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Zink of surface sediment in rural river basin as a potential priority to diffuse pollutants

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ABSTRACT

This study provides a baseline for the assessment of heavy metal contamination, especially zinc (Zn) contamination, in the sediments of Pyeongchang River in Korea. The zinc evaluation, along with that of other contaminants, for 20 study areas was done with respect to metal pollution load, ecological risk, enrichment of metal concentration, and geoaccumulated risk. Based upon the stated indices, a priority index (P_{index}) was proposed to rank the most contaminated sites. As expected, the values of pollution load, ecological risk, simplified enrichment factor, and simplified geoaccumulation risk index demonstrated lower zinc (and other heavy metal) contamination in upstream areas compared to areas downstream. Sediments were unpolluted to slightly polluted according to pollution load index, while high to extremely high ecological risks were observed in several sediment samples. The average quality of sediment indicated metal enrichment from point or non-point pollution sources to extremely high pollution. Further more, all the samples were uncontaminated as per geoaccumulation index. After simplification of enrichment factors and ecological risk indices, the P_{index} showed the most contaminated sediments with a value of 3.038, with a significant contribution from zinc. Notably, protective measures should be taken in highly contaminated areas prioritized by the P_{index}.

Keywords: Diffuse pollution; Heavy metal; Monitoring; Priority index; Surface sediment

1. Introduction

Although metals are present naturally in the environment, excessive amounts of heavy metals enter the coastal environment as contaminants from anthropogenic sources such as industrial processes, including untreated waste water, municipal sewage effluent, and surface runoff [1]. In many industrialized harbors and coastal regions around the world, a high concentration of heavy metals is often detected in sediments in aquatic environments [2]. A trace amount of metals is essential for providing the micronutrients necessary for the growth of many marine organisms. However, an excessive amount of heavy metals in the coastal environment is considered toxic to marine life [3]. Thus, high concentrations of heavy metals found in waters and sediments have raised serious environmental concerns not only for marine ecosystems but also for humans [1]. The sediment quality guideline (SQG) refers to the level that is likely to obstruct the health and properties of persons or rearing of animals and plants [4]. The SQG is categorized as unpolluted (SQG_u), moderately polluted (SQG_m), and heavily polluted (SQG_h).

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The distribution characteristics of organic and inorganic pollutants, including heavy metals in river sediments, have not been investigated. This study examines the evaluation of metal pollution levels and possible sources of background pollution for sediments. In addition, this study proposes a new index, priority index (P_{index}), to prioritize the most contaminated sediments.

2. Methods

Surface sediments from an approximately 41.78 km-long section of Pyeongchang River were collected from 20 points (named alphabetically **A–T**) upstream to downstream. The sediment collecting points indicate the direction of the river. River sediments were collected for assessing Cd, Cu, Pb, Zn, arsenic (As), chromium (Cr), mercury (Hg), nickel (Ni), total organic carbon (TOC), inorganic nitrogen (Ex-N), inorganic phosphorous (Ex-P), total nitrogen (TN), total phosphorous (TP), calcium (Ca^{2+}), sodium (Na^{+}), magnesium (Mg^{2+}), potassium (K^{+}), pH, and electric conductivity (EC).

A total of 20 sediments were collected, and each sample comprised a composite of four sub-samples taken from an area of 1 m^2. After transportation to the lab, large stones and plant debris were removed and air dried at room temperature until a constant weight was attained. Samples were disaggregated and passed through 2 mm and 150 µm sieves [2]. The pH and EC of sediment samples were determined by a 1:5 (w:v) ratio of sediment (150 µm) to de-ionized water. A simple test was performed by adding a few drops of HCl and observing the sample (2 mm) effervescences, afterward, samples were oven dried and analyzed using an element analyzer (1112EA, Thermo Quest) for the determination of TOC and TN.

Three grams of fine grained (150 µm) fraction samples were heated at 70°C for 1 h with 28 mL of aqua-regia (1:3 of nitric acid (HNO_3): hydrochloric acid (HCl)) for the extraction of Hg, Ni, and Zn from the topsoils. Afterward, all samples were cooled at room temperature, filtered as specified above, and diluted as required. Before analyzing, the filtrates were kept at 4°C. The concentrations of Ni and Zn were determined by inductively coupled plasma using an optical emission spectrophotometer (ICP–OES) (Optima 2000DV, Perkin Elmer) [3], whereas, time-saver system-reducing vaporization Hg analyzer (RA-3·SC-3, 3320, Nippon Instruments Corporation) was used for Hg determination. The sieved samples (2 mm) were mixed with a 1:5 (w:v) soil to 0.1N HCl solution ratio in a falcon tube for the extraction of Cd, Cu, Cr, and Pb, and the shaking, filtration, and storing processes followed as previously mentioned, while for As, the extraction solution and shaking duration were maintained as 1N HCl and 30 min.

3. Results and discussion

3.1. Concentration of cation and heavy metals

The percentages of cation and heavy metal concentrations are shown in Fig. 1 as ternary diagrams. The lowest concentrations of Ca^{2+}, Na^{+} and K^{+} were found in **A** as 202, 17 and 330 mg/kg, respectively, while the lowest Mg^{2+} concentration was observed as 85 mg/kg in **F**. It was found that the concentration of all heavy metals, except for Zn, Hg and Ni, maintained the unpolluted SQG (SQG_u) in all sites. The percentages of total sites that maintained moderately polluted SQG (SQG_m) were 80 for Zn and 25 for Ni, whereas highly polluted SQG (SQG_h) was observed in 15% of all sites for Zn, as shown in Fig. 2. The concentration of Hg in **K** surpassed the SQG_h as 1.77 mg/kg. The concentrations of Cu, Pb, and Hg were found as zero in 20%, 15%, and 30% of all site sediments. The concentrations of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, As, Cd, Cr, Cu, Hg, Ni, Pb and Zn were achieved as 3683, 423, 162, 2235, 0.4, 0.2, 0.3, 1.5, 0.2, 15.6, 2.4, and 152.1 mg/kg, respectively.

3.2. Pollution load assessment

Tomlinson's pollution load index (*PLI*) [5] of the samples was calculated using the heavy metal data and metal concentration for the world shale average as the background value [6]. The *PLI* is obtained as a concentration factor (*CF*) of each metal with respect to the background value in the sediment by applying the following equation:

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \times \cdots\cdots \times CF_n}$$

where, n is the number of heavy metals and $CF = C_{metal}/C_{background}$. The *PLI* of soils can be calculated by obtaining the nth root from the n number of obtained *CF* for all the metals [7]. The *PLI* values varied from 0.03 to 0.30 for sediments. As expected, the linear trend lines of *PLI* values, as shown in Fig. 3, increased with a positive slope of 0.3044 for sediments, from upstream to downstream areas. In sediment samples 4, 18, 5 and 14 sites, the concentrations of *CF* were over unity, respectively, for Cd, Zn, Ni and Hg. The concentration of Hg in **K**, for sediments, was about 32 times the background concentration, indicating extremely high Hg content in the sediment.

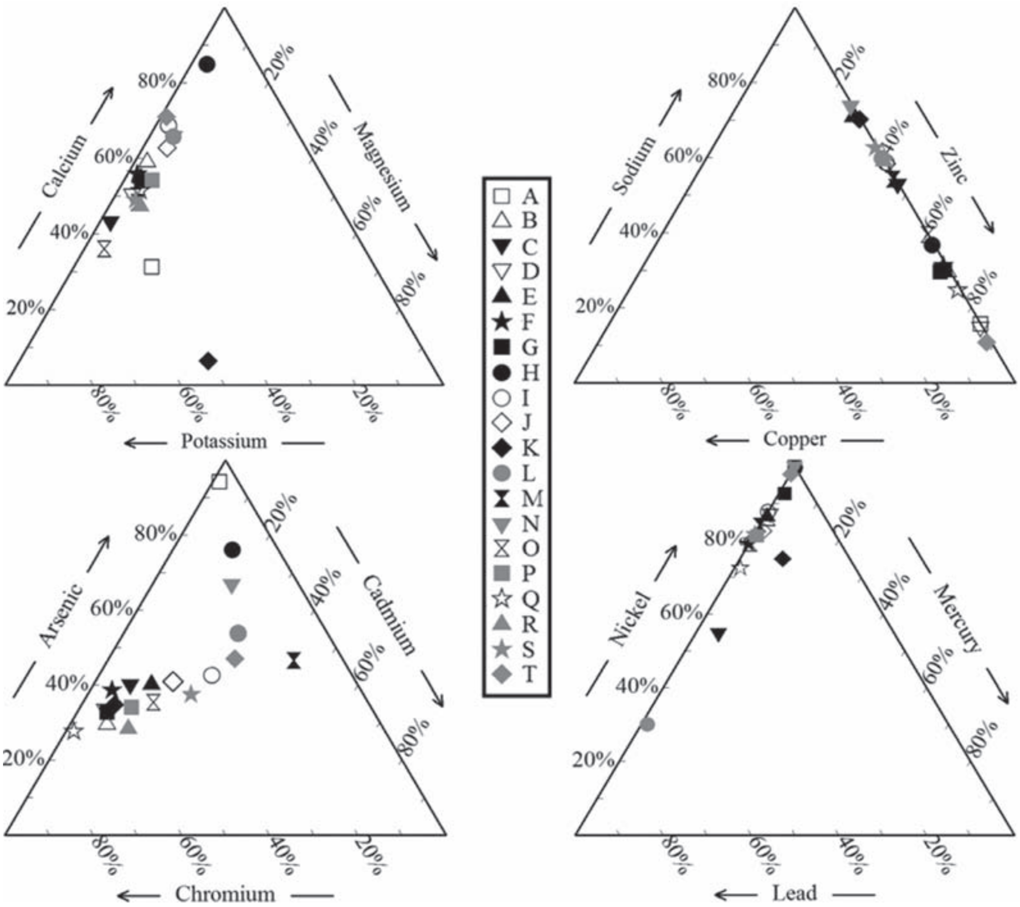

Fig. 1. Ternary chart of cation and metal amounts in sediments.

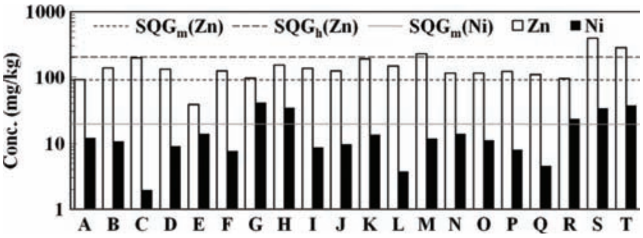

Fig. 2. Concentration of Ni and Zn in sediments.

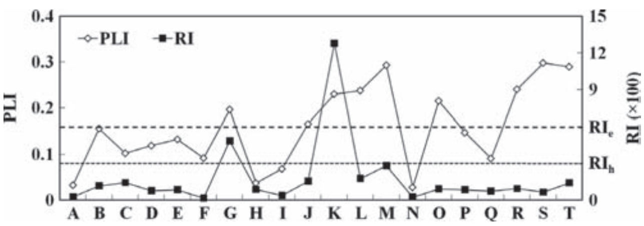

Fig. 3. PLI and RI values for sediments.

3.3. Ecological assessment

Ecological risk index (*RI*) [8] is defined as the summation of the change occurring in metals with respect to background values considering toxicological factors. The mathematical relation of *RI* can be shown as

$$RI = \sum_{i=1}^{n} \left(T_i \times \frac{C_i}{C_0} \right)$$

where, n is the number of heavy metals, T_i is the toxic-response factor for a given substance (for Hg, Cd, As, Cr, and Zn 40, 30, 10, 2, and 1, respectively, and 5 for Pb, Cu and Ni), C_i represents metal content in sediment, and C_0 is the regional background value of heavy metals. The regional background values of measured heavy metals were unavailable, consequently, metal concentrations for the world shale average [6] were chosen as the background value. Three contamination categories are recognized on the basis of ecological risks. $RI < 300$, $300 \leq RI \leq 600$ and $RI > 600$ state low to moderate, high (RI_h), and extremely high ecological risks (RI_e) [8] in heavy metals, respectively. Potential RI values of heavy metals in surface sediments lower than 300 suggest that sediment samples from the river catchment exhibited low and moderate ecological risks of heavy metals. However, 10% of samples from the sediments had RI values ranging from 300 to 600, which indicates a high ecological risk of heavy metals. RI value of the sediment in **K** was 1280, which reflects extremely high ecological risk of heavy metals. The values of RI are shown in Fig 3. As anticipated, positive slopes were found from upstream to downstream RI values, indicating lesser to higher ecological risk from sites **A** to **T**.

3.4. Metal enrichment

The enrichment factor (*EF*) of an element in the samples studied was based on the standardization of a measured element against a reference element. A reference element is often the one characterized by low-occurrence variability, as in the most commonly used elements, such as aluminum (Al), iron (Fe), K, and so on [9]. The EF is expressed below as

$$EF = \frac{(C_x / K)_{\text{soil}}}{(C_x / K)_{\text{background}}}$$

where, $(C_x/K)_{\text{soil}}$ is the metal to K ratio in the samples of interest, and $(C_x/K)_{\text{background}}$ is the natural background value of the metal to K ratio. In this study, the concentration of K^+ is assumed as K. As K and heavy metal background values for our study area are not available, the average continental shale metal values have been adopted. There is no accepted pollution ranking system or categorization of degree of pollution on the enrichment ratio and/or factor methodology [9]. The proposed EF classes along with the sediment quality at various values are shown in Table 1.

The values of *EF* for topsoil with qualities are shown in Table 2. For sediments, it was found that 5% (for Cd and As), 20% (for Ni), 55% (for Hg), and 60% (for Zn) of total sites surpassed class 5 *EF*. The values of *EF* for Cr and Cu were mostly below 0.5, indicating the enrichment entirely from point or non-point source pollution. The concentration of Cd for topsoil showed minimal to significant enrichment, while 80% of sediments showed the same enrichment. The observed Ni concentrations in 20% of sites, for sediment and topsoil, were moderately enriched starting from crustal materials. Minimal to moderate Pb enrichment was observed at 50% of total sites. The *EF* values of As in sediments in 50% of the sites showed minimal to extremely high in 75% of the sediments.

3.5. Priority assessment

The priority index (P_{index}) is proposed to prioritize the combined pollution or risk levels among sets of sediments from different locations. The mathematical equation is shown below with the range of P_{index} values.

$$P_{index} = \sum_{i=1}^{n} (I^N)i, \quad 0 \le P_{index} \le n$$

where the normalized index, $I^N = (y/y_{max})$, of any soil sample can be calculated by dividing the maximum pollution or risk index value (y_{max}) of any set of sediment samples with each pollution or risk index value (y) of sediment from that set of samples. n is the applied number of pollution or risk index to assess sediment sample-sets. The limitations of the proposed index are: (i) the pollution or risk indices whose rising values indicate higher contamination or risk should be applied, (ii) negative value from any index should be omitted during normalization, and (iii) the indices showing average contamination of soil should be applicable. In this study, the normalized *PLI* values (PLI^N) and normalized *RI* values (RI^N) are applied directly due to their average index criteria. However, as the values *EF* and I_{geo} do not show average index criteria, the normalization of these values follows after simplification of each value. The simplified enrichment factor (*sEF*) and simplified geoaccumulation index (sI_{geo}) can be shown as below:

$$sEF = \frac{1}{n}\sum_{i=1}^{n}\left[\frac{EF_i}{(EF_i)_{\max}}\right] \quad \text{and} \quad sI_{geo} = \frac{1}{n}\sum_{i=1}^{n}\left[\frac{I_{geoi}}{(I_{geoi})_{\max}}\right]$$

where, n is the total number of heavy metals; EF_i and I_{geoi} are the values of *EF* and I_{geo} of any heavy metal. These simplifications are done to form average index criteria. Therefore,

Table 1
Categorization of enrichment factors.

EF value	EF class	Level of enrichment
>40	6	Extremely high enrichment
20–40	5	Very high enrichment
5–20	4	Significant enrichment
2–5	3	Moderate enrichment
1.5–2	2	Minimal enrichment
0.5–1.5	1	Enrichment entirely from crustal materials
<0.5	0	Enrichment from point and non-point sources (E_p)

Table 2
Enrichment factor values with sediment quality.

Sites	EF values								Class
	Cr	Cu	Cd	Ni	Pb	As	Hg	Zn	
A	0.07	0.02	10.86	57.09	0.04	75.99	15.51	83.87	0-6
B	0.08	0.44	4.99	11.52	1.73	1.70	49.93	29.44	0-6
C	0.02	0.14	1.36	1.14	0.77	0.76	36.14	22.52	0-5
D	0.06	0.31	2.27	8.93	1.13	1.45	30.28	25.57	0-5
E	0.03	0.34	3.60	9.03	1.27	1.08	19.99	4.81	0-4
F	0.05	0.52	1.96	8.17	2.01	1.47	3.50	25.86	0-5
G	0.07	0.60	2.92	51.68	3.08	1.63	272.48	23.70	0-6
H	0.00	0.00	2.80	25.83	0.01	1.54	23.31	22.63	0-5
I	0.02	0.00	8.50	4.86	0.63	1.44	1.84	14.90	0-4
J	0.03	0.30	5.39	6.31	1.13	1.20	39.92	15.77	0-5
K	0.03	0.19	1.71	6.21	1.17	0.75	270.40	17.03	0-6
L	0.02	0.49	10.87	1.98	4.23	2.20	32.93	15.44	0-5
M	0.07	0.57	113.77	8.59	1.51	12.47	2.37	31.87	0-6
N	0.01	0.00	2.50	6.83	0.00	1.00	1.62	10.98	0-4
O	0.07	1.52	10.12	10.69	2.58	2.29	29.33	21.27	0-5
P	0.02	0.15	2.46	3.07	0.63	0.69	11.72	9.09	0-4
Q	0.10	0.44	0.64	6.33	2.12	1.74	42.91	29.95	0-6
R	0.06	1.17	6.34	15.90	3.29	1.24	21.12	12.83	0-5
S	0.04	0.83	10.78	15.40	3.20	1.73	1.51	35.31	0-5
T	0.04	0.92	22.16	24.17	0.41	3.56	19.97	35.46	0-5
Mean	**0.04**	**0.45**	**11.30**	**14.19**	**1.55**	**5.80**	**46.34**	**24.42**	**0-6**

Table 3
Ranking by P_{index} for sediments.

Site	Sediments					
	PLI^N	RI^N	sEF^N	$sIgeo^N$	P_{index}	Rank
A	0.108	0.019	0.966	0.000	1.093	11
B	0.523	0.088	0.568	0.100	1.279	9
C	0.342	0.110	0.231	0.347	1.030	12
D	0.398	0.059	0.411	0.021	0.889	14
E	0.444	0.064	0.281	0.021	0.810	15
F	0.307	0.012	0.444	0.000	0.763	17
G	0.660	0.378	**1.000**	**1.000**	**3.038**	**1**
H	0.124	0.066	0.223	0.385	0.797	16
I	0.227	0.029	0.185	0.000	0.441	19
J	0.556	0.119	0.309	0.157	1.140	10
K	0.772	**1.000**	0.499	0.764	3.035	2
L	0.798	0.136	0.491	0.181	1.605	6
M	0.984	0.219	0.768	0.873	2.843	3
N	0.091	0.017	0.085	0.000	0.194	20
O	0.722	0.071	0.738	0.021	1.551	8
P	0.493	0.064	0.180	0.021	0.758	18
Q	0.304	0.055	0.609	0.021	0.989	13
R	0.808	0.072	0.671	0.021	1.571	7
S	**1.000**	0.049	0.625	0.896	2.570	5
T	0.972	0.108	0.564	0.945	2.590	4

normalized *sEF* value (sEF^N) and normalized sI_{geo} value ($sI_{geo}{}^N$) are applied in the P_{index} relation to sort out the higher-to-lower affected sediments from 20 study areas. Thus, the final proposed P_{index} for this study is as follows:

$$P_{index} = \sum\left(PLI^N, RI^N, sEF^N, sI_{geo}{}^N\right) \qquad 0 \le P_{index} \le 4$$

The priority of sediments was assessed for eight heavy metals (Cr, Cu, Cd, Zn, Ni, Pb, As, and Hg) with respect to four indices: heavy metal pollution load, ecological risk, enrichment of heavy metal concentration, and geoaccumulated risk. The values of P_{index} with ranking are shown in Table 3. In sediments, the sequence was **G** > **K** > **M** > **T** > **S** > **L** > **R** > **O** > **B** > **J** > **A** > **C** > **Q** > **D** > **E** > **H** > **F** > **P** > **I** > **N**.

4. Conclusion

This study looked at river sediments to assess organic and inorganic pollution, including heavy metal contamination. The heavy metal contamination for the sediments was assessed with respect to metal pollution load, ecological risk, enrichment of heavy metal concentration, and geoaccumulated risk. Based upon the indices used, a priority index (P_{index}) was proposed to rank the most contaminated sites. Sediment quality guidelines in this study area implied that most of the sediments were moderately polluted by Zn. Significant risk of Hg contamination was observed for all indices, although the concentration in most of the sediments was below the guideline. As expected, positive linear trend lines were observed for the values of pollution load index and ecological risk index demonstrating lower heavy metal contamination in upstream areas compared to areas downstream. Sediments were un polluted to slightly polluted according to the pollution load index. The average sediment quality was observed up to extremely high enrichment. Furthermore, as per geoaccumulation index, all of the samples were unpolluted. After normalization followed by the simplifi cation of enrichment factors and ecological risk indices, the P_{index} showed the highest contaminated sediments **G** as 3.038. Therefore, remediation facilities should be applied to the affected sediments, which are prioritized by P_{index}.

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