Chinese Journal of Oceanology and Limnology
Vol. 34 No. 6, P. 1320-1331, 2016
http://dx.doi.org/10.1007/s00343-016-5112-3

Ecological risk assessment of heavy metals in surface seawater and sediment near the outlet of a zinc factory in Huludao City, Liaoning Province, China*

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Received May 5, 2015; accepted in principle Aug. 15, 2015; accepted for publication Sep. 8, 2015

Abstract At present, the methods widely applied to assess ecological risk of heavy metals are essentially single-point estimates in which exposure and toxicity data cannot be fully used and probabilities of adverse biological effects cannot be achieved. In this study, based on investigation of concentrations of six heavy metals (As, Hg, Pb, Cd, Cu, and Zn) in the surface seawater and sediment near the outlet of a zinc factory, located in Huludao City, Liaoning Province, China, a tiered approach consisting of several probabilistic options was used to refine ecological risk assessment for the individuals. A mixture of various heavy metals was detected in the surface seawater, and potential ecological risk index (PERI) was adopted to assess the potential ecological risk of heavy metals in the surface sediment. The results from all levels of aquatic ecological risk assessment in the tiered framework, ranging from comparison of single effects and exposure values to the use of distribution-based Hazard Quotient obtained through Monte Carlo simulation, are consistent with each other. Briefly, aquatic Zn and Cu posed a clear ecological risk, while Cd, Pb, Hg, and As in the water column posed potential risk. As expected, combined ecological risk of heavy metal mixture in the surface seawater was proved significantly higher than the risk caused by any individual heavy metal, calculated using the concept of total equivalent concentration. According to PERI, the severity of pollution by the six heavy metals in the surface sediment decreased in the following sequence: Cd>Hg>As>Pb>Cu>Zn, and the total heavy metals in the sediment posed a very high risk to the marine environment. This study provides a useful mathematical framework for ecological risk assessment of heavy metals.

Keyword: heavy metal; ecological risk assessment; zinc factory; joint probability curve; Monte Carlo; potential ecological risk index

1 INTRODUCTION

The discharge of domestic sewage and industrial wastewater, tends to increase with the urbanization and industrialization in coastal areas, and poses a serious threat to the environmental security of coastal marine ecosystems (Gao and Chen, 2012). Among various pollutants existing in wastewater, heavy metals have drawn much attention due to their strong biological toxicity, poor biodegradability in the environment, and easy accumulation and magnification in marine organisms (Zhuang and Gao, 2014). According to the Bulletin of Marine Environmental Status of China for the year of 2013, 20 743 tons of Zn, 3 703 tons of Cu, 2 004 tons of Pb, 138 tons of Cd, 40 tons of Hg, and 2 976 tons of As were discharged into the sea through terrigenous input in 2013 (State Oceanic Administration People's Republic of China, 2013). Hg posed a serious hazard to reproductive systems in humans and animals (Boujbiha et al., 2009). Pb, with levels as low as 10 μg/dl in plasma, leads to impaired cognitive

* Supported by the Science and Technology Project of North China Sea Branch of State Oceanic Administration (No. 2014B02)
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function, behavior difficulties, and reduced intelligence in children (Gasana et al., 2006). Chronic exposure to Cd is associated with occurrence of renal tubular dysfunction and proteinuria (Bremner, 1974). Heavy metals are a big threat to marine life.

At present, ecological risk assessment (ERA) of heavy metals mainly focuses on those deposited in sediments. Various risk assessment indices have been developed thereby, including sediment quality guidelines (SQGs) (Long et al., 1995; Macdonald et al., 1996), enrichment factor (EF) (Su et al., 2011), relative enrichment factors (REFs) (Tang et al., 2010), index of geo-accumulation (Igeo) (Liu et al., 2011), excess after regression analysis (Hilton et al., 1985), and potential ecological risk index (PERI) (Hakanson, 1980). For example, Gao and Chen (2012) used three empirically derived SQGs to assess the pollution of six heavy metals (Cd, Cr, Cu, Ni, Pb, and Zn) detected in the surface sediments of northwestern Bohai Bay. Li et al. (2013) applied EF, Igeo, and effect-range classification to evaluate the potential ecological risk of Cr, Cu, Ni, Pb, and Zn in surface sediments from the coastal Shandong Peninsula (Yellow Sea). Based on the effect-range classification, Cr, Cu, and Ni were estimated likely to pose environmental risks. Zhuang and Gao (2014) employed multiple indices and guidelines to assess the ecological risk of six heavy metals (Cd, Cr, Cu, Ni, Pb, and Zn) in the surface sediments of the Laizhou Bay and the surrounding marine area of the Zhangzi Island, and all the indices demonstrated that Cd posed the highest environmental risk in both areas.

These methods, widely applied to assess the ecological risk of heavy metals in sediment, are essentially single-point estimates in which exposure and toxicity data cannot be fully used and the probabilities of adverse biological effects cannot be estimated. Alternatively, probabilistic approaches, such as the joint probability curve (JPC) method and Monte Carlo simulation, can qualify the uncertainties of exposure and toxicity data, and provide quantitative probabilities of specific levels of adverse biological effects based on species sensitivity distributions (SSDs) (Wang et al., 2002; Zolezzi et al., 2005). In fact, probabilistic approaches have been adopted to refine high-level risk assessment of some organic environmental pollutants, such as endosulfan (Rand et al., 2010), chlorophenols (Jin et al., 2012), nonylphenol (Jin et al., 2014), hexachlorocyclohexanes and dichlorodiphenyltrichloroethanes (Hu et al., 2015). To obtain results that are more reliable for ERA, some researchers have suggested the use of a tiered approach, ranging from simple deterministic methods to probabilistic methods, for risk characterization (Zolezzi et al., 2005; Wang et al., 2009; Jin et al., 2012). Although exposure and toxicity data are also available for heavy metals, few authors have used probability method(s) to assess their ecological risk. On the other hand, while various index approaches were developed to assess the risk of heavy metals deposited in sediment, the ecological risk of heavy metals in the water column is largely overlooked. Although a large quantity of free metal ions get deposited in the sediments because of a combined action of adsorption, hydrolysis, and co-precipitation, heavy metals settled in sediments may be re-suspended and cause secondary contamination to the overlying water when environmental conditions change (Malferrari et al., 2009; Varol and Sen, 2012). Also, considering that the influence of heavy metals in the water column is more direct on zooplankton and fish, which play important roles in marine ecosystems, it is very important to perform aquatic ERA of heavy metals.

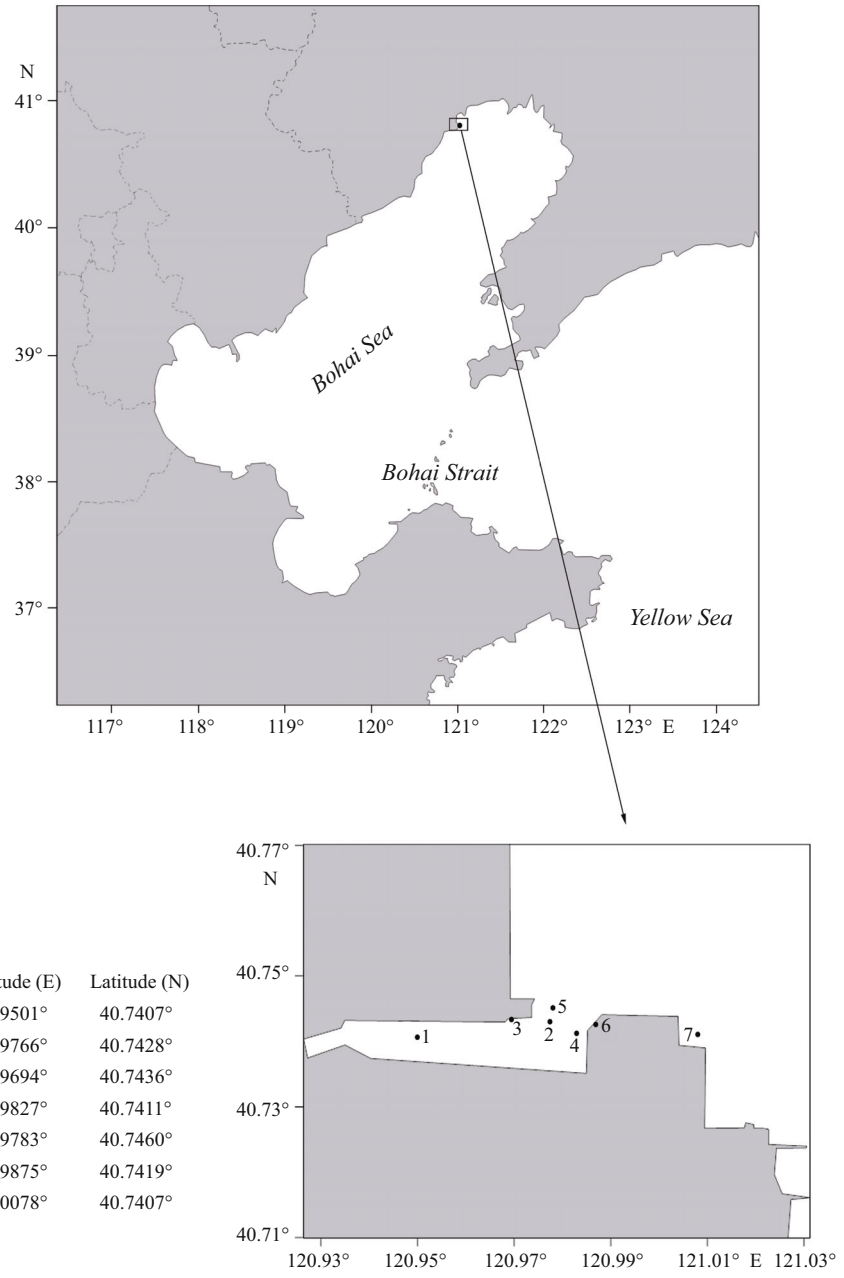
In this paper, the concentrations and potential ecological risk of heavy metals in the surface seawater and sediment near the outlet of a zinc factory, located in Huludao City, Liaoning Province, China, were evaluated. A tiered approach ranging from comparison of single effects and exposure values to the use of distribution based Hazard Quotient obtained through Monte Carlo simulation was used to refine aquatic ERA of individuals and mixture of various heavy metals detected in the surface seawater. The potential ecological risk of heavy metals in the surface sediment was assessed using typical PERI.

2 MATERIAL AND METHOD

The sampling and analysis methods were based on the Specification for Marine Monitoring (GB 17387-2007) (SPC, 2007).

2.1 Water and sediments sampling

Water samples at a depth of 0.5 m below the water surface were collected from seven different areas near the outlet of a zinc factory, located in Huludao City, Liaoning Province, China, in May and August, 2010 with permission of North China Sea Branch of SOA for each location. During the sample collection, a global positioning system (GPS) was used to locate the sites (Fig.1). Water samples for Hg detection were



	Longitude (E)	Latitude (N)
1	120.9501°	40.7407°
2	120.9766°	40.7428°
3	120.9694°	40.7436°
4	120.9827°	40.7411°
5	120.9783°	40.7460°
6	120.9875°	40.7419°
7	121.0078°	40.7407°

Fig.1 Map of sampling stations near the outlet of the zinc factory

obtained using glass bottles, and then acidified to pH<2 with sulfuric acid in order to minimize precipitation and adsorption on the walls of the container. Other water column samples were collected by plastic bottles, which were washed with hydrochloric acid, soaked with nitrate solution, and then rinsed with distilled water. After being filtered through 0.45-μm Millipore filters, these samples were acidified to pH<2 with sulfuric acid for As detection and acidified with nitric acid for Cu, Pb, Zn, and Cd. Surface sediment samples used for analysis of heavy metal fractions were taken by a grab sampler around each station at a depth of 0-5 cm, and quickly packed in airtight polythene bags for analysis of Cu, Pb, Zn, Cd, and As, and jars for Hg. After being transported back indoors, the sediment samples were air-dried, ground, passed through 160-mesh (96 μm) nylon sieves, and then stored in pre-cleaned sample bags for further analysis.

2.2 Sample analysis

Contents of heavy metals in all water and sediment samples were analysed based on the Specification for Marine Monitoring (GB 17387.4-2007 and GB 17387.5-2007). Specially, atomic fluorescence

Table 1 Statistical summary of acute species toxicity data (LC_{50}/EC_{50}) and the concentrations of heavy metals detected in the surface seawater near the outlet of the zinc factory

Compound	LC_{50}/EC_{50} (μg/L)				Concentration (μg/L)			
	N	Range	GM	GSD	N	Range	GM	GSD
As	20	9.20–150 000	9 232.70	6.98	12	3.11–24.70	8.30	2.26
Hg	126	3.34–9 000	93.35	5.83	12	0.03–0.10	0.06	1.51
Pb	101	5.00–500 000	4 539.30	8.13	12	0.16–20.10	0.49	4.58
Cd	258	8.00–560 000	1 904.90	8.18	12	0.27–7.50	1.43	4.10
Cu	399	1.85–231 000	286.34	7.99	12	0.25–3.06	0.89	2.80
Zn	232	12.90–150 951	1 897.60	7.66	12	30.60–265	98.69	1.77

LC_{50}: median lethal concentration; EC_{50}: median effect concentration; N: the number of data; GM: geometric mean; GSD: geometric standard deviation; similar hereinafter.

method was used for detection of As and Hg; flameless atomic absorption spectrometry was applied to analysing the concentrations of Cu, Pb, and Cd, and flame atomic absorption spectrophotometry was adopted for Zn monitoring.

2.3 Quality control

The analytical data quality was guaranteed by the use of standard operating procedures, calibration with standard reference material, analysis of reagent blanks, and analysis of replicate samples. The precision of the analytical procedures was tested by recovery measurements on the Chinese National Geostandard Samples (GBW-07333 and GBW-07314). The recoveries for these heavy metals in the standard reference were approximately 90%–110%, and the relative standard deviation (RSD) of all replicate samples was less than 10%. All analyses were carried out in duplicate, and the results are expressed as the mean.

2.4 Toxicity data

Acute toxicity data retrieved from the ECOTOX database (http://cfpub.epa.gov/ecotox/), including median effect concentration (EC_{50}) and median lethal concentration (LC_{50}) of heavy metals to marine organisms in various trophic levels, were used to develop SSDs in the following probabilistic ecological risk assessment (PERA) (Wang et al., 2009). The process of data screening mainly follows criteria described by Wheeler et al. (2002) and Duboudin et al. (2004). If multiple toxicity values were available for an individual species, the geometric mean of the data was used as a surrogate (Newman et al., 2000). The statistical summary and the data quantity of acute species toxicity data (LC_{50}/EC_{50}) are listed in Table 1 and Table 2, respectively.

Table 2 Data quantity of available aquatic toxicity in different taxonomic categories for heavy metals

Category	As	Hg	Pb	Cd	Cu	Zn
Algae, moss, fungi	1	14	19	27	51	21
Crustaceans	8	44	23	92	142	92
Fish	5	18	19	40	60	30
Invertebrates	0	6	7	17	33	14
Mollusks	5	27	18	59	88	53
Worms	1	17	15	23	25	22
Total	20	126	101	258	399	232

2.5 Tiered ERA of individual heavy metals in the surface seawater

The following tiered approach ranging from levels 1 to level 4 was adopted to perform ERA of the heavy metals detected in the seawater (EC, 2003).

(1) Level 1 utilizes deterministic Hazard Quotient (HQ), which is simply the ratio of single value of exposure divided by that of toxicity, calculated as follows:

$$HQ=EMC/ERC, \quad (1)$$

where geomean and maximum of aquatic heavy metals concentrations were respectively used as the environmental measuring concentration (EMC) to calculate general case (HQ_{GM}) and the worst case (HQ_{max}) of HQ. The predicted no effect concentration (PNEC), calculated by HC_5 (hazardous concentration for 5% of species) derived from SSD and a conservative safety factor (SF, set as 5), is adopted as the ecological risk criteria (ERC).

$$PNEC=HC_5/SF. \quad (2)$$

Two kinds of data (chronic toxicities and acute toxicities) can be used to derive SSD in ERA. Although chronic toxicity information is preferable,

the chronic toxicities of heavy metals retrieved from the ECOTOX database are insufficient to fit SSD, especially for As, Pb, and Hg. Thus, acute to chronic ratio (ACR) was adopted to transform acute data to chronic values under homogeneous test conditions (Raimondo et al., 2007). Generally, ACRs are less than 50 with a mean of 25 or less (Roex et al., 2000). In this study, considering the uncertainty of ACR, acute toxicity data were divided by ACRs of 1, 10, 25, 100, and 1 000 to yield chronic data to develop SSDs, where 1, 10, 100 and 1 000 were introduced as the bottom, the lower, the upper, and the top limits, respectively. HC_5 was derived from SSD with an ACR of 25.

In PERA, multiple tools, such as log-normal, log-logistic, Burr, Gamma, and Weibull methods were recommended for fitting of toxicity data (He et al., 2014). In this study, a log-logistic model for As, Hg, Pb, and Cu, a log-normal model for Zn, and a Burr model for Cd were adopted according to the P values of the KS-test (see Table S1), as well as the fitting results of SSD curves (see Fig.S1). The detailed parameters of SSDs are listed in Table S2.

(2) Level 2 obtains the probability that exposure levels exceeding pre-established effect levels or, conversely, effect levels exceeding pre-established exposure values, by comparing exposure concentration distribution (ECD) and fixed effects values or vice versa.

Level 2.1 assesses the probability of exposure concentration exceeding HC_5 and PENC. After a Kolmlgorov-Smirnov test (KS-test) has been performed, a log-normal model was generally applicable for fitting the data of heavy metals monitored in the surface seawater. The results of KS-test and model parameters are listed in Table S3.

Level 2.2 compares SSD to different levels of exposure (average and maximum concentrations for each heavy metal) to get the percentage of affected species.

(3) Level 3 involves both exposure and effect distributions. The 10th percentile for SSD was divided by the 90th percentile for ECD to generate the margin of safety (MOS_{10}) (Solomon et al., 1996). Then, the reverse cumulative distribution of exposure (or exceedance probability function, EXF) and the SSD were used to generate a JPC, which describes the probability of exceeding the concentration associated with a particular degree of effect. The distance between a JPC and its relative axes may be used as an indication of the associated risk. More specifically, the area under the curve indicates the overall risk probability (ORP) of the adverse effects expected to occur, which is calculated as:

$$\mathrm{ORP} = \int_0^1 \mathrm{EXP}(x)\mathrm{d}x, \tag{3}$$

where EXP(x) is the exceedance probability of the exposure data associated with 100x% species expected to be adversely affected.

(4) Level 4 involves the distribution-based HQs, in which the risk was expressed as the probability of exceeding certain HQ criteria (1, 1/10, 1/25, 1/100, 1/1 000) corresponding to a series of ACRs mentioned above. Monte Carlo simulations (Matlab 2012b) were conducted for 100 000 times, to randomly sample 100 000 EMC values from ECD and 100 000 toxicities from SSD, and then HQs (here, HQ=EMC/LC_{50}, or, HQ=EMC/EC_{50}) were calculated to generate its distribution.

2.6 ERA of heavy metal mixture in the surface seawater

Various chemical pollutants always exist as mixtures in real environments, and exposure to the mixture of heavy metals could lead to adverse biological effects that are more serious than those of an individual one. Thus, the joint risk of different heavy metals was calculated employing concentration addition (Altenburger et al., 2003). Generally, one compound was chosen as a reference substance, and the exposure concentrations of all of the others were converted to relative concentrations (C_r) with an effect equivalent to that of the reference. In this study, Zn was taken as the reference substance. Next, the joint risk of the mixture was calculated by integrating the distribution parameters for the relative concentrations of the mixture ($\sum C_r$) with those for the toxicity data of the reference. However, based on the probabilistic principles adopted in this study, C_r could not be estimated through a simple toxicity conversion factor (TCF), because no simple linear dependence had been determined between the toxicity data for different compounds. To solve this problem, the following formula was introduced to calculate $\sum C_r$ based on lognormal distributions of the toxicity data (Hu et al., 2015):

$$\begin{aligned} C_{\mathrm{equ,tol}} &= \sum C_r = \sum_{i=1}^{n} C_{r,i} \\ &= \sum_{i=1}^{n} 10\hat{}\left(\mu_r + \frac{\sigma_r(\lg C_i - \mu_i)}{\sigma_r} \right), \end{aligned} \tag{4}$$

Table 3 Mean concentrations (mg/kg) of heavy metals found in sediment near the outlet of the Zinc Factory compared to the reported average concentrations for other impacted coastal systems

Area	Cu	Zn	Pb	Cd	Hg	As	Reference
Lzmit Bay, Tukey	89.4	754	94.9	6.3	-	22.2	Pekey (2006)
Ribeira Bay, Brazil	24.6	109	22.9	0.207	-	-	de Carvalho Gomes et al. (2009)
Sepetiba Bay, Brazil	31.9	567	40	3.22	-	-	de Carvalho Gomes et al. (2009)
Mejilones Bay, Chile	-	29.7	-	21.9	-	-	Valdés et al. (2005)
Algeciras Bay, Spain	17	73	24	0.3	-	11	Díaz-de Alba et al. (2011)
Taranto Gulf, Italy	47.4	102.3	57.8	-	0.12	-	Buccolieri et al. (2006)
Gulf of Naples, Italy	27.2	602	221	0.57	0.70	2.0	Romano et al. (2004)
Malaga Bay, spain	15.08	-	19.05	0.076	-	-	Castillo et al. (2013)
Huludao, China	116.60	1008.75	104.65	4.11	0.56	88.25	This study

-: no data.

where C_i and $C_{r,i}$ represent the absolute and relative concentrations of compound i, respectively, μ_i and σ_i, are the means and standard deviations of the log-converted toxicity data for compound i, respectively, and μ_r and σ_r are the means and standard deviations of the log-converted toxicity data for the reference, respectively.

According to the distribution of $C_{\text{equ,tol}}$ and the SSD of the reference heavy metal (Zn), the combined ecological risk of all the detected heavy metals was then assessed by the JPC method and Monte Carlo simulation.

2.7 ERA of heavy metals in the sediment

Since no sufficient sediment data were available, the probability ERA cannot be implemented. Based on the assumption that the sensitivity of the aquatic system depends on its productivity, PERI methodology was developed (Hakanson, 1980). This method, integrating the measured concentration with ecological effect, environmental effect, and toxicology, was introduced to assess the degree of heavy metal pollution in sediments.

$$R_I = \sum E_r^i, \tag{5}$$

$$E_r^i = T_r^i C_f^i, \tag{6}$$

$$C_f^i = C_0^i / C_n^i, \tag{7}$$

where R_I is calculated as the sum of all risk factors for heavy metals in sediments, E^i_r is the monomial potential ecological risk factor, T^i_r is the toxic-response factor for a given substance, which accounts for the toxic requirement and the sensitivity requirement, as shown in Table S4, C^i_f is the contamination factor, C^i_0 is the concentration of heavy metals in the sediment, and C^i_n is the reference value for each heavy metal (Table S4).

Based on the reference values for these elements, the adjusted evaluation criteria for the ecological risk index PERI are listed in Table S5.

3 RESULT AND DISCUSSION

3.1 Occurrence of heavy metals in surface seawater and sediment

A statistical summary of concentrations of the six heavy metals (As, Hg, Pb, Cd, Cu, and Zn) measured in the surface seawater is listed in Table 1 (Since site 1 is fresh water, we did not consider it). Sediment samples were collected from site 6 and 7 only in August 2010 (Table S6). The mean concentrations of As, Hg, Pb, Cd, Cu, and Zn were 11.06, 0.06, 2.25, 2.92, 1.36, and 114.18 μg/L, respectively, in the surface seawater and 88.25, 0.56, 104.65, 4.11, 116.60, and 1 008.75 mg/kg, respectively, in the surface sediment. The heavy metal levels in the surface seawater met Grade IV of the Sea Water Quality Standard (GB 3097-1997), and heavy metals monitored in the surface sediment, except Zn, met Grade III of the Marine Sediment Quality (GB 18668-2002). The comparison of contaminant concentrations in sediment observed in this study with those reported for other impacted regions is shown in Table 3. The concentrations of heavy metals, especially Zn, Cu, and As, measured in this study were higher than other studies.

3.2 Ecological risk of individual heavy metals in the surface seawater

In the analysis of level 1, HQ_{GM} and HQ_{max} of heavy

metals to marine species were calculated based on HC_5 calculated from the SSDs, which was developed by an ACR of 25, as summarized in Table 4. HQ_{GM} were greater than 1 for As, Hg, Cd, Cu, and Zn and less than 1 for Pb, suggesting that the potential ecological risk posed by As, Hg, Cd, Cu, and Zn, but not that of Pb, was not acceptable. HQ_{max} values were greater than 1 for all the six heavy metals, suggesting that the potential ecological risk they posed was not acceptable in the worst case, especially for Zn.

Table 4 HQs and associated parameters for heavy metals in the surface seawater near the outlet of the zinc factory

Matter	HC_5 (μg/L)[a]	SF	PNEC (μg/L)	HQ_{GM}	HQ_{max}
As	38.54	5	7.708	1.08	3.20
Hg	0.18	5	0.036	1.67	2.78
Pb	6.56	5	1.312	0.37	15.32
Cd	1.66	5	0.332	4.31	22.59
Cu	0.32	5	0.064	13.91	47.81
Zn	2.67	5	0.534	184.81	496.25

HC_5 (μg/L) [a]: HC_5 were calculated from the SSDs, which was developed by an ACR of 25. SF: safe factor; PNEC: predicted no effect concentration; HQ: hazard quotient; similar hereinafter.

Table 5 The probabilities that exposure distribution of heavy metals exceeds HC_5 and PNEC and the proportion of species affected by the geometric mean and maximum of environmental measuring concentrations

Compound	Exceedance probability		Proportion of species affected (%)[a]	
	HC_5	PNEC	GM	Max
As	0.030	0.536	0.845	3.012
Hg	0.003	0.876	1.731	2.852
Pb	0.044	0.260	0.529	12.402
Cd	0.459	0.850	4.515	13.516
Cu	0.841	0.995	11.07	26.153
Zn	1.000	1.000	55.13	73.044

[a]: proportion of species affected were calculated from the SSDs, developed using by an ACR of 25.

Simplicity, transparency, and low data requirements are the major advantages of the HQ method, and it is the most commonly used tool for risk assessment of contaminated sites (Riccardi et al., 2001). However, this method cannot be used to calculate the probabilities of adverse biological effects, and it tends towards great uncertainty due to a high dependence on the values of SF (Zolezzi et al., 2005). Herein, probabilistic approaches were employed to refine the ERA performed.

In level 2.1, the probabilities that exposure distribution of heavy metals exceeded HC_5 and PNEC are shown (Table 5). The probability of exceeding HC_5 for As, Hg, and Pb are less than 0.05, indicating an acceptable ecological risk. However, the results of probability of exceeding PNEC (more than 0.2) indicated high ecological risk for all the six heavy metals.

In the analysis of level 2.2, we compare SSD curves of the six heavy metals to different levels of exposure (average and maximum concentration for each heavy metal), and the percentage of affected species are shown in Table 5. More than 5% of marine species could be affected by Zn and Cu, irrespective of whether the maximum or average of the measured environmental concentration was adopted. The maximum measured environmental concentrations of Cd and Pb also posed a hazard to more than 5% of marine species. Only a small proportion of marine species is likely to be affected by As and Hg and thereby their ecological risk is relatively low.

The values of MOS_{10} for heavy metals drawn from level 3 are listed in Table 6. The lower the MOS_{10} is,

Table 6 MOS_{10} and ORPs calculated from JPCs

Matter	MOS_{10}[a]	ORPs at various ACRs					Ranking
		1	10	25	100	1000	
As	3.068 6	2.99E-04	4.53E-03	1.32E-02	6.10E-02	4.19E-01	(5)
Hg	3.833 2	7.43E-04	7.37E-03	1.82E-02	6.84E-02	4.09E-01	(4)
Pb	4.412 2	7.64E-04	5.69E-03	1.24E-02	3.79E-02	1.82E-01	(6)
Cd	0.536 6	4.54E-03	2.28E-02	4.28E-02	1.07E-01	3.89E-01	(3)
Cu	0.233 2	1.17E-02	7.25E-02	1.38E-01	3.14E-01	7.11E-01	(2)
Zn	0.027 3	8.05E-02	3.78E-01	5.50E-01	7.83E-01	9.70E-01	(1)
Total	0.005 0	2.98E-01	7.18E-01	8.46E-01	9.54E-01	9.97E-01	

[a]MOS_{10} were calculated when ACR was 25.

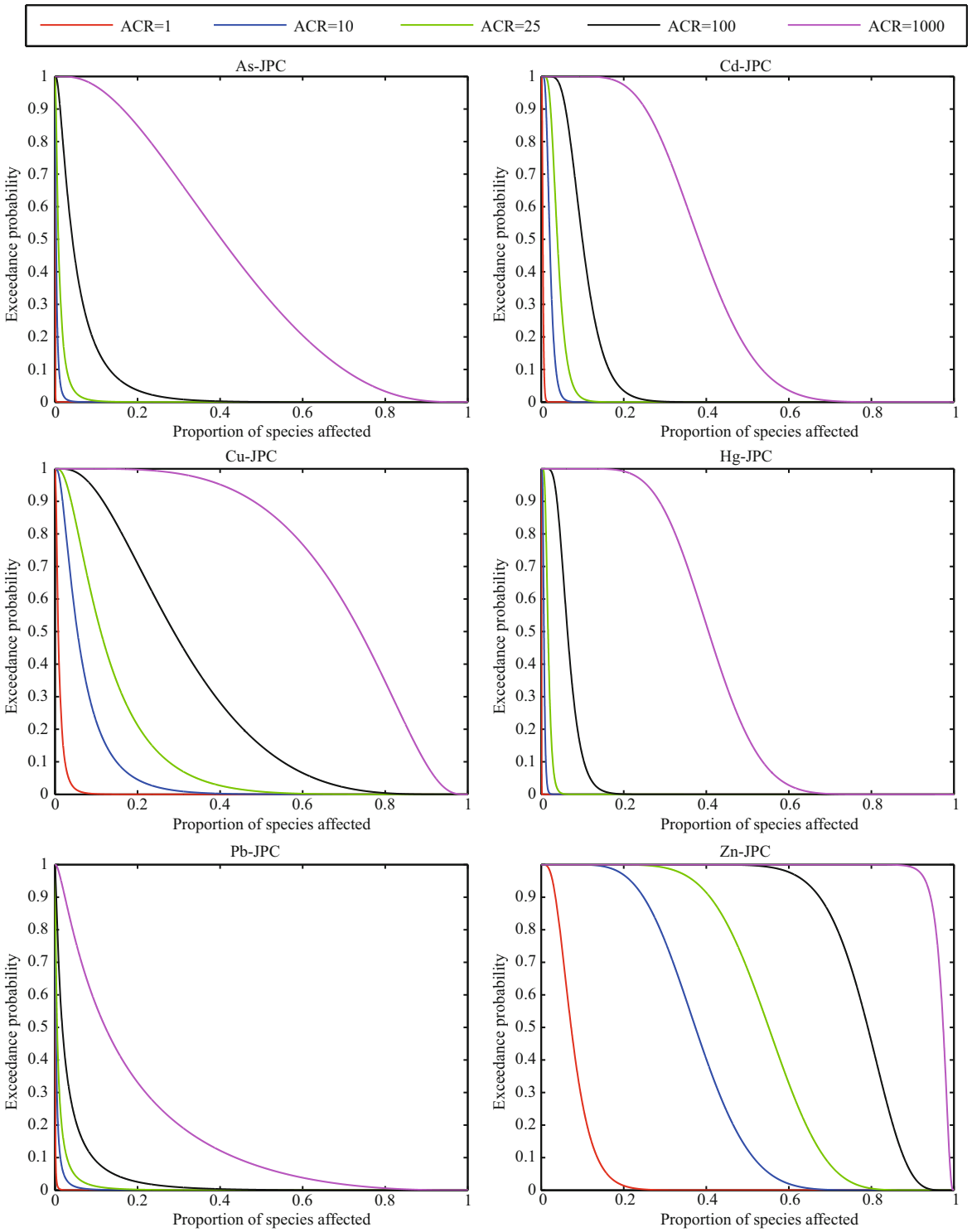


Fig.2 JPCs of six individual heavy metals to marine species in the surface seawater near the outlet of the zinc factory

the higher the risk is. In this study, MOS_{10}<1 indicates clear ecological risk. It was shown that Zn, Cu, and Cd posed potential ecological risk to the marine ecosystem, and this is consistent with the result of level 1 and level 2.

Although it uses both exposure distribution and effect distribution information, the MOS_{10} method only provides the general risk level and gives a deterministic value. Technically, MOS_{10} is not a real PERA method (Wang et al., 2009), while JPCs resulting from EXF and SSD offer a better representation of the overall risk. A series of JPCs

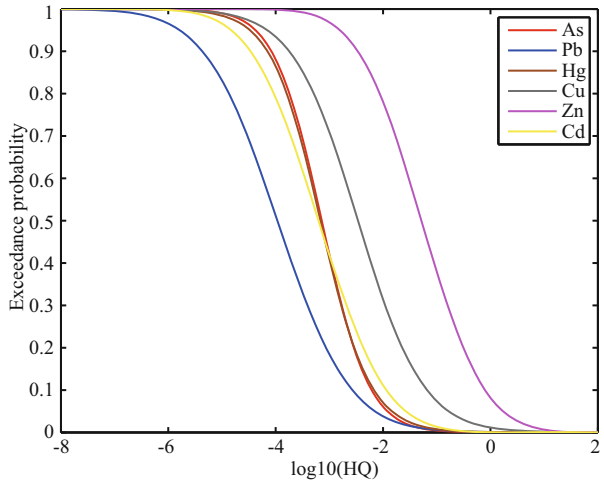


Fig.3 Exceedance probability curves of HQs based on 100 000-times Monte Carlo simulation

obtained by the application of different ACRs (1, 10, 25, 100, and 1 000) is shown in Fig.2.

The exceedance probabilities for 5% and 10% species were calculated from the JPCs. When ACR was 25, the exceedance probabilities of As, Hg, Pb, Cd, Cu, and Zn for 5% species were 2.98×10^{-2}, 3.24×10^{-3}, 4.44×10^{-2}, 2.83×10^{-1}, 8.39×10^{-1}, and 1.00×10^{0}, respectively, indicating that Zn posed the highest risk and Hg posed the lowest risk. In the case of non-conservative (ACR=1), the exceedance probabilities of As, Hg, Pb, and Cd were close to 0%, suggesting that the elements harbored an acceptable ecological risk to 5% of the most sensitive species. When the marine lives were over protected (ACR=1 000), all the six kinds of heavy metals posed high ecological risk.

The ORPs for As, Hg, Pb, and Cd were less than 5% when ACR was 1, 10, or 25, representing a critical level for management control. The ORPs for Zn and Cu, 8.05×10^{-2} and 1.17×10^{-2} on a non-conservative estimation basis (ACR=1), respectively, were slightly higher than that of the other four heavy metals. When ACR was 1 000, the ORP values of all the heavy metals were more than 5%, which indicated clear ecological risk. It is worth noting that ORPs will be underestimated if ACR is set as 1, and significantly overestimated if ACR is set as 1 000. According to the ORPs at an ACR of 25, the ORPs for different heavy metals were ranked in the following order: Zn>Cu>Cd>Hg>As>Pb (Table 6).

In the analysis of level 4, exceedance probability curves of HQs for six individual heavy metals were established based on 100 000-times Monte Carlo simulation. All of the curves were relatively far away from the axes, resulting in quite big areas below the curves (Fig.3). The exceedence probability for Zn and Cu were 8.04% and 1.19% for HQ>1 (corresponding to the application of ACRs of 1 in level 3), 37.8% and 7.39% for HQ>1/10 (corresponding to the application of ACRs of 10 in level 3), and 54.9% and 14.0% for HQ>1/25 (corresponding to the application of ACRs of 25 in level 3). The exceedence probability for Cd, Pb, Hg, and As were all less than 5% for HQ>1, HQ>1/10, and HQ>1/25. The exceedence probability for all heavy metals were more than 5% for HQ>1/100 and HQ>1/1 000 (corresponding to the application of ACRs of 100 and 1 000 in level 3, respectively), suggesting clear ecological risk. The probabilities of exceeding preselected HQ criteria are very close to ORPs at the corresponding ACRs using the JPC method. The JPC and Monte Carlo simulation methods are different risk characterization modes with the same essence (Wang et al., 2009). However, the distribution of HQs calculated by Monte Carlo simulation does not vary with ACR, and ORPs drawn from JPCs differ largely for different ACRs.

Combining the above tiered EPA results from four progressive levels, we proposed that aquatic Zn and Cu posed clear ecological risk while waterborne Cd, Pb, Hg, and As caused potential risk.

Uncertainty in ERA is inevitable even when high-level methods are used (Jin et al., 2014). The uncertainty may come from variability in ecosystem stressors, accuracy in exposure data and species effect data, risk characterization models, and lack of knowledge (Chen, 2005). In particular, the species used for SSDs are not local species and perhaps are not representative of the aquatic communities of the study area. Use of data on toxic potencies of chemicals for non-site specific species to ERA is controversial (Jin et al., 2014). However, this uncertainty could not be resolved previously in large part due to the paucity of toxicity data of heavy metals applicable for local species. To describe exposures more accurately, further information needs to be collected to describe concentrations of heavy metals at various spatial and temporal scales. Although the best probabilistic distribution model was selected for each heavy metal according to results of KS-test, there is still no guarantee that it has better extrapolation abilities.

3.3 Combined ecological risk of heavy metals in the surface seawater

Compared with the JPC curves for any particular heavy metal, the total ones were relatively far away

Table 7 PERIs of heavy metal in the surface sediment near the outlet of the zinc factory

Sample site	E^i_r						R_I
	As	Hg	Pb	Cd	Cu	Zn	
Site 6	103.44	99.80	34.52	306.00	34.51	22.04	600.32
Site 7	14.23	125.80	7.34	186.60	4.35	3.18	341.50
Mean	58.84	112.80	20.93	246.30	19.43	12.61	470.91

E^i_r: PERI of individual heavy metals; R_I: PERI of total heavy metals.

from the axes, indicating that the combined ecological risk of heavy metals was higher than that of any individual element. Combined exceedance probabilities for 5% and 10% species were all 100% for ACRs of 1, 10, and 25, which showed a very high ecological risk for 95% and 90% species protection. The combined probability of HQs exceeding 1, 1/10, and 1/25 was 0.301, 0.717, and 0.844, respectively, showing that the total heavy metals posed high ecological risk even in non-conservative cases.

Generally, three common additive reference approaches—concentration addition, effect summation, and independent action models—are available to determine the toxicity of chemical mixtures (Cedergreen et al., 2008; Martin et al., 2009). The results may be inconsistent according to different reference models applied. In this study, concentration addition was adopted to calculate the joint risk of different heavy metals, since it is often considered as a standard additive model for the toxicity prediction of mixture (Altenburger et al., 2003).

These heavy metals are of great concern because of their toxicities to not only marine organisms but also to human health. Zheng et al. (2007) found that the health risk of Hg, Pb, Cd, Zn, and Cu to the inhabitants close to Huludao Zinc Plant (<500 m) via consumption of vegetables is high, with the total metal target hazard quotient (TTHQ) > 1. Whether the emission of heavy metals into the sea leads to a population health risk via consumption of sea food product needs to be further discussed.

3.4 Ecological risk assessment of heavy metals in the sediment

Using Eqs.5–7 and parameters listed in Table S4, the potential ecological risk indices E^i_r and R_I for each site were obtained (Table 7). For different sites, the risk of each heavy metal varies widely. The average of PERIs for single regulator (E^i_r) indicated that the severity of pollution of the six heavy metals decreased in the following sequence: Cd>Hg>As>Pb>Cu>Zn. The average PERI of Cd in the studied area was 246.30, indicating that Cd posed a high risk to marine sediment environment, while each of deposited Zn, Cu, and Pb devoted low risk to the marine environment. The average PERI of total heavy metals (R_I) was 470.91, indicating that the mixture of the six heavy metals in the sediment posed a very high risk to marine environment.

4 CONCLUSION

Concentrations of heavy metals in surface seawater and sediment near the outlet of a zinc factory in Huludao City, Liaoning Province, China were investigated. The ERA of the risk posed by the six heavy metals to marine species was determined. The concentrations of these heavy metals in surface seawater and sediment were acceptable according to the Water Quality Standard (GB 3097-1997) and Marine Sediment Quality (GB 18668-2002). However, the potential risk posed by individual heavy metals and heavy metal mixtures to seawater column species was unacceptable according to the tiered approach, and the mixture of the six heavy metals in sediment posed a very high risk to the marine environment according to PERI. We hope that this work will aid in the management and regulation of heavy metals in the marine environment, aiming to minimize their ecological risk.

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Electronic supplementary material

Supplementary material (Supplementary Fig.S1 and Supplementary Tables S1–S6) is available in the online version of this article at http://dx.doi.org/10.1007/s00343-016-5112-3.