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"Contamination Assessment of Abandoned Mines by Integrated Pollution Index in the Han River Watershed"

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Abstract: Heavy metal contamination from abandoned mine areas is a major threat for the environment. The study objective was to categorize the most polluted mine areas among 44 mine sites at the four cities of *Chungcheongbuk-do* province in South Korea. Both water and soil samples were collected from the mine area. The pH of the water and soil ranged from 3.6 to 8.5 and from 4.1 to 9.1 respectively. A significant amount of arsenic (As), cadmium (Cd), copper (Cu), nickel (Ni), lead (Pb), zinc (Zn) and mercury (Hg) occurred in soil samples collected from the mine areas (0.2 to 42.4, 0.7 to 8.6, 10.7 to 430.2, 5.8 to 49.8, 2.1 to 122.8, 37.4 to 359.4 and 0.2 to 11.4 mg kg^{-1} respectively). The surrounding available waters also carried high contents of Cd, Cu, Pb and Zn, generally exceeding the fresh water acute and chronic criteria. Each mine site was ranked according to the Integrated Pollution Index (IPI). The normalized pollution index (PI^n) for water and soil, and the Survey Index (SI) were used to determine IPI. The highest polluted mine site exhibited an IPI value of 0.6394. IPI was introduced to prioritize the research sites for further precise investigation.

Key Words: Mine pollution, Integrated pollution index (IPI), Normalized pollution index (PI^n), Survey index (SI), Fresh water acute and Chronic criteria.

1. INTRODUCTION

Mine waste material containing sulphide waste is a major threat to the environment. Small quantities of metals occurring in the mined ores are not totally recovered by mill or processing operations, to be left in the tailing deposits. Such mining waste, containing significant metal concentrations, is a source of chemical pollution that may persist for a long time [1]. Mining and milling operations, together with grinding, concentrating ores and disposal of tailings, provide obvious sources of contamination in the surface environment, along with mine and mill wastewater [2]. Many studies have been conducted on heavy metal contamination in soils, plants, waters and sediments from metalliferous mines throughout the world [3-6]. The extent and degree of heavy metal contamination around the mines vary depending upon geochemical characteristics and mineralization of tailings. For example, tailings containing large quantities of sulfide minerals could influence nearby agricultural lands and streams.

In Korea, various mines were distributed all over the country and were actively mined until the early 1980s. However, in the last two decades, most of these mines were closed due to economic reasons. After mine closure, mine waste materials, including tailings, were left without full environmental treatment. Thus, soils, plants, waters and sediments in the vicinity of the mines have been contaminated by potentially toxic elements from tailings by clastic movement through wind and water.

The objective of this study was to assess the soil and water contamination in the vicinity of 44 abandoned mines distributed in the South *Han*-river watershed areas, by using the Integrated Pollution Index (IPI). The study purpose was to detect the most highly contaminated mine areas and thereby assist efforts to protect the river watershed.

2. MATERIALS AND METHODS

To investigate the impact caused by the abandoned mine sites, soil (top and/or, sub, 396 samples) and water (stream and/or, ground, 128 samples) samples were collected from the target mine sites. From each mine site 9 samples were collected from different locations around the mine, like the mine's front (0m) and control area, and at 200m, 400m, 600m, 800m and 1600m from the front. Sub soils were col-

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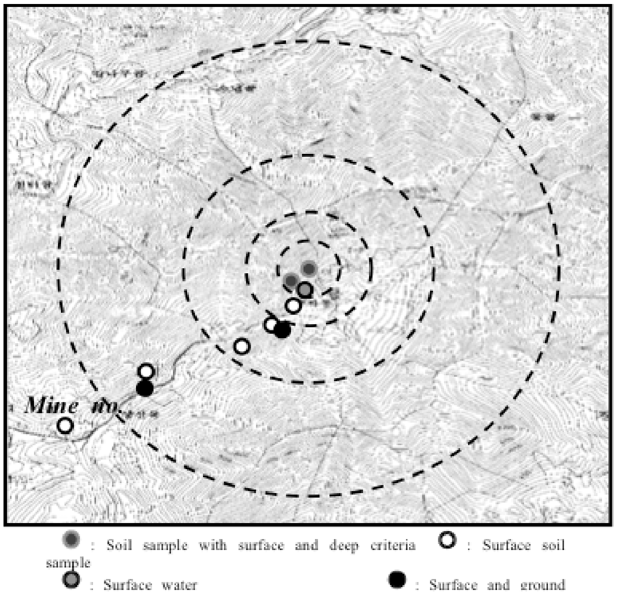

Fig. (1). Water and soil sampling location around mine no. 24 (no scale).

lected only from 0m and 200m, while top soils were collected from all the distances. Each soil sample comprised a composite of 4 sub samples taken from an area of 1 sq-m. Soil samples were air dried in room temperature for 2-3 weeks until a constant weight was attained. Samples were disaggregated and passed through 2.0mm and 250µm sieves. Following the Korean standard method [7], the sieved samples (< 2.0mm) were mixed with a 1:5 ratio of soil to 0.1N HCl solution in a falcon tube (volume of 50ml). For the final mixing, the solutions were shaken with the falcon tubes placed horizontally in a shaking machine at 185 rpm for 1hr and then filtered through a 0.45µm Millipore membrane filter using a hand pump.

Aqua regia solution can extract between 70 to 90% of the total contents of trace elements [8]. A fine grained (< 250µm) fraction of soil (3g) was added to 28ml of aqua regia (1:3 of HNO_3:HCl), heated to 70°C for 1hr [8], filtered and diluted as specified. The filtered aqueous samples were used to detect heavy metals [arsenic (As), cadmium (Cd), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn)] using Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES). A mercury analyzer was used to detect mercury (Hg) and the samples were sent to the Chungju Water Management Company for the detection of cyanide (CN^-) and hexavalent chromium (Cr^{6+}). The pH of the soil was determined by the 1:5 ratio of soil to de-ionized water.

In addition, 128 stream water samples were collected from inside of the mines / mine front / 100m / 200m / 400m / 600m / 800m / 1600m. Three water samples were collected from different locations at most of the mine areas. No water was sampled at two sites due to the absence of any surface water within 2km of the mine. In Fig. (**1**), the criteria of sampling are shown.

2.1. Method of IPI Estimation

IPI was calculated from a weighted ratio of site survey, soil pollution index (PIs) and water pollution index (PIw). According to the importance of the water, soil and survey, 50%, 30% and 20% values were used, respectively. The IPI ranged from 0 to 1.

$$IPI = \alpha PIw^n + \beta PIs^n + \gamma SI \qquad \text{(i)}$$

where, α, β and γ are constants with following values.

α = 0.5 for the presence of water and 0 for the absence of water,

β = 0.3 for the presence of water and 0.8 for the absence of water

γ = 0.2

PIw^n = Normalized Pollution Index of Water ($0 \le PIw^n \le 1$)

PIs^n = Normalized Pollution Index of Soil ($0 \le PIs^n \le 1$)

SI = Survey Index

2.2. Method of PI^n Estimation

PI^n is the amount of the pollution normalized to the highest Pollution Index (PI). This relation is common for both water and soil samples. Simply,

$$PI^n = \frac{\text{Each mine site's}}{\text{Highest PI}}$$

This PI was used in this study to evaluate the degree of trace metal contamination [9-12]. The tolerable level is the element concentration in the soil that supports crop production considered safe for human consumption [13, 14]. The tolerable levels for soil and water are shown in Table **1** and Table **2** respectively.

$$PIs = \frac{\sum \frac{\text{Heavy metal concentration in soil}}{\text{Tolerable Level}}}{\text{Number of heavy}}$$

Table 1. Tolerable Level for Soil*

Heavy Metals	Tolerable Level (mg kg^{-1})
Cadmium (Cd)	1.5
Lead (Pb)	100
Nickel (Ni)	40
Zinc (Zn)	300
Copper (Cu)	50
Arsenic (As)	6
Mercury (Hg)	4
Hexavalent Chromium (Cr^{6+})	4
Cyanide (CN^-)	2

* NIER and HERC, 2007.

Similarly, for the water samples, PIw was measured to evaluate the contamination of water as specified in the Korean standard.

$$PIw = \frac{\sum \frac{\text{Heavy metal concentration in water}}{\text{Tolerable Level}}}{\text{Number of heavy}}$$

Table 2. Tolerable Level for Water*

Heavy Metals	Tolerable Level (mg L^{-1})
Cadmium (Cd)	0.005
Lead (Pb)	0.05
Arsenic (As)	0.05
Mercury (Hg)	0 (< 0.001)
Hexavalent Chromium (Cr^{6+})	0.05
Cyanide (CN^{-})	0 (< 0.01)

*NIER and HERC, 2007.

2.3. Method of SI Estimation

SI indicates the evaluation of each mine site according to the following listed survey pattern. Ten evaluation items, as shown in Table **3**, were selected for the mine area survey. The sulphuration and chlorosis indicate the change of the color of the soil, stone and plants within the mine area, compared to the nearby area. The value of SI ranges from 0 to 1.

$$SI = \frac{\sum \ Score \ of \ evaluated}{10}$$

Table 3. Survey Criteria with Score*

Evaluation Item	Criteria	Score
1. Overflow of water from mine	Yes / No	1 / 0
2. pH of mine inside water	<5.0 / >5.0	1 / 0
3. pH of soil	<5.0 / >5.0	1 / 0
4. Existence of debris	Yes / No	1 / 0
5. Debris position (Slope criteria)	Slope / Flat	1 / 0
6. Peoples affected by mine	Yes / No	1 / 0
7. Damage prevention facility	Yes / No	0 / 1
8. Sulphuration and Chlorosis phenomena	Have / Haven't	1 / 0
9. Plants around mine	Many / Few	0 / 1
10. Inflow of stream water to the mine	Yes / No	1 / 0

*NIER and HERC, 2007.

3. RESULT AND DISCUSSION

3.1. Pollution Index of Soil (PIs)

The plots of the mean and median values of trace element concentration from the 0.1N HCl-treated soil samples are shown in Fig. (**2**). The logarithmic trend line of mean values remained mostly above the trend line for the median values. The sites with a median concentration above the mean value

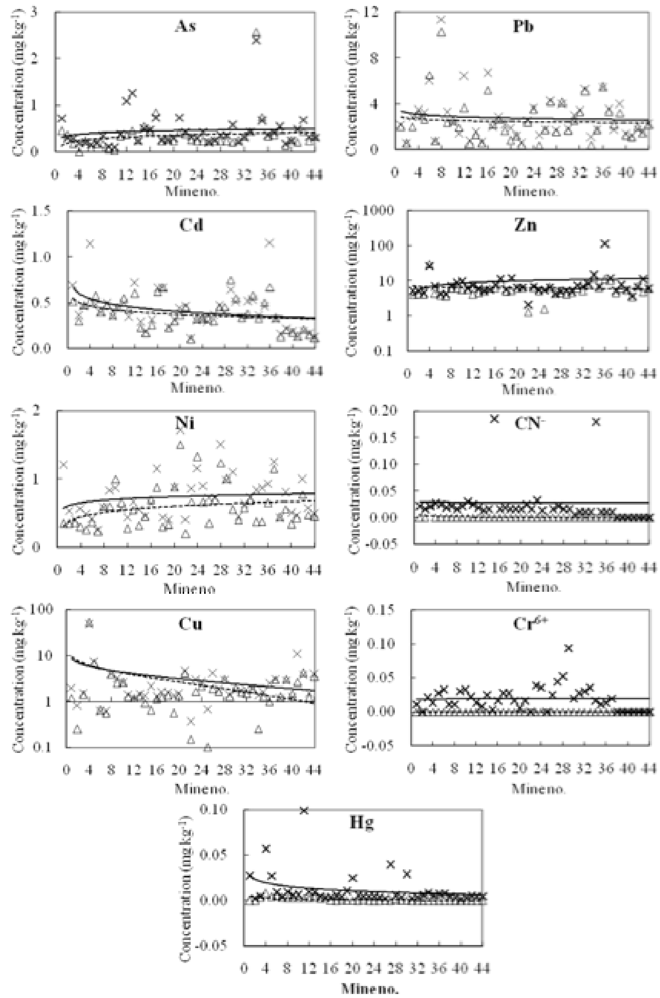

Fig. (2). Plots of the mean (×) and median (Δ) values of the soil contamination of 0.1N HCl treated soil samples with logarithmic line of mean (**▬**) and median (---).

indicated that among the sampling points, the metal concentration at one or two points was very high with respect to the other points. Individually, the PIs varied from 0.0174 to 0.5556. After that, the mean PIs value of each mine site was determined. The maximum and minimum mean PIs values were 0.2127 and 0.0174 in site no. 4 and site no. 22 respectively.

Practically, the PI of aqua regia-treated soils was greater than that of 0.1N HCl-treated soils. Among all sites, the mean PIs varied from 0.2117 to 2.0682. Moreover, PIs at 8 sites was higher than 1, which indicated highly contaminated soil according to PIs. Fig. (**3**) shows the maximum and minimum trace element concentrations of all sites. In the control area of most of the mines, the metal concentrations of Cd, Cu, Pb and Zn were higher than the world average of 0.35, 30, 35 and 90 mg kg^{-1} respectively [15].

3.2. Pollution Index of Water (PIw)

Water has vast importance in IPI evaluation. The PIw among all sites varied from 0, in mine no. 7 and no. 38, to 0.4 in mine no. 42**.** The concentrations of Cd, As, Hg, CN^{-} and Cr^{6+} in most of the water samples were less than the given tolerable level. PIw was below 0.1 at 16 (36.4%) of the

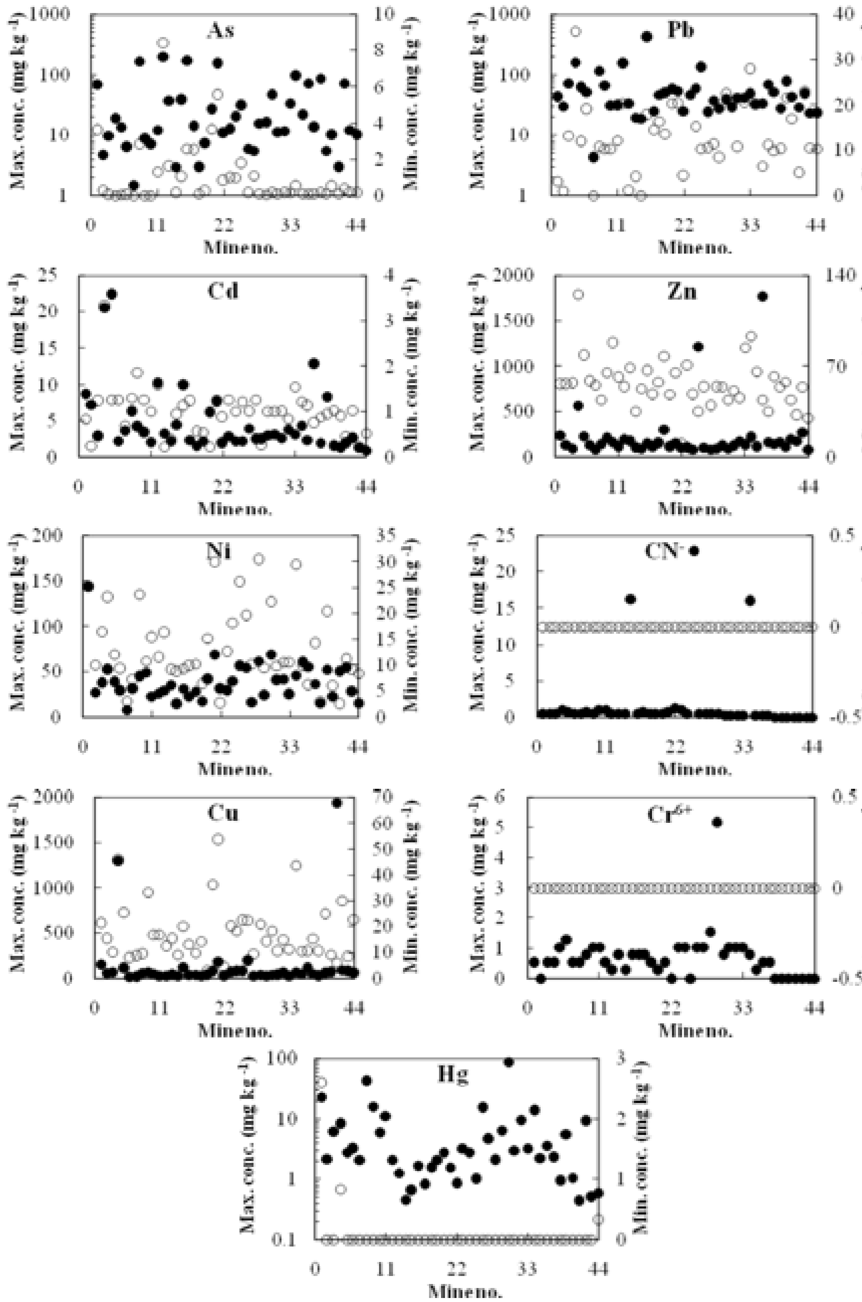

Fig. (3). Scattered plots of the aqua regia treated samples with the maximum (●) and minimum (o) concentrations of experimented trace metals for 44 mine sites.

sites, between 0.1 to 0.3 at 27 (61.4%), and greater than 0.4 at 1 (2.2%). The concentration of Hg, CN^- and Cr^{6+} remained below detection at all sites. Fig. (**4**) shows the bar charts of the heavy metal concentrations of the water samples with arithmetic mean and standard deviation, which were used to understand the water contamination range of the mine sites.

3.3. Fresh Water Acute and Chronic Criteria

The water around most of the mine areas exceeded the acute and chronic effect levels proposed by the US Environmental Protection Agency (USEPA) in 2007 [16]. Fig. (**5**) shows the heavy metal concentrations at the top five ranked sites, which exceeded the fresh water aquatic life acute and chronic criteria. The tolerable acute and chronic levels for fresh water are 340 and 150 µg/l for As, 2 and 0.25 µg/l for Cd, 13 and 9 µg/l for Cu, 65 and 2.5 µg/l for Pb and 120 µg/l for both for Zn. Among all the studied areas, 95.5% of the mine areas' water exceeded the acute and chronic limit of Cd, while 91% of the sites exceeded the chronic limit of Pb. However, the acute limit for Pb was exceeded in only two mine areas. The acute concentration for Zn was surpassed in 6.82% of the mine areas.

3.4. Survey Index

The survey index was measured at each site and the highest score of 6 was obtained by mine no. 4, indicating the highest risk. Half of the 44 sites had a survey score above 1 and the other 50% had a survey index of 0.1, which indicated sites.

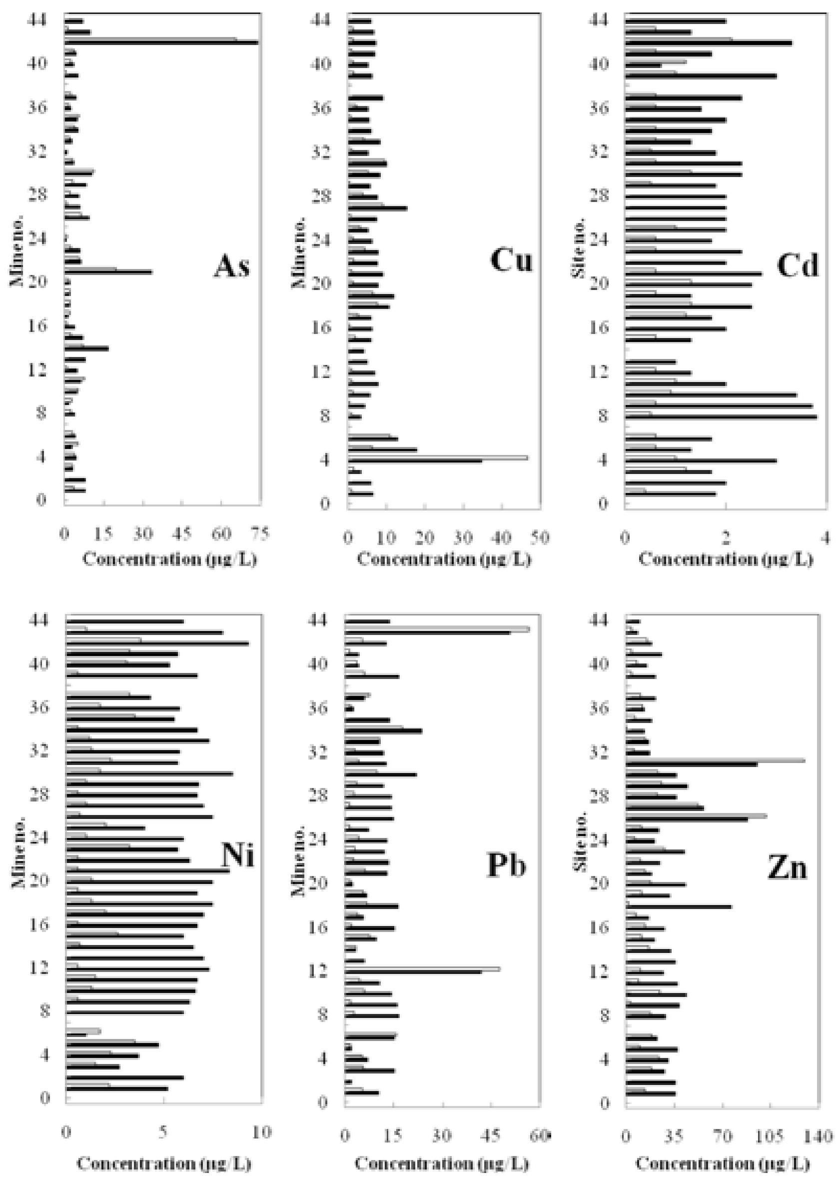

Fig. (4). Bar charts of heavy metal concentration with Arithmetic Mean (■) and Standard Deviation (□) of the mine water samples.

that the surrounding areas were physically and visually less affected by the mine. Table **4** shows the survey index values.

3.5. Integrated Pollution index (IPI)

The values of PIs^n, PIw^n, SI and IPI for the top five ranked sites are shown in Table **4**. The values of $\alpha = 0$ and $\beta = 0.8$ were only used in the two mine areas that suffered an absence of water. The PIs values from the aqua regia-treated soils were 5- to 25-fold greater than that of 0.1N HCl-treated soils. PIs > 1 indicated the degree of importance. All 0.1N HCl-treated PIs were below 1, indicating low pollution criteria. However, this problem was successfully solved by IPI. The IPI ranking for both 0.1N HCl- and aqua regia-treated samples showed similar values. The top five ranked sites were nearly the same for both treated systems. IPI normalized the PIs values by comparing them with the maximum value. Moreover, SI showed the importance of justifying the pollution index. For the 0.1N HCl-treated samples, only 8 mine areas had an IPI value below 0.2. However, two mines had an IPI value over 0.5. Similarly, for the aqua regia-treated samples, the IPI values ranged from 0.1185 to 0.6394. In common, the top five ranked mine areas were significantly affected by trace metals in the soils and water. Importantly, various contamination index such as index for chemistry of the sediment quality triad component (I), marine sediment pollution index (MSPI) [17], enrichment index (EI) [18], combined pollution index (CPI) [19]; ecological risk index such as the mean sediment quality guideline quotient (SQG-Q) [20], and mean sediment quality guideline quotient as an indicator of contamination and acute toxicity (SQG-QI) [21-22], all have an averaging nature capable of aggregating all contaminants into one value. Similarly, IPI has the same property to aggregate all contaminants into one value. IPI is therefore a superior method to prioritize the

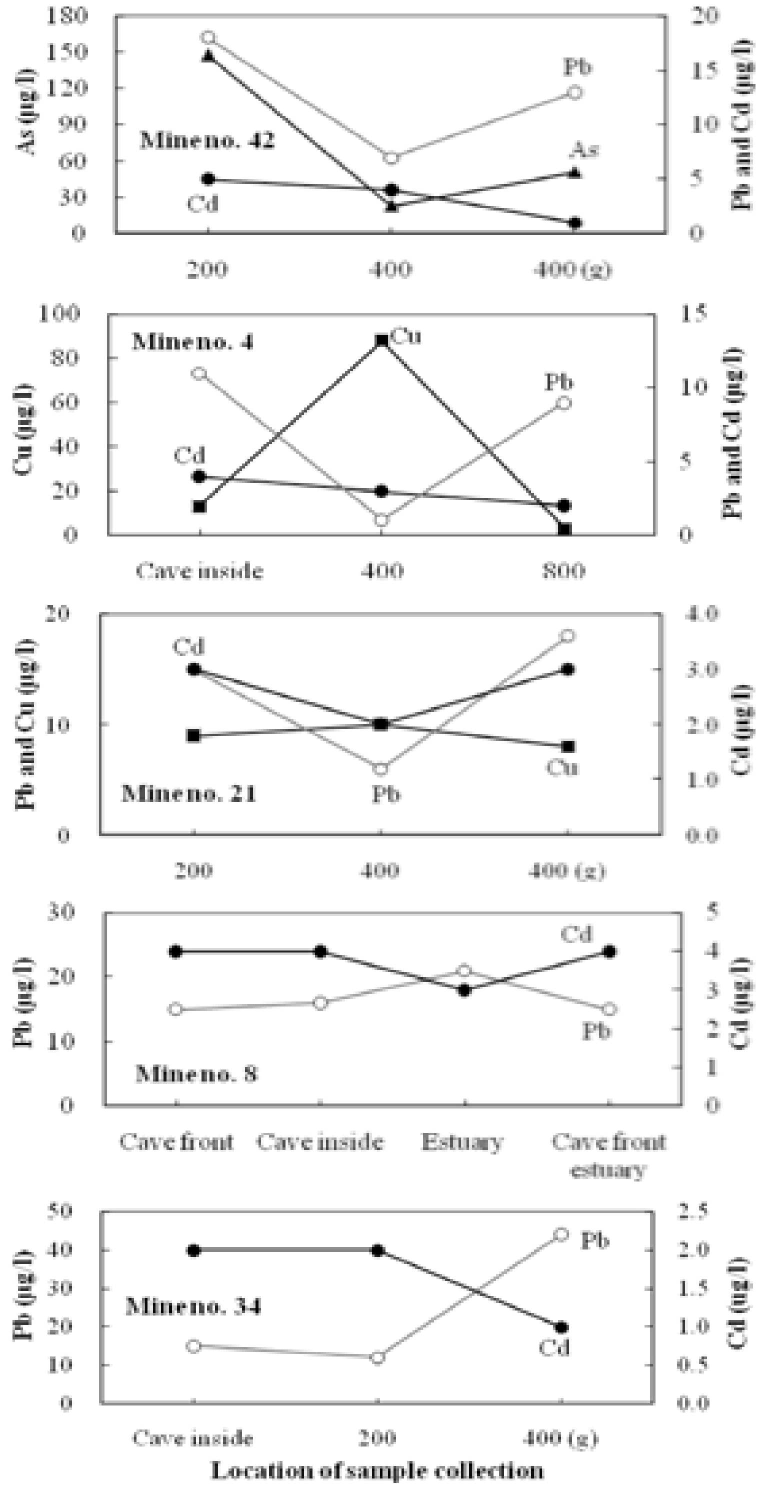

Fig. (5). Plots of the exceeded limits of fresh water criteria including ground water (g) at various distances (mostly in meter) for the top 5 ranked mine sites.

comparison of site contamination. IPI is only applicable on a group of sites to determine the contamination from higher to lower values among those sites.

4. CONCLUSION

Both soil and water in all of the mine areas were contaminated by past mining activity. The mean PIs values of the 44 mines were determined and site no.4 and no. 22 had maximum and minimum values of 0.2127 and 0.0174, respectively, according to the Korean standard method. The concentrations of Cd, As, Hg, CN^- and Cr^{6+} were lower than the tolerable levels for most of the water samples. The concentrations of Hg, CN^- and Cr^{6+} were below detectable limits in all the sites' water samples. PIw was below 0.1 at 16 (36.4%) of the sites, between 0.1 to 0.3 at 27 (61.4%), and greater than 0.4 at 1 (2.2%). Among the 44 mines, the top

Table 4. Values of 5 Top Most IPI with Ranking for Different Extraction Methods

Mine no.	0.1N HCl Treated Soil		Aquaregia Treated Soil		Water		0.1N HCl Treated Soil		Aquaregia Treated Soil		Survey
	IPI	Rank	IPI	Rank	PIw	PIw^n	PIs	PIs^n	PIs	PIs^n	SI
42	0.5705	2	0.6394	1	0.4000	1.0000	0.0358	0.1683	0.8231	0.3980	0.1000
4	0.5936	1	0.5936	2	0.1389	0.3472	0.2127	1.0000	2.0682	1.0000	0.6000
21	0.4722	3	0.5698	3	0.2433	0.6083	0.0624	0.2933	1.2796	0.6187	0.4000
8	0.4020	4	0.4978	4	0.1933	0.4833	0.0570	0.2678	1.2146	0.5873	0.4000
34	0.3971	5	0.4432	5	0.1522	0.3806	0.0899	0.4228	1.1922	0.5764	0.4000
Maximum	**0.5936**	---	**0.6394**		**0.4000**	---	**0.2127**	---	**2.0682**	---	**0.6000**

five ranked mine areas were significantly contaminated with heavy metals. The maximum and minimum IPI values were 0.6394 and 0.1185, respectively. According to the SI survey, none of the mines had any damage prevention facility, indicating a high risk of contamination. A comprehensive program should be developed to promote measures that best fit the rehabilitation of the environmentally affected sites. Site selection preference should be followed by the IPI ranking.

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APPENDIX

All relevant data tables are available from "Environmental Water Quality Lab., Department of Environmental Engineering, Chungju National University, *Daehak-ro* 72, *Chungju-si*, *Chungcheongbuk-do*, 380-702, Korea."

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