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Contamination assessment of pollutants and sediments of abandoned mines using integrated pollution index (IPI)

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ABSTRACT

The objective of this paper is to classify the major polluted mine areas established by the integrated pollution index (IPI) for soil, water, and sediments to provide a baseline to extend further study. Besides, the present study aimed to investigate the pollutant levels of heavy metals in the soil, water, and sediments generated from waste mine areas. Almost all the mine areas river water, soil, and sediment carried high contents of heavy metals generally exceeding the freshwater, and soil criteria. The study consists of the assessment of three mines of heavy metal contamination in water, soil, and sediments near the Han River basin. Samples collected at different mine sites and analyzed according to the standard method. Based on the study results water, soil, and sediment quality guidelines are compared. The concentrations of heavy metals Cr, Cu, Cd, Zn, Ni, in soil and water are below the countermeasure levels whereas, sediments are moderately polluted by Zn. In sediments, the significant amount of heavy metals are Zn (35.31–491.87 mg/kg), Ni (13.44–132.25 mg/kg), As (0.15–8 mg/kg), Cd (0.05–3.51 mg/kg), Cu (0.001–39.85 mg/kg), Pb (0.03–32.79 mg/kg), Hg (0.19–1.68 mg/kg), and Cr^{6+} (0.01–0.78 mg/kg). The mining areas have obvious risks of contamination in the surface environment waters, and sediments through abundant precipitation. This study, intended for the classification of mines, by the IPI throughout each pollution index.

Keywords: Abandoned Mine; Heavy metal; Integrated Pollution Index (IPI); Pollutant; Sediment

1. Introduction

The mines that cause soil, water and sediment contamination are mainly abandoned metal mines, abandoned asbestos mines, and abandoned coal mines. In Korea, there are 5,396 mines distributed nationwide and 98% are abandoned. Most of the mines continuously discharge heavy metals in the environment. As a result, soil, plant, water, and sediment of surrounding mine areas are contaminated by potentially toxic elements from tailings by clastic movement through wind and water [1–3]. The Ministry of Environment conducts surveys on contaminated mines across the country, but it is difficult to predict the accumulation of sediment contamination. The abandoned mine survey, monitoring, and measurement system are insufficient to continuously monitoring the pollution of the mine water and sediment. However, the Ministry of Environment established a sediment monitoring network in 2011 together with a water quality monitoring network to manage the contamination of sediment. While compared with all abandoned mines in the

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whole country, 286 sediment monitoring networks are insufficient to identify the ecosystem contamination by water quality and sediment contamination. Therefore, an integrated pollution index (IPI) is required to build a convenient monitoring system, assessment of sediment contamination and toxicity according to the pollutants and concentration. The purpose of this study is to establish an IPI through sediment index which can analyze heavy metals of sediment as well as soil and water contamination.

2. Material and methods

2.1. Methods for estimating pollution index

The IPI is calculated from a weighted ratio of site survey (SI), soil pollution index (PIs) and water pollution index (PIw) [4]. Moreover, the sediment pollution index (SP_{index}) is assessed to three indices, heavy metal pollution load (PL^N), ecological risk (RI^N) and geoaccumulation risk (sI^N_{geo}) [1]. The metal pollution index (MPI) [5] is calculated to enable present the metal (As, Cd, Cu, Ni, Pb, Zn, Hg, Cr) concentrations of sediment as a single value.

The IPI is proposed to prioritize the combined pollution or risk levels among soil, water, and sediment samples from different abandoned mine locations. The IPI belongs to three conditions depend on the pollution status of heavy metal of abandoned mines. The mathematical relations are shown below:

A. $IP_{index} = \alpha PIw^n + \beta PIs^n + \gamma SI \quad (0 \le IP_{index} \le 1)$
B. $SP_{index} = \sum (PLI^N, RI^N, sI^N_{geo}) \quad (0 \le SP_{index} \le 1)$
C. $MPI = (Cf_1^{\chi}\, Cf_2^{\chi} \ldots\ldots\ldots Cf_k)^{1/k} \quad (0 \le MPI \le 1)$

Condition 1. IPI = $\sum$ (A, B, C)
Condition 2. IPI = $\sum$ (A, B)
Condition 3. IPI = $\sum$ (A, C)

Herein, several data on water, soil, and sediment heavy metals concentration accumulated from experiment results, and narratively analyzed. According to the analysis, a new pollution index has been re-established to prioritize the abandoned mines by pollutants level.

2.2. General status of the sampling site

The mines located near the Han River basin (Fig. 1). The total target area of mine 'A' was 4,108 ha (hectare) located in Gangwon-do and known as a copper mine. In terms of land use status, forests accounted for 97.8% (4,017 ha) of total land area and less than 10% of cultivated land. The B mine located in Chungcheongbuk-do and the total target area was 913 ha. Regarding the land use, forests accounted for 75.7% (691 ha) of the total area, and cultivated land accounted for 21%. The total area of the mine C was 871 ha and located in Chungcheongbuk-do. In respect of land use status, forests accounted for 70% (610 ha) of total area, and cultivated land accounted for less than 20.4%.

2.3. Sampling and analysis of mine water

For the sampling of the mine water, samples collected considering the affected point of the river, and the point where the flow can be measured was selected. Municipal water of 2 points, 4 points of river water, 2 points of groundwater total of eight sampling points where samples were collected from February to October and analyzed for 28 water quality indicators. Samples were collected under the water pollution process standard, and 2 L sterilized bottles were used to carefully collect samples of possible impurities. During the early sampling period, the flow rate of the stream was very small due to the winter drought.

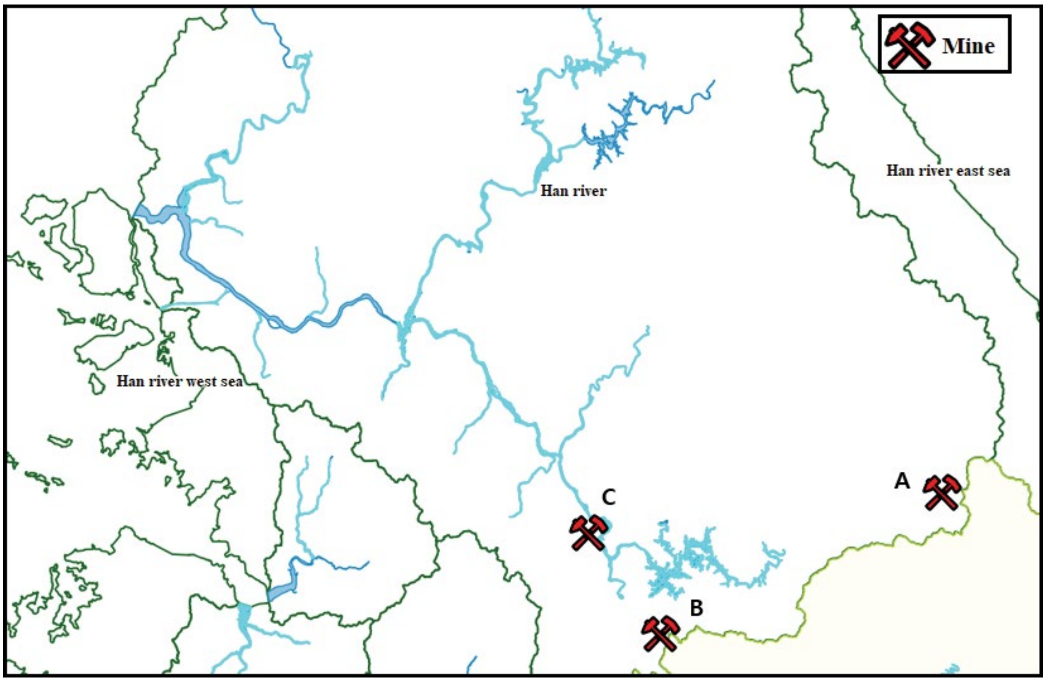

Fig. 1. Sampling areas near the Han River basin.

The collected samples were immediately transported and analyzed according to the sample storage method except those immediately measured.

The analysis items were pH, water temperature, dissolved oxygen (DO), electrical conductivity (EC), total suspended solids, turbidity, hardness, alkalinity, Cl^-, SO_4^{2-}, total nitrogen (TN), total phosphorus (TP), Ca, Mg, Na, K, Al, Fe, Cd, Pd, Cu, Mn, Zn, and Ni. All analysis was carried out by the water pollution process test method. The pH of the analysis items was measured by a pH meter, water temperature, DO and EC was measured using a multifunction meter (HI9828, HANNA, Manufactured in Romania), and turbidity was measured immediately using a turbidity meter (2100P, HACH, USA) in the field.

An inductively coupled plasma optical emission spectrometry (ICP-OES) was used for the quantitative determination of metal materials. The implanted plasma was injected into an argon plasma formed by a high-frequency induction coil, and the atoms were excited at high temperature (6,000~8,000 K). It was a method of qualitatively and quantitatively measuring an element by measuring a light emission line and a light emission intensity that was emitted when moving. ICP was plasma generated by the induction coil in the 27.13 Hz region (radio wave) generated from a high-frequency generator, which was an oscillation type, using argon gas as plasma gas. The instrument consists of a sample introduction part, a high-frequency power part, a light source part, a light-emitting part, an associative processing part and a recording part, and the spectroscopic part was a sequential monochromator and a multi-element simultaneous measurement device.

2.4. Sampling and analysis of soil and sediment

Soil samples were collected starting from the shaft and near the mine shaft at 2.0 km at twenty points. Each soil sample was composed of 4 subsamples taken from the mine area. Collected soil samples transported to the laboratory, large stones, and plant debris were removed from the soil and air-dried at room temperature until a constant weight was attained then sieved with 2 mm, 300 μm, and 150 μm sieves [6].

The survey area of sediment sampling was 1.0 km away from the mine shaft, and samples were collected sequentially from upstream to downstream near the mine shaft. The analysis of sediment samples was carried out on nine items such as pH, As, and heavy metals in the same way as soil samples.

Soil samples were analyzed for pH, As and heavy metals. The pH of soil and sediment samples were measured by the 1:5 (w:v) ratio of soil to de-ionized water [4]. Total organic carbon and TN determined by the simple test by adding a few drops of hydrochloric acid (HCl) and observed the sample effervesces [7], next samples were oven-dried and analyzed by the element analyzer (1112EA, Thermo Quest, Italy).

The heavy metals determined by the ICP-OES. 3 g of the sample accurately measured and heated at 70°C for 1 h with 28 ml of aqua-regia (1:3 of nitric acid (HNO_3):HCL) for extraction of Hg, Ni, and Zn from soils and sediments. Then, all samples were cooled, in-room temperature, and filtered through ϕ150 mm filter papers by the gravity filtration method. The filtrates were kept at 4°C before analysis. The concentrations of Ni and Zn were measured by the ICP-OES (Optima 2000DV, Perkin Elmer, USA) [8]. To determine the Hg concentration time saver system reducing vaporization Hg analyzer (RA-3.SC-3, 3320, Nippon Instruments Corporation, Japan) was used.

According to the Korean standard method As, Cd, Cu, Cr, and Pb were determined. The sieved samples were mixed with a 1:5 (w:v) ratio of soil to 0.1N HCl solution in a falcon tube for the extraction of Cd, Cu, Cr, and Pb, and the shaking, filtration and reserving process were followed as previously explained methods. Also, for the extraction of As the solution and shaking duration were maintained as 1 N HCl and 30 min accordingly.

For TP measurement, digestion with perchloric acid (70% $HClO_4$) ascorbic acid method was used. In the tubes used in block digester, 2 g of samples were mixed with 30ml of $HClO_4$ (70%) and heated at 130°C until precipitation. After that, the solutions were cooled at room temperature and diluted. The diluted solutions were filtered as the followed method. Then, 2 ml of filtrates were mixed with 8 ml of 2.4% H_3BO_3 and 2 ml of an ascorbic acid solution made by ascorbic acid and ammonium paramolybdate solution. Before measuring through a spectrophotometer, the final solutions were kept for 1 h at room temperature.

To determine Inorganic N and P, the samples were pretreated before analysis. For N determination the samples were pretreated as 1:10 (w:v) of soil to potassium chloride solution (2 M KCl) and filtered as the above method. Then, 30 ml of filtrate sample was mixed with 1 g of magnesium oxide (MgO) and 1 g of Devarda's alloy, and the solution was operated through a distillation unit (Kjeltec™ 2100, Foss, Denmark) for 10 min. Afterward, the distilled solution was mixed with 5 ml of 2% boric acid (H_3BO_3) and then titrated with 0.01 N sulfuric acid (H_2S0_4) to get the concentration of inorganic N. As above method the samples were pre-treated with calcium chloride solution (0.01 M $CaCl_2$) as 1:10 (w:v) by mixing for 24 h and then filtrated for extraction of inorganic P. The final solution making and measuring processes were the same as the extraction of T-P.

3. Results and discussion

3.1. Heavy metal concentration in water

The heavy metals were analyzed from water and important to evaluate the PI_w among all mine sites for the evaluation of IPI. PI_w is measured to evaluate the contamination of water as specified in the Korean standard tolerable levels for water. [4,9]. Fig. 2 shows the bar charts of heavy metal concentrations in the water samples also evaluates the water contamination range of the mine sites. The following graph shows that among 3 mines, the As and Zn concentrations are stronger than other pollutants. The highest concentration of As and Zn in the mine site of A and C, 0.0213 and 0.0313 mg/kg accordingly. Besides, the concentration of heavy metals in almost all sites of the mine is less than the tolerable level.

3.2. Heavy metal concentration in soil

In the south-west regions, subsoil and surface soil were strongly contaminated by lead and arsenic [10]. In

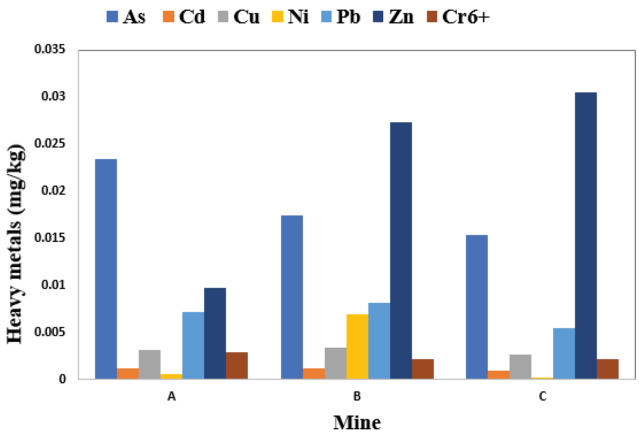

Fig. 2. Heavy metal concentration in water.

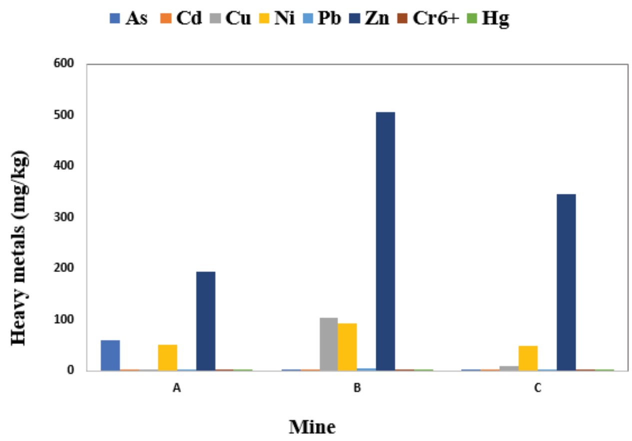

Fig. 3. Heavy metal concentration in soil.

this study area, Zn and Ni contaminations are very high in all mine sites. Mostly contaminated by Zn is the highest 505.65 mg/kg in mine B. In some areas, high levels of arsenic and copper are visible. Also, at two points found Ni and Cu contamination is very high, 92.75 and 104.25 mg/kg respectively. Fig. 3 shows the maximum and minimum trace element concentration of all mine sites. Most of the sampling point areas, the metal concentrations of Cu, Cd, Pb, Cr, and CN are lower than the tolerable values (50, 2, 100, 4, 2) mg/kg accordingly.

3.3. Heavy metal concentration in sediment

In sediment Zn and Ni, concentrations are dominated compared to the other metals. Sediment pollution is considered the largest risk to the aquatic environment. Fig. 4 shows the most pollutant elements in sediment are Zn and the highest polluted sites are B and A whereas the metal concentrations are 407.31 and 296.04 mg/kg. On the other hand, the second-most effective heavy metal is Ni and the highest Ni contamination is 97.47 mg/kg in mine B and the lowest is 35.82 mg/kg in mine C, where the tolerable level for Ni is 18.6 mg/kg. Compare to water and soil the heavy metals concentration in sediment is rich and above tolerable level. Sediment with the high concentration of heavy metals poses a potential threat to the marine ecosystem [11].

3.4. Metal pollution index

The MPI [5] is used to compare the total content of metals at various sampling sites of the abandoned mine. The values of the MPI are 1.186, 5.751, and 5.629 accordingly. In these three mines, the metal contamination is very high at B mine shown in Fig. 5. Therefore, the indication is that the strong metal enrichment nears the mine shaft. The concentration of Ni, Hg, and Zn are significant in sediment with extremely high contamination.

3.5. Primary integrated pollution index IP_{index}

The primary integrated pollution index IP_{index} [12] values varied from 0.35 to 1.00 for water and 0.028 to 1.00 for

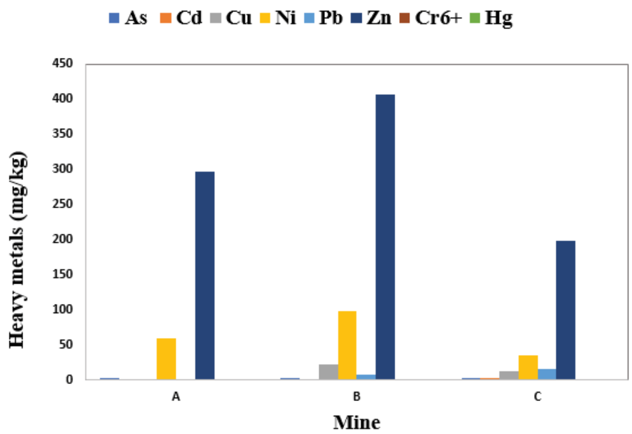

Fig. 4. Heavy metal concentration in sediment.

soil. The survey index according to the mine survey is 0.2, 0.4 and 0.6. The IPI range is 0.25 to 0.78. The Highest point of IP_{index} is 0.78 where the soil pollution is high. However, Fig. 6 shows the primary IPI can rank the mines depend on water, soil and survey results where sediment has also dominant pollutants from the abandoned mines.

3.6. Sediment pollution index SP_{index}

The pollution load index (PLI) [13,14] of heavy metals is calculated using heavy metal data and metal concentration for the world shale average as the background value [1,15–18]. The PLI values varied from 0.048 to 1.104 for sediment. Fig. 7 shows the variation of three sediment pollution indices metal concentration. The concentration of Zn, Ni and Hg are over the tolerable level. Specifically, the concentration of Hg in sediments is extremely high where the limit is (0.056 mg/kg). The ecological risk index RI [19] of heavy metals in sediment is high and mine site C has the highest contamination of all sites. The mean values of geoaccumulation index I_{geo} [18,20,21] for sediments have moderate contamination. High geoaccumulation contamination is found in the sediment of mine B site. Therefore, according to

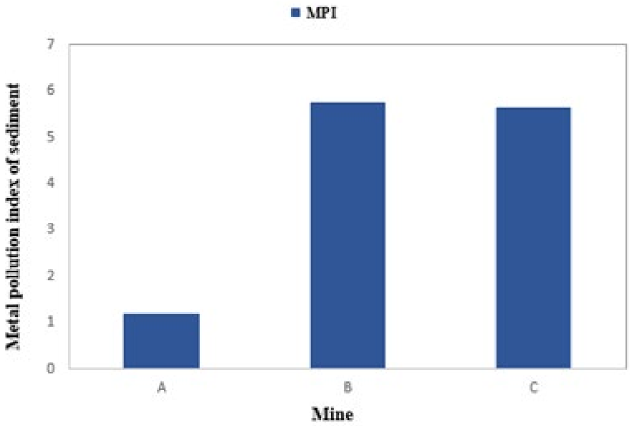

Fig. 5. Metal pollution index of sediment.

the sediment pollution index mine B has the heaviest metal contamination.

3.7. IPI ranking through pollution indices

Three mine areas are ranked according to the contamination of heavy metals. According to the graph 8, all indices are comparably significant for the utmost contaminated sites. The IPI determines the most pollutant sites of mine areas, which is an indicator of prioritizing surveys for future research. The pollution index is used to compare the total content of metals at different sampling points. Therefore, the mines are prioritized from higher to lower values of IPI as C > B > A. The values of IPI are 2.204, 2.082 and 1.616, accordingly. However, protective measures should be taken for the utmost contaminated mine areas.

4. Conclusions

In this study, a new IPI is proposed based on the pollutant levels of heavy metals in the abandoned mine sites soil, water, and sediments. The IPI provides the measurement of most polluted mine sites according to their pollutant levels which becomes more convenient to conduct prioritize surveys and evaluation method for abandoned metal mine contamination. According to the study results, Mine C is the most polluted mine. The primary pollution index of three mines are 0.418, 0.521 and 0.735, Sediment pollution index are 0.690, 0.728 and 0.685. Finally, the IPI of three mines are 0.509, 0.833 and 0.784 respectively. The study results show the accumulation of three indices of the major pollutant mine upon IPI ranking. However, water, soil, and sediment quality guidelines are compared and the concentrations of Cr, Cu, Cd, Zn, Ni in soil and water are below the countermeasure levels whereas sediments are comparatively polluted by Zn. In sediments, the significant amount of heavy metals are Zn (35.31–491.87 mg/kg), Ni (13.44–132.25 mg/kg), As (0.15–8 mg/kg), Cd (0.05–3.51 mg/kg), Cu (0.001–39.85 mg/kg), Pb (0.03–32.79 mg/kg), Hg (0.19–1.68 mg/kg) and Cr^{6+} (0.01–0.78 mg/kg). The sediment contamination sites are the most polluted abandoned mine sites according to the survey. Sediment quality is a good indicator

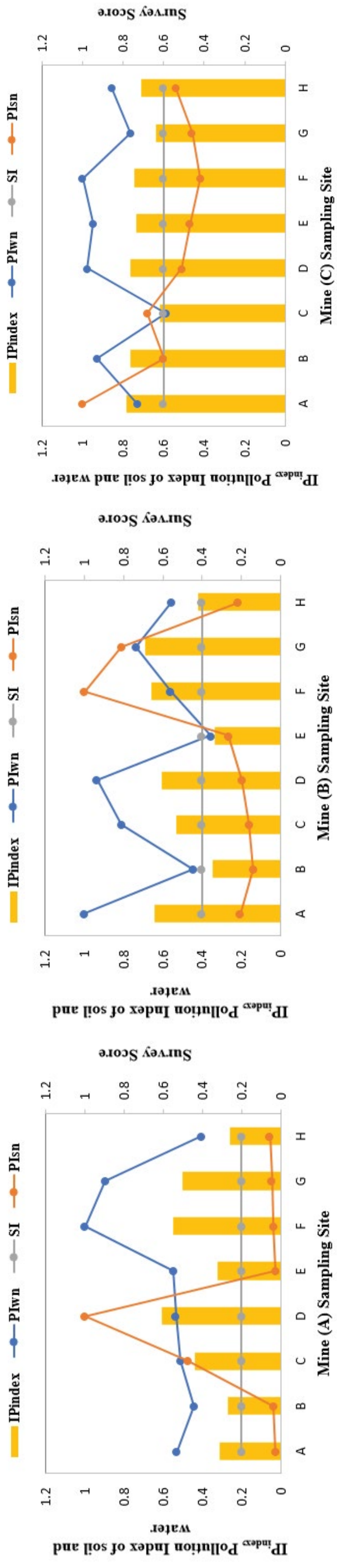

Fig. 6. Primary integrated pollution index if soil and water.

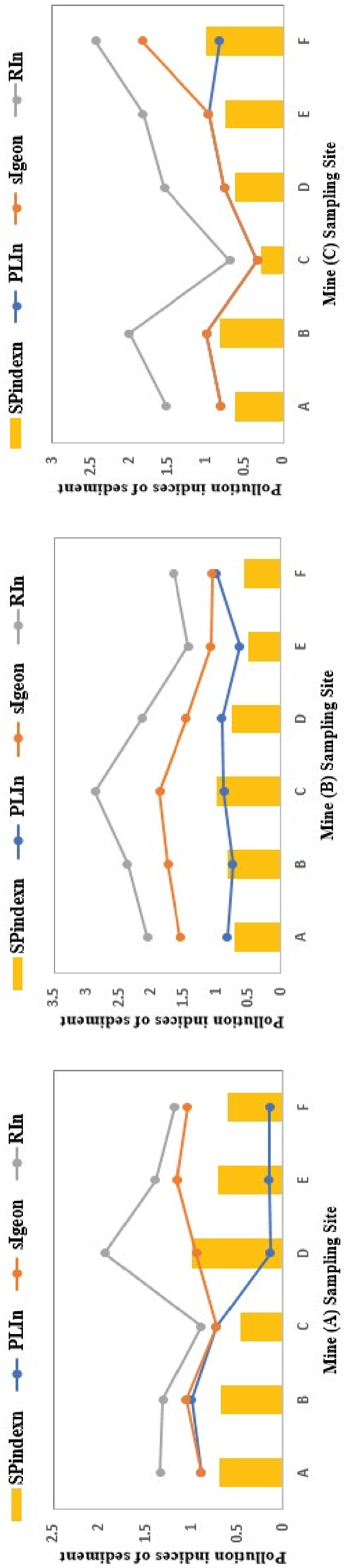

Fig. 7. Sediment pollution index.

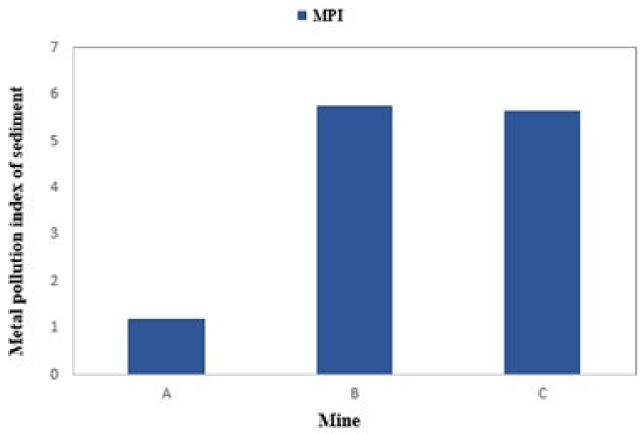

Fig. 8. IPI ranking through pollution indices.

of pollution in the water, where heavy metals and other organic pollutants tend to concentrate. Therefore, the prioritization is given to the most contaminated sediment drainage basins according to the contamination level. Future prevention and protective measures should be possible for the highly contaminated mine areas, which are prioritized by IPI.

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