Chr ¹⁾	2,3,6-tmPhe	2-mAnt
Fish (FW)	6	2	19	55	53
Daphnid (FW)	11	4	24	62	61
Green Algae (FW)	105	37	157	313	316
Fish (SW)	73	34	155	323	324
Mysid (SW)	0.064	0.018	0.346	2	1.96
	1-mPhe	3-mPhe	9-mPhe	1,7-dmPhe	Ret
Fish (FW)	53	53	53	20	4
Daphnid (FW)	61	61	61	25	6
Green Algae (FW)	316	316	316	158	51
Fish (SW)	324	324	324	157	48
Mysid (SW)	1.96	1.96	1.96	0.4	0.028 8

Note: 1) Data from Wang et al. (2016). FW represents fresh water and SW seawater.

Table A5. Distribution parameters of exposure concentration (ng/L) for ten PAHs in seawaters from the Dalian Bay

	BaP	DbA	Chr	2,3,6-tmPhe	2-mAnt
Min	1.50	0.30	1.16	2.54	0.56
Max	5.58	1.88	6.03	7.04	2.88
Average	2.87	0.87	3.43	5.24	1.90
St Dev	1.20	0.41	1.69	1.55	0.67
<i>n</i>	14	14	14	14	14
	1-mPhe	3-mPhe	9-mPhe	1,7-dmPhe	Ret
Min	2.61	5.41	4.03	2.00	5.12
Max	6.86	11.76	14.68	5.60	9.88
Average	4.77	8.48	11.26	3.80	6.70
St Dev	1.10	1.70	2.83	1.02	1.30
<i>n</i>	14	14	14	14	14

Table A6. Distribution parameters of exposure concentration (ng/g) for ten PAHs in sediments from the Dalian Bay

	BaP	DbA	Chr	2,3,6-tmPhe	2-mAnt
Min	0.69	0.17	3.44	1.34	0.50
Max	26.84	3.29	37.12	8.01	13.51
Mean	6.88	0.89	12.39	3.99	3.97
St Dev	7.75	0.89	10.40	2.17	3.84
<i>n</i>	13	13	13	13	13
	1-mPhe	3-mPhe	9-mPhe	1,7-dmPhe	Ret
Min	3.66	5.80	4.15	3.34	2.20
Max	20.74	30.32	27.22	13.76	32.88
Mean	8.94	13.53	10.87	7.36	11.71
St Dev	5.12	6.85	6.61	3.42	10.73
<i>n</i>	13	13	13	13	13

Table A7. Risk quotients for ten PAHs in surface seawaters from the Dalian Bay

Sample site	BaP	DbA	Chr	2,3,6-tmNaP	2-mAnt	1-mPhe	3-mPhe	9-mPhe	1,7-dmPhe	Ret
1	0.125	0.017	0.004	0.002	0.002	0.002	0.005	0.005	0.007	0.113
2	0.465	0.065	0.012	0.003	0.001	0.003	0.006	0.005	0.009	0.141
3	0.317	0.038	0.012	0.002	0.001	0.002	0.004	0.004	0.007	0.103
4	0.316	0.042	0.012	0.002	0.002	0.002	0.005	0.004	0.006	0.092
5	0.203	0.036	0.007	0.002	0.001	0.002	0.004	0.004	0.008	0.087
6	0.229	0.028	0.006	0.002	0.001	0.001	0.003	0.003	0.003	0.085
7	0.269	0.027	0.007	0.003	0.001	0.002	0.004	0.004	0.005	0.073
8	0.130	0.026	0.003	0.002	0.002	0.002	0.004	0.004	0.005	0.091
9	0.378	0.037	0.009	0.001	0.000	0.001	0.003	0.003	0.004	0.079
10	0.228	0.024	0.008	0.001	0.001	0.002	0.004	0.005	0.007	0.114
11	0.193	0.01	0.004	0.002	0.002	0.002	0.005	0.005	0.008	0.110
12	0.142	0.012	0.002	0.001	0.001	0.001	0.004	0.001	0.005	0.078
13	0.159	0.021	0.004	0.002	0.002	0.002	0.005	0.005	0.007	0.090
14	0.196	0.039	0.006	0.002	0.001	0.002	0.004	0.004	0.006	0.082

Table A8. Risk quotients for ten PAHs in sediments from the Dalian Bay

Sample site	BaP	DbA	Chr	2,3,6-tmNaP	2-mAnt	1-mPhe	3-mPhe	9-mPhe	1,7-dmPhe	Ret
1	0.051	0.001	0.008	0.012	0.012	0.010	0.028	0.017	0.182	0.075
2	0.170	0.004	0.016	0.009	0.011	0.010	0.030	0.017	0.168	0.050
3	0.017	0.001	0.004	0.003	0.001	0.004	0.013	0.006	0.068	0.006
4	0.316	0.006	0.024	0.007	0.012	0.009	0.028	0.016	0.179	0.043
5	0.071	0.002	0.009	0.003	0.003	0.005	0.017	0.009	0.100	0.014
7	0.014	0.001	0.003	0.002	0.001	0.003	0.009	0.005	0.055	0.005
8	0.045	0.001	0.006	0.005	0.002	0.004	0.013	0.006	0.073	0.011
9	0.074	0.002	0.004	0.006	0.003	0.005	0.015	0.008	0.080	0.018
10	0.557	0.012	0.036	0.011	0.023	0.016	0.048	0.030	0.225	0.070
11	0.034	0.001	0.006	0.004	0.002	0.005	0.017	0.008	0.096	0.009
12	0.164	0.003	0.012	0.004	0.005	0.005	0.020	0.009	0.093	0.011
13	0.039	0.001	0.005	0.003	0.002	0.003	0.012	0.006	0.075	0.009
14	0.302	0.006	0.022	0.006	0.010	0.009	0.030	0.018	0.169	0.027