Depth profiles and the behavior of heavy metal atoms contained in the soil around a Il-Kwang disused mine in Kyung Nam

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경남 일광 폐광 부근 토양에 함유된 중금속의 깊이별 분포와 거동

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Abstract : We investigated the content of heavy metals contained in the soil at an Il-Kwang disused mine in Kyung Nam. Three sampling points were selected, each point was digged to 210 or 240cm, sampled each 30cm depth. After air drying, each sample was digested in aqua regia and then analyzed with an Inductively Coupled Plasma Atomic Emission Spectrometer. We determined the content of Zn, Pb, Cr, Cd, Cu, Mn, and Fe, maximum content of Pb, Cd, and Zn was observed to $(4.6\pm0.1)\times10^3$, $9.4(\pm3.6)$, and $2.7\pm0.1)\times10^2 \mu g/g$ respectively. Mean pH values of soil sampled at No. 1, 2, and 3 regions were 3.2, 2.6, and 2.8, respectively. These values are remarkably lower than pH of the conventional standard soil which usually shows pH level around 4.9. At each sampling point, maximum content of heavy metals was observed from 30cm to 60cm depth. The depth profiles of Zn, Cd, Pb, and Cr showed very similar tendencies to each other, but those of Fe, Cu, and Mn showed different tendencies to former ones.

요약 : 본 실험은 경남 일광 지역의 한 폐광의 토양에 함유된 중금속의 함량을 연구한 것이다. 세 지점을 선택하여, 각 지점마다 30cm씩 210 또는 240cm까지 굴착하였다. 각 시료는 풍건한 후 왕수분 해법으로 추출한 다음, 유도결합쌍 플라즈마 원자방출분광법(ICP-AES)으로 정량분석하였다. Zn, Pb, Cr, Cd, Cu, Mn 및 Fe를 대상으로 분석하였고, Pb, Cd 및 Zn의 함유량의 최대값은 $(4.6\pm0.1)\times10^3$, $9.4(\pm3.6)$ 및 $(2.7\pm0.1)\times10^2 \mu g/g$으로 각각 나타났다. 1번 지역의 평균 pH값은 3.2, 2번 지역은 2.6, 그리고 3번 지역은 2.8로 나타났다. 그 값들은 4.9로 나타난 표준 시료 토양의 pH값에 비해 현저히 낮다. 각 시료 채취 지점에서, 중금속의 최대값은 30cm부터 60cm 깊이 사이에서 관찰되었다. Zn, Cd, Pb 및 Cu의 깊이에 따른 중금속 함량들은 분포된 경향이 비슷하게 나타나지만, Fe, Cu 및 Mn 은 앞의 중금속들과는 분포된 경향이 다르게 나타났다.

Key words : depth profiles, heavy metal atoms, leaching rate, soil

1. Introduction

Recently, enviromental problem has become the most popular interest of all nations on earth and even our survival problem. The soil can act as vast reserviors for the retention of heavy metals. The

several factors, such as pH and composition of the soil, can affect the amount of metal atoms contained in. The heavy metals which exist as the soluble chemicals in soil, should give a serious effect on human body because of accumulation through food chain. The relative toxicity of heavy metals can be classified as follows : Cd > (Cu, Pb) > (Mn, Zn) > (Fe, Cr).[1] After accumulation of heavy metals in soil, they were gathered and moved by the capillary phenomenon to subterranean water. So the behavior of heavy metals in soil must be discussed very carefully. We have studied the depth profiles of heavy metals contained in soil around a disued mine. The purpose of this study is to investigate the content of heavy metals along the depth, the effect of pH or moisture of soil on the content of heavy metals, and the relationship between contents of heavy metals.[2]

2. Sampling

Sampling has obtained around a disused mine at Il-Kwang Myun in Kyung-Nam, which is shown in *Fig*. 1. Three sampling points were selected along the watercourse. Each point was digged upto 210 or 240cm, and sampled at every 30cm depth. To investigate the content of heavy metals in the water-
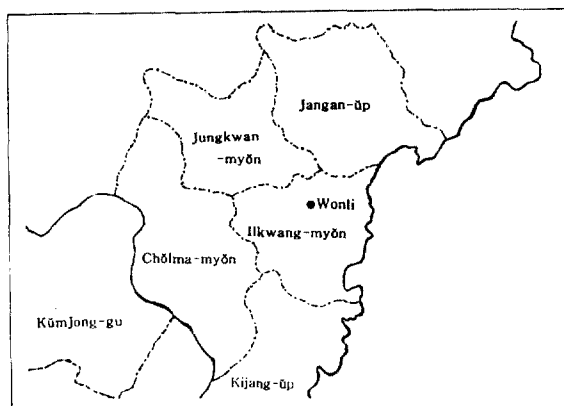

Fig. 1. Location of the sampling point.(Il-Kwang disused mine at Il-Kwang Myun in Kyung-Nam)

course, water was sampled at 2m away from one of the sampling points. The soil was collected by using a sampler(hand made in Germany). Each sample was put in a polyethylene bag to minimize the secondary contamintion by containers. In the laboratory, sample was kept at 4℃ in the refrigerator. Water sample was collected in a polyethylene bottle rinsed with acidic solution and stored in a refrigerator. The moisture content was determined as a weight difference between before and after drying the soil samples in the oven at 100±2℃ for 24 hours. After drying, the sample was passed through a 2mm-standard sieve to homogenize the particle size of the soil.[3,4]

3. Materials and methods

The pH values of soil was measured as follows : 5g of homogenized soil sample was immersed in 25mL distilled-deionized water in a 100mL conical flask. And then the sample solution was stirred for an hour and filtered. The pH of the filterate was determined by a pH meter(pH meter 50, Fisher Scientific Co).

Extraction of heavy metals in the soil sample was done as follows : 10g of soil sample was digested with 50mL aqua-regia(1:3 mixture of concentrated HNO_3 and HCl) in a shaking bath at 30℃ for two hours and then filtered into a 100mL volumetric flask and filled up with distilled-deionized water. The filtered solution was analyzed by an Inductively Conpled Plasma Atomic Emission Spectrometer(ICP-AES, Spectra 1200-A, Seiko Co.) for heavy metals(Cr, Cd, Pb, Fe, Mn, Cu and Zn).

Extraction of heavy metals in the water sample was performed as follows : 5mL of HNO_3 was added to 100mL water sample in an evaporating dish and was evaporated in water bath. After the volume of solution was reduced to 10mL, 5mL of HNO_3 and 10mL of H_2SO_4 was added. After solution was boiled until the fume of H_2SO_4 was observed, it

Table 1. Depth profiles of heavy metals(μg/g)

depth	Cr±STD	Zn±STD	Pb±STD	Cd±STD	Mn±STD	Fe(%)±STD	Cu±STD
No.1, 30cm	4.4±0.4	63±6	$(4.5±0.1)×10^2$	57±5	41±5	6.9±0.0	$(6.0±0.5)×10^2$
60	4.9±0.2	$(3.7±0.6)×10^2$	$(7.9±1.7)×10^2$	79±4	21±4	3.3±0.0	$(3.2±0.0)×10^3$
90	8.4±1.2	47±9	89±1	33±2	17±3	1.5±0.2	$(2.9±0.4)×10^2$
120	4.7±0.7	31±3	73±19	30±1	18±1	1.2±0.0	$(1.3±0.1)×10^2$
150	4.0±0.3	196±1	57±11	24±2	25±2	0.65±0.01	55±13
180	4.7±0.2	27±1	$(1.2±0.3)×10^2$	28±3	57±3	1.4±0.1	51±8
210	3.0±0.3	35±1	66±15	17±1	57±1	2.4±0.0	49±6
240	2.1±0.1	28±3	52±8	4.0±0.1	54±10	1.3±0.2	39±0
No.2, 30cm	6.1±0.0	61±1	$(3.3±0.9)×10^2$	100±0	20±3	6.8±0.1	$(8.3±0.5)×10^2$
60	3.5±0.5	$(1.4±0.1)×10^2$	$(8.2±3.9)×10^2$	160±0	18±2	5.7±0.0	$(1.4±0.0)×10^3$
90	2.4±0.2	54±1	$(2.3±0.6)×10^2$	97±2	23±4	4.9±0.4	$(3.2±0.2)×10^2$
120	2.0±0.3	37±5	27±3	73±6	15±3	3.3±0.1	$(2.4±0.4)×10^2$
150	2.3±0.3	23±1	28±1	0.83±0.07	13±2	0.83±0.06	$(2.6±0.2)×10^2$
180	3.8±0.7	37±23	$(2.0±3.1)×10^2$	6.2±5.3	19±1	1.3±0.6	$(4.2±3.9)×10^2$
210	2.2±0.2	19±0	10±1	1.0±0.0	21±1	1.1±0.0	$(1.2±0.0)×10^2$
No.3, 30cm	1.0±0.1	$(1.7±0.2)×10^2$	$(2.9±0.6)×10^2$	8.0±1.9	12±2	2.0±0.0	$(1.6±0.7)×10^3$
60	2.3±0.1	$(2.7±0.1)×10^2$	$(4.6±0.1)×10^2$	9.4±0.4	16±0	2.0±0.1	$(2.3±0.3)×10^3$
90	3.0±0.2	76±4	$(5.6±0.8)×10^2$	3.8±0.2	17±1	2.0±0.0	$(1.0±0.1)×10^3$
120	2.4±0.3	25±1	71±7	2.5±0.1	17±1	2.0±0.0	$(2.6±0.2)×10^2$
150	4.2±1.0	25±4	45±5	1.0±0.3	30±8	1.0±0.2	$(3.5±0.2)×10^2$
180	3.6±0.2	23±3	35±1	0.90±0.07	33±2	0.92±0.04	$(1.8±0.2)×10^2$
210	3.3±0.2	25±5	59±2	0.84±0.03	37±9	0.92±0.01	$(1.7±0.0)×10^2$

STD : standard deviation

was cooled to room temperature and filled up with distilled-deionized water in a 100mL volumetric flask. Heavy metals were analyzed by an ICP-AES. The content of heavy metals was determined according to the calibration curve procedure.

Acids for the extraction of the heavy metals were analytical grade(Junsei Co.). Working sloutions were made by diluting a 1000ppm standard solution. The distilled-deionized water was provided by the Millipore water system.

For the leaching experiment of the soil, we prepared three aliquots of 5g sample in 100mL of 0. 01N NaNO₃ into a 250mL flask.[36] One sample was kept at the original pH, and the others were kept at the original pH±1 respectively. The pH values of sample solutions were determined after shaking it for 2 hours and contents of heavy metals were measured by an ICP-AES. The most and least contaminated soil were selected as the samples for the leaching experiment.
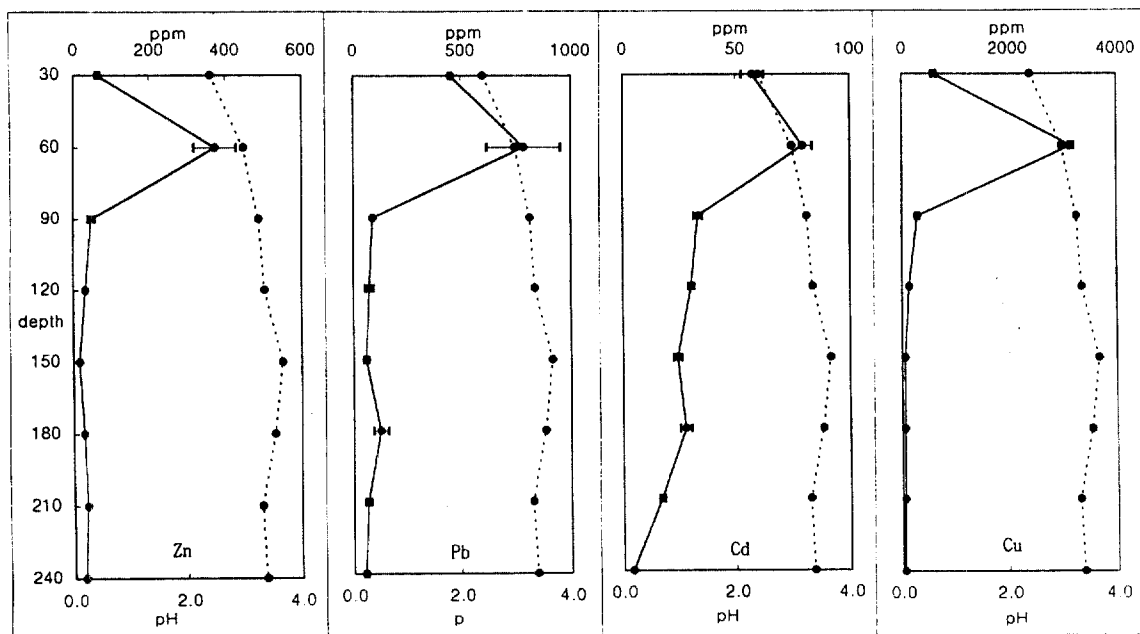
4. Results and discussion

4.1. Depth profiles of heavy metals

The content of heavy metals along the depth is shown in *Table* 1. It shows that most highly contaminated depth ranged from 30cm to 60cm. Concentrations of Zn, Cd, Pb and Cu in this depth at the sampling point No. 1 were $(3.7\pm0.6)\times10^{2}$, $(7.9\pm1.7)\times10^{1}$, 79 ± 4, and $(3.2\pm0.0)\times10^{3}\mu g/g$ respectively. The largest concentration of Cr, Mn, and Fe at the sampling point No. 1 were (8.4 ± 1.2), $(57\pm3)\mu g/g$, and $(6.9\pm0.0)\%$ respectively.

The contents of Zn, Cd, Pb, and Cu along the depth are shown in *Fig.* 2, which show similar distribution tendencies. It seems that the depth between 30cm and 60cm may be contaminated as the result of human activities.

Correlation coefficients between content of each heavy metal are shown in *Table* 2. Calculation of correlation coefficients about each heavy metal(Cr, Zn, Pb, Cd, Mn, Fe, and Cu) was done according to the following equation[8] :

Solid line : mean value. Error bar : standard deviation. Dotted line : pH
Fig. 2. Depth profiles of heavy metals

Table 2. Correlation coefficients between content of each heavy metal at the sampling point No. 1, No. 2, and No. 3

at the sampling point No. 1

	Cr	Zn	Pb	Cd	Mn	Fe	Cu
Cr	1.0	0.12	0.10	0.36	-0.64	-0.02	0.14
Zn		1.00	0.91	0.82	-0.34	0.29	1.00
Pb			1.00	0.94	-0.25	0.64	0.93
Cd				1.00	-0.46	0.62	0.86
Mn					1.00	0.11	-0.37
Fe						1.00	0.34
Cu							1.00

at the sampling point No. 2

	Cr	Zn	Pb	Cd	Mn	Fe	Cu
Cr	1.00	0.33	0.44	0.33	0.25	0.60	0.56
Zn		1.00	0.98	0.88	0.12	0.70	0.95
Pb			1.00	0.82	0.19	0.67	0.97
Cd				1.00	0.22	0.91	0.80
Mn					1.00	0.37	0.05
Fe						1.00	0.70
Cu							1.0E+0

at the sampling point No. 3

	Cr	Zn	Pb	Cd	Mn	Fe	Cu
Cr	1.00	-0.64	-0.65	-0.78	0.79	-0.76	-0.64
Zn		1.00	0.99	0.97	-0.64	0.61	0.99
Pb			1.00	0.96	-0.62	0.58	0.97
Cd				1.00	-0.80	0.75	0.98
Mn					1.00	-0.97	-0.71
Fe						1.00	0.68
Cu							1.00

$$\gamma = \frac{\sum_i (x_i - \overline{x})(y_i - \overline{y})}{\{\sum_i (x_i - \overline{x})^2 \cdot \sum_i (y_i - \overline{y})\}^{1/2}}$$

$$-1 \leq \gamma \leq 1$$

The content of Zn, Cd, Pb, and Cu show good correlation($\gamma > 0.80$) at the sampling point No. 1, No. 2 and No. 3.[9] Here, γ can get values in the range of $-1 \leq \gamma \leq 1$, and it must be greater than 0.76, in this case, to be considered as a sigificant correlation. Correlation between contents of Zn, Cd, Pb, and Cd are shown in *Fig. 3*.

Zn, Cd, Pb, and Cu are known as chalcophile elements. They have a strong affinity for sulfur and their adsorption mechanisms in soil are nearly the same.[10] High correlation between these elements indicates that they are likely to pass similar contamination pathways. In common, if pH decreases, the contents of heavy metals desorbed from the soil increases. Inclination of pH at the sampling point No. 1, No. 2, and No. 3 are shown in *Fig. 4*.

Mean pH values of soil from the No. 1, No. 2, and No. 3 points were 3.2, 2.6, and 2.8 respectively. These values are remarkably lower than that of the conventional standard soil which usually shows pH level around 4.9. The pH values along the depth show an increasing tendency. The content of most heavy metals along the depth show a decreasing tendency as shown in *Fig. 2*. The contents of heavy metals in soil depend on pH, constituents of soil, and the type of heavy metal. At high pH values, retention of heavy metals by precipitaion mechanism becomes predominant, whereas at low pH, retention by cation exchange mechanism becomes dominant. In water sample Cr, Pb, Cd, Ni, and Be were not detected. The contents of heavy metals in a small stream nearby the sampling points are shown in *Table 3*. Content of Zn, Mn, Cu, and Fe in the water sample were 8.6, 3.4, 110, and 6.8 $\mu g/g$ respectively, which are relatively high as compared with those in the soil. This is in accord with the result of leaching experiment.

4.2. Leaching experiment

Leaching experiment was conducted to examine the influence of contamination of soil on the water quality and to figure out leaching rate of heavy metals from the soil. Leaching rate may be an index of water pollution by means of heavy metals leached from the soil. Leaching rate of Zn, Mn, and Cu were 11, 38, and 6.2% at the sampling point No. 1(30~60cm region), and 55, 11, and 16% at the sampling point No. 2(210~240cm) respectively, which are shown in *Table* 4. But Pb, Cr, and Cd were hardly leached, and Fe showed very low leaching rate. The plot of leaching rate of Zn, Mn, and Cr is shown in *Fig.* 5.

High leaching rate of Zn, Mn, and Cu may indicate that large portions of these metals exist as water soluble types, i.e. as the exchangebles. Pb, Cr, Cd, and Fe contained in the soil do not have a serious effect on pollution of water because their leaching rates are very low. To investigate the type of chemical species containing heavy metals in soil, sample was prepared with the selective sequential extraction method and analyzed by an ICP-AES. The selective sequential extraction method is based on the fact that different forms of heavy metals retained in soil(e.g., as the exchangeables, hydroxides, carbonates, bound with organic matter, or residues) can be extracted selectively by using appropriate reagents. Neutral salts such as $MgCl_2$, $CaCl_2$, and $NaNO_3$ are commonly used as ion displacing extractants to promote the release of ions physically bound by electrostatic attraction to the negatively charged sites on the soil particle surfaces. The content of the exchangeable fractions of heavy metals in soil was compared with the result of aqua-regia extraction[11], which is shown in *Table* 5.

The exchangeable fractions of Zn, Mn, and Cu, were 10, 28, and 38%, whereas those of Pb, Cd, and Fe were 3.4, 1.3, and 1.5% respectively. The exchangeable fractions of Cr was below the detection
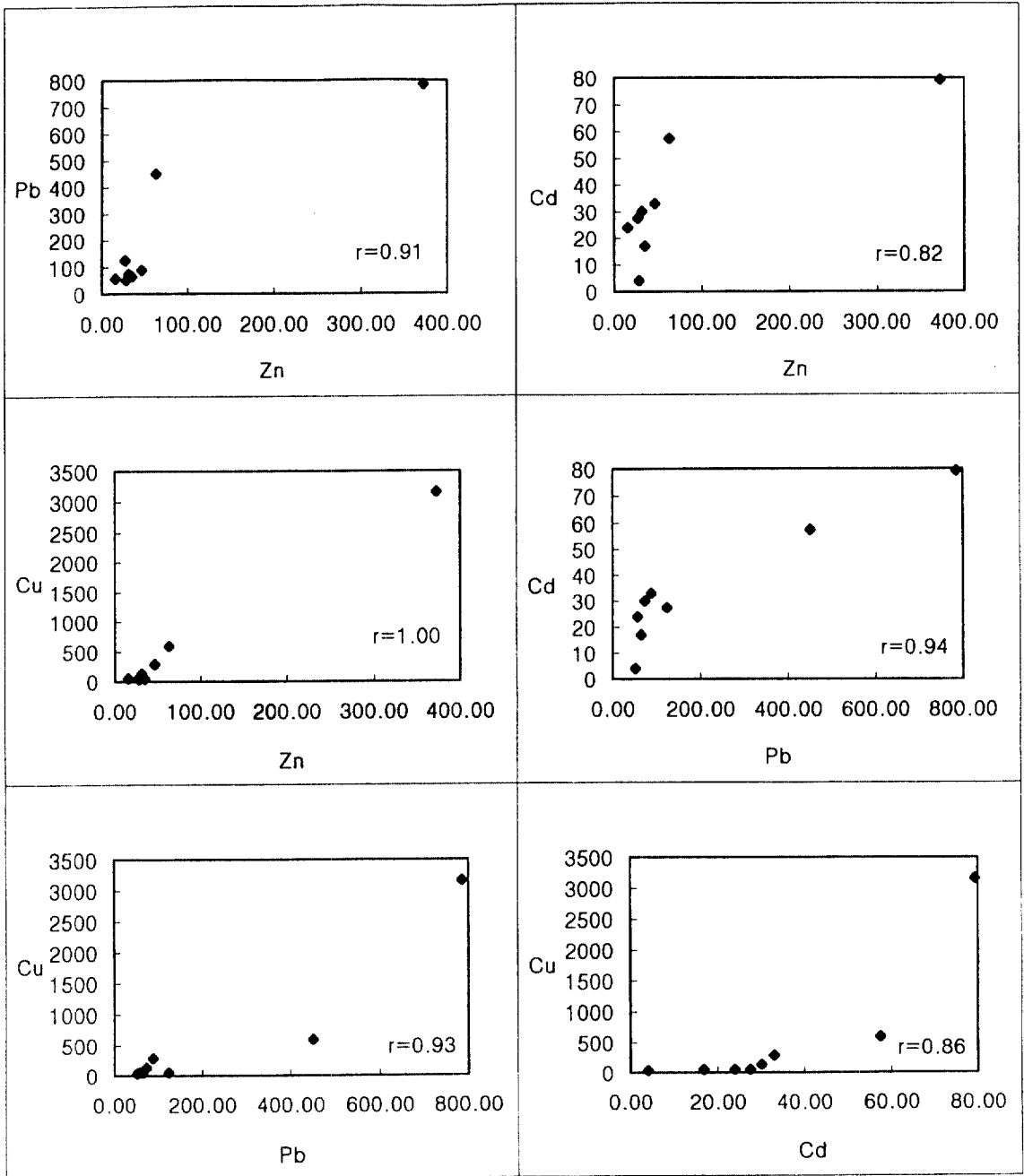
Fig. 3. Plot of correlation between content of heavy metal atoms.

limit. The exchangeable fractions of Zn, Mn, and Cu was higher than those of Pb, Cr, Fe, and Cd. Therefore, these results well accord with their high leaching rate.

5. Conclusion

The purpose of this study is to investigate content of heavy metals along the depth in soil of a

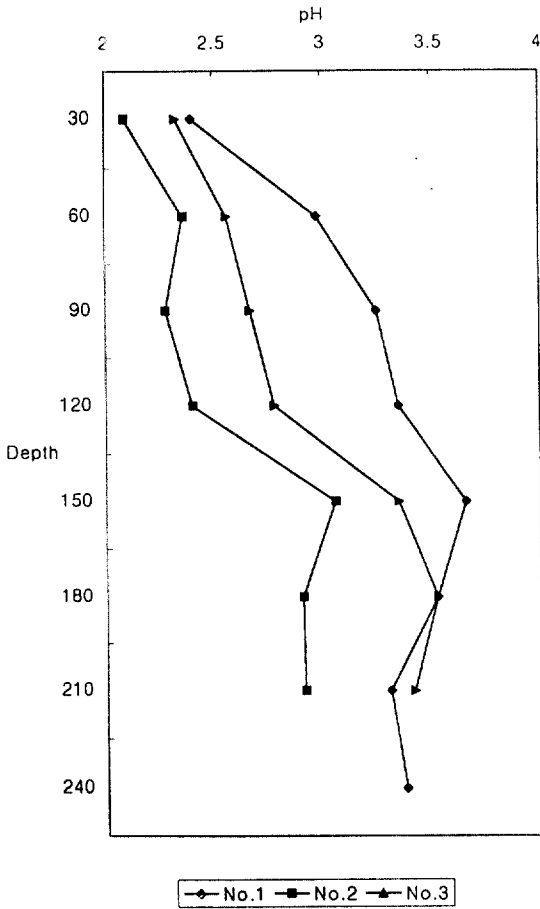Fig. 4. Plot of pH at the sampling point No. 1, No. 2, and No. 3

disused mine and to find correlation between the contents of heavy metals and behvior of soil according to pH. The contents of Cr, Cd, Pb, Zn, Mn, Fe, and Cu were determined. Results showed that Pb, Cu, Cd, and Zn were seriously contaminated. The relatively higher correlation between the contents of Pb, Cu, Cd, and Zn indicates that pollution pathways and geochemical behaviors of these metals are similar to each other. Mean pH values at the sampling point No. 1, No. 2, and No. 3 were 3.2, 2.6, and 2.8 respectively. At each sampling
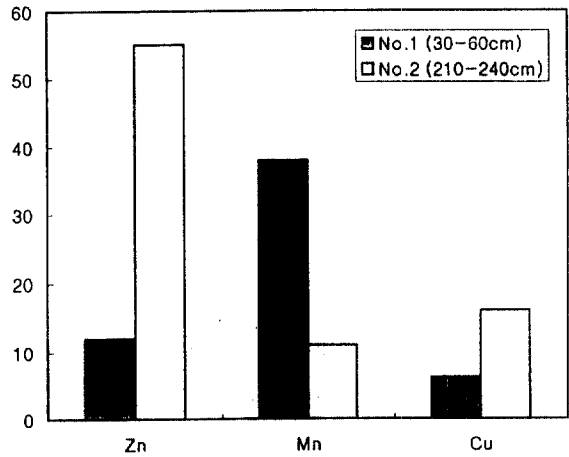

Fig. 5. Plot of leaching rate of Zn, Mn, and Cu from the soil sample.

Table 3. Content of heavy metal in a small stream nearby the sampling points

Metal	Cr	Zn	Pb	Cd	Mn	Fe	Cu
$\mu g/g$	ND	8.6	0.14	0.14	3.4	111.0	6.8

Table 4. The leaching rate of Zn, Mn, Cu, and Fe from the soil(%)

	Zn	Mn	Cu	Fe
No. 1(30~60cm)	12	38	6.2	0.4
No. 2(210~240cm)	55	11	16	0.1

point, the maximum content of heavy metal was observed from 30cm to 60cm depth. In leaching experiment, Pb, Cr, and Cd were not leached and Mn, Cu, and Zn were well leached. The high leaching

Table 5. The contents of exchangeable fraction of heavy metals in soil between 30cm and 60cm depth at the sampling point No. 1

	Cr	Zn	Pb	Cd	Mn	Fe	Cu
Content of exchangeable fraction of each heavy metal	ND	38	27	1.0	5.9	480	1200.0
Content of aqua regia extraction fraction of each heavy metal	4.9	370	790	79	21	33000	3200
percent of exchangeables($\%$)	–	10	3.4	1.3	28	1.5	38

rates of Mn, Cu, and Zn indicate that large portions of chemical species containing these metals in soil consist of water-soluble components.

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