

## Arsenic Movement in the Soils around a Closed Zinc Mine

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The sediments and soils around a mine are likely to be exposed to contamination of arsenic (As) through mining operations. In this study, the factors associated with As movement in soils around a closed zinc (Zn) mine were evaluated by the relationship of As distributions to physico-chemical properties of soils. A sequential extraction scheme, based on a soil P fractionation, was used to assess the As distributions in solid phases. A significant difference in As distributions was found between paddy and upland soils. While As contents of paddy soils increased with soil depth, those of upland soils decreased with soil depth. In upland soils, As showed additional significant relationships to oxides of Si, Al and Fe. Although a major fraction of As in soils was found to be in the NaOH extractable fraction, As exhibited highly significant relationship to the Zn species that apparently originated from the mine. Therefore, As mobility around Zn mine seems to be governed by mass flow of the particulates containing As-associated Zn in paddy soils, whereas retention reactions such as adsorption, complexation, and precipitation seem to predominate in upland soils.

**Key words:** Arsenic distribution, Sequential extraction, Physico-chemical properties, Mine tailing

### Introduction

Contamination of soils by toxic metal species has been a long-term concern. Among various metal contaminants, special concern has been given to As because of its high mobility in soils and toxicity to humans and animals. As species such as arsenite and arsenate in soils are readily propagated into aqueous systems and biosystems including human beings. Although there are many studies on As behavior in soils (McLaren et al., 1998; Cai et al., 2002), heterogeneity of soil properties makes it difficult to fully understand and precisely predict As mobility in soil environments.

Arsenic contamination of soils results primarily from anthropogenic sources like metallurgical processes, tanneries, and pesticide application. In particular, on-site metal extraction processes in mines have significantly

contributed to As contamination of soils and water environments because arsenic acid and sulfuric acid are usually employed as extraction agents. Distributions of As around mine areas have been extensively investigated (Mok and Wai, 1989; Donahue et al., 2000; Lee et al., 2003). Because many mines are located in mountainous regions, there is a high potential of As to contaminate soils and water. As is likely to be discharged from abandoned mines through the processes like accidental flooding and/or permeation. In fact, most mines in Korea are also located in mountainous areas, and several closed mines still have potential to pollute the nearby soils and streams.

Many studies have been undertaken to evaluate the relationship of As mobility to various soil components, because it can provide essential information in understanding As fate in the environment (McLaren et al., 1998; Lombi et al., 2000; Schlieker et al., 2001). As in soils can be subjected to various geo-chemical reactions such as adsorption/desorption, precipitation/dissolution, and oxidation/reduction (Jacobs et al., 1970; Elkhatib et al., 1984; McGeehan and Naylor, 1994; Roussel et al.,

2000; Lumsdon et al., 2001). Depending on various factors such as colloidal surface properties, pH, redox potential, soluble electrolytes, soil texture etc, As in soils could be either released into solution or retained on/in colloidal particles (Smith et al., 1999; Zobrist et al., 2000; Smith et al., 2002). Because both arsenate and arsenite can be adsorbed on colloid surfaces by ligand exchange with surface hydroxyl groups, it is generally accepted that adsorption/desorption reactions play a crucial role in mobility of As in soils, especially iron-rich soils (Fendorf et al., 1997; Jain et al., 1999). Soil physical properties, including soil texture and hydraulic conditions, are also significantly involved in As fate (Darland et al., 1997; Ma et al., 1997; Chen et al., 2002). These physico-chemical properties of soils govern the chemical forms of As species which, in turn, affect its mobility and plant-availability (Johnston and Barnard, 1979; Tessier et al., 1979; McLaren et al., 1998; Wenzel et al., 2001). Thus, it is suggested that the relationships of soil properties to the vertical and horizontal distributions of As reflect a wide range of the soil factors, which are involved in As fate in soils.

In this study, As distributions around the closed Suksan Zn mine in Korea are investigated to elucidate the soil factors involved in As movement. In particular, the relationships of its vertical distributions to chemical properties of soils are evaluated.

## Materials and methods

**Site description** The Suksan Zn mine is located at Suksan-ri (N 36°12'15", E 128°52'25") of Gunwi county in Korea. It is characterized by rugged topography with steep slopes and narrow valleys. The underlying bedrock around the mine is composed of felsite, quartz and granite porphyries. Mining was undertaken from 1964 to 1972. About 23,000 tons of ore deposit and mine tailings were dumped into the tailings reservoir near the mine.

In rainy season, water flow in a creek near the mine is rapid and frequently floods into adjacent farmlands. A fraction of mine tailings and metal rich particles had been released into creek and soils from the tailings reservoir. The mine waste had devastated the soils along the creek until a concrete wall was constructed as protection fence and the upper part of the tailings reservoir was covered with soil in 1999.

**Sample collection** Fourteen sites for soil sampling

were selected near Yusa creek passing by the mine. Seven paddy soils and seven upland soils were collected by excavating discrete sections at 15 cm-depth interval to a maximum depth of 30 cm. Each site was examined by three soil samples taken within 100 m<sup>2</sup> area at random. Six sediment samples were also taken from the creek with plastic shovels. Locations of the sampling sites are shown in Fig. 1. After collection, samples were sealed in polyethylene bags and stored at 4°C.

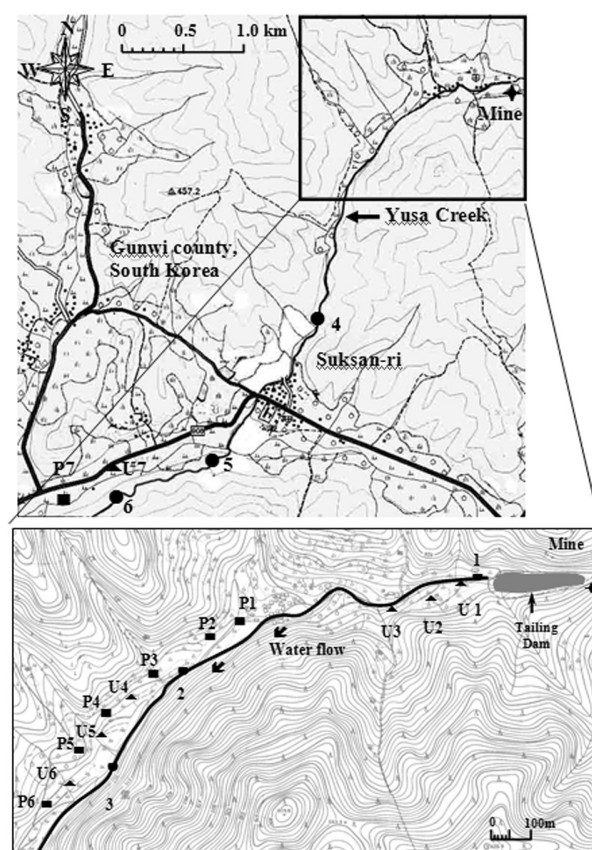


Fig. 1. Location of Suksan zinc mine and sampling collecting site. ■ : paddy, — : upland, • : sediment.

**Sample characterization** Soil samples were air-dried and ground to pass a 2 mm sieve. Particle size analyses of samples were carried out by the pipette method (Elkhatib et al., 1984). Soil pH was measured in soil-distilled water suspension using a pH electrode. Organic matter was determined by acid-dichromate digestion (Veneman et al., 1983). To determine total contents of As, Fe, Mn, Zn and Al, a sample (1.0 g) was digested with concentrated HNO<sub>3</sub> in a Teflon vessel by a microwave digestion system (CEM, Mars 5, USA). For acid oxalate extraction, 1.0 g sample was weighed into a

centrifuge bottle and 50 mL of acid oxalate reagent (0.2 M ammonium oxalate, 0.2 M oxalic acid, pH=3) was added. The suspension was shaken for 4 hours in the dark and then filtered through a filter paper. Concentrations of metal (Fe, Mn, Zn, Al) were determined by an inductively coupled plasma spectrophotometry (Perkin Elmer, Optima 3200RL, USA).

Fractionation of As was conducted by sequential extraction (Onken and Adriano, 1997) because of geo-chemical similarity of As to P. A sequential extraction method using a modified Chang and Jackson procedure (1957) for phosphorous has been adopted to fractionate As pool. One gram of sample was extracted in a centrifuge tube with 25 mL of the extraction solution (vide infra) at 25°C. The tubes were centrifuged at  $5,000 \times g$  for 10 min. The supernatants were used for arsenic analysis. Sequential extraction was conducted in 1 N  $\text{NH}_4\text{Cl}$  solution ( $\text{NH}_4\text{Cl}$ -As) for 30 min, in 0.5 N  $\text{NH}_4\text{F}$  solution ( $\text{NH}_4\text{F}$ -As) for 1 h, in 0.1 N NaOH solution (NaOH-As) for 17 h, in 0.5 N  $\text{H}_2\text{SO}_4$  solution ( $\text{H}_2\text{SO}_4$ -As) for 1 h, with intervening washings with 25 ml of saturated NaCl. Total As and sequentially extracted As were determined by an atomic absorption spectrometer (Perkin Elmer, AAS 3300, USA) equipped with the FIAS 100 hydride generation system. The instrumental variability was

checked with  $0.05 \text{ mg L}^{-1}$  of As solution, and recovery of total As was also examined from standard reference material (SRM 2711). All experiments were conducted in triplicate and average values are given. Significance between two treatments was calculated by Wilcoxon signed rank test.

## Results and Discussion

**Soil properties** The soils examined in this study are classified as sandy clay loams. Physico-chemical properties of the selected soils are represented in Table 1.

Paddy soils show slightly higher pH values compared with those of upland soils. Soil organic matter decreases with soil depth in paddy, whereas content of manganese (Mn) and zinc (Zn) increase. Any significant differences in the contents of other element were not found with soil depth, and the values are within the range observed in typical granite-derived soils (Kabata-Pendias and Pendias, 1984). In particular, Zn contents of the selected soils were found to be higher than those of granite-derived soils. This result implies that the soils were continuously affected by the Zn mine.

**Table 1. The summary of physico-chemical properties of soils.**

Soil	Depth (cm)	Statistic	pH (1:5)	Soil organic matter (%)	Total				NH <sub>4</sub> -oxalate extractable			Clay	Silt	Sand
					Fe	Al	Mn	Zn	Fe	Al	Mn			
					----- % -----	--- mg kg <sup>-1</sup> ---	----- mg kg <sup>-1</sup> -----			----- % -----				
Paddy (n=7)	15	Mean	5.8	2.1	2.1	2.9	396	264	5363	720	176	21.8	13.8	64.4
		Range	5.7 ~ 6.0	1.5 ~ 3.6	1.4 ~ 2.6	1.9 ~ 3.6	163 ~ 520	82 ~ 379	1985 ~ 9237	182 ~ 1676	53 ~ 226	18.6 ~ 25.7	6.8 ~ 17.4	58.4 ~ 74.6
	30	Skewness	0.2	0.2	-0.4	-0.6	-1.1	-0.8	0.2	1.0	-1.7	0.2	-1.5	0.9
		Mean	6.1	1.7	2.1	2.8	497	275	4776	472	314	20.9	16.7	62.4
		Range	5.9 ~ 6.3	1.1 ~ 2.7	1.3 ~ 2.9	1.6 ~ 3.7	119 ~ 998	71 ~ 373	2052 ~ 7763	153 ~ 830	34 ~ 866	18.5 ~ 23.9	7.7 ~ 28.4	49.3 ~ 73.8
		Skewness	1.2	1.2	-0.1	-0.4	0.8	-1.0	0.3	0.1	1.5	0.4	0.5	-0.3
Upland (n=7)	15	Mean	5.1	1.6	2.3	2.8	916	317	4738	751	688	21.6	16.4	62.1
		Range	4.6 ~ 5.8	0.6 ~ 3.3	1.4 ~ 3.0	2.2 ~ 3.5	131 ~ 1807	70 ~ 807	3801 ~ 5316	300 ~ 1238	32 ~ 1315	17.3 ~ 25.4	6.8 ~ 22.7	53.6 ~ 75.9
	30	Skewness	0.3	1.1	-0.5	0.4	0.6	1.4	-1.2	0.0	0.1	-0.4	-0.8	0.9
		Mean	5.3	1.3	2.3	2.8	970	312	5541	719	902	21.9	19.2	59.0
		Range	4.8 ~ 5.7	0.6 ~ 2.8	1.6 ~ 2.6	1.9 ~ 3.5	213 ~ 1581	75 ~ 748	5012 ~ 6479	397 ~ 957	141 ~ 1689	17.7 ~ 26.4	13.3 ~ 23.3	50.3 ~ 69.0
		Skewness	0.5	1.7	0.2	0.3	0.4	1.2	0.9	0.0	0.0	0.3	0.2	0.3

**Table 2. Chemical properties of the sediments in the creek.**

Distance* (km)	pH(1:5)	Arsenic				Total				NH <sub>4</sub> -oxalate extractable		
		Total	NH <sub>4</sub> F**	NaOH	H <sub>2</sub> SO <sub>4</sub>	Fe	Al	Mn	Zn	Fe	Al	Mn
		mg kg <sup>-1</sup>				mg kg <sup>-1</sup>				mg kg <sup>-1</sup>		
0.4	6.9	300.8	2.9	52.0	18.4	24,006	23,247	1,805	2,222	2,342	126.0	916.5
1.5	6.6	196.0	4.7	55.3	13.3	23,520	18,538	1,307	767	2,064	65.9	628.7
2.2	6.6	202.3	7.2	70.8	15.0	21,651	14,428	1,317	843	1,809	98.6	685.9
3.8	6.7	145.9	3.8	37.9	11.6	31,971	14,991	1,142	541	1,024	89.5	498.4
5.0	6.8	49.9	2.2	33.6	6.7	19,000	7,648	475	114	1,223	209.8	1,003.1
5.5	6.6	83.6	4.7	41.3	10.3	24,860	8,550	754	222	1,004	125.0	309.8

\* Sampling distance from the closed mine.

\*\* NH<sub>4</sub>F, NaOH, H<sub>2</sub>SO<sub>4</sub> : sequentially extracted As fraction by 0.5 N NH<sub>4</sub>F, 0.1 N NaOH and 0.5 N H<sub>2</sub>SO<sub>4</sub>.

**As movement in the stream** Various chemical properties of the sediments are given in Table 2. Total As contents in the sediments decreased with the distance from the mine, ranging from about 300 mg kg<sup>-1</sup> at 0.4 km to about 83 mg kg<sup>-1</sup> at 5.5 km from the mine. It was found that total Zn and Mn contents decreased in a similar trend to show their significant relationship to that of As. Acid oxalate extractable Fe content in the sediments also showed a significant relationship to that of As (Table 2). Iron oxides and oxyhydroxides are well known to show high affinity for As species, especially arsenate (Mok et al., 1988; Mok and Wai, 1989). Only trace amounts of 1 N NH<sub>4</sub>Cl extractable As were detected in the sediments (data not shown), indicating that As in this fraction was easily removed from weak adsorption sites on solid phase. A great difference between the total and extractable As contents indicates that a considerable amount of As is tightly incorporated into sediment constituents.

These results suggest that As-bearing particulates have been washed out of the tailings and Zn ore dumps by heavy rain. Because the stream flows downhill with a relatively steep slope, As-rich particulates originating from the mine could migrate into the stream either by surface run-off of water or long-term leaching.

**As distribution with depth of soils** Distributions of As in the paddy soils around the mine are given in Fig. 2. Total As content increased with soil depth. The fractions of NaOH-As and H<sub>2</sub>SO<sub>4</sub>-As also increased with soil depth. In addition, NaOH-As was the major fraction regardless of the depth. However, a decrease was observed in the relative ratio of NH<sub>4</sub>F-As/total extractable As and NaOH-As/total extractable As with soil depth, while that of H<sub>2</sub>SO<sub>4</sub>-As increased from 11.2% at 0-15 cm

to 19.1% at 15-30 cm (Table 3). Typically, most of the paddy soils exhibited a clear tendency of As distribution that increased with the depth (Fig. 2). On the other hand, the vertical As distribution in the upland soils is markedly different from that of the paddy soils (Fig. 3. and Table 3). There was no significant change in their relative ratios of NH<sub>4</sub>F-As/total and NaOH-As/total in upland soils. However, the NaOH-As fraction was most abundant in upland soils as in the paddy soils and the sediments.

Paddy soils are continuously irrigated during rice cultivation, while upland soils are mostly subjected to a dry state. Continuous irrigation in paddy soils induces their environment to be reduced and soil particles to settle as sediment. In particular, arsenite, which is stable in the reduced condition, could be leached at a higher rate in paddy soils than in upland soils.

The observed difference in the vertical distribution of As between paddy and upland soils clearly indicated the profound effect of water flow on As movement in soils. The vertical movement seems to take place mainly by mass flow although relative ratios of each extractable As implies adsorption-desorption reaction to be involved.

**Table 3. Percentage of extractable As against total extractable As in paddy soils and upland soils.**

As fraction	Paddy		Upland	
	15 cm	30 cm	15 cm	30 cm
NH <sub>4</sub> F-As*	17.0±8.8**	12.9±5.7	11.9±2.7	11.4±7.1
NaOH-As	71.8±4.2	68.0±6.7	66.1±15.8	69.0±6.3
H <sub>2</sub> SO <sub>4</sub> -As	11.2±7.0	19.1±10.2	22.0±15.5	19.6±11.6

\*NH<sub>4</sub>F-As, NaOH-As, H<sub>2</sub>SO<sub>4</sub>-As : sequentially extracted As fraction by 0.5 N NH<sub>4</sub>F, 0.1 N NaOH and 0.5 N H<sub>2</sub>SO<sub>4</sub>.

\*\* mean±standard deviation.

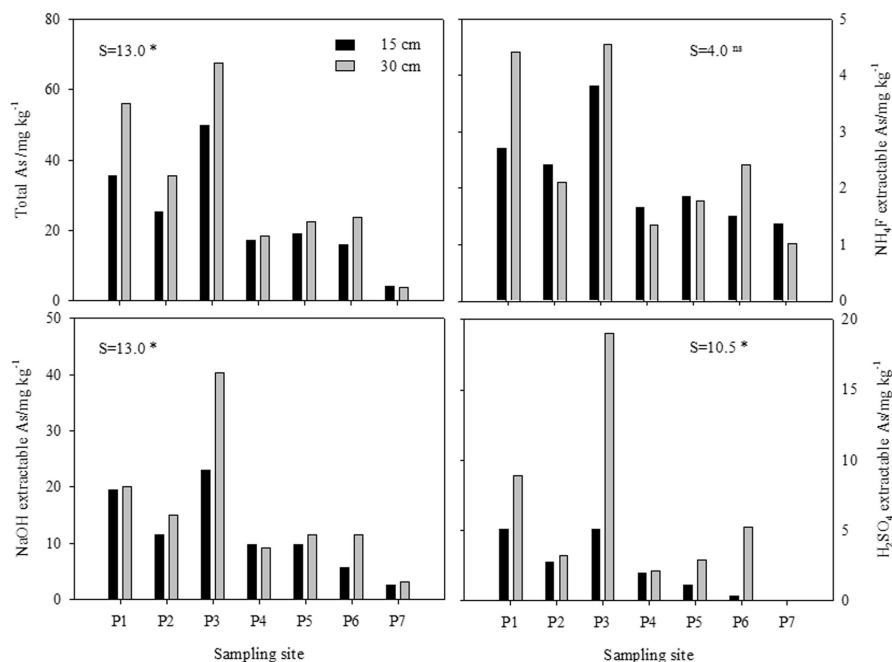


Fig. 2. Vertical distributions of arsenic in paddy soils. Significance between two treatments was calculated by Wilcoxon signed rank test,  $P \leq 0.05$ .

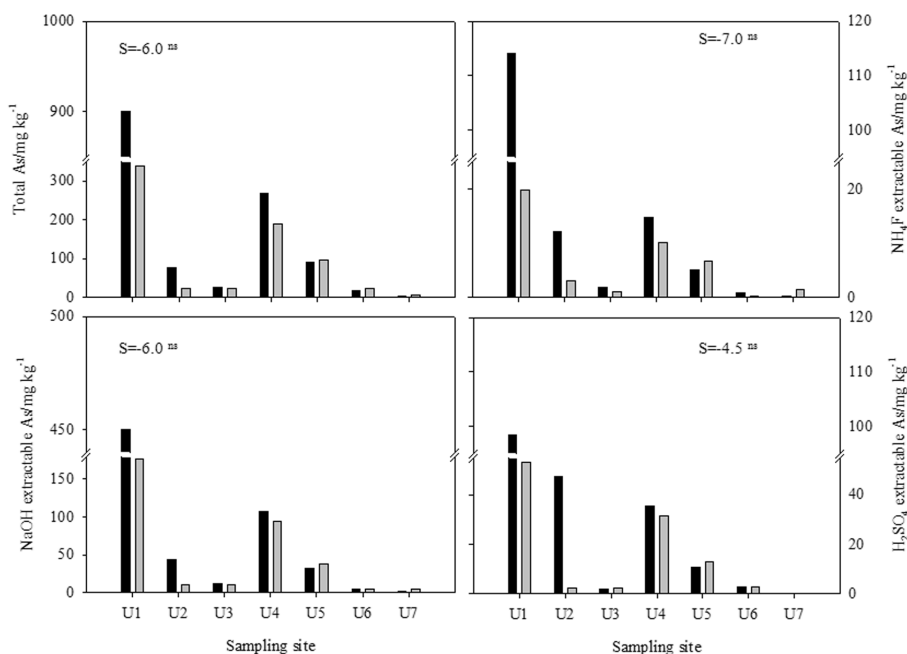


Fig. 3. Vertical distributions of arsenic in upland soils. Significance between two treatments was calculated by Wilcoxon signed rank test,  $P \leq 0.05$ .

Therefore, it is strongly suggested that mass flow plays a crucial role in As mobility in the soils.

**Relationship of As fractions to chemical properties of sediment and soils** Relationship of As fractions to various chemical properties of soils was evaluated to elucidate the effect of soil chemical property on As

movement in soils. Correlation coefficients in the sediment and the soils are given in Tables 4, and 5, respectively. The correlation coefficients indicate that the chemical behavior of As in the sediments is quite different from those in the soils. In the sediment, any significant relationships are not observed between  $\text{NH}_4\text{F}$ -As or NaOH-As and the inorganic species. Only total As content

and H<sub>2</sub>SO<sub>4</sub>-As fraction exhibit significant relationship to several fractions of inorganic species. As indicated in Table 4, As is mainly bound with Zn and Mn species and H<sub>2</sub>SO<sub>4</sub>-As fractions are associated with Fe, Al and Si oxides.

On the other hand, Zn species are significantly

correlated with most of As fractions in paddy soils. The upland soils exhibit similar tendencies to those in paddy soils. However, additional significant correlations are observed with the oxides of Si, Fe, and Al in the upland soils. No significant relationship was found between As fractions and other chemical properties such as pH,

**Table 4. Correlation coefficients between As and inorganic constituents of sediments in creek (n=6).**

Variables	Total As	NH <sub>4</sub> F extractable As	NaOH extractable As	H <sub>2</sub> SO <sub>4</sub> extractable As
Total Fe	0.1285	0.0021	-0.2398	0.1538
Total Mn	0.9918***	0.2307	0.6250	0.9777***
Total Zn	0.9415**	-0.0704	0.4365	0.9100*
Oxalate extractable Fe	0.8708*	0.1306	0.6724	0.8068
Oxalate extractable Mn	0.2303	-0.4729	0.0189	0.0873
Oxalate extractable Al	-0.5202	-0.6172	-0.5476	-0.5606
1 N NH <sub>4</sub> Cl extractable Zn	0.9074*	-0.0997	0.4131	0.8840*
0.5 N NH <sub>4</sub> F extractable Si	0.2201	-0.7194	-0.4073	0.1940
0.5 N NH <sub>4</sub> F extractable Zn	0.8560*	-0.2789	0.2430	0.8054
0.5 N NH <sub>4</sub> F extractable Al	0.8885*	0.0279	0.4800	0.9035*
0.1 N NaOH extractable Si	0.8745*	-0.1165	0.4691	0.8137*
0.1 N NaOH extractable Fe	0.8639*	-0.2360	0.2848	0.8231*
0.1 N NaOH extractable Zn	0.9087*	-0.2025	0.3412	0.8425*
0.1 N NaOH extractable Al	0.8042	-0.2754	0.2338	0.7745
0.5 N H <sub>2</sub> SO <sub>4</sub> extractable Si	-0.8438*	-0.1289	-0.5147	-0.7452
0.5 N H <sub>2</sub> SO <sub>4</sub> extractable Fe	0.8356*	0.3316	0.7075	0.7974
0.5 N H <sub>2</sub> SO <sub>4</sub> extractable Mn	0.9664**	0.0860	0.5320	0.9342**
0.5 N H <sub>2</sub> SO <sub>4</sub> extractable Zn	0.9579**	-0.0808	0.4412	0.9012*
0.5 N H <sub>2</sub> SO <sub>4</sub> extractable Al	-0.8700*	-0.0320	-0.4093	-0.7795

**Table 5. Correlation coefficients between As and inorganic constituents in paddy soils and upland soils.**

	Paddy soils (n=14)				Upland soils (n=14)			
	Total As	NH <sub>4</sub> F-As <sup>§</sup>	NaOH-As	H <sub>2</sub> SO <sub>4</sub> -As	Total As	NH <sub>4</sub> F-As	NaOH-As	H <sub>2</sub> SO <sub>4</sub> -As
Total Fe	-0.0975	-0.1730	-0.2000	0.2802	0.3699	0.2457	0.3232	0.3632
Total Mn	0.2010	0.0565	0.1503	0.0396	0.7028**	0.5829*	0.6924**	0.7108**
Total Zn	0.6271*	0.5013	0.5470*	0.4019	0.8655***	0.7494**	0.8676***	0.8687***
Oxalate extractable Fe	-0.0125	0.0077	-0.1500	-0.2063	-0.1397	-0.1718	-0.1240	-0.1262
Oxalate extractable Mn	0.1505	0.0260	0.1147	0.0530	0.4886	0.3321	0.4866	0.5371*
Oxalate extractable Al	-0.4664	-0.3810	-0.4746	-0.4432	-0.6389*	-0.4682	-0.6080*	-0.6109*
1 N NH <sub>4</sub> Cl extractable Zn	0.4894	0.4357	0.4012	0.2700	0.8244***	0.7039**	0.8334***	0.8303***
0.5N NH <sub>4</sub> F extractable Si	-0.5697*	-0.4581	-0.6871**	-0.6235*	0.1922	0.1111	0.1691	0.1366
0.5 N NH <sub>4</sub> F extractable Zn	0.5453*	0.4482	0.6103*	0.5684*	0.7128**	0.5954*	0.7346**	0.7769**
0.5 N NH <sub>4</sub> F extractable Al	-0.5418*	-0.4321	-0.5987*	-0.5212*	-0.6196*	-0.5345*	-0.6030*	-0.7621**
0.1 N NaOH extractable Si	-0.2788	-0.1773	-0.4342	-0.4066	-0.6955**	-0.6687**	-0.7083**	-0.6665**
0.1 N NaOH extractable Fe	-0.1308	-0.0592	-0.2731	-0.3153	-0.7146**	-0.6066*	-0.6870**	-0.6538**
0.1 N NaOH extractable Zn	0.5481*	0.5085	0.4915	0.4247	0.4021	0.2253	0.4185	0.5532*
0.1 N NaOH extractable Al	-0.4765	-0.4659	-0.5902*	-0.5532*	-0.7805**	-0.6522**	-0.7660**	-0.7444**
0.5 N H <sub>2</sub> SO <sub>4</sub> extractable Si	0.0635	0.1131	0.0922	-0.2004	0.6201*	0.5223*	0.6063*	0.6556**
0.5 N H <sub>2</sub> SO <sub>4</sub> extractable Fe	0.1521	0.1763	0.0257	0.0633	0.5396*	0.4866	0.5608*	0.5815*
0.5 N H <sub>2</sub> SO <sub>4</sub> extractable Mn	0.3776	0.2744	0.3570	0.2692	0.5532*	0.4566	0.5511*	0.6079*
0.5 N H <sub>2</sub> SO <sub>4</sub> extractable Zn	0.7471**	0.6840**	0.6685**	0.5403*	0.7851***	0.6373*	0.7957***	0.8133***
0.5 N H <sub>2</sub> SO <sub>4</sub> extractable Al	-0.2815	-0.2464	0.3430	-0.4762	0.3144	0.3267	0.3251	0.5269*

\*, \*\*, \*\*\* is significant at P<0.05, <0.01, and <0.001, respectively. <sup>§</sup>0.5 N NH<sub>4</sub>F extractable As, 0.1 N NaOH extractable As, 0.5 N H<sub>2</sub>SO<sub>4</sub> extractable As.

organic content and textural properties (data not shown).

Chemical properties of As in soils are affected by a wide range of factors including metal oxyhydroxide/oxide content, redox potential, pH, the type of clay mineral and the oxyanion competing with As species (Frost and Griffin, 1977; Onken and Adriano, 1997; Smith et al., 1999; Zobrist et al., 2000; Goldberg et al., 2001; Gustafsson, 2001; Smith et al., 2002; Brouwere et al., 2004). Amorphous as well as crystalline hydrous oxides of Fe, Al and Mn are known to play a major role in controlling As movement through adsorption and desorption reactions (Pierce and Moore, 1980; Livesey and Huang, 1981; Elkhatib et al., 1984). As associated with these oxides could be immobilized by several reactions like precipitation and adsorption reactions (Oscarson et al., 1980; Pierce and Moore, 1982). The presence of oxyanions such as phosphates, silicate etc., inhibits these reactions by competition (Gustafsson, 2001; Smith et al., 2002; Brouwere et al., 2004).

The highly significant relationship of H<sub>2</sub>SO<sub>4</sub>-As to the oxides of Si, Fe, and Al indicates that As species are precipitated or strongly adsorbed on the surfaces of these oxides. Additionally, a significant relationship of total As to total and 0.5 N H<sub>2</sub>SO<sub>4</sub> extractable Zn reflects considerable incorporation of As into Zn containing particles. These results show that As is mobilized in the forms of particles rather than precipitation-dissolution and adsorption-desorption. Therefore, the movement of As in this study appears to take place mainly through mass flow of the mine-derived particulates in the creek because most of Zn species would result from the Zn mine. Movement of As through mass flow of the particulates are also indicated in both paddy and upland soils. Most of Zn fractions are more significantly correlated with all As fractions in soils than in the creek sediment. Sequentially extracted As profiles and results of correlations between paddy soils and upland soils imply that precipitates of As-Zn mainly moved down to the lower profile of soils.

The significant relationships of NH<sub>4</sub>F-As and NaOH-As to the Zn fractions indicate that adsorption and desorption reactions also take place on the surfaces of these oxides in the soils. However, these complexation reactions are more active in upland soils than in paddy soils. The As fractions in upland soils exhibit additional significant correlation with various oxide fractions besides the Zn fractions. Particularly, the H<sub>2</sub>SO<sub>4</sub>-As shows a positively significant relationship with 0.5 N

H<sub>2</sub>SO<sub>4</sub> extractable Si fraction in upland soil, while a negative correlation is found with 0.1 N NaOH extractable Si fraction. This result may be explained by the high dependence of As adsorption with pH on the silica surface (Frost and Griffin, 1977; Smith et al., 1999). In addition, a negative relationship of As to 0.5 N NH<sub>4</sub>F extractable Al may result from negatively charged group of aluminosilicates.

## Conclusions

This study clearly shows the decisive role of water flow in As movement in soils. Because water flow facilitates both reduction and mass flow in soils, As mobility significantly increases. Reduced conditions in paddy soils led to an increase in soluble As species that could be easily adsorbed on the surface of various metal oxides, especially Zn and Mn species as found in this study. Therefore, As movement in soils around Zn mine seems to be governed mainly by mass flow of the particulates containing arsenic-associated Zn and Mn species in paddy soils. On the other hand, retention reactions such as adsorption, complexation, and precipitation seem to predominate in upland soils, where the movement by mass flow is very limited.

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## 폐 아연 광산 주변 토양에서 비소의 이동양상

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광산 주변 토양 및 하천퇴적물은 광산활동기간 뿐만 아니라 폐광 이후에도 비소 (As)의 오염에 노출될 가능성이 높다. 본 연구에서는 아연 (Zn) 광산 주변 토양의 비소 이동 특성을 규명하기 위한 방법으로 토양 중 비소의 분포와 토양이화학성과의 상관관계를 조사하였다. 인 분획법 (P fractionation) 을 이용하여 토양중 비소의 분포 특성을 조사한 결과, 논토양과 밭토양에서 큰 차이를 나타내었다. 논토양의 비소함량은 깊이가 깊어짐에 따라 증가하였으나, 밭토양은 감소하였다. 또한 밭토양에서 비소는 Si, Al 및 Fe 산화물과 밀접한 상관관계를 보였다. 토양에서 비소는 주로 NaOH용액으로 추출가능한 형태로 발견되었지만, 광산으로부터 유입된 아연과도 높은 상관관계를 보였다. 포화상태의 수리조건이 형성되는 논토양과 비교적 건조한 상태인 밭상태에서 비소의 분포양상이 다르고 이들의 상관관계 결과를 고려할 때 비소의 이동에 물의 영향은 매우 결정적인 요인으로 작용하였다. 특히 논토양에서 비소의 이동은 공극을 통한 물의 mass flow에 영향을 받는 반면, 밭토양에서는 교질표면에 비소의 adsorption, surface complexation, surface precipitation 등 retention 반응에 더 큰 영향을 받는 것으로 판단되었다.

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