TYPE Original Research
PUBLISHED 06 December 2024
DOI 10.3389/fenvs.2024.1509277

OPEN ACCESS

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RECEIVED 10 October 2024
ACCEPTED 14 November 2024
PUBLISHED 06 December 2024

CITATION
Liu Z, Wu Q, He C, Zhang P, Wang X, Luo Z, Yang L and Huang C (2024) Ecological risk and chemical speciation of heavy metals in surface sediments of the Pearl River Estuary for comprehensive assessment.
Front. Environ. Sci. 12:1509277.
doi: 10.3389/fenvs.2024.1509277

Ecological risk and chemical speciation of heavy metals in surface sediments of the Pearl River Estuary for comprehensive assessment

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The Pearl River Estuary, a vital ecological and economic zone in Southern China, has been heavily impacted by industrial discharges, leading to significant heavy metal contamination. To address the ecological implications of different chemical forms of heavy metals, this study systematically evaluated the total concentrations and chemical speciation of Cu, Zn, Cd, and Pb in surface sediments (0–2 cm) collected from 17 sites. Chemical speciation was determined using a modified BCR sequential extraction procedure, and pollution and ecological risks were assessed via the geo-accumulation index (I_{geo}), potential ecological risk index (RI), and risk assessment code (RAC). The results showed that all four metals exceeded background values, with Cd presenting the highest enrichment (39 times) and contributing 97% of the ecological risk. Speciation analysis revealed that Cd predominantly exists in bioavailable forms, posing severe ecological threats. This study highlights the urgent need for targeted remediation strategies to mitigate Cd contamination and its ecological impact on the estuary.

KEYWORDS

heavy metal contamination, chemical speciation, ecological risk assessment, surface sediments, Pearl River Estuary

1 Introduction

The estuarine region is a critical transitional zone between terrestrial and marine ecosystems, where intricate interactions occur among physical, chemical, biological, and geological processes. Due to their inherent ecological sensitivity and fragility, estuarine environments are highly vulnerable to anthropogenic disturbances (Elliott and Quintino, 2007; Min et al., 2021). The Pearl River Estuary, one of China's three largest estuaries, serves as a critical breeding and conservation ground for juvenile fish and shrimp and provides habitat for numerous rare aquatic species (Chan and Wang, 2019). Recent rapid industrial, agricultural, and marine fishery development along the estuary's coastline has led to excessive pollutant discharges, resulting in severe environmental degradation-most notably, the pervasive contamination by heavy metals (Zhao et al., 2020; Niu et al., 2021a). Similar studies in other coastal and lagoon systems have shown comparable pollution patterns, highlighting the importance of understanding regional environmental conditions and pollution trends (Ustaoglu et al., 2024).

Heavy metals are characterized by their intrinsic biological toxicity, environmental persistence, and bioaccumulation potential. Once introduced into aquatic systems, such as rivers and estuaries, these metals accumulate in sediments, posing severe threats to benthic organisms and aquatic life, and may ultimately impact human health through biomagnification along the food chain. Consequently, heavy metals are considered a priority pollutant in aquatic ecosystems (Ndimele, 2012; Fu et al., 2014; Li et al., 2014). Research on the bioaccumulation of metals across different species offers further insight into the potential health risks and ecological implications (Yuksel et al., 2024). In response to these environmental challenges, the *Guangdong Province Heavy Metal Pollution Prevention Plan* and several ecological restoration projects have been implemented to reduce heavy metal emissions and improve water quality in the Pearl River Estuary (Zhen et al., 2016; Zhao et al., 2020). The Pearl River Estuary, acting as a "source-sink" transition zone, is heavily influenced by hydrodynamic and tidal forces, which intensify the dispersal and accumulation of heavy metals, making it a significant pollution hotspot for surrounding cities such as Guangzhou, Dongguan, and Shenzhen in the Greater Bay Area (Niu et al., 2021a). Therefore, a systematic evaluation of heavy metal contamination in the estuarine sediments is urgently needed (Wang et al., 2011; Huang et al., 2018; Wang et al., 2023).

The bioavailability and mobility of heavy metals in sediments are influenced not only by their total concentrations but also by their chemical forms and binding states. Sequential chemical extraction methods have been widely adopted to investigate these chemical forms in solid media such as sediments and soils (Choleva et al., 2020). Tessier first introduced the sequential extraction approach in 1979, and the European Community Bureau of Reference (BCR) later developed a widely used three-step sequential extraction protocol in 1987. The BCR protocol has since undergone numerous modifications to enhance its precision and applicability (Usero et al., 1998; Zemberyová et al., 2006). The fundamental principle of these multi-step extraction methods is to simulate varying environmental conditions using chemical reagents of increasing strength, gradually isolating different chemical forms of heavy metals. Tessier's method categorizes heavy metals into five chemical forms: exchangeable, carbonate-bound, iron-manganese oxide-bound, organic matter-bound, and residual. Subsequently, Rauret improved the BCR method in 1999 by grouping metals into four forms: acid-extractable, reducible, oxidizable, and residual. The acid-extractable form encompasses the exchangeable and carbonate-bound metals from Tessier's classification (Rauret et al., 1999; Anju and Banerjee, 2010). The exchangeable form is primarily adsorbed onto clay or humic substances. It is the most susceptible to release and migration, while the carbonate-bound form is quickly released under acidic conditions (Morera et al., 2001). The acid-extractable form is generally the most responsive to environmental changes, presenting high ecological risk and toxicity. Conversely, the residual form is bound within mineral and silicate lattices, rendering it relatively stable and posing minimal ecological risk (Sundaray et al., 2011). The distribution of heavy metals in various chemical forms indicates their mobility and transformation potential in sediments and soils, reflecting their bioavailability and ecological risks (Kim et al., 2015).

Numerous studies have assessed the ecological risks of heavy metals in surface sediments by analyzing their total concentrations, chemical forms, and distribution patterns using various technical methods (Yu et al., 2011). Among these, the Index of Geo-Accumulation (I_{geo}) and the Potential Ecological Risk Index (RI) are commonly employed to evaluate the overall pollution status and potential ecological risks of heavy metals in sediments (Cui et al., 2014; Maanan et al., 2015). The I_{geo} provides a straightforward reflection of natural and anthropogenic influences on sediment quality. At the same time, the RI considers the concentrations, toxicities, and environmental sensitivities to heavy metals, thus offering a comprehensive risk assessment framework (Zhang et al., 2016). However, both indices fail to consider the varying chemical forms of heavy metals, which play a decisive role in determining their toxicity and mobility in aquatic environments. The Risk Assessment Code (RAC), which emphasizes the chemical forms of heavy metals, offers a more accurate evaluation by correlating the bioavailable fractions with environmental risks (Yang et al., 2014).

Although extensive research has been conducted on heavy metal accumulation in the Pearl River Estuary, most studies have focused on total concentrations and pollution risks (Ip et al., 2004; Yang et al., 2012; Zhao et al., 2020), with limited attention paid to the chemical forms and their associated ecological risks. Comparative studies across various regions can provide a broader context, highlight unique pollution characteristics, or align them with global patterns (Yuksel et al., 2021; Topaldemir et al., 2023). Therefore, this study aims to bridge this gap by employing the I_{geo}, RI, and RAC methodologies to comprehensively analyze the accumulation characteristics, chemical speciation, and ecological risks of four common heavy metals (Cu, Zn, Cd, and Pb) in the surface sediments of the Pearl River Estuary. The results of this study will provide a valuable theoretical foundation for the long-term management and mitigation of heavy metal pollution in the Pearl River Estuary.

2 Materials and methods

2.1 Study area overview

The Pearl River, formed by the convergence of the Xi River, Bei River, Dong River, and numerous tributaries within the Pearl River Delta, is the most extensive river system in southern China. The third longest in the country, spanning 2,320 km with a drainage area of 450,000 square kilometers, of which 440,000 square kilometers are within Chinese territory (Chen et al., 2008). The Pearl River's annual runoff exceeds 330 billion cubic meters, second only to the Yangtze River, and it produces seven times the annual runoff of the Yellow River (Xu et al., 2010). This study focuses on the surface sediments of the Pearl River Estuary, extending from Duntouji in Guangzhou (113.51°E, 23.05°N) in the north to near the Jitimen Bridge in Zhuhai (113.26°E, 22.09°N), including the Lingding Yang region, which is characterized as a tide-dominated estuarine bay. Sampling was

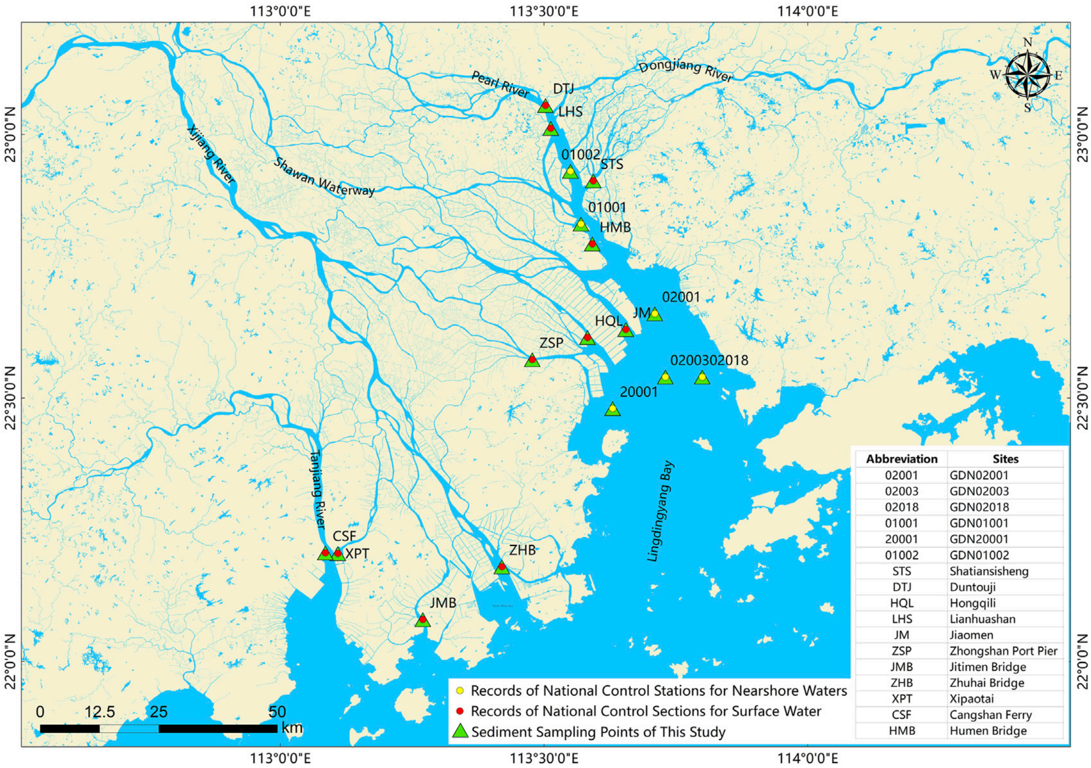

FIGURE 1
Distribution of sediment sampling points in the Pearl River Estuary.

conducted in January 2022, with 17 sampling sites established across the study area, as depicted in Figure 1.

2.2 Sample collection and processing

Due to the mild and consistent climate conditions in the Pearl River Estuary region throughout the year, coupled with the continuous and stable industrial activities along its banks, the levels of heavy metal pollution in this area are generally consistent year-round (Ye et al., 2020). Sediment samples were collected using a grab sampler to obtain undisturbed surface sediments (0–2 cm) and stored in polyethylene bags at 0°C–4°C. The samples were air-dried, and visible gravel, plants, and animal residues were removed. Subsequently, the sediments were oven-dried at 105°C to a constant weight, ground using an agate mortar, and sieved through a 200-mesh screen. The processed samples were stored in a desiccator for further analysis. According to the GB 15618–2008 Environmental Quality Standards for Soils, Cu, Zn, Cd, and Pb were selected as target heavy metals of concern (Ministry of Environmental Protection of China, 2008). The total concentrations of these metals in the sediment samples were determined after digestion using a mixture of HCl, HNO_3, HF, and $HClO_4$, following the four-acid digestion method (GB/T17140) (Standardization Administration of China, 1997). Cd and Pb concentrations were measured using a graphite furnace atomic absorption spectrophotometer, while Cu and Zn were quantified using a flame atomic absorption spectrophotometer. These different analytical techniques are chosen based on the concentration sensitivity and detection requirements specific to each metal. The graphite furnace atomic absorption spectrophotometer (GFAAS) offers a significantly higher sensitivity compared to FAAS, making it ideal for detecting trace levels of metals like Cd and Pb, which are often present in lower concentrations. In contrast, flame atomic absorption spectrophotometry (FAAS) is suitable for metals such as Cu and Zn, which are generally found in higher concentrations in environmental samples. FAAS is also efficient for rapid analysis when ultra-trace sensitivity is not required. Utilizing these methods in tandem ensures accurate measurement across different concentration ranges, enhancing the precision and reliability of the heavy metal quantification (Garnier et al., 2006; Medeiros et al., 2020).

TABLE 1 Assessment of geo-accumulation index (I_{geo}) and sediment pollution degree.

I_{geo}	Level	Pollution degree
<0	0	Practically unpolluted
0–1	1	Unpolluted to moderately polluted
1–2	2	Moderately polluted
2–3	3	Moderately to heavily polluted
3–4	4	Heavily polluted
4–5	5	Heavily to extremely polluted
>5	6	Extremely polluted

TABLE 2 Classifications of potential ecological risk index (ERI).

Assessment criterion	Ecological risk index				
	Low	Moderate	Considerable	High	Very high
E_r^i	E_r^i < 40	40 ≤ E_r^i < 80	80 ≤ E_r^i <160	160 ≤ E_r^i < 320	E_r^i ≥ 320
RI	RI < 150	150 ≤ RI < 300	300 ≤ RI < 600	RI ≥ 600	

TABLE 3 Classification standards for risk assessment method (RAC).

Acid-extractable content (%)	Risk level
RAC < 1	No risk
1 ≤ RAC < 10	Low risk
10 ≤ RAC < 30	Medium risk
30 ≤ RAC < 50	High risk
RAC > 50	Very high risk

The chemical forms of the heavy metals were extracted using the modified BCR sequential extraction procedure (Rauret et al., 1999; Sungur et al., 2014). The specific extraction protocol consisted of (1) Acid-extractable fraction (F1), including exchangeable and carbonate-bound metals, extracted using 0.11 mol·L^{-1} acetic acid; (2) Reducible fraction (F2), representing metals bound to iron-manganese oxides, extracted using 0.5 mol·L^{-1} hydroxylamine hydrochloride; (3) Oxidizable fraction (F3), representing metals bound to organic matter and sulfides, extracted by digesting the F2 residue with 30% (8.8 mol·L^{-1}) hydrogen peroxide followed by 1 mol·L^{-1} ammonium acetate; and (4) Residual fraction (F4), representing metals bound to silicates or within the mineral lattice, extracted by digesting the F3 residue using a mixture of three acids.

Three parallel samples and an environmental standard reference material (ESS-4) were used for quality control to ensure analytical precision and accuracy. The relative error of heavy metal concentrations in parallel samples was maintained below 10%, and the recovery rates of standard reference materials ranged from 95% to 120%. The detection limits for Cu, Zn, Cd, and Pb were 0.5 mg·kg^{-1}, 7.0 mg·kg^{-1}, 0.07 mg·kg^{-1}, and 2.0 mg·kg^{-1}, respectively.

While the BCR sequential extraction procedure is widely used for assessing heavy metal speciation, potential limitations exist. Interferences from other sediment components, such as organic matter or carbonate content, may affect the extraction accuracy, particularly for acid-extractable and reducible fractions. Additionally, the four-acid digestion method used for total concentration measurement could lead to variations in recovery rates for certain metals due to complex matrix effects (Ryan et al., 2008).

2.3 Data analysis

2.3.1 Pollution characteristics and risk assessment based on total heavy metal concentrations

2.3.1.1 Index of geo-accumulation (I_{geo})

The Index of Geo-Accumulation (I_{geo}), is widely used to evaluate the extent of heavy metal pollution in sediments (Karbassi et al., 2008; Ke et al., 2017). It is calculated using Equation 1 as follows:

$$I_{geo} = log_2\left(\frac{C_i}{1.5B_i}\right) \tag{1}$$

I_{geo} is the geo-accumulation index, C_i is the measured concentration of element I in the sediment, and B_i is the geochemical background value of element I in the region. In this study, the background values for Cu, Zn, Cd, and Pb are derived from the geometric mean values for soils in Guangdong Province (China National Environmental Monitoring Center, 1990). The background values used are Cu (12.1 mg·kg^{-1}), Zn (42.7 mg·kg^{-1}), Cd (0.026 mg·kg^{-1}), and Pb (32.0 mg·kg^{-1}). Based on the calculated I_{geo} values, the degree of heavy metal pollution is categorized into seven classes, as shown in Table 1 (Forstner et al., 1993).

2.3.1.2 Potential ecological risk assessment method (RI)

The potential ecological risk assessment method, proposed by Hakanson (1980), evaluates the ecological risks posed by heavy metals in sediments (Maanan et al., 2015; Zhang et al., 2016). The values are calculated using Equation 2 as follows:

$$E_i^T = T_i \times \frac{C_s^i}{C_n^i} \tag{2}$$

where E_i^T is the potential ecological risk factor for element i, T_i is the toxic response factor for element i, which depends on its toxicity and the sensitivity of the ecosystem to the element. In this study, the toxic response factors (T_i) for heavy metals (Cu = 5, Zn = 1, Cd = 30, and Pb = 5 (Suresh et al., 2011; Ke et al., 2017). C_s^i is the measured concentration of element I in the sediment (mg·kg^{-1}), and C_n^i is the background concentration of element I, derived from Guangdong Province soil background values.

The comprehensive ecological risk of multiple heavy metals is calculated using Equation 3 as follows:

$$\mathrm{RI} = \sum E_i^r \tag{3}$$

RI represents the comprehensive potential ecological risk index for multiple heavy metals, and $\sum E_i^r$ is the sum of the individual potential ecological risk factors for each heavy metal. The classification standards for RI are shown in Table 2 (Ke et al., 2017; Wang et al., 2018).

2.3.2 Risk assessment based on different chemical forms of heavy metals

The Risk Assessment Code (RAC) method provides a deeper understanding of the relationship between bioavailability, mineral mobility, and the environmental risks of heavy metals (Yang et al., 2014). RAC is calculated as the proportion of the acid-extractable fraction relative to the total content of an element (Lv et al., 2013), as shown in Equation 4 below:

$$\mathrm{RAC} = \frac{C_{F1}}{C_{F1} + C_{F2} + C_{F3} + C_{F4}} \times 100\% \quad (4)$$

where C_{F1} is the acid-extractable fraction content (mg·kg^{-1}), C_{F2} is the reducible fraction content (mg·kg^{-1}), C_{F3} is the oxidizable fraction content (mg·kg^{-1}), and C_{F4} is the residual fraction content (mg·kg^{-1}). The risk levels based on RAC values are classified as shown in Table 3.

3 Results

3.1 Descriptive statistics of total Cu, Zn, Cd, and Pb in sediments

3.1.1 Concentrations of Cu, Zn, Cd, and Pb in surface sediments of the Pearl River estuary

The concentrations of Cu, Zn, Cd, and Pb in surface sediments of the Pearl River Estuary are illustrated in Figure 2. The measured concentrations varied as follows: Cu ranged from 30.14 to 150.74 mg·kg^{-1}, Zn from 78.63 to 367.16 mg·kg^{-1}, Cd from 0.18 to 2.63 mg·kg^{-1}, and Pb from 40.57 to 115.11 mg·kg^{-1}. All sampling sites exhibited heavy metal concentrations exceeding the background values for soils in Guangdong Province. Among these, Cd showed the most significant elevation, with a mean concentration of 1.05 mg·kg^{-1}, surpassing the background value by 39 times. The mean concentrations of Cu (58.71 mg·kg^{-1}), Zn (88.23 mg·kg^{-1}), and Pb (67.17 mg·kg^{-1}) exceeded the background values by 3.85, 2.54, and 1.10 times, respectively.

3.1.2 Geo-accumulation index (I_{geo}) and pollution degree assessment of heavy metals

The geo-accumulation index (I_{geo}) and corresponding pollution assessment for the four heavy metals across 17 sampling sites are summarized in Table 4. Results indicate varying pollution levels for different metals based on I_{geo} values. Cd exhibited the highest pollution level, with an average I_{geo} of 4.47 (ranging from 2.09 to 6.08), classified as severely polluted (Class 5). Conversely, Pb showed a relatively low pollution level with an average I_{geo} of 0.42 (ranging from −0.12 to 1.26), indicating a clean status (Class 1). The mean I_{geo} values for Cu and Zn were 1.50 and 1.07, respectively, both classified as moderately polluted (Class 2).

Overall, the pollution ranking for the four metals from highest to lowest is: Cd (Class 5) > Cu (Class 2) > Zn (Class 2) > Pb (Class 1). The average I_{geo} values for the 17 sampling sites ranged from 1.05 to 3.19, corresponding to pollution levels between Class 2 and Class 4. The most severe pollution was observed at Site S5, which was classified as moderately to heavily polluted (Class 4), while Sites S4, S8, and S15 were categorized as moderately polluted (Class 3). The remaining 13 sampling sites were moderately polluted (Class 2).

3.1.3 Potential ecological risk assessment of heavy metals in sediments

The potential ecological risk indices (ERI) for Cu, Zn, Cd, and Pb in the surface sediments of the Pearl River Estuary are presented

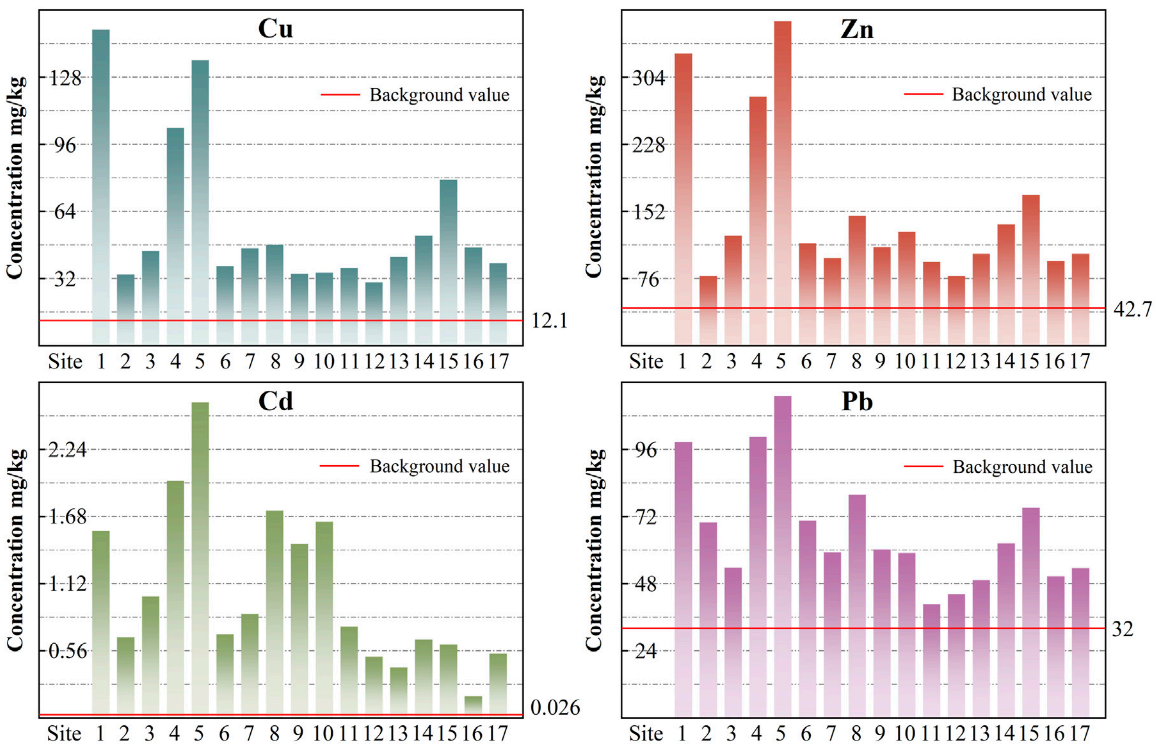

FIGURE 2
Descriptive statistics and comparative parameters of Cu, Zn, Cd, and Pb in surface sediments of the Pearl River Estuary (unit: mg·kg^{-1}).

TABLE 4 Geo-accumulation index (I_{geo}) and pollution degree assessment for Cu, Zn, Cd, and Pb in surface sediments of the Pearl River Estuary.

Sampling site	Cu		Zn		Cd		Pb		Average	
	I_{geo}	Pollution degree	I_{geo}	Pollution degree	I_{geo}	Pollution degree	I_{geo}	Pollution degree	I_{geo}	Pollution degree
S1	3.05	MHP	2.37	MP	5.32	SP	1.04	MMP	2.95	MP
S2	0.90	LP	0.30	LP	4.11	HP	0.54	C	1.46	MMP
S3	1.31	MMP	0.96	LP	4.70	HP	0.16	C	1.78	MMP
S4	2.52	MP	2.14	MP	5.66	SP	1.07	MMP	2.85	MP
S5	2.91	MP	2.52	MP	6.08	SP	1.26	MMP	3.19	MHP
S6	1.06	MMP	0.86	LP	4.16	HP	0.56	C	1.66	MMP
S7	1.35	MMP	0.63	LP	4.47	HP	0.30	C	1.69	MMP
S8	1.41	MMP	1.20	MMP	5.47	SP	0.73	C	2.20	MP
S9	0.92	LP	0.80	LP	5.22	SP	0.33	C	1.82	MMP
S10	0.94	LP	1.01	MMP	5.39	SP	0.30	C	1.91	MMP
S11	1.03	MMP	0.57	LP	4.29	HP	0.24	C	1.41	MMP
S12	0.73	LP	0.30	LP	3.71	MHP	0.12	C	1.15	MMP
S13	1.22	MMP	0.70	LP	3.43	MHP	0.04	C	1.35	MMP
S14	1.53	MMP	1.10	MMP	4.07	HP	0.38	C	1.77	MMP
S15	2.12	MP	1.41	MMP	3.97	MHP	0.65	C	2.04	MP
S16	1.36	MMP	0.58	LP	2.19	MHP	0.08	C	1.05	MMP
S17	1.11	MMP	0.70	LP	3.78	MHP	0.16	LP	1.44	MMP
Average	1.50	MMP	1.07	MMP	4.47	HP	0.42	C	1.87	MMP

Note: C = clean, LP, lightly polluted; MP, moderately polluted; MMP, mildly to moderately polluted; MHP, moderately to heavily polluted; HP, heavily polluted; SP, severely polluted.

in Table 5. The ERI values for Cu ranged from 12.45 to 62.29, indicating low to moderate risk, whereas Zn and Pb showed low risk at all sampling points, with ERI values ranging from 1.84 to 8.60 and 6.34 to 17.99, respectively. In contrast, Cd exhibited extremely high ERI values, ranging from 205.93 to 3,036.77, suggesting severe ecological risk across all sites.

The average ERI values in descending order were as follows: Cd (1,214.46) > Cu (24.26) > Pb (10.49) > Zn (3.54). The comprehensive potential ecological risk index (RI) for the four heavy metals ranged from 235.39 at Site S16 to 3,119.60 at Site S5, with an average RI value of 1,252.75. Among the 17 sampling sites, Site S5 was categorized as a moderate ecological risk, Site S15 as a considerable ecological risk, and the remaining 15 as a high ecological risk.

3.2 Descriptive statistics of different chemical forms of Cu, Zn, Cd, and Pb in sediments

3.2.1 Percentage content of different chemical forms of Cu, Zn, Cd, and Pb in surface sediments

Figure 3 presents the percentage content of different Cu, Zn, Cd, and Pb chemical forms in the surface sediments. The distribution of chemical forms for each metal is as follows:

Cu: The acid-extractable form accounted for 2.52%–12.38%, the reducible form 3.56%–23.98%, the oxidizable form 43.00%–63.66%, and the residual form 7.93%–37.50%. On average, the proportions of the chemical forms were ranked as follows: oxidizable (52.13%) > residual (22.75%) > reducible (17.57%) > acid-extractable (7.55%).

Zn: The acid-extractable form ranged from 7.21% to 29.73%, the reducible form from 12.15% to 27.22%, the oxidizable form from 17.13% to 40.48%, and the residual form from 14.89% to 50.93%. The average proportions were residual (33.07%) > oxidizable (28.08%) > reducible (19.58%) > acid-extractable (19.28%).

Cd: The acid-extractable form ranged from 17.37% to 50.63%, the reducible form from 13.63% to 34.33%, the oxidizable form from 8.87% to 51.49%, and the residual form from 4.52% to 19.91%. On average, the chemical form distribution was acid-extractable (35.45%) > reducible (32.82%) > oxidizable (21.86%) > residual (9.87%).

Pb: The acid-extractable form accounted for 1.07%–4.27%, the reducible form 21.23%–46.33%, the oxidizable form 15.38%–53.26%, and the residual form 21.04%–35.16%. The average distribution was: reducible (34.76%) > oxidizable (34.66%) > residual (28.45%) > acid-extractable (2.12%).

TABLE 5 Potential ecological risk assessment of Cu, Zn, Cd, and Pb in surface sediments of the Pearl River Estuary.

Sampling site	ERI (Cu)	Risk level	ERI (Zn)	Risk level	ERI (Cd)	Risk level	ERI (Pb)	Risk level	RI	Risk level
S1	62.29	M	7.74	L	1797.23	VH	15.41	L	1882.67	H
S2	14.00	L	1.84	L	775.10	VH	10.92	L	801.86	H
S3	18.61	L	2.91	L	1,166.53	VH	8.38	L	1,196.44	H
S4	42.90	M	6.61	L	2,281.40	VH	15.70	L	2,346.60	H
S5	56.25	M	8.60	L	3,036.77	VH	17.99	L	3,119.60	H
S6	15.67	L	2.71	L	802.25	VH	11.02	L	831.65	H
S7	19.18	L	2.32	L	999.19	VH	9.23	L	1,029.93	H
S8	19.87	L	3.44	L	1993.50	VH	12.46	L	2029.28	H
S9	14.16	L	2.61	L	1,676.15	VH	9.41	L	1702.33	H
S10	14.35	L	3.02	L	1886.46	VH	9.20	L	1913.03	H
S11	15.33	L	2.22	L	877.46	VH	6.34	L	901.35	H
S12	12.45	L	1.84	L	588.05	VH	6.91	L	609.25	H
S13	17.48	L	2.43	L	484.15	VH	7.69	L	511.77	C
S14	21.66	L	3.21	L	754.05	VH	9.75	L	788.67	H
S15	32.66	L	4.00	L	702.97	VH	11.73	L	751.36	H
S16	19.30	L	2.24	L	205.93	VH	7.91	L	235.39	M
S17	16.24	L	2.44	L	618.56	VH	8.37	L	645.60	H
Average	24.26	L	3.54	L	1,214.46	VH	10.49	L	1,252.75	H
RERL	L		L		VH		L		H	

Note: L = low, M = moderate, C = considerable, H = high, VH, very high; RERL, regional ecological risk levels.

3.2.2 Risk assessment code (RAC) for different chemical forms of heavy metals

The Risk Assessment Code (RAC) values and corresponding risk levels for Cu, Zn, Cd, and Pb are shown in Figure 4. The results are summarized as follows:

Cu: RAC values ranged from 2.52% to 12.38%. Only two sampling sites (S15 and S16) were classified as medium risk (11.76%), while the remaining 15 sites showed low risk (88.24%).

Zn: RAC values ranged from 7.21% to 29.73%. Only Site S9 was classified as low risk, whereas the remaining 16 sampling sites were categorized as medium risk (94.12%).

Cd: RAC values ranged from 17.37% to 50.36%, indicating medium to very high risk. Seven sampling sites (S1, S4, S5, S2, S8, S7, and S9) were classified as medium risk (41.18%), nine sites (S15, S14, S11, S12, S16, S17, S10, S3, and S6) as high risk (52.94%), and Site S1 as very high risk.

Pb: RAC values ranged from 1.07% to 4.27%, indicating low risk across all sites.

The average RAC values across all sites rank as follows: Cd (35.45%) > Zn (19.28%) > Cu (7.55%) > Pb (2.12%). Based on these values, Cd is classified as high risk, Zn as medium risk, and Cu and Pb as low risk.

3.3 Comprehensive assessment of total and speciated heavy metal pollution risk

A comprehensive assessment of the total and speciated pollution risks for Cu, Zn, Cd, and Pb is presented in Table 6, using the I_{geo}, ERI, and RAC indicators. Results indicate that Cd poses the highest risk levels across all three indicators. Cu is categorized as moderately to mildly polluted (MMP) according to the I_{geo}, with both its single-element ecological risk and bioavailable fraction risk being classified as low risk. Zn is also classified as MMP by I_{geo} and as low risk in terms of its single-element ecological risk; however, its bioavailable fraction presents a medium risk, indicating a higher potential ecological risk than Cu. Pb is considered clean according to I_{geo}, with its single-element ecological risk and bioavailable fraction risk classified as low risk.

This assessment highlights that Cd poses the most significant risk across all indicators, necessitating prioritized mitigation efforts, whereas Cu and Pb present minimal risks. Despite Zn's lower total concentration, its higher bioavailable fraction contributes to a medium risk, warranting attention to potential ecological impacts.

These ecological risks are closely linked to the chemical forms of the metals. For Cd, the dominance of its acid-extractable fraction indicates high bioavailability, which increases its mobility and

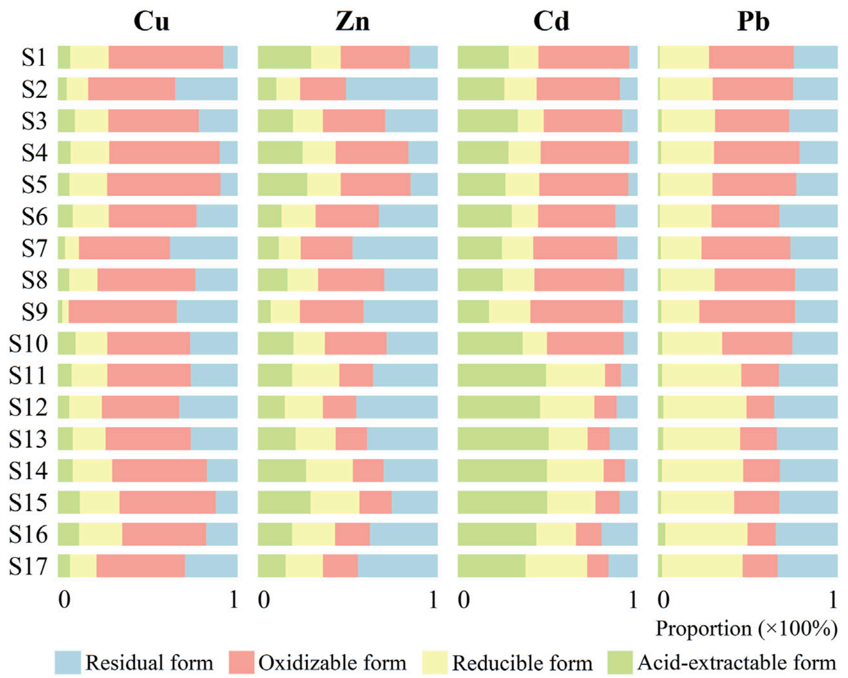

FIGURE 3
Percentage content of different chemical forms of Cu, Zn, Cd, and Pb in surface sediments.

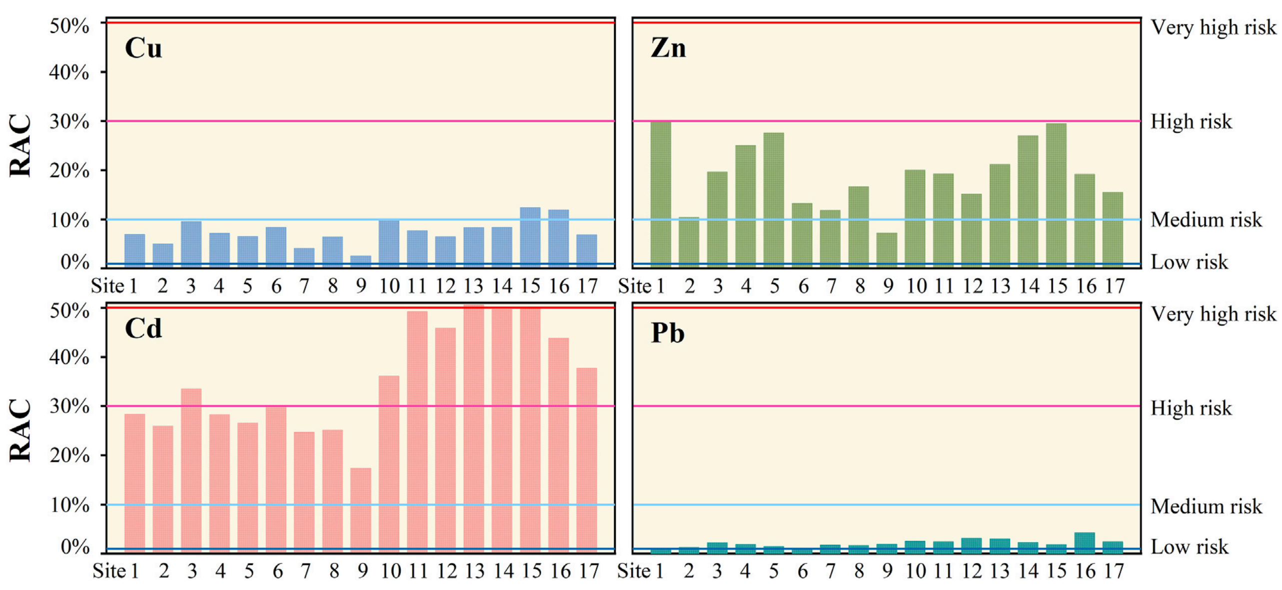

FIGURE 4
Risk levels of heavy metals based on risk assessment code (RAC).

potential for uptake by aquatic organisms, posing severe ecological threats. In contrast, Zn, although lower in total concentration, shows a substantial bioavailable fraction, highlighting its potential for mobility and ecological impact under variable environmental conditions. On the other hand, Cu and Pb have lower proportions of bioavailable forms and higher residual fractions, suggesting they are less mobile and present a reduced ecological risk (Xu et al., 2016; Liu et al., 2021).

TABLE 6 Comprehensive assessment of total and speciated pollution risk for Cu, Zn, Cd, and Pb.

Heavy metal	I_{geo} level	ERI level	RAC level
Cu	MMP	LR	LR
Zn	MMP	LR	MR
Cd	MP	VER	EHR
Pb	C	LR	LR

Note: MMP, moderate to mildly polluted; MP, moderately polluted, C = clean, LR, low risk; MR, medium risk; VHR, very high risk; HER, extremely high risk.

TABLE 7 Comparison of metal ion concentrations (mg·kg^{-1}) in surface sediments of the Pearl River Estuary and other rivers in China.

Heavy metal	Cu	Zn	Cd	Pb	Reference
This Study (Pearl River Estuary)	58.71	151.23	1.05	67.17	—
Guangdong Province Soil Background	12.1	42.7	0.026	32.0	China National Environmental Monitoring Center (1990)
Yangtze River	44.75	120.42	0.4	39.32	—
Bortala River	30.09	99.19	0.17	31.98	Zhang et al. (2016)
Liao River	17.83	50.24	1.2	10.57	Ke et al. (2017)

4 Discussions

4.1 Total heavy metal pollution and ecological risk in the Pearl River Estuary

Cu, Zn, Cd, and Pb concentrations in the Pearl River Estuary are substantially higher than other major river systems in China, such as the Yangtze River and Bortala River (Xinjiang), as shown in Table 7. While the sediment Cd concentrations in the Yangtze and Liao Rivers slightly surpass those in the Pearl River Estuary, Cu, Zn, and Pb concentrations are significantly lower. This finding underscores that the Pearl River Estuary remains one of the most heavily contaminated estuaries in China concerning heavy metal pollution in sediments, likely due to the highly industrialized nature of the lower Pearl River region. Furthermore, all heavy metal concentrations in the sediments exceed the background values for Guangdong Province soils (Table 7), indicating substantial anthropogenic contributions to heavy metal contamination, particularly for Cd, which is elevated by 39 times compared to the background level. Numerous studies have consistently identified Cd as the most severe contaminant in this estuary over the years (Xie et al., 2012; Liu et al., 2017; Jia et al., 2021). Despite the implementation of stringent control measures in recent years, the persistence and accumulation of these metals imply that heavy metal pollution remains a critical environmental challenge in the region, especially for Cd, which necessitates sustained remediation efforts.

Regarding potential ecological risk, the single-element ecological risk index (ERI) for Cu, Zn, and Pb at all sampling points indicates low risk (Table 5). In contrast, Cd poses a high ecological risk across the 17 sites. The contribution of each metal's ERI to the comprehensive potential ecological risk index (RI) is ranked as follows: Cd (96.94%) > Cu (1.94%) > Pb (0.84%) > Zn (0.28%), clearly indicating Cd's dominant role in the overall ecological risk. This result aligns with a study by Zhang et al. (2016), which assessed the potential ecological risk of heavy metals in the Bortala River. Their findings similarly showed that Cd accounted for 97% of the total ecological risk, followed by Pb, Cu, and Zn. The congruence between these studies further confirms that Cd exhibits the highest single-element ecological risk and makes the most significant contribution to the comprehensive ecological risk in the Pearl River Estuary.

4.2 Correlation analysis of heavy metals in sediments of the Pearl River estuary

Heavy metals in sediments often exhibit complex interrelationships, influenced by factors such as the original composition of heavy metals in the parent rock, soil formation processes, and anthropogenic activities. High and significant correlations between heavy metals can imply a common source of contamination (Zhang et al., 2016; Ke et al., 2017; Fu et al., 2022). This study conducted Pearson correlation analysis to examine the interrelationships between Cu, Zn, Cd, and Pb in the sediments from 17 sampling sites. As shown in Table 8, all four metals exhibited significant correlations ($P < 0.01$), suggesting that they share a common source, potentially linked to the intense industrial development in the lower reaches of the Pearl River. Many heavy metals are discharged into the river through industrial effluents, leading to severe sediment contamination in the estuary. These findings are consistent with research by Zhang et al. (2016), who studied the distribution of heavy metals in sediments from the Lingding Yang area of the Pearl River Estuary over the past century. Their results indicated that the strong correlations between heavy metals suggest a common source or that the environmental conditions and biogeochemical processes have remained highly consistent and stable. Other studies have attributed the primary sources of heavy metals in the Pearl River Estuary to

TABLE 8 Correlation analysis of Cu, Zn, Cd, and Pb in the Pearl River Estuary.

	Cu	Zn	Cd	Pb
Cu	1.000			
Zn	0.969**	1.000		
Cd	0.629**	0.778**	1.000	
Pb	0.863**	0.913**	0.786**	1.000

Note: ** represents a highly significant correlation at P < 0.01 (two-tailed); * represents a significant correlation at P < 0.05 (two-tailed).

industrial activities, shipping, and agricultural production, with Cd contamination particularly associated with the lead-zinc mining and smelting industries in the upper reaches of the Beijiang and Dongjiang Rivers in Guangdong Province (Gu et al., 2014; Du et al., 2019; Lu et al., 2020; Niu et al., 2021b). Pollutants from these industries are transported downstream, exacerbating heavy metal contamination in the estuarine sediments.

4.3 Chemical speciation and environmental risks of heavy metals

The RAC results indicate that Cd poses the highest pollution and ecological risk among the four metals. The acid-extractable fraction of Cd, representing its most bioavailable form, constitutes more than one-third of its total concentration, the highest proportion among the studied metals. Furthermore, the combined content of the acid-extractable, reducible, and oxidizable forms of Cd exceeds 90% of its total concentration, with the residual fraction contributing less than 10%. This distribution pattern suggests that anthropogenic activities heavily influence Cd in the surface sediments of the Pearl River Estuary, which are present predominantly in bioavailable forms. Consequently, Cd is highly susceptible to environmental changes, such as variations in water chemistry, and can be quickly released back into the water, where it may be assimilated by aquatic organisms, adversely impacting their growth and survival.

In contrast, Pb exhibits the lowest RAC value, with the acid-extractable fraction accounting for only 2.12% of its total concentration and a relatively high residual fraction (28.45%), indicating low ecological risk. Cu also has a low proportion of acid-extractable content but shows the highest percentage of oxidizable forms, exceeding 50% of its total concentration. This suggests Cu may migrate from sediments to the water column under oxidative conditions. On the other hand, Zn has a relatively high proportion of acid-extractable content and a substantial residual fraction (33.07%), the highest among the four metals. The other chemical forms of Zn (acid-extractable, reducible, and oxidizable) are present in relatively similar proportions, ranging from 19.28% to 28.08%, indicating that Zn can quickly shift between its bioavailable forms under both oxidative and reductive conditions.

Although research on heavy metals in river sediments across China began relatively late, most major river basins have been comprehensively studied. The distribution of heavy metal chemical forms shows significant variation among different river systems, likely due to the diverse anthropogenic activities and environmental conditions that influence heavy metal partitioning in sediments (Jiang et al., 2020; Deng et al., 2023).

The estuarine environmental conditions, such as pH, salinity, and organic matter content, are considered to interpret the observed speciation patterns further. For instance, the high bioavailability of cadmium (Cd) in the Pearl River Estuary may be attributed to the estuary's slightly acidic conditions and moderate salinity levels, which enhance the solubility and mobility of Cd. Similarly, the presence of oxidizable forms of Cu is likely influenced by the organic-rich sediments found in this region, which provide binding sites for metal-organic complexes. These environmental factors contribute to the differential bioavailability and mobility observed for each metal.

5 Conclusion

The concentrations of Cu, Zn, Cd, and Pb in surface sediments across all sampling sites in the Pearl River Estuary significantly exceed the background values for soils in Guangdong Province, with Cd (1.05 mg·kg^{-1}) showing the most pronounced contamination, surpassing the background value by a factor of 39. The geo-accumulation index (I_{geo}) values for the sampling sites indicate varying pollution levels, ranging from Class 2 to Class 4, with the pollution severity ranked as follows: Cd (Class 5) > Cu (Class 2) > Zn (Class 2) > Pb (Class 1). The average single-element ecological risk index (ERI) for heavy metals in descending order is Cd > Cu > Pb > Zn, with Cd classified as an extremely high risk. At the same time, Cu, Zn, and Pb are categorized as low-risk. The comprehensive potential ecological risk index (RI) classifies the Pearl River Estuary sediments as high ecological risk, with Cd contributing 97% of the total risk. The Risk Assessment Code (RAC) analysis further ranks the metals in terms of risk as Cd > Zn > Cu > Pb. Cd is classified as high risk, Zn as medium risk, and Cu and Pb as low risk.

This study reveals that Cd poses the highest ecological risk among the four metals, with its predominantly bioavailable forms making it highly susceptible to environmental changes and, thus, a significant threat to the estuarine ecosystem. These findings highlight the need for continuous, targeted management strategies to mitigate Cd contamination and reduce its ecological impact in the Pearl River Estuary. By focusing on heavy metal contamination and ecological risks within the estuary's specific context, we used background values relevant to the region. While international standards, such as those from the European Union or EPA, provide useful comparative benchmarks, they may not fully capture the unique environmental and regulatory conditions of this estuarine ecosystem in southern China. Future research should incorporate these benchmarks, examine the long-term impacts of Cd bioavailability on aquatic health, and assess the efficacy of remediation techniques over time to support adaptive management in this unique ecological context.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding authors.

Author contributions

ZhL: Conceptualization, Data curation, Methodology, Writing–original draft, Writing–review and editing. QW: Data curation, Investigation, Software, Visualization, Writing–review and editing. CH: Data curation, Investigation, Software, Visualization, Writing–review and editing. PZ: Conceptualization, Data curation, Methodology, Supervision, Writing–original draft, Writing–review and editing. XW: Data curation, Investigation, Software, Visualization, Writing–review and editing. ZiL: Investigation, Validation, Writing–review and editing. LY: Investigation, Validation, Writing–review and editing. CQH: Conceptualization, Data curation, Methodology, Supervision, Writing–original draft, Writing–review and editing.

Funding

The author(s) declare that financial support was received for the research, authorship, and/or publication of this article. This work was supported by the Key Research and Development Program Project in Guangdong Province (2020B1111350001), the Science and Technology Innovation Project in Guangdong Forestry (2024KJCX005), and the UNEP/GEF "Implementation of the Strategic Action Plan for the South China Sea and Gulf of Thailand" (Mangroves, seagrass beds, wetlands) (S1-32GFL-000631, SB-009056).

Conflict of interest

Author LY was employed by Guangzhou Hongjing Ecological Technology Co., Ltd.

The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Generative AI statement

The author(s) declare that no Generative AI was used in the creation of this manuscript.

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Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fenvs.2024.1509277/full#supplementary-material

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