Chapter

Water Quality Ecological Risk Assessment with Sedimentological Approach

Limin Ma and Changxu Han

Abstract

The potential ecological risk index (ERI) is a useful diagnostic tool for water system assessment. It's based on sedimentology and combined with environmental chemistry and ecotoxicology. This chapter introduces the approach, including basic theory, calculation formula, evaluation criteria, and its parameters. Using a case study, the modification of the classification of the potential ecological risk is discussed. The water quality of the Liaohe River is assessed by the potential ecological risk index with the sedimentological approach. The sediments samples were collected from 19 sites and were analyzed for seven substances (Cd, As, Cu, Ni, Pb, Cr, and Zn) to assess the potential ecological risk. According to the results, Cd was found to be the main pollutant in the Liaohe River. The consequence of the monomial potential ecological risk factor E_r^i (mean) of each element is ranked as: Cd (93.39%) > As (3.13%) > Cu (1.26%) > Ni (0.97%) > Pb (0.70%) > Cr (0.34%) > Zn (0.22%). The ERI results (358.35) indicate the Liaohe River poses a very high potential ecological risk.

Keywords: water quality assessment, sedimentological method, Håkanson index, potential ecological risk index, methodologies

1. Introduction

The water and sediments are the main storage medium for pollutants in lake environments. The sediments adsorb various kinds of pollutants which could accumulate in sediments for a long time. When external conditions change, pollutants adsorbed in sediments may be released back into the water and taken up by organisms. Eventually, these pollutants may affect human health through the food chain. Therefore, how to assess the risk of the water system with contaminated sediments has become an important issue. If ecological risk assessment can be used as a diagnostic tool to evaluate the potential risks accurately, it is of great significance to pollution control [1, 2].

Until now, various approaches, which are based on the different perspectives of the chemical, biological and toxicological indices, have been proposed to assess the water quality ecological risk of the environment. For example, the enriched factor (EF) can evaluate the accumulation of elements in the sediment. It is calculated by comparing the concentration of the sample with the background value [3]. The geo-accumulation index (I_{geo}) assesses the risk by comparing the total concentration, the background value, and the background matrix correction factor of lithogenic effects is considered in it [4]. The pollution load index (PLI) is defined as the nth root of the product of the ratios between the concentration of each metal to the background values [5]. The sediment quality guidelines (SQGs) include threshold effect concentrations (TECs) and probable effect concentrations (PECs). Bioavailability is taken into account in this approach [6]. It is not adequate to assess the ecological risk by using only concentrations without factors of toxicity. The potential ecological risk index (ERI) posed by Swedish geochemist Lars Håkanson (The National Swedish Environment Protection Board, Water Quality Laboratory Uppsala) is based on the "abundance principle", "sink-effect", and "sensitivity factor" [7]. As a diagnostic tool for pollution control, the potential ecological risk index has been widely used since its development in the 1980s [8–10].

This chapter describes an approach to assess water quality risks using its basic theory, calculation formula, evaluation criteria, and parameters calculation. This approach combines environmental chemistry with ecotoxicology in order to assess the potential risks accurately. The approach integrates the concentration of substances with ecological effects, environmental effects, and toxicity. Furthermore, the model is used to explain in detail a water quality case study of the Liaohe River, China [11].

2. The potential ecological risk index

2.1 Theoretical hypothesis

Considering the different aspects that could affect ecological risk, Håkanson [7] made four hypotheses about the potential ecological risk index (ERI) value when he proposed the approach. They are:

1. The concentration requirement. The ERI value should increase as the pollutant contamination increases.

2. The number requirement. The ERI value should increase as the number of pollutant species increase.

3. The toxic factor requirement. Various substances have different toxicological effects. ERI value should differentiate between mildly, moderately and very toxic substances.

4. The sensitivity requirement. Various lakes and water systems do not have the same sensitivity to toxic substances.

2.2 Equations

Based on the above hypothesis, the potential ecological risk index is calculated by the following equations:

$$C_f^i = \frac{C_{0-1}^i}{C_n^i} \tag{1}$$

$$C_d = \sum_{i=1}^{n} C_f^i = \sum_{i=1}^{n} \frac{C_{0-1}^i}{C_n^i} \tag{2}$$

where C_f^i is the contamination factor of the substance i, C_{0-1}^i is the measured value of the substance i, C_n^i is the preindustrial reference value of the substance i, and C_d is the degree of contamination.

$$E_r^i = T_r^i \cdot C_f^i \tag{3}$$

$$ERI = \sum_{i=1}^{n} E_r^i = \sum_{i=1}^{n} T_r^i \cdot C_f^i \tag{4}$$

where E_r^i is the potential ecological risk factor for the given substance i, T_r^i is the "toxic-response" factor for the given substance i, and ERI is the potential ecological risk index for the basin/lake.

2.3 The parameters

2.3.1 The contamination factor C_f^i

To get the value of the contamination factor (C_f^i), more information needs to be known about the measured value of substance i (C_{0-1}^i) and the preindustrial reference value of substance i (C_n^i). In order to reflect the risk of the lake accurately, Håkanson proposed that "undisturbed" samples should be collected from accumulation areas in the lake targeting the 0–1 cm layer. Håkanson provides two methods to determine the accumulation areas for a given lake. The first method, the ETA-diagram (**Figure 1**), uses only the water depth and the effective fetch. The second method uses the water content of sediments (W_{0-1}). In this second method, researchers have to collect and analyze sediments to determine the bottom dynamic condition. The method requires 5 g wet sediment dried for 6 h at 105°C, then expressed as the water content as wet sediment. Accordingly, if the W_{0-1}>75%, it may mean the sediments are from an accumulation area.

In addition, Håkanson gives the types of contaminants that could be included in this contamination factor index. These contaminants include PCB, Hg, Cd, As, Cu, Pb, Cr, and Zn. Of course, it is possible to study other pollutants

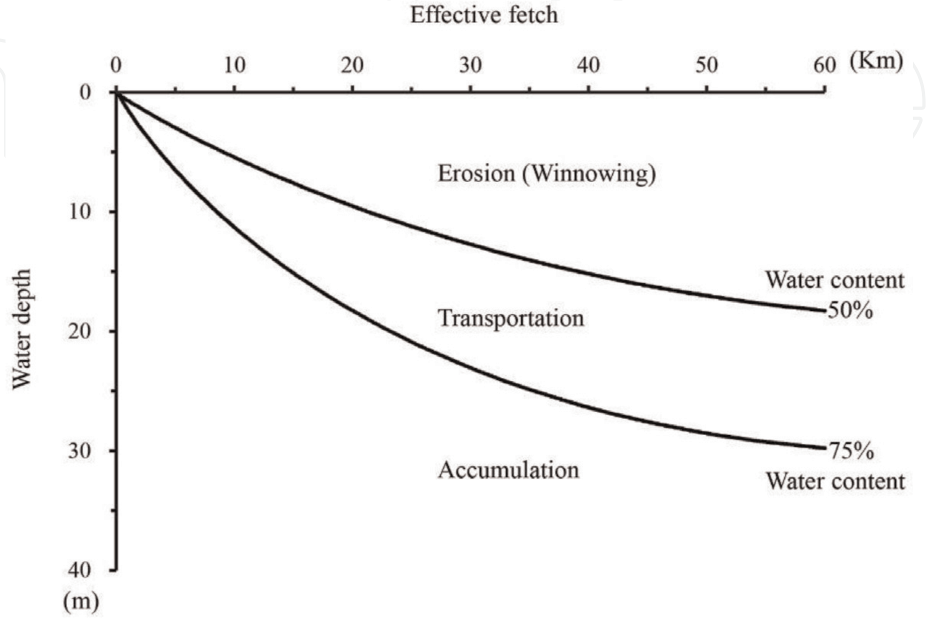

Figure 1.
The ETA-diagram [12].

(e.g., Ni, V, Mo, Co). Fe, Mn, and P are unsuitable as sediment parameters in this approach because their concentration is often influenced by physical or chemical processes in the sediments.

According to the contamination factor (C_f^i), single elements, C_f^i are classified as follows:

$C_f^i < 1$, low contamination factor;
$1 \leq C_f^i < 3$, moderate contamination factor;
$3 \leq C_f^i < 6$, considerable contamination factor;
$C_f^i \geq 6$, very high contamination factor.

For the preindustrial reference condition $\left(C_n^i\right)$, Håkanson chose preindustrial background reference values as PCB = 0.01, Hg = 0.25, Cd = 1.0, As = 15, Cu = 50, Pb = 70, Cr = 90, and Zn = 175 (ppm). Different researchers [13–15] have selected other reference values for C_n^i, for example, the national standards and the background reference value.

2.3.2 The degree of contamination C_d

The degree of contamination value (C_d) is the sum of all C_f^i, which accounts for the total of the sediment pollution. C_f^i are classified as follows:

$C_d < 8$, low degree of contamination;
$8 \leq C_d < 16$, moderate degree of contamination;
$16 \leq C_d < 32$, considerable degree of contamination;
$C_d \geq 32$, very high degree of contamination.

The thresholds are determined by the number of substances. Eight substances were analyzed in Håkanson's research; therefore, the threshold is 8 for the low degree of contamination. C_d classification thresholds should be modified for different assessments. For example, if there are five substances analyzed in an assessment, then the threshold for the low degree of contamination should be 5.

2.3.3 The toxic factor St^i

In this risk index approach, the toxic factor (St^i) primarily provides two important pieces of information—the threat to man and the threat to the aquatic ecological system. Håkanson calculated the "toxic-response" factor based on "abundance principle" and "sink-effect". The potential biotoxicity of a metal element is inversely proportional to its abundance.

To evaluate the "abundance principle", the following methodology has been used:

1. The basic data for the evaluation is given in **Table 1**. It illustrates the abundance of various elements in igneous rocks, soils, fresh water, land plants, and land animals.

2. Relative abundance of elements in different media are shown in **Table 2**. The value of 1.0 is given to the element with the highest mean concentration in each media. For example, Zn has the highest value in land animals, so Zn should be given the value of 1.0.

Element	Igneous rocks	Soils	Freshwater	Land plants	Land animals
As	1.8	6.0	0.0004	0.2	≤ 0.2
Cd	0.2	0.06	< 0.08	0.6	≤ 0.5
Cr	100	100	0.00018	0.23	0.075
Cu	55	20	0.01	14	2.4
Hg	0.08	0.03–0.8	0.00008	0.015	0.046
Pb	12.5	10	0.005	2.7	2.0
Zn	70	50	0.01	100	160

Table 1.
The abundance of various elements in different media ($\times 10^{-6}$) [16].

Order	Igneous rocks	Soils	Fresh water	Land plants	Land animals	$\sum_1^5$	$\sum_1^4$	Abundance number
1	1.0-Cr	1.0-Cr	1.0-Zn	1.0-Zn	1.0-Zn			
2	1.4-Zn	2.0-Zn	1.0-Cu	7.1-Cu	67-Cu			
3	1.8-Cu	5.0-Cu	2.0-Pb	37-Pb	80-Pb			
4	8.0-Pb	10-Pb	25-As	167-Cd	320-Cd			
5	56-As	17-As	31-Cd	435-Cr	800-As			
6	500-Cd	240-Hg	56-Cr	500-As	2130-Cr			
7	1250-Hg	1670-Cd	125-Hg	6670-Hg	3480-Hg			
Cr	1.0	1.0	56	435	2130*	2623	493.0	110.0
Zn	1.4	2.0*	1.0	1.0	1.0	6.4	4.4	1.0
Cu	1.8	5.0	1.0	7.1	67*	81.9	14.9	3.4
Pb	8.0	10	2.0	37	80*	137	57.0	13.0
As	56	17	25	500	800*	1398	598	140.0
Cd	500	1670*	31	167	320	2688	1018	230.0
Hg	1250	240	125	6670*	3480	11,765	5095	1160.0

**To avoid the inappropriate weight to the sum, the largest value for each element should be omitted.*

Table 2.
Relative abundance of elements in different media [17].

3. The "relative abundance" in each media is calculated by comparing the highest mean concentration with others in each media. For example, the value of Zn is 80 times higher than that of Pb in land animals, so Pb should be given 80. The results of relative abundance are given in **Table 2**.

4. The "abundance numbers" are determined by the sum of the five relative abundance numbers for each element. It is shown in the $\sum_1^5$ column. To balance the effect of extreme "abundance numbers" and to avoid the inappropriate weight to the "abundance numbers", the largest value marked "*" for each element should be omitted. The results of every element are given in the column marked $\sum_1^4$. In the end, the "abundance numbers" are obtained by division by the value of 4.4 (the value of Zn). For example, the "abundance

numbers" of Cr is obtained by dividing 493.0 (the sum of 1.0, 1.0, 56, and 435 in the line of Cr) by 4.4. The results of the "abundance numbers" are following: Zn < Cu < Pb < Cr < As < Cd < Hg.

5. The "corrected abundance numbers" are closely related to the toxicity coefficient, but it cannot represent "toxic-response" factor directly. Håkanson modified the "abundance numbers" by multiplying it by the "sink-factors", where the sink factor is determined as:

$$\text{Sink factor} = \frac{\text{Natural background concentration in fresh water}}{\text{Preindustrial reference value for lake sediments}}$$

Table 3 lists the data of natural background values for freshwater and preindustrial reference values. This results in the following "corrected abundance numbers": Zn = 57, Cr = 220, Cu = 680, Pb = 920, As = 3780, Cd = 46,000 and Hg = 371,200.

6. In order to match the dimensions of the contamination factors, first, divide all "corrected abundance numbers" by 57 (the value of Zn), then to take the square root of these figures, and then round off the values. This gives the following results: Zn = 1, Cr = 2, Cu = 5, P b = 5, As = 10, Cd = 30, and Hg = 80. The result of Hg is too high compared to Cd, therefore the toxic factor of Hg was determined as 40 by Håkanson. In addition, Håkanson hypothesized that the sedimentological toxic factor for PCB should be the same magnitude as that of Hg. Therefore, the St^i value for PCB was given 40. This gives the following St^i: Zn = 1, Cr = 2, Cu = 5, Pb = 5, As = 10, Cd = 30, Hg = 40, and PCB = 40.

2.3.4 The "toxic-response" factor T_r^i

It is well known that the sensitivity of organisms to the toxic substances is related to the biological characteristics of the aquatic systems [18]. This section describes sensitivity to toxic substances and how it varies from lake to lake. Håkanson uses the bioproduction index (BPI) value to represent the sensitivity. The BPI value is calculated by measuring the ignition loss (the IG value) and the nitrogen content (the N value) of sediment samples. The BPI value is defined as the nitrogen content on the regression line for IG = 10%. The nitrogen content is

Element	Background concentration in fresh water	Preindustrial reference value for lake sediments	Sink factor (10^{-3})	Abundance number	Corrected abundance numbers
Cr	0.2	90	2	110.0	220
Zn	10	175	57	1.0	57
Cu	10	50	200	3.4	680
Pb	5	70	71	13.0	920
As	0.4	15	27	140.0	3780
Cd	0.2	1	200	230.0	46,000
Hg	0.08	0.25	320	1160.0	371,200

Table 3.
Sink factors of elements [16].

determined using the standard Kjeldahl method [19]. The IG value is the ignition loss of dried sediment samples (550°C for 1 h). The N value and IG value are given in mg/g and % ds (ds = dry substance), respectively. After Håkanson's analysis, the relationships between the BPI value and St^i are the following (**Table 4**).

2.3.5 The monomial potential ecological risk factor E_r^i

The monomial potential ecological risk factor $\left(E_r^i\right)$ is used to express the potential ecological risk for a substance. E_r^i values are classified as follows:

$E_r^i < 40$, low potential ecological risk;
$40 \le E_r^i < 80$, moderate potential ecological risk;
$80 \le E_r^i < 160$, considerable potential ecological risk;
$160 \le E_r^i < 320$, high potential ecological risk;
$E_r^i \ge 320$, very high ecological risk.

It is should be noted that the thresholds of low potential ecological risk are determined by the largest T_r^i value of substances. This means that even though there is no contamination ($C_f^i = 1$), the E_r^i can reach a value of 40 [20].

2.3.6 The comprehensive potential ecological index ERI

The comprehensive potential ecological risk index (ERI) is the sum of all E_r^i values which is used to express the potential ecological risk for a given aquatic system. ERI values are classified as follows:

$\text{ERI} < 150$, low potential ecological risk for the water system.
$150 \le \text{ERI} < 300$, moderate potential ecological risk for the water system.
$300 \le \text{ERI} < 600$, considerable potential ecological risk for the water system.
$\text{ERI} \ge 600$, very high ecological risk for the water system.

The thresholds of C_d and E_r^i values are determined by the number and type of contaminants. The thresholds of ERI value are determined similarly. ERI values are determined by the sum of all the T_r^i values of every substance in an assessment. It could consider that there is a reference lake in which each substance's C_f^i

Substance	St^i value	T_r^i value
PCB	40	40·BPI/5
Hg	40	40·5/BPI
Cd	30	$30\cdot\sqrt{5/\sqrt{BPI}}$
As	10	10
Cu	5	$5\cdot\sqrt{5/\sqrt{BPI}}$
Pb	5	$5\cdot\sqrt{5/\sqrt{BPI}}$
Cr	2	$2\cdot\sqrt{5/\sqrt{BPI}}$
Zn	1	$1\cdot\sqrt{5/\sqrt{BPI}}$

Table 4.
The St^i and T_r^i of elements [7].

value = 1.0, BPI value = 5.0. This means that there is no contamination in the reference lake. The data from one's samples would be compared with the reference lake. The ERI classification thresholds are modified for different assessments. For example, if there were eight substances analyzed in Håkanson's research and the sum of all the T_r^i values is 155, the thresholds of the first level could be 150. Moreover, Håkanson ignores the influence of BPI value on the T_r^i value because of the C_f^i value is 1.0. Therefore, he regards the sum of St^i value as the threshold.

3. Case application

This section illustrates the potential ecological risk index by using a case study. The data for the ERI values is taken from [11]. The main steps for creating a potential ecological risk index to assess the Liaohe River system are:

1. Determine the substances of interest (As, Cd, Cr, Cu, Ni, Pb, and Zn) in the study area (the Liaohe River);

2. Determine the accumulation areas for the river and collect the samples from the 0–1 cm layer in the sediments;

3. Calculate or look up the St^i value;

4. Measure the IG value and N value to calculate the BPI and T_r^i value; and,

5. Calculate the potential ecological risk to assess the water quality.

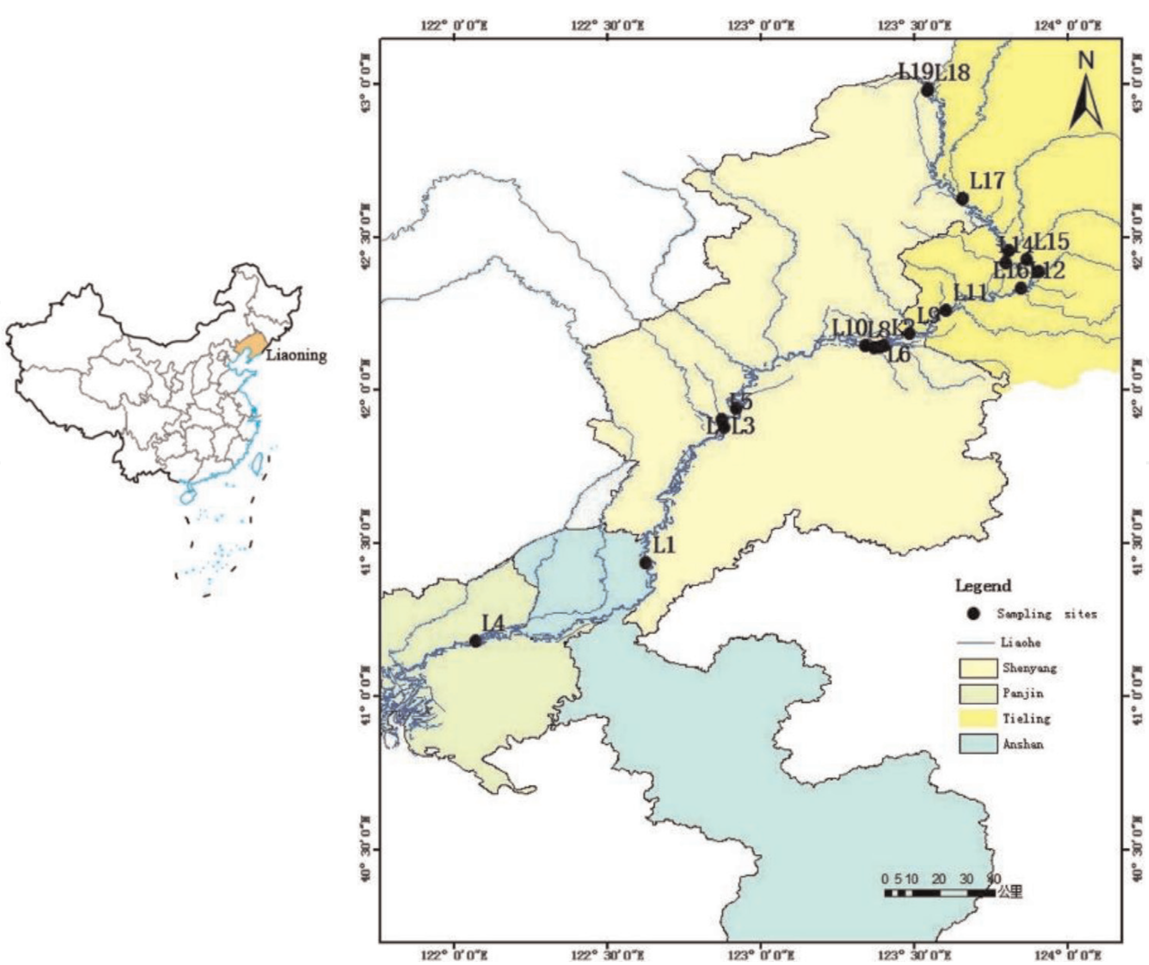

Figure 2.
The location of sampling sites along the Liaohe River protected area [11].

3.1 Description of the study area

The Liaohe River is located in the south of northeast China (**Figure 2**). It is one of the seven major rivers in China. As an important aquatic ecosystem, it plays an important role in the local economic and social development. Because of anthropogenic activities, the pollution of the Liaohe River is becoming a more serious problem. The Liaohe River has become one of the most polluted rivers in China. Therefore, it is significant to assess the quality of the Liaohe River [21].

3.2 Data collection and processing

Nineteen superficial sediment samples were collected along the Liaohe River protected area. At each site, three surface sediments were collected and placed into polyethylene bags and sealed. An Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) was applied for the determination of heavy metals (As, Cd, Cr, Cu, Ni, Pb, and Zn). The details are found in [11].

	C_f^i							C_d
	Cd	**As**	**Cu**	**Pb**	**Ni**	**Cr**	**Zn**	
L1	3.70	0.70	0.40	0.38	0.48	0.67	0.42	6.75
L2	4.94	1.28	0.57	0.43	0.62	0.53	0.49	8.86
L3	19.75	0.82	0.78	0.47	0.56	0.44	1.15	23.97
L4	20.06	0.44	0.57	0.37	0.43	0.37	1.07	23.31
L5	20.99	0.57	0.87	0.47	0.66	0.32	1.22	25.09
L6	19.44	0.81	1.08	0.57	0.79	0.62	1.47	24.78
L7	18.21	0.39	0.66	0.34	0.36	0.36	0.81	21.13
L8	5.87	1.33	0.63	0.44	0.64	0.84	1.02	10.77
L9	5.56	1.38	2.08	0.59	1.38	0.89	1.00	12.86
L10	6.79	1.64	1.49	0.57	1.31	0.99	0.84	13.63
L11	5.56	1.31	1.01	0.51	0.82	0.83	0.79	10.83
L12	5.25	1.27	0.69	0.46	0.71	0.69	0.67	9.72
L13	6.48	1.07	1.17	0.50	0.90	0.84	0.71	11.67
L14	4.35	0.91	0.80	0.38	0.59	0.49	0.42	7.94
L15	9.91	1.16	0.60	0.54	0.47	0.47	0.53	13.67
L16	5.83	1.11	0.57	0.47	0.41	0.46	0.50	9.34
L17	13.43	1.59	1.45	0.70	0.76	0.63	0.57	19.13
L18	25.00	2.00	0.57	0.72	0.47	0.49	0.58	29.83
L19	10.83	1.57	1.14	0.60	0.79	0.63	0.76	16.32
Min	3.70	0.39	0.40	0.34	0.36	0.32	0.42	6.75
Max	25.00	2.00	2.08	0.72	1.38	0.99	1.47	29.83
Mean	11.16	1.12	0.90	0.50	0.69	0.61	0.79	15.77
Reference lake ("unpolluted")	1.00	1.00	1.00	1.00	1.00	1.00	1.00	7.00

Table 5.
Contamination factors (C_f^i) of different elements detected in sediments.

3.3 Methods

The potential ecological risk index is used to assess the ecological risk of the Liaohe River. The computational formula was shown as Eqs. (1)–(4). The T_r^i for Cd, As, Cu, Pb, Ni, Cr, and Zn are 30, 10, 5, 5, 5, 2, and 1, respectively [7, 22].

3.4 Results

3.4.1 The degree of contamination C_d

Table 5 shows the contamination factor C_f^i of the substances in the sediments from the Liaohe River. In Håkanson's research, seven metals (Hg, Cd, As, Cu, Pb, Cr, and Zn) and one organic pollutant (PCBs) were considered. However, in this study, there are only seven metals considered. Therefore, the C_d classification thresholds are modified. According to Håkanson's approach, the threshold for the "low degree of contamination" is 7, corresponding to the number of substances (7). The classification of C_f^i and C_d are classified in **Table 6**.

Table 5 shows that the C_f^i values of sampling sites range from 0.32 to 25.00. The average C_f^i value of each element and the percentage of that in C_d are in the following

Threshold	Modified threshold	Degree of risk
$C_f^i < 1$	/	Low
$1 \leq C_f^i < 3$	/	Moderate
$3 \leq C_f^i < 6$	/	Considerable
$C_f^i \geq 6$	/	Very high
$C_d < 8$	$C_d < 7$	Low
$8 \leq C_d < 16$	$7 \leq C_d < 14$	Moderate
$16 \leq C_d < 32$	$14 \leq C_d < 28$	Considerable
$C_d \geq 32$	$C_d \geq 28$	Very high
$E_r^i < 40$	$E_r^i < 30$	Low
$40 \leq E_r^i < 80$	$30 \leq E_r^i < 60$	Moderate
$80 \leq E_r^i < 160$	$60 \leq E_r^i < 120$	Considerable
$160 \leq E_r^i < 320$	$120 \leq E_r^i < 240$	High
$E_r^i \geq 320$	$E_r^i \geq 240$	Very high
ERI < 150	ERI < 60	Low
150 ≤ ERI < 300	60 ≤ ERI < 120	Moderate
300 ≤ ERI < 600	120 ≤ ERI < 240	Considerable
ERI ≥ 600	ERI ≥ 240	Very high

Table 6.
Classification of the potential ecological risk.

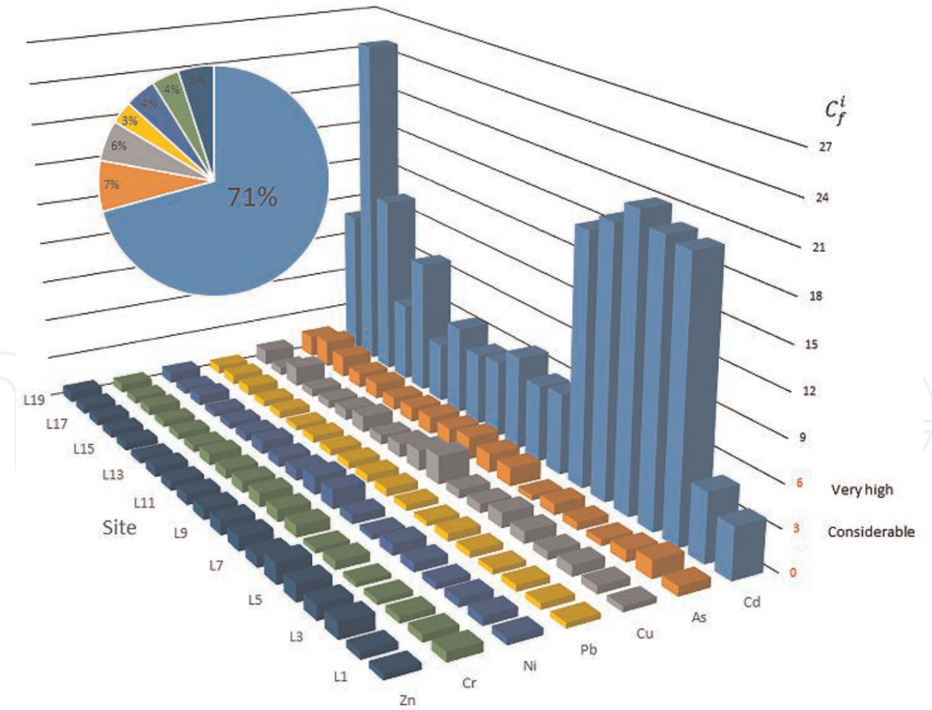

Figure 3.
Contamination factors (C_f^i) of different elements detected in sediments.

	Elements (St^i value)							
	Cd	As	Cu	Pb	Ni	Cr	Zn	$ERI = \sum_{i=1}^{7} E_r^i$
	30	10	5	5	5	2	1	
L1	111.11	6.97	1.99	1.90	2.41	1.34	0.42	126.14
L2	148.15	12.84	2.84	2.15	3.12	1.05	0.49	170.64
L3	592.59	8.22	3.92	2.34	2.81	0.87	1.15	611.90
L4	601.85	4.39	2.85	1.87	2.17	0.73	1.07	614.93
L5	629.63	5.68	4.33	2.36	3.29	0.63	1.22	647.14
L6	583.33	8.07	5.38	2.86	3.96	1.24	1.47	606.31
L7	546.30	3.90	3.31	1.71	1.80	0.71	0.81	558.54
L8	175.95	13.33	3.15	2.20	3.21	1.67	1.02	200.53
L9	166.67	13.79	10.38	2.95	6.89	1.77	1.00	203.45
L10	203.70	16.36	7.44	2.87	6.56	1.98	0.84	239.75
L11	166.67	13.14	5.03	2.57	4.11	1.65	0.79	193.96
L12	157.41	12.69	3.43	2.28	3.53	1.38	0.67	181.39
L13	194.44	10.68	5.86	2.50	4.52	1.67	0.71	220.38
L14	130.56	9.13	3.99	1.90	2.93	0.98	0.42	149.91
L15	297.22	11.56	2.98	2.70	2.36	0.94	0.53	318.29
L16	175.00	11.06	2.85	2.33	2.04	0.92	0.50	194.70
L17	402.78	15.91	7.26	3.50	3.79	1.26	0.57	435.07
L18	750.00	20.03	2.85	3.60	2.34	0.98	0.58	780.38
L19	325.00	15.65	5.68	3.01	3.96	1.26	0.76	355.32
Min	111.11	3.90	1.99	1.71	1.80	0.63	0.42	126.14

	Elements (St^i value)							
	Cd	As	Cu	Pb	Ni	Cr	Zn	$ERI = \sum_{i=1}^{7} E_r^i$
	30	10	5	5	5	2	1	
Max	750.00	20.03	10.38	3.60	6.89	1.98	1.47	780.38
Mean	334.65	11.23	4.50	2.51	3.46	1.21	0.79	358.35
Reference lake ("unpolluted")	30	10	5	5	5	2	1	58

Table 7.
The potential ecological risk factor (E_r^i) of different elements detected in sediments [11].

order: Cd (70.74%) > As (7.12%) > Cu (5.71%) > Zn (5.01%) > Ni (4.39%) > Cr (3.84%) > Pb (3.18%). Every C_f^i value of Pb and Cr is less than 1.0. For the average C_f^i value, Cd and As have a very high and moderate contamination factor, respectively. Whereas, Cu, Zn, Ni, Cr, and Pb have low contamination factors.

The resulting C_d values of each sample site ranged from 6.75 to 29.83. According to the category of C_d (**Table 6**), only sample L1 has the low degree of contamination. Ten sampling sites are classified as moderate and 7 sampling sites as having high contamination factors, sample L19 is classified into very high contamination factor. **Figure 3** clearly shows that Cd has the highest contamination factor. That means the Liaohe River is dominated by the pollution of one element—Cadium.

3.4.2 The potential ecological risk E_r^i and ERI

If the classification thresholds of C_d are modified, the E_r^i and ERI should also be modified. The first level of E_r^i is fixed by the T_r^i value of the most toxic element. This means that the results of the given water body are compared with a reference lake which has no contamination (C_f^i = 1). Similarly, the first level of ERI is fixed by the sum of T_r^i value of all the elements.

In the Liaohe River case study, the most toxic element is Cd and the T_r^i of Cd is 30. Therefore, the classification threshold of E_r^i is 30. The sum of T_r^i of all elements

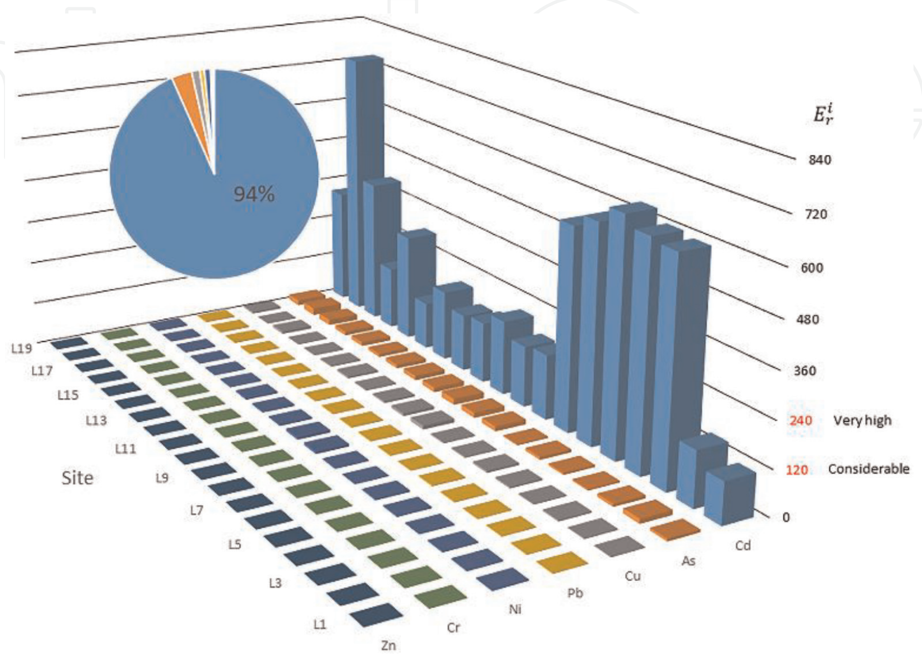

Figure 4.
The potential ecological risk factor (E_r^i) of different elements detected in sediments.

is 58, so the classification threshold of ERI could be 60. The classification of E_r^i and ERI are classified in **Table 6**.

Table 7 illustrates the potential ecological risks of the heavy metals in the sediments from the Liaohe River. The E_r^i values of sampling sites range from 0.42 to 750.00. The consequence of E_r^i (mean) of the 7 heavy metals are ranked as: Cd (93.39%) > As (3.13%) > Cu (1.26%) > Ni (0.97%) > Pb (0.70%) > Cr (0.34%) > Zn (0.22%). The E_r^i value of As, Cu, Pb, Ni, Cr, and Zn are all below 30. According to the category of E_r^i (**Table 6**), these six heavy metals have a low potential ecological risk. Cd at L1 posed a considerable potential ecological risk (111.11), while at other sampling sites, it shows high or very high potential ecological risk. The very highest E_r^i value is observed for Cd (750.00) at L18, indicates extremely severe pollution. The ERI values for the sampling sites range from 126.14 to 780.38. According to the listing of the ERI values (**Table 6**), the lowest ERI value for site L1 is over 120; therefore, all the sampling sites all have the considerable or very high potential ecological risk. The mean value of ERI (358.35) for the sediments in the Liaohe River indicates very high potential ecological risk (**Figure 4**).

4. Discussion

The Liaohe River is used as a case study to illustrate this approach. The investigation of seven heavy metals (Cd, As, Cu, Ni, Pb, Cr, and Zn) in the sediments suggest that the Liaohe River is dominated by the pollution of Cd which contributes around 94% potential ecological risk. The E_r^i means of the remaining sites are ranked as: Cd (93.39%) > As (3.13%) > Cu (1.26%) > Ni (0.97%) > Pb (0.70%) > Cr (0.34%) > Zn (0.22%). All elements except cadmium have low potential ecological risk. According to the ERI results, due to the serious pollution of cadmium, all the sampling sites have the considerable or very high potential ecological risk. Thus, it is important to control the pollution of cadmium. This study assesses the risk of Liaohe River by the modified risk classification criterion. Therefore, the results are different from [11], the risks assessed by this study are more serious. It is worth discussing how to use the risk classification criterion. This study suggests using the modified risk classification criteria.

Because of the "toxic-response" factor, compared with other approaches, the potential ecological risk index can distinguish the differences among substances and aquatic systems. Therefore, this approach has outstanding advantages to assess the risk of water system as a widely used approach which can provide a better overall ecological risk to the aquatic system. However, two main problems are neglected in the application of this method. (1) T_r^i is replaced by St^i. More attention should be given to the BPI value. Different aquatic systems have different sensitivities to toxic substances. According to Eq. (3) and **Table 4**, the effect of BPI value on the results depends on the degree of contamination of the aquatic system. If the pollution of the study aquatic system is serious, the BPI value will have large effect on the index calculation. Ecological risks can be evaluated more accurately by measuring the BPI value of the study aquatic system. (2) According to Håkanson's research [7, 23], the classification thresholds should be modified for different assessments. In this chapter, a reasonable suggestion for modification is suggested as well as applied. For C_d, the threshold for the "low risk" is modified by the number of substances. For E_r^i, the threshold for the "low risk" is modified by the T_r^i value of the most toxic element. For ERI, the threshold for the "low risk" is modified by the sum of T_r^i of all elements. There are still other problems deserve researchers concerns in the application of this approach, for example, the determination of accumulation areas in the aquatic system and calculation of St^i value. This study provides detail information for the potential ecological risk index and discusses several problems of the approach. And it is helpful for researchers to assess the ecological risk of aquatic system by this approach.

Acknowledgements

This work was supported by the Key Program of China (2018YFC1803103) and National Natural Science Foundation of China (No. 21377098). We also thank the anonymous reviewers and the editors for their comments which improved the manuscript.

Author details

Limin Ma[1,2,3]* and Changxu Han[1]

1 State Key Laboratory of Pollution Control and Resources Reuse, Tongji University, Shanghai, China

2 Key Laboratory of Yangzi River Water Environment, Ministry of Education, Tongji University, Shanghai, China

3 Shanghai Institute of Pollution Control and Ecological Security, Shanghai, People's Republic of China

*Address all correspondence to: lmma@tongji.edu.cn

References

[1] Li F, Huang J, Zeng G, et al. Spatial risk assessment and sources identification of heavy metals in surface sediments from the Dongting Lake, Middle China. Journal of Geochemical Exploration. 2013;**132**:75-83

[2] Wu Y, Xu Y, Zhang J, et al. Evaluation of ecological risk and primary empirical research on heavy metals in polluted soil over Xiaoqinling gold mining region, Shaanxi, China. Transactions of the Nonferrous Metals Society of China. 2010;**20**:688-694

[3] Taylor SR. Abundance of chemical elements in the continental crust: A new table. Geochimica et Cosmochimica Acta. 1964;**28**:1273-1285

[4] Müller G. Index of geo-accumulation in sediments of the Rhine River. Geochemical Journal. 1969;**2**:108-118

[5] Tomlinson DL, Wilson JG, Harris CR, et al. Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index. Helgoländer Wissenschaftliche Meeresuntersuchungen. 1980;**33**: 566-575

[6] MacDonald DD, Ingersoll CG, Berger TA. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Archives of Environmental Contamination and Toxicology. 2000; **39**:20-31

[7] Håkanson L. An ecological risk index for aquatic pollution control. A sedimentological approach. Water Research. 1980;**14**:975-1001

[8] Sun C, Zhang Z, Cao H, et al. Concentrations, speciation, and ecological risk of heavy metals in the sediment of the Songhua River in an urban area with petrochemical industries. Chemosphere. 2019;**219**: 538-545

[9] Zhang M, He P, Qiao G, et al. Heavy metal contamination assessment of surface sediments of the Subei Shoal, China: Spatial distribution, source apportionment and ecological risk. Chemosphere. 2019;**223**:211-222

[10] Zhang Z, Lu Y, Li H, et al. Assessment of heavy metal contamination, distribution and source identification in the sediments from the Zijiang River, China. Science of the Total Environment. 2018;**645**:235-243

[11] Ke X, Gui S, Huang H, et al. Ecological risk assessment and source identification for heavy metals in surface sediment from the Liaohe River protected area, China. Chemosphere. 2017;**175**:473-481

[12] Håkanson L. The influence of wind, fetch, and water depth on the distribution of sediments in Lake Vänern, Sweden. Canadian Journal of Earth Sciences. 1977;**14**:397-412

[13] Liu R, Bao K, Yao S, et al. Ecological risk assessment and distribution of potentially harmful trace elements in lake sediments of Songnen Plain, NE China. Ecotoxicology and Environmental Safety. 2018;**163**:117-124

[14] Ram SS, Aich A, Sengupta P, et al. Assessment of trace metal contamination of wetland sediments from eastern and western coastal region of India dominated with mangrove forest. Chemosphere. 2018;**211**: 1113-1122

[15] Tran TAM, Leermakers M, Hoang TL, et al. Metals and arsenic in sediment and fish from Cau Hai lagoon in Vietnam: Ecological and human health risks. Chemosphere. 2018;**210**: 175-182

[16] Bowen HJM. Trace Elements in Biochemistry. London/New York: Academic Press; 1966

[17] Forstner U, Müller G. Schwermetalle in Flüssen und Seen als Ausdruck der Umweltverschmutzung. Berlin Heidelberg: Springer; 1974

[18] Dauvalter VA, Kashulin NA. Assessment of the ecological state of the Arctic Freshwater system based on concentrations of heavy metals in the bottom sediments. Geochemistry International. 2018;**56**:842-856

[19] Kjeldahl J. Neue methode zur bestimmung des stickstoffs in organischen körpern. Fresenius' Zeitschrift für Analytische Chemie. 1883;**22**:366-382

[20] Carballeira JAFA. Evaluation of contamination, by different elements, in terrestrial mosses. Archives of Environmental Contamination and Toxicology. 2001;**40**:461-468

[21] Ke X, Gao L, Huang H, et al. Toxicity identification evaluation of sediments in Liaohe River. Marine Pollution Bulletin. 2015;**93**:259-265

[22] Xu Z, Ni S, Tuo X, et al. Calculation of heavy metals' toxicity coefficient in the evaluation of potential ecological risk index. Environmental Sciences. 2008;**2**:112-115

[23] Liu C, Wang Z, He G, et al. Evaluation on the potential ecological risk for the river mouths around Bohai Bay. Research of Environmental Sciences. 2002;**15**:33-37