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Original Research

Content and Spatial Distribution of V and Ni in Coastal Sediments and Waters of China's Shuangtaizi Estuary

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Abstract

In order to assess the spatial distribution and the potential pollution risk of nickel (Ni) and vanadium (V) in Shuangtaizi Estuary in China, the water and the surface sediments were collected to determine V and Ni content in specified sites. The data indicated that the estuary was contaminated by Ni, while V content was low. Total concentrations of V in river water ranged from 0.212 to 0.374 μg/L, and in surface and bottom seawater from 0.214 to 0.559 μg/L and 0.231 to 0.684 μg/L, respectively. V content in river sediments ranged from 0.093 to 0.119 μg/g and in ocean sediments were 0.032 to 0.123 μg/g. Total Ni concentrations in river waters ranged from 23.667 to 118.667 μg/L, and in surface and bottom seawaters were 32.000 to 90.323 μg/L and 42.000 to 100.333 μg/L, respectively. Ni content in sediments of river ranged from 15.303 to 21.732 μg/g and in sediments of ocean were 11.197 to 21.107 μg/g. Ni content was higher than that of V. An ecological risk assessment study shows that Ni has potential ecological risk in water and no risk in sediment. V has no potential ecological risk in Shuangtaizi Estuary. V and Ni concentrations increased from the inner estuary to the outer estuary. The anthropogenic emissions from land are the main sources of Ni and V in the study area.

Keywords: vanadium (V), nickel (Ni), spatial distribution, water and sediment, potential ecological risk assessment

Introduction

As one of the 20th most abundant elements, vanadium (V) is widely distributed in the earth's crust [1]. It is an essential trace element due to its significant role in environmental and physiological systems involving participation in different enzymatic reactions as an inhibitor and cofactor. V can be found in trace amounts in foods, soils, sediments, natural waters, air, plants, etc. [2-5], and is used widely in industrial processes. With the development of industry, V content in environment is getting higher and higher. At high concentrations V has a toxic effect on the environment and health. V could damage the biota and consequently damage humans through processes of bioaccumulation and biomagnification [6-8]. V and its compounds seemed as one kind of pollution in the environment. In the petroleum and derivatives processing industry, control of V is

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required because of its ability to poison catalysts. Due to its toxic effect on biological systems, there is increasing interest in determining V in environmental samples [9-10].

Nickel (Ni) is one of the most abundant elements in the earth crust, at 0.018% [11]. Ni has toxic effects at high concentrations. Ni and nickel salt could cause allergic dermatitis and has an obvious toxic effect on aquatic organisms, and some reports believe nickel to be carcinogenic [12-13]. With the development of industry, more and more Ni and its compounds are discharged into the environment, which will cause some environmental pollution, and there is increasing interest in determining Ni in the environment [14-16]. Studies have shown that as a result of anthropogenic inputs, many coastal areas were strongly polluted with metals such as As, Pb, Ni, and so on [17-20].

A natural wetland is a complex ecosystem providing numerous benefits to the environment. The wetland of Shuangtaizi Estuary has been ranked as the second largest swamp and the largest bulrush wetland in the world. In recent years, the wetland environment has suffered serious damage due to the rapid industrial development, plus economic and social activities. Therefore, the State Oceanic Administration of China set up two key ecological monitoring areas in Liaodong Bay, one of which is Shuangtaizi Estuary. Many researchers have studied the marine economy and the ecohydrological processes of the estuary due to its important strategic position [21-22], but few studies have been conducted on the distribution of Ni and V in the estuary. In order to study the Potential ecological risks of those elements in the estuary, the water and surface sediments were collect to study the contents and the distribution of Ni and V.

Material and Methods

Collecting and Preparing Samples

The samples of water were collected in 20 sites; samples of surface sediments were collected in 12 sites in Shuangtaizi Estuary (Fig. 1).

The water was collected by surface water and bottom water in 20 sites. R1-R4 were sample sites in the upstream river and S1-S16 were sample sites in the ocean. The surface water (sampled approximately 0.5 m below the surface) and bottom water (sampled approximately 0.5 m above the bottom) samples (1 L) were collected with a stainless steel water sampler and stored in glass bottles with screw caps. Because the river is shallow, only a mixed water sample was taken from the river. The sediments were collected by grab from the stations and were taken from the center of the grab into a glass container with a plastic spoon. The samples were stored at 4ºC.

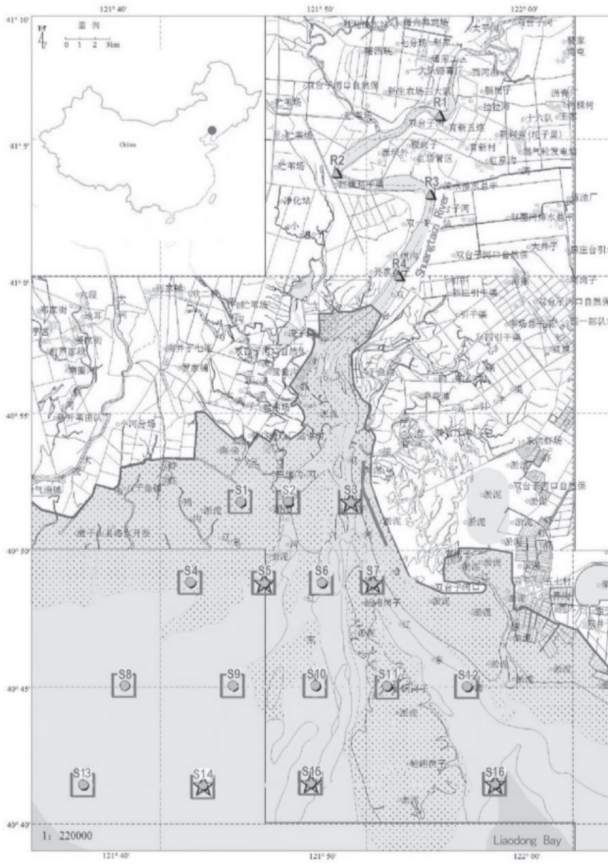

Fig. 1. Sampling locations in Shuangtaizi Estuary: R1-R4 for river water samples, S1-S16 for seawater samples; R1-R4 for river sediment samples; and S1, S3, S4, S5, S6, S7, S11, S13 for ocean sediment samples.

Pretreatment of Samples and Analysis Method

Ni and V content were analyzed by atomic absorption spectrometry [23-24]. Ni in water was chelated by DDTC (sodium diethyldithiocarbamate) and extracted by CCl_4, and then analyzed by atomic absorption spectrometry. V in water was enriched with resin of Chelex-100 [25], and then analyzed by atomic absorption spectrometry.

The sediments samples were dried at 60ºC until constant weight and sieved through a 100 μm mesh to remove large particles. 1 g of dried and sieved sediment was digested in 2 mL of hydrofluoric acid and perchloric acid using a WX-6000microwave digestion instrument (China, 2016) and then diluted to a final volume of 25 mL with deionized water. V and Ni content in both matrixes were then measured by atomic absorption spectrometry [26].

Data Analysis

All samples were measured at least three times to assess the reproducibility of the measurement. The standard deviations were controlled to within 5%. The contamination factor was used to determine

Table 1. Content of V in water.

Station	Surface water V (μg/L)	Bottom water V (μg/L)	Mean V (μg/L)
R1	0.310	0.310	0.310
R2 L3	0.212	0.212	0.212
R3	0.374	0.374	0.374
R4	0.374	0.374	0.374
S1	0.328	0.367	0.347
S2	0.227	0.231	0.229
S3	0.214	0.684	0.449
S4	0.400	0.457	0.428
S5	0.374	0.371	0.372
S6	0.450	0.470	0.460
S7	0.474	0.534	0.504
S8	0.428	0.462	0.445
S9	0.463	0.450	0.456
S10	0.465	0.533	0.499
S11	0.505	0.461	0.483
S12	0.481	0.507	0.494
S13	0.476	0.450	0.463
S14	0.503	0.503	0.503
S15	0.443	0.468	0.455
S16	0.559	0.426	0.493

the contamination status of the water and sediment. Contamination factor is calculated according to Thomilson and Wilson et al. [27].

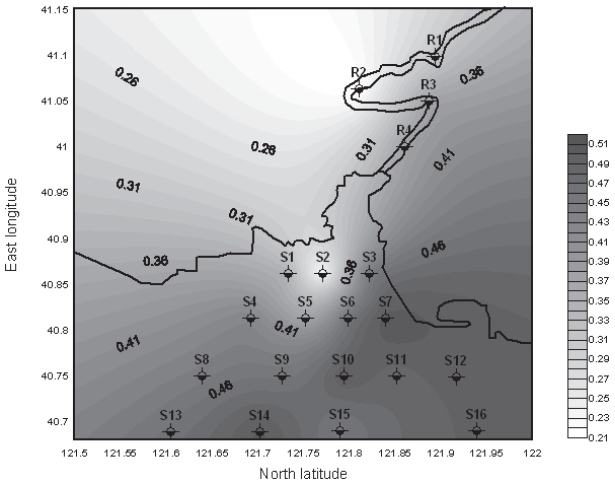

Fig. 2. Distribution of V in water.

$$C_f^i = \frac{C_{n\_1}^i}{C_n^i} \qquad C_d = \sum_{i=1}^{n} C_f^i$$

…where C_{n-1}^i is the content of substance from the sample sites and C_n^i is the background value.

The potential ecological risk index was proposed by Hakanson [28] to evaluate the characteristics and environmental behavior of heavy metal pollution in coast sediments, and has been used to evaluate the pollution degree of heavy metal by many researchers [29-32]. The ecological risk index was calculated by the following equation [33-34]:

$$E_{RI} = \sum_{1}^{m} E_r^i = \sum_{1}^{m} T_r^i C_f^i$$

…where C_f^i is the contamination factor, T_r^i is the toxic factor of heavy metal, and the values for Ni and V are both 6. E_r^i is the monomial potential ecological risk factor and E_{RI} indicates the integrated ecological risk index.

Results and Discussion

Content and Distribution of Ni and V in Shuangtaizi Estuary

Content and Distribution of V in Water

The content of V in water in Table 1 shows that the average concentration of V in the river water was 0.318 μg/L in the range 0.212-0.374 μg/L. The mean concentration of V in the surface seawater was 0.357 μg/L in the range 0.214-0.559 μg/L, and in the bottom seawater was 0.388 μg/L in range 0.231-0.684 μg/L. It could be seen that V content in the river is generally the same as that in seawater.

The spatial distribution characteristic of V in the estuary water (Fig. 2) showed clearly that there is an increasing trend from the inner estuary to the outer estuary and from the northern shore to the southern shore. In river samples in R1 to R4, the V content gradually increased, and in seawater samples from S1~S3 to S4~S7, to S8~S12, and to S13~S16 V concentration increased gradually. This result shows that the V can accumulate in water.

Table 2. Content of V in sediment.

Station	V (μg/g)	Station	V (μg/g)	Station	V (μg/g)
R1	0.091	S1	0.0613	S6	0.100
R2	0.108	S3	0.0320	S7	0.103
R3	0.119	S4	0.111	S11	0.123
R4	0.093	S5	0.112	S13	0.106

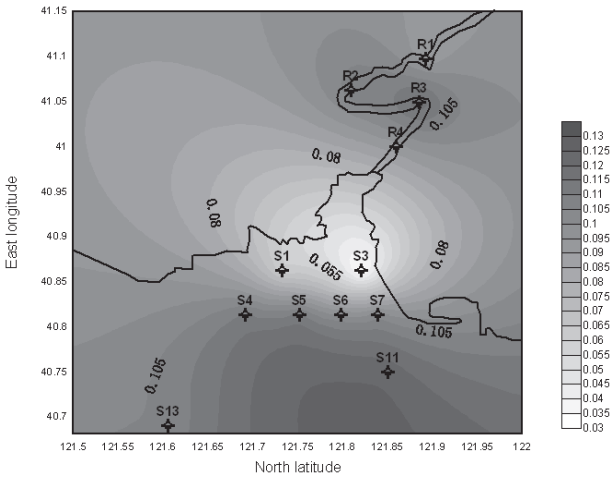

Fig. 3. Distribution of V in sediment.

Fig. 4. Distribution of Ni in water.

Content and Distribution of V in Sediments

The concentration of V in sediment samples is shown in Table 2. The average concentration of V in the river sediments was 0.103 μg/g in the range 0.093-0.119 μg/g, and in the marine sediments was 0.0936 μg/g in the range 0.032-0.123 μg/g. The distribution of V in sediment samples (Fig. 3) shows that V content in sediments of river is higher, while in marine sediments it is lower and changes significantly. Overall, V content in river mouth sediments is lower, while it increases along with the distance to the inner estuary.

The spatial distribution of V in sediments shows that there is V in the seawater and the upstream estuary, and the marine V mainly comes from terrestrial sources. Because of the low velocity of upstream river, V would deposit gradually, and in the mouth of the estuary V content was low by the dilution of seawater, while in outer estuary V would accumulate gradually, and V content in sediments increased in the outer estuary.

Table 3. Content of Ni in water.

Station	Surface water Ni (μg/L)	Bottom water Ni (μg/L)	Mean Ni (μg/L)
R1	107.000	107.000	107.000
R2	78.667	78.667	78.667
R3	118.667	118.667	118.667
R4	23.667	23.667	23.667
S1	54.376	58.667	56.522
S2	38.667	43.667	41.167
S3	32.000	42.000	37.000
S4	73.667	83.667	78.667
S5	67.000	70.333	68.666
S6	82.000	88.667	85.334
S7	85.333	83.667	84.500
S8	83.667	80.333	82.000
S9	90.333	92.000	91.167
S10	85.333	90.333	87.833
S11	90.333	93.667	92.000
S12	82.456	85.333	83.895
S13	90.333	93.667	92.000
S14	80.333	100.333	90.333
S15	80.333	83.667	82.000
S16	92.000	98.667	95.334

Content and Distribution of Ni in Shuangtaizi Estuary

Content and Distribution of Ni in Water

The content of Ni in the water samples is shown in Table 3. It could be seen that the average concentration of Ni in the river water was 82.003 μg/L in the range 23.667-118.667 μg/L in the surface seawater was 63.588 μg/L in the range 32.000-90.323 μg/L, and in the bottom seawater was 67.825 μg/L in range 42.000-100.333 μg/L. The content of Ni in river water is a little higher than that in bottom seawater and higher than that in surface seawater.

Table 4. Content of Ni in sediment.

Station	Ni (μg/g)	Station	Ni (μg/g)	Station	Ni (μg/g)
R1	15.482	S1	12.178	S6	16.197
R2	15.303	S3	11.197	S7	16.554
R3	16.018	S4	15.661	S11	15.840
R4	21.732	S5	21.107	S13	19.411

Table 5. Sediment-accumulated trace elements of Ni of other coastal regions.

Regions	Shuangtaizi Estuary	Pearl River Estuary, China	Coast Bohai Bay	Northwestern Gulf of Thailand	Coastal sites, Singapore	Coastal Belt, Pakistan	Arabian Gulf Coast
Ni (μg/g)	16.39	41.7	23.4-52.7	0-14.63	13.27-20.00	34	34
Regions	Fadiouth, Senegal	Red Sea, Egypt	Gulf of Mannar, India	Southeast Coast	South Port Klang, Malaysia	Sado Estuary, Portugal	Surface sediments, Tuticorin Coast
Ni (μg/g)	2.5	22	24	38.61	13.9	15.09	30

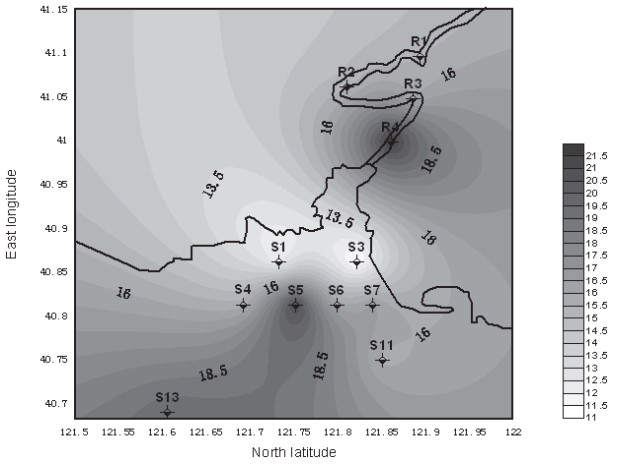

Fig. 5. Distribution of Ni in sediment.

The distribution of Ni in water (Fig. 4) shows that the Ni content in river water is higher. As the dilution of seawater, the content of Ni in the mouth of the estuary is low, and increased along with the distance to the outer estuary.

Content and Distribution of Ni in Sediment

Table 4 shows the content of Ni in the estuary sediment samples. The mean concentration of Ni in river sediments was 17.134 μg/g in the range 15.303-21.732 μg/g, and in marine sediments was 16.018 μg/g in the range 11.197-21.107 μg/g, which is a little lower than that in river sediment. In a study, Ke et al. analyzed the metal content in the area of the Liaohe River adjacent to the studied area and showed that the mean content of Ni in the sediments was 17.73 μg/g [30], which is the same as the studied result. To gain a comprehensive understanding of the pollution status of Ni in Shuangtaizi Estuary, we compared Ni concentrations in our work with the results of other estuaries (Table 5). This indicates that the concentrations of Ni in the estuary is at the general level of other estuaries [15-16, 18, 29].

The distribution of Ni in sediments was shown in Fig. 5. It could be seen that the distribution of Ni in the sediments of the area is the same as that in water samples. The higher content of Ni was located in the river and the outer estuary.

The results of Ni in water and sediment samples show that there is Ni pollution in the estuary, and the distribution of Ni in the area indicates that Ni in seawater mainly comes from terrestrial emissions. Sanderson et al. showed that river runoff could account for 29-34% of the total input of metals in most wetlands [35]. With the dilution of seawater, Ni content decreased at the position of the estuary mouth while increasing by accumulation with the distance of the outer estuary. The Ni in water could sediment to the bottom by a certain time.

Potential Ecological Risk of Ni and V in Shuangtaizi Estuary

The contamination factor was used to determine the contamination status of the water and sediment in the study. The potential ecological risk index was proposed by Hakanson [28] to evaluate the characteristics and environmental behavior of heavy metal pollution in coast sediments, and has been used to evaluate the pollution degree of heavy metals by many researchers [29-32]. The potential ecological risk posed by heavy metals can be classified into five categories (Table 6).

Table 6. Ecological risk index and grades of potential heavy metal contamination.

C_f^i	C_d	Pollution degree	E_r^i	E_{RI}	Grades of potential ecological risk
<1	<5	Clean	<30	<60	Low
1-3	5-10	Low	30-50	60-90	Moderate
3-6	10-20	Moderate	50-100	90-120	Considerable
6-9	<20	Considerable	100-150	120-180	High
>9		High	>150	>180	Very high

Table 7. Contamination of V and Ni in water.

Station	E_r^i		E_{RI}
	V	Ni	
R1	1.86	64.20	66.06
R2	1.66	47.22	48.88
R3	2.22	71.22	73.44
R4	2.22	14.22	16.44
S1	2.10	33.90	36.00
S2	1.38	24.72	26.10
S3	2.70	24.90	27.60
S4	2.58	49.80	52.38
S5	2.22	43.44	45.66
S6	2.76	53.94	56.70
S7	3.00	53.70	56.70
S8	2.70	51.90	54.60
S9	2.76	57.48	60.24
S10	3.00	55.68	58.68
S11	2.88	58.08	60.96
S12	2.94	53.28	56.22
S13	2.76	57.96	60.72
S14	3.00	57.18	60.18
S15	2.76	51.96	54.72
S16	2.94	60.12	63.06
Average	2.50	49.80	51.30

Table 8. Contamination of V and Ni in sediments.

Station	E_r^i		E_{RI}
	V	Ni	
R1	0.0042	1.26	1.26
R2	0.0048	1.20	1.20
R3	0.0054	1.26	1.27
R4	0.0042	1.74	1.74
S1	0.0030	0.96	0.96
S3	0.0018	0.90	0.90
S4	0.0054	1.26	1.27
S5	0.0054	1.68	1.69
S6	0.0048	1.32	1.32
S7	0.0048	1.32	1.32
S11	0.0060	1.26	1.27
S13	0.0048	1.56	1.56
Average	0.0048	1.32	1.32

Tables 7 and 8 showed the potential ecological risks index of V and Ni, and Figs 6-9 showed the distribution of potential ecological risk of V and Ni in the studied area. It could be seen that the values of E_r^i of V in water and in sediments are all very low (<30). The values of E_r^i of Ni in sediments are low (<30), while E_r^i of Ni in waters are high and in some samples are higher than 50. These results suggest that the sediments in the area are clean, and that V and Ni had no potential ecological risk to the sediments. The water in the area was not contaminated with V while it contaminated with Ni, and the contaminated degree of Ni was low to moderate. Above all, except for the water samples of R1, R3, S9, S11, S13, S14, and S16 being in the grade of moderate potential ecological risk, all the other samples were all at low potential ecological risk.

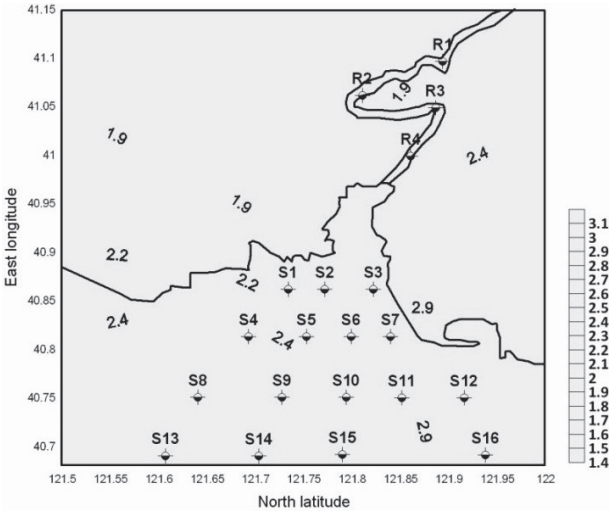

Fig. 6. Distribution of potential ecological risk of V in water.

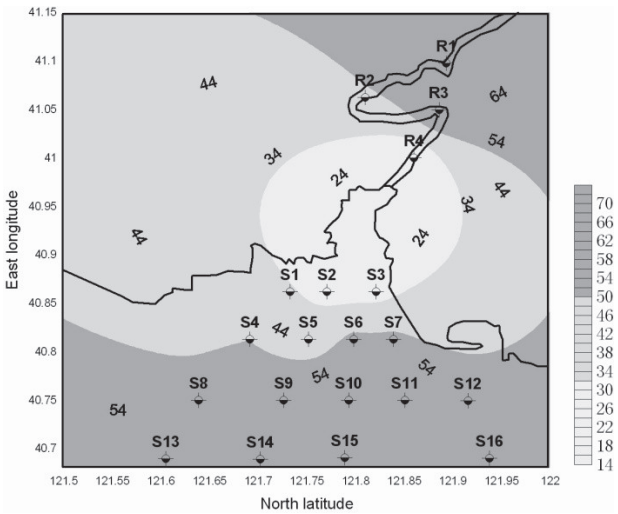

Fig. 7. Distribution of potential ecological risk of Ni in water.

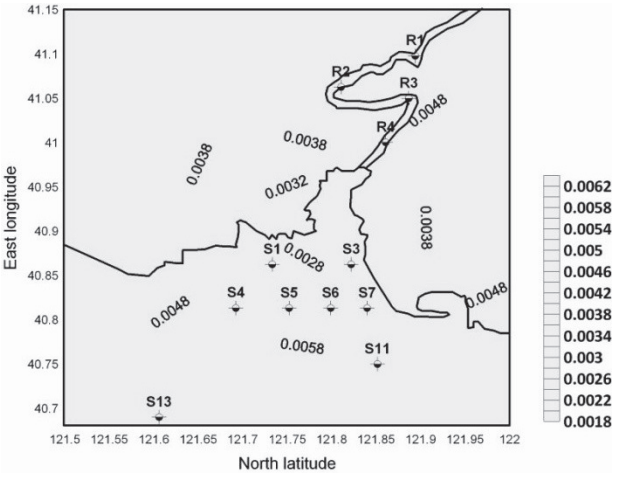

Fig. 8. Distribution of potential ecological risk of V in sediment.

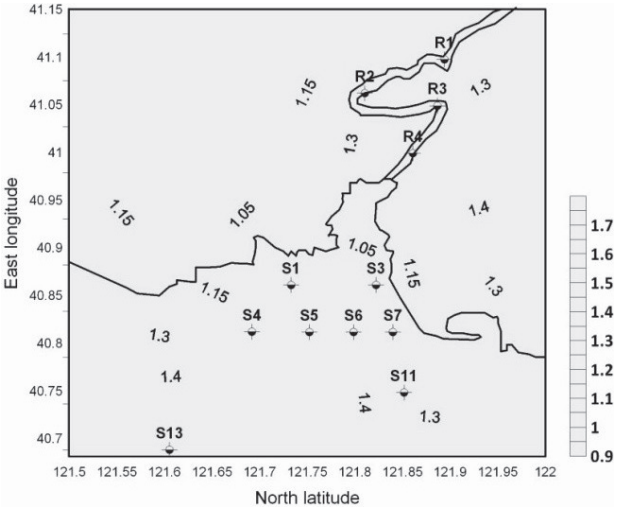

Fig. 9. Distribution of potential ecological risk of Ni in sediment.

Conclusions

This study demonstrated that Shuangtaizi Estuary was commonly contaminated by Ni and V. The V content is lower while the Ni content in water is higher. V and Ni in Shuangtaizi estuary clearly have spatial distribution. The content of Ni and V in the marine mouth is low, and increases along with the distance to the outer estuary. The distribution results indicate that the V and Ni in marine mainly come from terrestrial emissions. V and Ni in water could sediment to the bottom over a long period of time and distance. V and Ni in marine have some accumulation effects. In the estuary, V has no potential ecological risk, while Ni has moderate to considerable potential ecological risk in water. The total pollution grades of V and Ni were low.

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