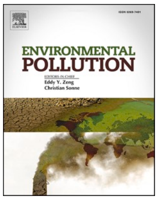
Environmental Pollution 368 (2025) 125811

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol



Spatial distribution and potential toxicity of PAHs in contaminated sediments in Korea using a passive sampler-based approach☆

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ARTICLE INFO

Keywords:
Passive sampler
Ex-situ method
Freely dissolved concentration
Biota-sediment accumulation factor
Interstitial water toxicity unit
Chemical activity

ABSTRACT

Due to the bioaccumulation and adverse health effects of polycyclic aromatic hydrocarbons (PAHs) on aquatic organisms, evaluating their potential toxicity in sediments is essential. Particularly, as industrial activities and urbanization expand, PAHs are increasingly being introduced into marine ecosystems. Passive samplers (PS) have been widely used to measure the concentration of freely dissolved (C_{free}) PAHs and assess their potential toxicity in sediment porewater. In this study, C_{free} was measured using passive samplers to assess the potential toxicity of contaminated sediments near industrial facilities in Korea. The maximum C_{free} levels in OS, JS, and OP were 201 ng/L, 70 ng/L, and 77 ng/L, respectively, indicating relatively high levels compared to other areas in Korea. Additionally, the spatial distribution of C_{free} was influenced by regional characteristics and sediment properties. The potential toxicity was evaluated using four key factors: C_{free}, biota-sediment accumulation factor (BSAF), interstitial water toxicity units (IWTUs), and chemical activity (a). Although the sedimentary PAH levels in these three harbors may not currently exhibit adverse effects on organisms based on these factors, inner sites could pose potential toxicity risks in the future. The findings of this study suggest the necessity for further research using PS techniques at potentially contaminated sites to enhance understanding of ongoing contamination, ecological risks, and strategies for improving sediment management.

1. Introduction

Marine ecosystems are increasingly subjected to elevated inputs of polycyclic aromatic hydrocarbons (PAHs) as a result of expanding industrial activities and urbanization. Due to their low solubility in water, PAHs exhibit a high affinity for organic carbon and particulate matter, which enhances their adsorption onto sediments and leads to bioaccumulation in benthic organisms (Guo et al., 2010), resulting in higher PAH concentrations being measured in sediments than in water (Qiu et al., 2009). Therefore, sediments serve as a sink for PAHs accumulation and are important for the assessment of ecotoxicity. Additionally, PAHs are of significant concern due to their carcinogenic and mutagenic properties, underscoring the importance of monitoring the levels of PAHs in the marine environment is consequently essential (Kannan et al., 2005).

Contaminated sediments are managed through remediation strategies such as capping and dredging to restore environmental quality. During the implementation of strategies, it is essential to conduct ecological risk assessments to monitor the effectiveness of the remediation efforts and to ensure that environmental risks are being adequately addressed throughout the project. The ecological risks of hydrophobic organic contaminants (HOCs) are commonly evaluated using either bulk sediment concentrations or total extractable concentrations (Ng et al., 2010; USEPA, 2000). The Sediment Quality Guidelines (SQGs) are commonly used as indicators for ecological risk assessment of sediments. SQGs express the potential effects of contaminants on organisms in sediments through the Effect Range Low (ERL) and Effect Range Median (ERM), which correspond to thresholds for predicting biological impacts at different contamination levels (Long et al., 1995). However, the method based on bulk sediment concentrations may overestimate the actual risk, as it assumes that all contaminants are entirely available for uptake by organisms (Kim et al., 2024; Muijs and Jonker, 2012).

☆ This paper has been recommended for acceptance by Eddy Y. Zeng.

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https://doi.org/10.1016/j.envpol.2025.125811
Received 3 December 2024; Received in revised form 9 January 2025; Accepted 4 February 2025

Previous studies have used direct water extraction methods and equilibrium partitioning (EqP) theory to estimate freely dissolved concentration (C_{free}) in sediment porewaters (Di Toro et al., 1991; Ololade, 2010; Yan et al., 2022). However, these direct measurements of C_{free} using conventional methods often result in unpredictable overestimates or underestimates due to inaccuracies caused by the presence of small particles (e.g., colloidal) (Carr and Nipper, 2003). Notably, the EqP theory predicts freely dissolved concentrations using the partition coefficient between water and organic carbon, but it has been found to overestimate concentrations by 1–3 orders of magnitude compared to those obtained from passive samplers (PS) (Baldwin et al., 2024; Borrelli et al., 2018; Burgess et al., 2021; Reininghaus et al., 2020). Although some conventional methods, such as raw porewater and air-bridge techniques in water, have shown good agreement with concentrations obtained from passive sampler (Fernandez et al., 2009a), these methods are challenging to handle depending on the experimenter, involve high costs, and require complex experimental procedures.

Passive samplers (PS), functioning as biomimetic devices, can measure C_{free}, allowing for the accurate prediction of concentration in organisms, within a factor of 2–4 (Minick et al., 2019; Muijs and Jonker, 2012). Moreover, a 1:1 linear relationship has been observed between concentrations measured by passive samplers and those found in biota (Heijden and Jonker, 2009; Kreutzer et al., 2022). As a result, research focused on monitoring contaminants and assessing ecological risks through the measurement of C_{free} using passive samplers has been emphasized instead of relying on bulk sediment concentrations. HOCs are often monitored with materials including poly(methyl methacrylate), low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), silicon rubber (SR), and polydimethylsiloxane (PDMS) (Jang et al., 2022; Kim et al., 2014; Kim et al., 2023a; Lao et al., 2016; Maruya et al., 2015). In contrast, hydrophilic contaminants and heavy metals are typically measured using polar organic chemical integrative samplers (POCIS), Chemcatcher, and organic diffusion gradients in thin films (o-DGT) (Chen et al., 2012; Kingston et al., 2000; Morin et al., 2012). Furthermore, the rise of emerging organic contaminants (EOCs) is leading to an increase in the development of new passive samplers designed to mimic the physicochemical properties of these target compounds (Gao et al., 2019; McDermett et al., 2022; Rong et al., 2024). These passive samplers have low detection limits, allowing trace analysis, and are advantageous for determining spatiotemporal concentration distributions (Oh et al., 2024) due to their ease of handling, minimal solvent requirements, and small footprint. Particularly, LDPE has been extensively studied as a passive sampler under various analytical conditions, enabling it to serve as a reliable and standard tool for use (Charrasse et al., 2014; Estoppey et al., 2016; Taylor et al., 2021).

In sediments, both in-situ and ex-situ methods can be used to measure C_{free} in porewater (Endo et al., 2020; Kim et al., 2024; Lang et al., 2015; Lee et al., 2022; Maruya et al., 2015). However, in-situ methods present a higher risk of loss and require divers for installation, which increases costs. In contrast, the ex-situ method is more cost-effective and allows for the assessment of spatial concentration distribution and toxic potential at multiple sampling points. An advantage of the ex-situ method is that it remains unaffected by environmental factors such as temperature or salinity changes (Apell and Gschwend, 2016). The aim of this study is to evaluate the potential toxicity of PAHs in contaminated sediments from selected locations in South Korea using the ex-situ method. Despite PAHs constituting 84% of the total concentration of organic pollutants detected in sediments across South Korea (Choo et al., 2024), studies on bioavailable PAHs are still limited. To the best of the authors' knowledge, this study is the first to measure C_{free} in sediments from industrial sites in Korea using a passive sampler. Additionally, the spatial distribution of C_{free} was evaluated based on the sediment characteristics in each region. Finally, the potential toxicity of PAHs in the sediments to organisms was evaluated using a tiered approach based on four key factors. This research serves as an initial investigation into contaminated sediments in South Korea and is anticipated to contribute significantly to future risk assessment and monitoring efforts.

2. Materials and methods

2.1. Sampling locations

Ulsan City, one of South Korea's special management areas, encompasses Onsan Harbor (OS) and Jangsaengpo Harbor (JS), both of which are located in national industrial complexes. OS mainly includes lubricants production, non-ferrous products, automobile and ship-related parts, and petroleum plants, while JS contains oil, chemical, and automobile plants. Kim et al. (2023b) found that OS and JS contribute 15% and 8.9%, respectively, to the pollution sources in the outer part of Ulsan Bay. Additionally, PAH inputs occur predominantly in areas connected to the Weohwang River. The Okpo harbor (OP) in Geoje-do is surrounded mainly by shipyards. These areas are contaminated with PAHs, organochlorine compounds, and persistent organic pollutants (POPs) originating from industrial and other anthropogenic activities, necessitating continuous environmental monitoring and remediation efforts (An et al., 2020; Choi et al., 2011; Khim et al., 2001; Kim et al., 2023b; Seo et al., 2020).

The sediments were collected using grab samplers in April for OS (20 sites), May for OP (26 sites), and August for JS (9 sites) in 2023 (Fig. 1 and Table S1). These samples were stored in a freezer until analysis. To measure water content (WC%), a 5 g subsample of wet sediment was placed in an oven at 60 °C for 24 h. The total organic carbon contents (TOC%) in sediments at OS, OP, and JS were obtained from Chungnam National University and GeoSystem Research Corporation. Black carbon (BC) was measured using CHN Elemental Analyzer (Flash 2000, Thermo Scientific) after removing OC, following the method described by Gustafsson et al. (1996) (Table S3).

2.2. Materials and agents

Information on materials and agents is provided in the Supporting Information.

2.3. Measurement of the concentration in whole sediment (C_S)

The sediments in OS, JS and OP were collected using a grab sampler and stored in 500 mL amber bottles, placed in an icebox, and quickly transported to the laboratory under cooled conditions for analysis. The detailed experimental procedures are described in Kim et al. (2023b). Briefly, freeze-dried sediment samples (~10 g each) were extracted using an accelerated solvent extractor (ASE, Dionex ASE 350, Thermo Scientific, Salt Lake, UT) with dichloromethane. The samples, placed in a stainless-steel cell (34 mL), were extracted at 120 °C for 10 min. The extracts were concentrated using N_2 gas (TurboVap LV, Biotage, Uppsala, Sweden) and activated copper powder (Merck, Darmstadt, Germany) was added to remove sulfur. The extracts were purified using open column chromatography packed with 8 g of activated silica gel (70–230 mesh, Merck) and eluted with 60 mL of a hexane:dichloromethane (8:2, v/v). Finally, the eluents were exchanged with hexane and concentrated to 1 mL.

The wet sediments (~20 g each) in JS were spiked with 30 μL of a surrogate standard (concentration: 10 μg/mL) and extracted using the Soxhlet method with 200 mL of dichloromethane for 16 h. The extracts were concentrated using a rotary evaporator, and copper was added to remove sulfur. The samples were purified using a column packed with 20 g of deactivated silica gel (5%), 10 g of alumina (1%), and sodium sulfate (Na_2SO_4). The extracts were eluted through the column with 100 mL of DCM. The eluents were then concentrated and exchanged with hexane.

The samples were concentrated to 1 mL using N_2 gas and then spiked with 30 μL of gas chromatography/internal standard (GC/IS) at a concentration of 10 μg/mL.

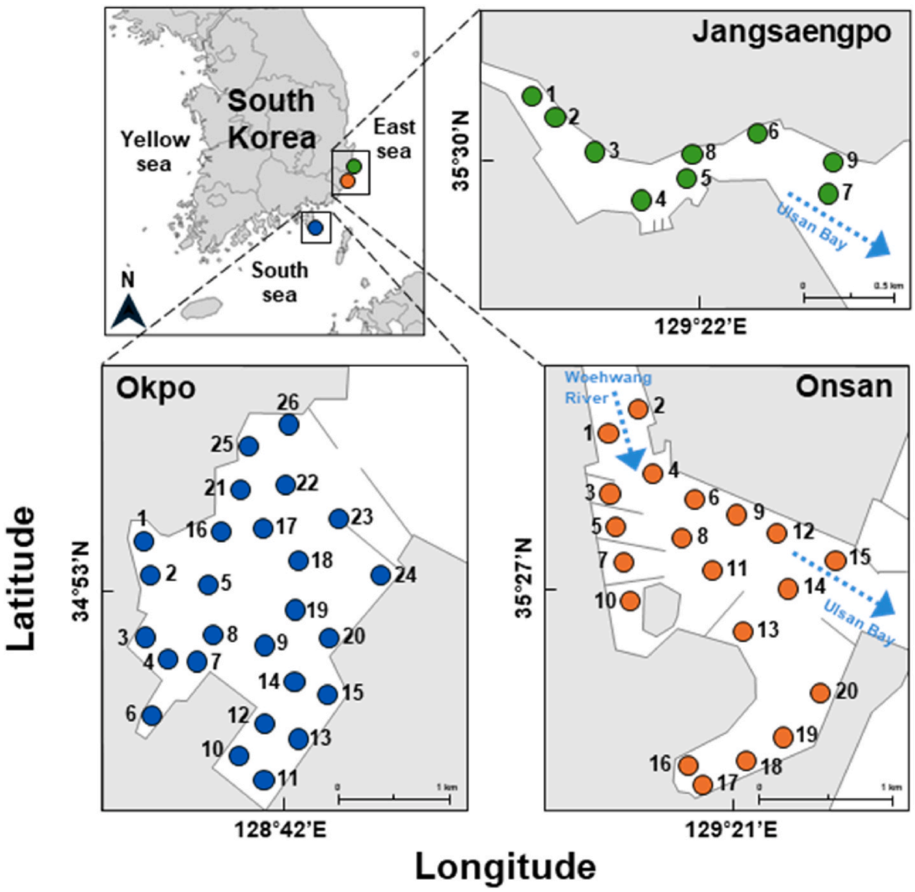

Fig. 1. Sediments were collected in Onsan Harbor (OS, orange point), Jangsaengpo Harbor (JS, green point), and Okpo Harbor (OP, blue point), Korea. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

2.4. Measurement of C_{free}

If the mass of passive sampler (m_p) is greater than the mass of the sediment (m_s), chemical depletion will occur between the sediment and the passive sampler, thus requiring a low m_p/m_s ratio. Additionally, the mass of organic carbon (m_{oc}) is considered in the determination of the non-chemical depletion condition. Therefore, the ratio of m_p to m_{oc} should be maintained below 0.05 (Ghosh et al., 2014; Mayer et al., 2014). In this study, 10 mg of LDPE was used for all sediments, and 30 g–50 g of wet sediments were used to maintain a low m_p/m_s ratio, with the overall protocol following that of Lao and Kim. (2024). The m_p/m_{oc} ratio of sediment in OS, OP, and JS ranged from 0.02 to 0.03, indicating that non-chemical depletion conditions were considered.

The sediment was placed in a 230 mL amber bottle, and additional water was added to achieve 80% moisture content to maintain a resuspended state. NaN_3 was included to inhibit microbial degradation, and 10 mg of LDPE ($n = 2$) was added. The bottles were then shaken on an orbital platform shaker at 180 rpm for 30 days. After the exposure time, the retrieved LDPE was carefully wiped using Kimwipe and frozen in a 1.5 mL GC vial until analysis. A 30 μL of the surrogate standard (concentration: 10 μg/mL) was added to a 1.5 mL GC vial containing LDPE, followed by extraction in a sonication extractor with 1.5 mL of dichloromethane for 15 min, repeated three times. The extracts were combined in a 15 mL vial, concentrated under N_2 gas, and the solvent was exchanged to hexane. The final concentrate volume was 0.2 mL and spiked with 30 μL of GC/IS (concentration: 10 μg/mL).

2.5. Instrumental analysis and quality assurance

Information on instrumental analysis and quality assurance is provided in the Supporting Information.

2.6. Tiered approach for assessing potential toxicity

PAHs have higher concentrations in sediments than in the water column and can be released or resuspended into the water, providing a secondary source (Liu et al., 2018). Therefore, it is important to assess the toxic potential of PAHs in sediments. Based on the C_{free} measured in sediment porewater, the biota-sediment accumulation factor (BSAF), interstitial water toxicity units (IWTUs), and chemical activity (a) can be calculated to assess the toxic potential of sediments. This study presents

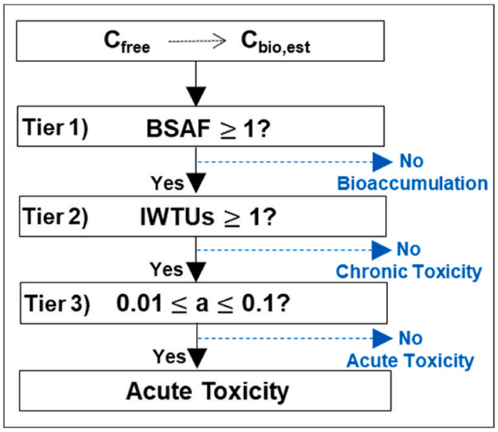

Fig. 2. Tiered approach for assessing potential toxicity of PAHs to biota in sediments.

a protocol, following the steps outlined in Fig. 2, to evaluate whether PAHs in sediments pose an acute toxic threat to organisms.

First, the C_{free} (ng/L) can be obtained from the ratio of the passive sampler-water partition coefficient (K_{PW}, L/kg) and the concentration of contaminant (ng/Kg) absorbed by the passive sampler.

$$C_{free} = \frac{C_{PS}^{\infty}}{K_{PW}} \tag{1}$$

Although the concentration in organisms typically requires consideration of the lipid-water partition coefficient ($K_{lip\text{-}w}$), it can be approximated as being equal to the octanol-water partition coefficient (K_{OW}, L/Kg) (Hawker and Connell, 1986; Hussain et al., 2024; Lu et al., 2011; Mackay et al., 1991). The estimated PAH concentrations in biota ($C_{bio,est}$, ng/Kg) were derived from C_{free} and K_{OW} as follows:

$$C_{bio,est} = C_{free} \times K_{OW} \tag{2}$$

Second, the assessment of PAHs bioavailability in the environment often involves comparing the concentrations of individual PAHs in benthic organisms with those found in sediment (Keshavarzifard et al., 2017). The bioaccumulation of contaminants in sediments is evaluated through ecological assessments through the calculating of BSAF. However, BSAF with OC-normalized concentration (C_{OC}, ng/g) overestimated the concentration in organisms by a factor of more than 2, while LDPE had a ratio of mean concentration in organisms closer to 1 (Fernandez and Gschwend, 2015). Additionally, Paulik et al. (2016) found that LDPE predicted bioaccumulation on average within a factor of 2, indicating that C_{free} obtained from passive samplers can be used to predict bioaccumulation, resulting in more accurate BSAF. Thus, BSAF was estimated according to the following equation:

$$BSAF = \frac{C_{bio,\ est_i}}{C_{OC_i}} \tag{3}$$

If the BSAF for individual PAHs exceeds the theoretical value of 1, the contaminants in sediments must be considered for bioaccumulation potential (Cortazar et al., 2008).

Third, IWTUs are key factors for assessing chronic toxicity and calculated from C_{free} in porewater.

$$IWTUs = \sum \frac{C_{free}}{C_{free,\ PAH_i,FCV_i}} \tag{4}$$

Here, $C_{free,\ PAHi,FCVi}$ represent the final chronic value for individual PAHs (USEPA, 2003). These toxic units (TUs) can be used to evaluate the additive or mixed effects of PAHs in sediments, which represent the sum of 34 PAH concentrations. If this value is greater than 1, this indicates that the PAHs in the sediment are toxic to organisms. Therefore, these sedimentary environments should be carefully managed and monitored to prevent ecological harm.

Fourth, chemical activity is a parameter that quantifies the concentration of a compound and is also an indication of the potential for distribution in an organism (Mayer and Holmstrup, 2008). Passive sampling techniques for measuring C_{free} in porewater have been successfully used to determine the relationship between toxicity and chemical activity (Schmidt et al., 2013; Schmidt and Burgess, 2020). The difference between C_{free} and chemical activity reflects the thermodynamic gradient for diffusion and partitioning processes, which influence whether sediments act as a source or sink for hydrophobic organic pollutants (HOCs) (Reichenberg and Mayer, 2006). Moreover, chemical activity allows for the identification of which compounds are more likely to diffuse into organisms based on the composition of individual compounds.

$$a = \sum \frac{C_{free_i}}{S_{L_i}} \tag{5}$$

Chemical activity is calculated using sub-cooled liquid solubility (S_L) and C_{free}, and baseline toxicity occurs when chemical activity is within the range of 0.01–0.1. This range represents acute toxicity to living organisms.

3. Results and discussion

3.1. Spatial distribution of C_{free}

This study seeks to measure freely dissolved PAHs in sediments collected from areas near industrial facilities and to investigate their spatial distribution patterns (Fig. 3 and Table S6). In OS, the sum of C_{free} ranged from 2.2 (± 0.05) to 201 (± 9.7) ng/L, with PAHs in the porewater predominantly comprising 3-ring compounds (mean 74%), followed by 4-ring (mean 25%), 5-ring (mean 0.37%), and 6-ring compounds (mean 0.24%) (Fig. S1a). At sites 1 to 15 in OS, ACY, FLR, and PYR were predominant PAHs, while at sites 16 to 20, PHE and ANT were more prevalent. In JS, the sum of C_{free} ranged from 16 (± 1.2) to 70 (± 6.7) ng/L, with 3 ring compounds dominating at 86% (Fig. S1b). There were no significant differences in the compositional ratios of PAH compounds across all sampling stations in JS ($p > 0.05$), with ACY, FLR, and PHE being the predominant 3 ring compounds. In OP, the sum of C_{free} ranged from 1.4 (± 0.35) to 77 (± 7.0) ng/L, with PYR and FLR being predominant. The C_{free} was predominantly observed in the following order: 3 rings (mean 64%), 4 rings (mean 34%), 5 rings (mean 1.7%), and 6 rings compounds (mean 0.46%) (Fig. S1c). Among the 7 carcinogenic compounds, CHR and BaA were predominant across all areas, although their contribution to the sum of C_{free} was marginal. Notably, the sum of C_{free} and the 7 carcinogenic compounds tended to increase towards inner harbors in all areas (Fig. 4a).

Kim et al. (2023b) found that PAH concentrations in whole sediment at OS (ng/g OC) were higher at upstream stations (near sites 1–2 in Fig. 2) near the Woehwang River, which flows into Ulsan Bay, with concentrations decreasing downstream stations (near sites 14–15 in Fig. 2) (Fig. S2a). This trend is likely attributed to the re-suspension and dilution of surface sediments downstream, caused by increased water flow and volume in the Woehwang River (Dong et al., 2013). Additionally, higher levels of PHE were observed at stations near the Woehwang River and JS, potentially due to their proximity to docks associated with the petroleum and oil industry (Ulsan Regional Office of Oceans and Fisheries), which may contribute to contamination. In contrast, the C_{free} in OS showed higher concentrations at inner sites (16–20). At these inner sites, PHE and ANT were more prevalent than at other sites. The increase in low molecular weight PAHs at these sites is likely due to the semi-enclosed characteristics and emissions from nearby non-ferrous and petrochemical industrial complexes. Additionally, the concentration may be higher at inner sites in OS due to restricted water circulation caused by marine structures such as breakwaters.

Since the early 2000s, concerns over sediment contamination in JS have been highlighted (Kim et al., 2023b; Khim et al., 2001; Moon et al., 2001). Previous studies have reported the highest PAH concentrations at inner sites of JS, attributed to the discharge of oils and solvents from nearby petrochemical industrial complexes into the Gosacheon Stream (Seo et al., 2020). Consequently, the Korean government implemented capping measures between 2015 and 2019 to prevent the release of pollutants from sediments. The method involved capping the contaminated sediment surface with a 20 cm thick layer of clean sand followed by a 20 cm thick layer of gravel, for a total capping thickness of 40 cm. Despite the completion of this project, PAH concentrations in whole sediment remained high at inner sites (1–2) even four years later (Fig. S2b). Similarly, the C_{free} in porewater at sites 1 and 2 was at higher levels, showing a decreasing trend towards the outer sites (3–9) (Fig. 4b). It should be noted that the surface sediment samples were collected using grab sampling four years after capping. Smedes et al. (2013) measured the accessible concentration (C_{AS}) released from sediments to porewater using multi-ratio passive sampling. The accessibility of contaminants tends to decrease as contact time with the

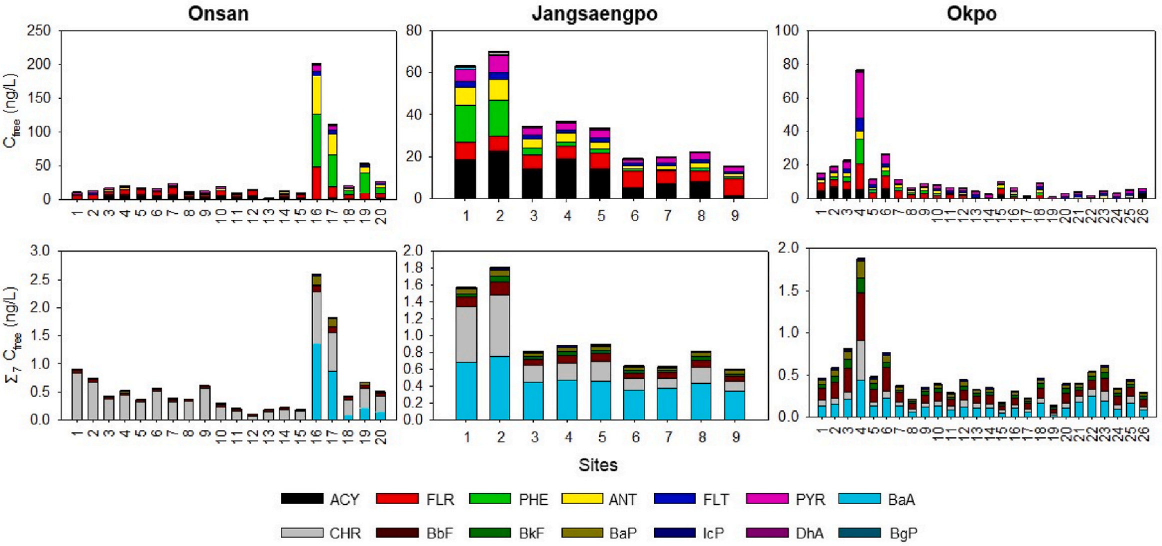

Fig. 3. Sum of C_{free} (first low) and C_{free} for 7 carcinogenic compounds (second low) (ng/L) in OS, JS, and OP.

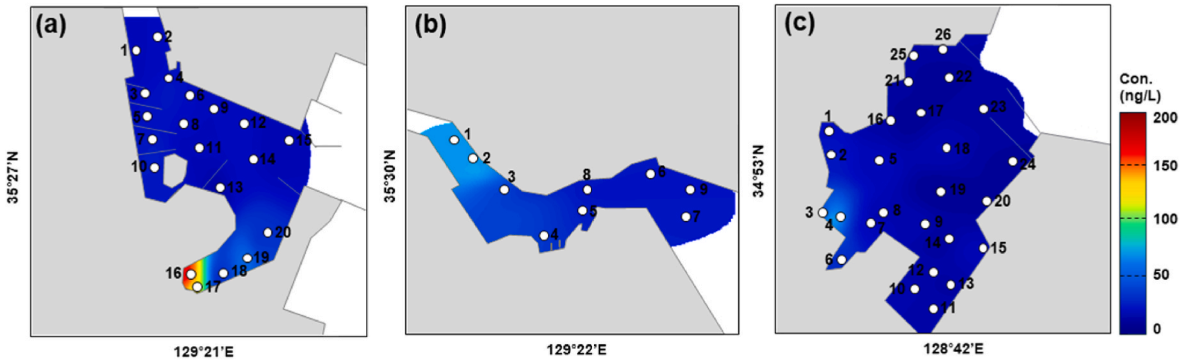

Fig. 4. Spatial distribution patterns of C_{free} in (a) OS, (b) JS, and (c) OP.

sediment matrix increases, as it takes time for contaminants to find binding sites within the sediment and migrate internally (Luthy et al., 1997; Pignatello and Xing, 1995). Therefore, the relatively high levels of C_{free} in the inner sites are considered to result from recently introduced contaminants, which have had less contact time with the sediment and weaker binding, leading to higher accessibility. This suggests that the C_{free} is likely associated with recently accumulated PAHs in surface sediments. While it is possible that PAHs in the source sediments may already be in equilibrium with the newly deposited sediments, the high concentrations observed at inner sites also suggest ongoing contamination, likely from industrial or other potential sources such as municipal and stormwater discharges (Hussain et al., 2024). The high concentrations observed at the inner sites, therefore, likely reflect ongoing contamination from industrial complexes, also consistent with the concentration (C_S) trends observed in previous studies (Kim et al., 2023b; Khim et al., 2001) (Fig. S2b).

In OP, the C_{free} was generally high at sites 1 to 7, located near the shipyard. As a semi-enclosed harbor, high C_{free} concentrations were anticipated at the inner sites (8–12) (Fig. 4c), while the highest concentration was actually observed at site 4, showing a trend similar to that of C_S (ng/g dw) (Fig. S2c). In contrast to OS and JS, which contain multiple industrial complexes, OP contains only a shipyard. Thus, the elevated concentrations observed at site 4 are potentially attributable to anthropogenic activity in the shipyard.

3.2. *Variations in C_{free} according to sediment characteristics*

The OC contents in OS, JS, and OP ranged from 0.25% to 2.15% (mean 1.7%), 1.72%–3.06% (mean 2.1%), and 0.21%–2.14% (mean 1.4%), respectively (Table S3). Therefore, Pearson correlation analysis was conducted between C_{free} of individual PAHs and OC content measured in the three regions (Table S7). The results showed differences in sediment characteristics that were influenced by regional factors.

In OS, a very high positive correlation was observed between OC and BC ($r = 0.751$, $p < 0.01$). Additionally, a significant correlation was observed between the sum of C_S and BC/OC ($r = 0.77$, $p < 0.01$), suggesting a common source for PAHs and BC in the sediment. In contrast, the sum of C_{free} showed a negative correlation with both OC and BC ($r = -0.494$, $p < 0.05$; $r = -0.581$, $p < 0.01$). OC and BC/OC were higher at sites near the Woehwang River compared to downstream and inner harbor sites. Therefore, at the inner sites, where BC and OC levels are lower than those of upstream sites, adsorption is weaker, potentially resulting in higher C_{free}. The sediment-porewater distribution coefficient ($K_D = C_S/C_{free}$) also exhibited a lower slope in OS compared to other regions, indicating a higher tendency for PAHs to diffusion into porewater rather than into sediment (Fig. S3). Low molecular PAHs are more likely to be released from sediment into porewater (Smedes et al., 2013). Thus, in the inner harbor of OS, the high concentration of low molecular PAHs in porewater may be attributed to relatively low BC and OC contents, indicating the need for further research on the C_{AS}.

In contrast, the seven low molecular PAHs and the sum of C_{free} in JS showed a positive correlation with OC, and the sum of C_{free} and C_S also showed a positive correlation ($r = 0.716$, $p < 0.05$). However, C_S did not show a significant correlation with OC and BC. As discussed in Section 3.1, this may result from the fact that recently introduced PAHs have accumulated in the surface sediments, providing insufficient time for them to become strongly absorbed onto OC or BC.

In OP, a negative correlation was observed between OC and the eight PAHs, as well as the sum of C_{free}. However, the sum of C_{free} and C_S exhibited a significant positive correlation ($r = 0.67$, $p < 0.01$). This indicates that while OC does not contribute to an increase in C_{free}, the increase in C_S is associated with a consistent increase in C_{free}. This pattern is consistent with the observations in JS.

The grain size of sediments plays a crucial role in influencing their adsorption behavior. In OS and OP, the C_{free} showed a significant negative correlation with the mean grain size (phi) ($r = -0.459$, $p < 0.05$; $r = -0.673$, $p < 0.01$), whereas no significant correlation was found in JS. As the grain size of sediments increases (becomes coarser), the surface area available for PAHs adsorption decreases (Mehler et al., 2011; Yu et al., 2009; Wang et al., 2015a). Therefore, the high C_{free} in porewater at inner sites may have been influenced by lower mean grain sizes (phi) compared to other sites (Fig. S4).

The EqP method, which is derived from the ratio of C_{OC} to partition coefficient between organic carbon and water (K_{OC}), has been used to estimate C_{free} in sediments. The C_{free} estimated by the EqP method ($C_{free,\ EqP}$) was up to 57, 49, and 289 times higher in OS, JS, and OP, respectively, compared to the C_{free} calculated from passive sampler ($C_{free,\ PS}$) (Fig. S5), consistent with the findings of previous studies (Apell and Gschwend, 2016; Fernandez et al., 2009b; Kim et al., 2024). Particularly at site 4 in OP, the EqP method could overestimate C_{free} due to the substantial effects of OC and particle size.

The field-based log K_{OC} (log $K_{OC,\ field}$) for the three regions is presented in Table S8. For PAHs, a linear correlation was observed between log K_{OW} and log $K_{OC,\ field}$ in all areas (Fig. S6). The generic log K_{OC} predicted using the Karickhoff regression was higher than log $K_{OC,\ field}$ by an average of 2.0 (5-ring) to 18 (3-ring) log units in OS, 1.5 (5-ring) to 3.9 (6-ring) log units in JS, and 1.9 (5-ring) to 4.2 (3-ring) log units in OP (OS: mean 2.8; JS: mean 2.2; OP: mean 2.8 log units). This suggests that while bioavailable phases may decrease due to OC, PAHs present in the sediment may exhibit weak adsorption to OC. Similar findings were reported by Yu et al. (2009), where field-based log K_{OC} for high molecular weight PAHs with log $K_{OW} > 5.5$ were 1.2–3.1 log units lower than the generic log K_{OC}, likely due to the slow adsorption equilibrium typically observed for highly hydrophobic PAHs (Pignatello and Xing, 1995). In this study, the log $K_{OC,\ field}$ for low molecular weight PAHs was lower than that of high molecular weight PAHs in OS and OP, indicating that low molecular weight PAHs may exhibit higher concentrations in porewater. Therefore, measuring the spatial distribution of C_{free} should be considered based on the characteristics of the sediment, and using a passive sampler offers a more reliable and stable approach compared to the EqP method.

3.3. Comparison of C_{free} level

Compared to the values reported by Jeong et al. (2020) and Lee et al. (2022), who measured freely dissolved PAHs in contaminated sediment in South Korea, the maximum C_{free} levels in OS, JS, and OP, which were 2.8–31 times higher (Table 1). The C_{free} levels in JS and OP were similar to the maximum levels measured in the Ohio River (Kim et al., 2024), although still lower than those in other highly contaminated areas (Fig. S7). The sediment in JS has already undergone a remediation and restoration project addressing contamination. Nevertheless, the concentration levels remain high compared to previous studies. Furthermore, the high C_{free} at site 16 in OS was comparable to the maximum C_{free} reported by Kreutzer et al. (2023), Endo et al. (2020), and Wu et al. (2020). Notably, Endo et al. (2020) reported that the highest concentration was found near an effluent of a carbon manufacturing plant. In addition, the C_{free} at site 16 in OS was slightly higher than the maximum concentration reported in industrialized areas by Allan et al. (2012). The sampling sites in this study, as described in Section 2.1, include complex industrial areas and large shipyards. The C_{free} levels at the inner sites in OS, JS, and OP cannot be ignored compared to results from other countries. In the case of OS, it is determined that sites 16 and 17 exhibit high levels of PHE and ANT due to their relatively finer mean grain size (phi) compared to other sites (see Fig. S4). According to previous studies, the fossil fuel combustion at the inner site in OS contributes 66.2% of the pollution, while vehicle emissions account for 51.5% in JS (Kim et al., 2023b). As a result, consistently high concentrations are observed in the inner site due to the influence of nearby ongoing

Table 1
Comparison of C_{free} in sediments with other regions. An explanation of the specific area has been provided in the description.

Country	Location	No. of PAHs	Type of PS	Con. (ng/L)	Description	Refer.
USA	Baltic Sea region	9	PDMS	2.7–8.5		Lang et al. (2015)
	North Sea	8	SPME	1–5		Niehus et al. (2019)
	North Sea and Wadden Sea	16	SPME	30-460 (North Sea) and 15–205 (Wadden Sea)	- The North Sea is located near dumping site - Core porewater	Kreutzer et al. (2023)
	Narragansett Bay	20	LDPE	3.3–18		Yonis et al. (2023)
	Massachusetts	3	LDPE	2.92 (Pioneer Village, Sandy beach) and 1992 (Island End, Chelsea Creek)	- Core porewater - Island End is coal-tar contaminated site	Fernandez and Gschwend. (2015)
	5 Great lakes	22	LDPE	4.4–30624 (median 116)	- Watershed	Baldwin et al. (2024)
	Kentucky lake and Ohio river	6–12	LDPE	0.53–81		Kim et al. (2024)
Norway	Oslo harbor	14	PDMS	1.1–310	- Presence of hotspot	Cornelissen et al. (2008)
	Coastal	19	LDPE	0.014–176	- Industrialized areas	Allan et al. (2012)
China	Dongjiang River	16	LDPE	50–218	- Core porewater	Wu et al. (2020)
Japan	Tanoura Bay	10	LDPE	12–257	- The station showing the highest concentration is located near a carbon manufacturing plant effluent.	Endo et al. (2020)
UK	River	31	SR	7.4–208		Yates et al. (2011)
South Korea	Dongho harbor	3	PMMA	6.6		Lee et al. (2022)
	Harbor and bay	13	LDPE	12–28	- Nationwide	Jeong et al. (2020)
	Onsan harbor	13	LDPE	2.22–201	- Industrialized areas	This study
	Jangsaengpo harbor	14		15.7–69.8	- Industrialized areas	
	Okpo harbor	14		1.38–76.7	- Shipyard	

pollution sources. Therefore, these regions are considered critical for assessing pollution levels and ecological toxicity.

3.4. *Potential toxicity based on C_{free}*

The potential toxicity of sediments was assessed based on four key factors: C_{free}, BSAF, TUs, and chemical activity (Fig. 5). The passive sampler, acting as a biomimetic polymer, has been shown to predict concentrations in organisms within a factor of 2 (Minick et al., 2019). BSAF is typically calculated using the EqP method; however, utilizing C_{free} calculated from passive sampler for BSAF calculations provides a more accurate estimation (Cornelissen et al., 2006). Therefore, BSAF was derived from concentrations estimated in organisms ($C_{bio,\ est}$), based on C_{free} obtained from the passive sampler, was measured across three regions to assess bioaccumulation. In OS, the most sites contained PAHs with theoretical values exceeding 1, whereas in OP and JS, PAHs approximating or exceeding the theoretical values were observed at most sites, with a few exceptions (Fig. S8). Notably, sites 16 and 17 in OS, which exhibited elevated C_{free}, demonstrated the highest BSAF compared to other sites. For OS and JS, BSAF exhibits a decreasing trend with increasing molecular weight, consistent with findings from previous studies (Tuikka et al., 2016). In OP, the BSAF at site 4, which exhibited the highest C_{free}, was relatively low. Although C_{free} was elevated, the low BSAF could be attributed to the limited bioavailability of PAHs, influenced by sediment characteristics, biological metabolic processes, and the structural properties of PAHs (Esmaeili et al., 2022; Kaag et al., 1997; Lyytikäinen et al., 2003; Wang et al., 2015b).

The hazard quotient (HQ) and SQGs based on C_S were used to assess the potential toxicity of individual and total PAHs in contaminated sediment (Zhao et al., 2017). However, these methods have limitations in accurately predicting ecological toxicity effects due to the complexity of mixed contaminants and the variability in sediment composition and geochemical properties across different geographic locations (Long, 2006). In contrast, the approach based on passive sampling used in this study could better predict the potential toxicity in contaminated sediment because the spatial distribution of bioavailable concentrations varies according to sediment characteristics. Therefore, in most of the sites across the three regions where high BSAF over one was observed, Equilibrium partitioning sediment benchmarks toxicity units (ESBTUs) and IWTUs were calculated based on C_{OC} and C_{free} to evaluate whether the accumulated PAHs pose toxic effects to organisms. TUs were below 1 in all regions, except for site 4 in OP, where the ESBTUs exceeded 1 (Fig. S9). ESBTUs at OS, JS, and OP were on average 5.3, 11, and 23 times higher than IWTUs. This result suggests that ESBTUs based on derived C_{OC} may overestimate biotoxicity assessments, consistent with the findings of Kim et al. (2024) and Endo et al. (2020). Since the IWTUs remained below 1, PAHs in contaminated sediments from the three regions expected to exhibit no toxicity to organisms. However, since the IWTUs are calculated based on the sum of 34 PAHs rather than just a few, there is a potential that this threshold could be exceeded.

Chronic toxicity was not observed at all sites in this study. However, if chronic toxicity were to occur, the chemical activity could be calculated to assess the potential for acute toxicity in the next step. Baseline toxicity, also known as narcosis, represents the minimum toxicity that a compound can cause upon membrane penetration, with “a” value between 0.01 and 0.1 (Escher and Schwarzenbach, 2002), and is significant in complex environmental mixtures where acute effects such as lethality can occur within this range (Reichenberg and Mayer, 2006). TUs may not fully reflect toxicity since the concentrations of individual contaminants are simply summed for calculation. Chemical activity quantifies the energy state of a substance that drives spontaneous physicochemical processes, such as diffusion and partitioning (Schwarzenbach et al., 2016). Therefore, chemical activity is crucial for understanding bioavailability.

In this study, the effects of chronic toxicity were not observed. However, chemical activity was calculated as a subsequent step to provide a comprehensive approach for assessing sediment toxicity in high-risk areas. Chemical activity at all sites was 10–100 times lower than the baseline toxicity range, consistent with the findings of Lang et al. (2015) and Witt et al. (2009). However, inner sites in three regions with high C_{free} showed chemical activity approximately 10 times lower than baseline toxicity. Moreover, chemical activity at the inner sites is comparable to values reported for composted manufactured gas plant soils (Reichenberg and Mayer, 2006). Although chemical activity was calculated as the sum of 9 PAHs, the presence of additional PAHs in the sediment may indicate a very high level of contamination.

Analyzing the contribution of individual compounds to chemical activity allows the identification of compounds exhibiting higher

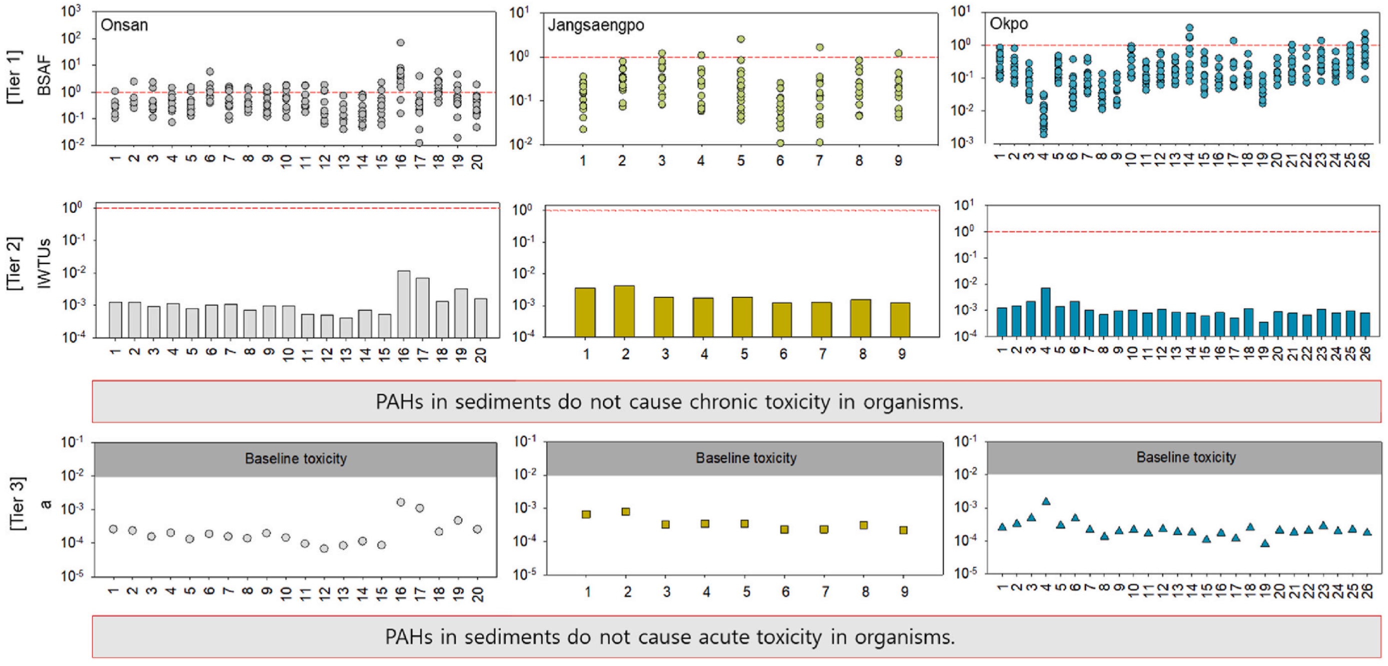

Fig. 5. Potential toxicity assessment across study areas, presented as BSAF (first row), IWTUs (second row), and chemical activity (third row).

spontaneous energy for organisms. In OS, chemical activity showed a high contribution in the order of CHR > PYR and PHE > ANT, with site 16 being dominated by PHE and ANT (Fig. S10), which is similar to the composition of $C_{free.}$ At JS, BaA and PYR were dominant, with site 2 showing a similar contribution. In OP, while PYR dominated in C_{free}, BbF was the most dominant in chemical activity, accounting for 30%. These results suggest that, depending on the region, the composition of compounds contributing to the baseline toxicity of PAH mixtures may differ from those contributing to the C_{free} (Lang et al., 2015).

Management strategies, including capping to reduce risks from contaminated sediments, may be ineffective due to significant ongoing sources such as stormwater (Ghosh et al., 2003; Gidley et al., 2022). Therefore, in areas like JS where capping has been implemented, inadequate management strategies for surrounding industrial complexes have resulted in persistently high levels of Cs and C_{free}. Furthermore, the inner sites of the three regions with elevated C_{free} and chemical activity may exhibit significant toxic effects in the future.

4. Conclusions

While numerous studies in Korea have measured C_{free} using passive sampler, this study is the first to apply a passive sampler-based tiered approach to assess the potential toxicity in contaminated sediments near industrial complexes of Korea. High C_{free} levels were observed at inner sites in three regions, indicating potential for bioaccumulation. However, the potential toxicity assessment, conducted using a passive sampler-based tiered approach including BSAF, IWTUs, and chemical activity, revealed no evidence of chronic or acute toxicity. Despite restoration and remediation efforts in areas like JS, the persistently high concentrations observed are attributed to continuous inputs from ongoing pollution sources, highlighting the limitations of pollution source management in Korea. Passive samplers proved effective in evaluating the spatial distribution influenced by local and sediment characteristics. The findings of this study provide a foundational PS-based tiered approach for assessing potential toxicity, which could inform contamination evaluations and subsequent management strategies. As demonstrated in Allan et al. (2024), the tiered approach incorporating passive samplers can be effectively employed to assess potential toxicity not only in seawater but also in sediment-dwelling organisms, particularly in regions where direct sampling is challenging, serving as an animal-free step in environmental assessments. However, it is important to note that replacing K_{OW} with BCF when predicting concentrations in biota lead to a 1-log unit discrepancy. Moreover, in environments rich in black carbon, limitations exist in the predictability of BSAF for high molecular weight compounds. Therefore, to strengthen the relationship between C_{free} and BSAF, adjustments reflecting sediment properties and biological factors may be necessary.

CRediT authorship contribution statement

Na Yeong Kim: Writing – original draft, Formal analysis, Conceptualization. **Joonhyeong Park:** Investigation, Formal analysis. **Youngnam Kim:** Investigation, Formal analysis. **Seongjin Hong:** Resources, Conceptualization. **Taeha Kim:** Resources, Conceptualization. **Gi Beum Kim:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Gi Beum Kim reports financial support was provided by Korea Institute of Marine Science and Technology Promotion. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the Development of source identification and apportionment methods for toxic substances in marine environments program of Korea Institute of Marine Scinece & Technology Promotion (KIMST) funded by the Ministry of Oceans and Fisheries, Korea [RS-2022-KS221655]: Development of Technology for Impact Assessment and Management of HNS discharged from Marine Industrial Facilities of Korea Institute of Marine Science & Technology Promotion (KIMST) funded by the Ministry of Oceans and Fisheries, Korea [RS-2021-KS211535]: and Development of risk managing technology trackling ocean and fisheries crisis around Korean Peninsula by Kuroshio Current of Korea Institute of Marine Science & Technology Promotion (KIMST) funded by the Ministry of Oceans and Fisheries, Korea [RS-2023-00256330].

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2025.125811.

Data availability

Data will be made available on request.

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