Speciation of Arsenic from Soil Organic Matter in Abandoned Gold and Silver Mines, Korea

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Organic forms of arsenic (As) were determined through fractionation procedure of soil organic matter (SOM) in soil, sediments and mine tailing samples from the Myungbong, Dongil, and Okdong mining areas of southern Korea. An alkaline extraction method was applied to soil samples followed by the fractionation procedures of SOM by the DAX-8 and XAD-4 resin adsorption method. Major fraction of organic As species (42% to 98%) was found in acid-soluble fraction, whereas minor fraction (0.1% to 67.8%) was present in the humic-associated As. In acid-soluble fractions, the transphillic- and hydrophilic-associated As were dominant in addition to As binding with humic and fulvic SOM. Arsenic binding was the strongest between pH 6 to 8 and reduced to about 70% at both low and high pH regions. The amount of both transphillic and hydrophillic associated As was less changed than humic and fulvic-associated As, in both low and high pH regions. This apparently indicates that As has stronger affinity towards hydrophillic rather than hydrophobic organics. From the experimental observation of As-binding SOM in natural soil, the ligand exchange model may be a feasible explanation of transphillic and hydrophillic affinity of As.

Key words : *alkaline extraction, arsenic, soil organic matter, speciation*

Arsenic (As) has become an emerging issue in environmental research because of its use in agricultural activities, industrial and mining wastes, and other geological sources [Del Razo et al., 1990; Chen et al., 1994; Nickson et al., 1998; Smedley and Kinniburgh, 2002]. Arsenic in soil environments is released to the wider ecosystem, and consequently human beings, through inorganic and organic As species [Cullen and Reimer, 1989]. The role of arsenic species in soil environments, as both carcinogenic and non-carcinogenic compounds, is significant because of their bioavailability, toxicity and mobility, which is dependent on chemical forms [Manning and Martens, 1997; Datta et al., 2006]. The toxicity of As species is dependent on its organic and inorganic chemical speciation. Inorganic forms of As

such as As(III) and As(V) are more toxic than methylated As. Some complicated organic structures, like arsenobetaine and arsneosugar, are non-toxic. Organic As species such as MMA (monomethylarsonic acid), DMA (dimethylarsinic acid) and arsenobetaine occur as less toxic forms as a result of the detoxification process [Cullen and Reimer, 1989; Huang and Matzner, 2007]. Furthermore, arsenobetaine and some arsenosugars are relatively recalcitrant organic As species.

In soil horizon, As speciations are deposited through percolation along with seepage water movement, and further supported if the soil horizon is rich in carbon, which acts as a sink for As deposition [Huang and Matzner, 2007]. Soil organic matter (SOM) as organic constituents in the soil includes undecayed plant and animal tissues, their partial decomposed products, and the soil biomass. This contains well-known high-molecular-weight organic materials such as polysaccharides and proteins, simpler substances such as sugars and amino acids, and other small molecules of humic substances. The SOM can bind with As in soils, particularly, in the

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presence of mineral particles such as iron oxyhydroxides mineral [Sposito, 1984]. On the other hand, As mobility can be increased in organic rich horizons of forest soils due to soluble organic binding with As. Some researchers analyzed organic As fractions as recalcitrant organic As species in soil samples by subtracting the total As from $NaBH_4$-reducible As (as MMA and DMA are not reducible by $NaBH_4$) [Gustafsson and Jacks, 1995]. In general, metal cations have higher binding affinity to surface-bound and dissolved humic substances [Davis, 1984; Laxen, 1985; Christl and Kretzschmar, 2001]. However, oxyanions such as AsO_4^{2-}, AsO_3^{3-}, SO_4^{2-}, HPO_4^{2-}, $H(BO)_4^-$, MoO_4^{2-}, SeO_4^{2-} and SeO_3^{2-} have low adsorption capacities for composted organic matter [Sposito, 1984]. Arsenic, as oxyanionic species, also forms an organic complex with humic substances through bridging metals or ligand exchanges [Redman et al., 2002; Ko et al., 2004]. In another proposed mechanism, the ligand exchange reaction model also provides possible reaction between oxyanionic As and various types of organic ligands, such as nitrate and phosphate ions [Thanabalasingam and Pickering, 1986]. Risk of As-contaminated soils may be significantly assessed by As speciation which is related with SOM.

In the optimal determination of organic As speciation from soil samples, the SOM fractionation procedure using alkaline extraction can solubilize As binding to humic substances and various metal oxyhydroxides [Stevenson, 1994; Seby et al., 1997]. Silica-based anion- and resin-based cation-exchange cartridges were used for the separation of the inorganic and organic As fractions in each bulk alkali extractant solution obtained from the SOM fractionation procedure in this study. The solid resin cartridge is cheap (about US $ 2) [Impellitteri, 2004], and possibly applicable for the in-situ analysis of water samples by instant separation of inorganic As(III), As(V) and organic As species [Le et al., 2000]. In our previous studies [Ko et al., 2004 and 2006], the cartridge method was employed in the determination of organic As species. In this study, we aim to conduct determination of organic As species associated with various organic fractions, such as humic SOM, fulvic SOM, transphillic SOM and hydrophillic SOM during the SOM fractionation procedure, by the alkaline extraction. Because alkaline extraction includes both inorganic and organic As species in bulk extractant solutions, reasonable separation method should be accompanied for the separation of organic As speciation. Some studies have tried to interpret organic As species, but their separation and extraction methods from soil samples were limited to only within hydrophobic SOM fractions [Thanabalasingam and Pickering, 1986; Gustafsson and Jacks, 1995; Seby et al., 1997]. The

objectives of this study are; (a) to determine the content of organic As fraction in soil, sediment and mine tailing samples from the Au-Ag mining areas, and (b) to examine the effect of solution pH on the extractability of organic As species from the SOM fractionation procedure.

Materials and Methods

Sampling of soil, sediment and tailings. Soil, sediment and mine tailing samples around Au and Ag mining areas in the southern part of Korea were collected to investigate organic As speciation (Fig. 1a). Mining activities in these locations were ceased during the 1970s, and have been abandoned since. It is well known that Au and Ag mining sites release As from the source minerals of arsenopyrite or As-bearing pyrite. Myungbong [Kim et al., 2003], Dongil [Ko et al., 2003] and Okdong mining areas [Yi et al., 2004] have been reported to be highly contaminated with As and heavy metals from mine drainage, tailings, and waste rocks in the abandoned Au and Ag mining areas. Consequently, these mines have been used in this study, where soil, sediment and mine tailings contaminated with As were collected down to the depth of 30 cm using a shovel. In the Dongil mine, tailing sample (DI-T), control soil (DI-S) and two paddy soils (DI-PS1 and DI-PS2) were collected within about 500 meters distance from the mining pit (Fig. 1b). In the Okdong mine, tailing sample (OD-T), sediment (OD-ST), control soil (OD-S), two paddy soils (OD-PS1 and OD-PS2), and farmland soil (OD-FS) samples were collected within about 700 meters from the mining pit (Fig. 1c). In the Myungbong mine, tailing sample (MB-T), control soil (MB-S) and sediment (MB-ST) samples were collected within about 300 meters distance from the mining pit (Fig. 1d).

Fractionation procedure of SOM. The alkali-extraction method was performed for the extraction of SOM (Fig. 2). Two-hundred and fifty milliliters of 0.5 N NaOH solution was added to 40 g of soil in a HDPE (high density polyethylene) centrifuge bottle. This mixture was agitated in a shaking incubator at 200 rpm at 25°C. The SOM-concentrated supernatant was passed through 0.45 μm-glass filter after centrifugation at 4,000 rpm for 20 min to remove suspended particles. The pH of the supernatant was adjusted to about 1.5 with concentrated HCl. The concentrated SOM solution stood for 1 hr and was separated from the precipitated humic SOM by centrifugation at 6,000 rpm for 20 min.

The SOM fractionation was accomplished by passing through columns of DAX-8 and XAD-4 resins (Supelite TM DAX-8 and Amberlite® XAD-4) using the procedure of Malcolm and McCarthy [1992]. Humic and non-humic
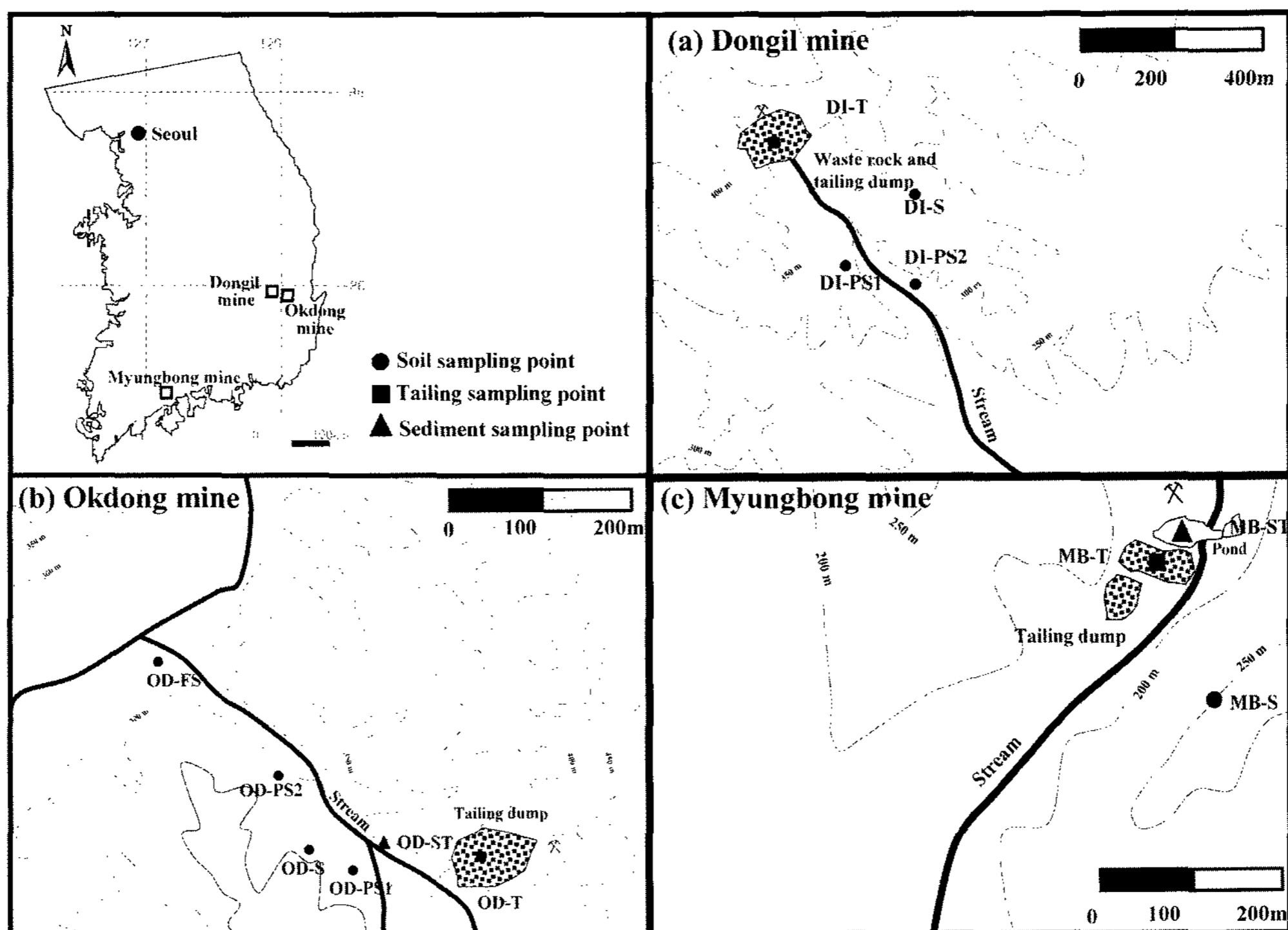
Fig. 1. Location map of studying sites; (a) Dongil mine, (b) Okdong mine, & (c) Myungbong mine, and sampling sites with I.D. of soils, sediment & mine tailing samples.

substances were considered as hydrophobic and hydrophilic, respectively [Leenheer, 1981; Thurman, 1985]. The humic substance consists of humic and fulvic SOM, while non-humic substance consists of the transphillic SOM and hydrophillic SOM. The SOM-concentrated samples were processed through DAX-8 resin followed by XAD-4 resin and were fractionated into fulvic SOM (DAX-8 adsorbable), transphillic SOM (XAD-4 adsorbable), and hydrophillic SOM (neither DAX-8 nor XAD-4 adsorbable). The adsorbed fulvic SOM and transphilic SOM were eluted using 0.1 N NaOH solution. In addition, both inorganic As and organic As species were readily eluted with 1 M HCl and ethanol to recover the adsorbed As onto both of the resin columns (ϕ=2.5 cm, h=10 cm). Figure 2 shows the fractions of the organic As species during SOM fractionation, while the organic As species were divided into two categories of non-acid and acid soluble As. The non-acid soluble As is humic-associated, with the acid soluble As consisting of fulvic-, transphillic-, and hydrophillic-associated As. Humic SOM, fulvic SOM, transphillic SOM, and hydrophillic SOM obtained from the fractionation of SOM were analyzed for determination of total concentration of As species. Arsenic was analyzed in order to distinguish its organic and inorganic species. Due to the use of chemicals such as HCl or NaOH, the separation procedure of As(III) and As(V) can not be significant, but the concentration of total As in each SOM extractant may be meaningful. Although organic As species were low in the SOM fractionation, they may be discriminated against for the better understanding of As binding to SOM [Gustafsson and Jacks, 1995].

Arsenic speciation and chemical analysis. The solution pH of each organic fraction extractant was adjusted from 3 to 11 using 1.0 M HCl and 1.0 M NaOH. The As in the pH-adjusted solution was instantly separated as inorganic and organic As species following the separation method. In order to separate the inorganic and organic forms of As, their species were determined by the solid cartridge method [Le *et al.*, 2000]. Yalcin and Le developed the separation method of As species by passing through a resin-based strong cation cartridge (Alltech, Canada) followed by a silica-based strong anion exchange cartridge (Supelco, Canada) [Yalcin and Le, 2001]. The DMA is retained on a resin-based strong cation exchange cartridge and eluted with 1.0 M HCl. Both MMA and As(V) are retained on a silica-based strong anion exchange cartridge and sequentially eluted with 60 mM acetic acid for MMA and 1.0 M HCl for As(V). Both cartridges were preconditioned with 50% methanol and deionized water before the separation of each species. After the collection of supernatant through 0.2 μm membrane filter, 3 mL of the same solution sample was allowed to flow sequentially through a resin-based strong
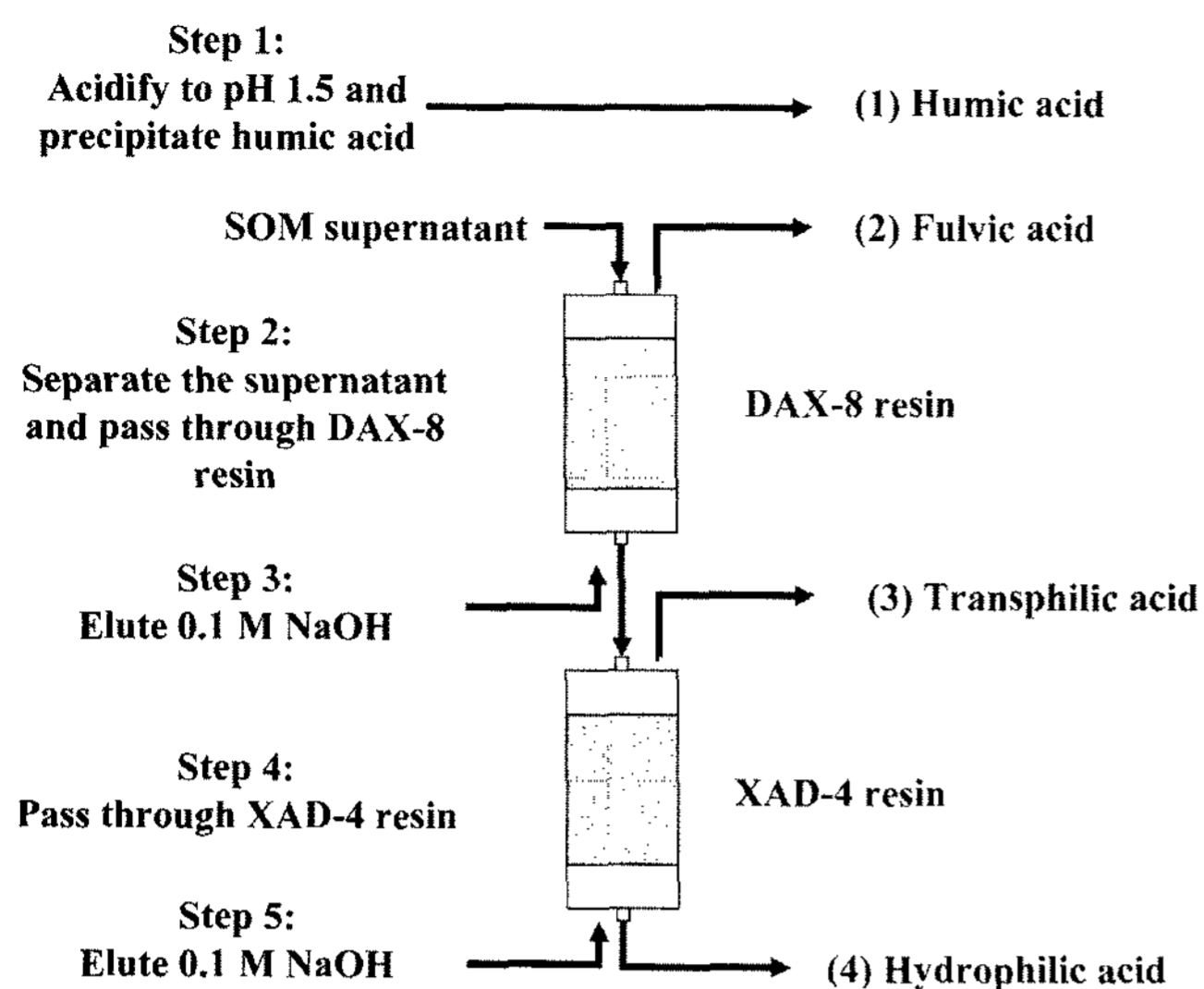
Fig. 2. Experimental schematic diagram showing the determination of organic fraction during SOM fractionation procedure based on alkali extraction.

cation and a silica-based strong anion exchange cartridge at about 2 mL min^{-1} via a peristaltic pump. After passing the supernatant through the cartridges, each eluting buffer solution was allowed to flow through the cartridges 3 times by using 3 mL eluting solutions for complete elution of As species. Arsenic species in both solutions and elutions from the cartridges were stored at 4°C before the chemical instrumental analysis.

The total concentration of As in the aqueous phase was determined by hydride generation atomic absorption spectrometry (HG-AAS: Perkin Elmer ZL 5100, USA), with detection limit of 1 μg L^{-1} As. Total concentration of As and non-alkali extractable As was determined using aqua-regia (HCl : HNO$_3$=3 : 1) decomposition. Total metal concentrations and dissolved organic carbon of each SOM extractant were determined using inductively coupled plasma atomic emission spectrometry (ICP-AES: Thermo Jarrel Ash, USA) and TOC (Total Organic Carbon: PPM Lab Co., Korea) analyzer, respectively. Molecular size was measured by high performance size exclusion chromatography (HPSEC) using a SEC column (protein-pak 125, Waters, Milford, USA) [Aiken et al., 1992]. Standard solutions were made using various polystyrene sulfonates to produce a relative molecular mass (RMM) calibration curve [Ko et al., 2005]. For the analysis of physico-chemical properties of soil samples, all samples were air-dried and passed through the 2 mm sieve. The soil texture analysis was carried out by determining the percentage of sand, silt and clay in each given soil using a combination of wet sieving. Those determinations were plugged into a texture analysis USDA textural triangle to determine soil classification.

Soil pH was determined in 0.01 M CaCl$_2$ with 1 : 10 wt wt^{-1} as a soil to solution ratio. The measurement of SOM was loss-on-ignition (LOI), which was determined from the percentage of loss weight (wt%) after ignition in a furnace at 550°C over 16 hrs.

Results and Discussion

Characterization of soil, sediment and mine tailing samples. The chemical compositions of toxic metals in soil, sediment, and tailing samples were determined, (Table 1). The soil samples (DI-S, OD-S and MB-S) consisted of 'control' forest soils uncontaminated with toxic metals in the vicinity of the mining sites. Sediment samples (OD-ST and MB-ST) as well as paddy and farmland soils (DI-PS1, DI-PS2, OD-PS1, OD-PS2 and OD-FS) were highly contaminated with As. For the mine tailings, we analyzed the samples DI-T, OD-T, and MB-T, to possess high concentrations of As; 7,001, 77.4, and 5,769 mg kg^{-1}, respectively. Tailing samples were acidic with lower soil pH (3.5-5.2) compared to soil and sediment samples of pH 5.7-6.7. Most of sampled soils were loam, silt loam or clay loam. In contrast, tailing samples consisted of silty clay textures (DI-T and OD-T).

Table 2 shows the average molecular weight and the percentage of each fraction of SOM in soil, sediment and tailing samples. Two sediment samples had higher levels of SOM (15.28 wt% for OD-ST and 10.46 wt% for MB-ST) compared to those of mine tailing samples (less than 1 wt% actually for DI-T, OD-T and MB-T). The amounts of SOM in tailing samples was less than 1 wt%, and in particular less frequently detected in subsurface layer of tailings dump, comparing with those of topsoil layers (data not shown here). This indicates that the low hydraulic conductivity of mine tailings permitted less movement of pore water. The amounts of humic SOM in soils ranged from 49.9% to 70.7%. However, humic SOM content in paddy soil samples were observed at 15.2% for DI-PS1 and 15.5% for OD-PS2. Average ratio of humic to non-humic substances was about 3 : 1, and the order of the relative content of SOM followed; humic SOM > transphillic SOM > fulvic SOM. The SOM fraction consisting of humic substances, can be high with up to 80% of SOM fraction in mineral soils extractable with NaOH classified as humic and fulvic SOM [Stevenson, 1994]. Furthermore, it is possible for some paddy soils (DI-PS1 and OD-PS2) to have less humic substances if the decomposition of plant litter takes longer than usual. The average molecular weights of fulvic SOM and transphillic SOM were lower than that of humic SOM. Since each SOM fraction is a kind of various organic mixtures, molecular weight values can be considered as average

Table 1. Soil properties of soil, sediments & mine tailing samples, and their mean concentration of As & heavy metals

Sampling site	Sample	Soil type	As*	Cd	Cr	Cu	Pb	Zn	Soil pH**	Soil texture
Dongil mine	DI-T	Tailing	7,001±16	9.5±0.3	10.5±1.1	2,221±36	4,469±41	976±14	4.2	Silty clay (14, 44, 42)***
	DI-S	Control soil	0.25±0.02	nd****	nd	7.29±0.4	0.74±0.02	2.6±0.02	5.8	Clay loam (32.1, 33.4, 34.5)
	DI-PS1	Paddy soil	88.2±3.8	7.9±0.6	12±0.7	134.3±5.4	73.19±6.1	95.4±0.3	6.1	Clay loam (34, 32.6, 33.4)
	DI-PS2	Paddy soil	44.4±5.4	0.3±0.02	16.5±0.9	115.7±14	40.51±2.7	91.9±11	5.7	Silty clay (14, 44, 45)
Okdong mine	OD-T	Tailing	77.37±8.1	7.2±0.8	10.5±0.6	187±9	1,079±31	6,810±26	5.2	Silty clay (12.4, 44, 43.6)
	OD-S	Control soil	8.4±0.8	4.9±0.1	22.5±1.2	23.6±1.1	18.5±0.9	56±1.8	6.6	Loam (45, 33, 22)
	OD-ST	Sediment	9.9±0.4	3.6±0.02	16.5±1.6	42.8±2.5	26.9±1.1	69.3±4.3	5.9	Silt loam (35, 13.8, 56.2)
	OD-PS1	Paddy soil	11.5±0.4	1.1±0.02	21±2.5	93.9±9.6	22.4±1.2	70.9±3.8	5.8	Clay loam (32, 38.6, 29.4)
	OD-PS2	Paddy soil	18.9±2.7	1.7±0.02	36±2.8	93.5±5.5	46.7±0.8	148.7±11	6.3	Loam (40.5, 40.3, 20.2)
	OD-FS	Farmland soil	14.8±1.1	3±0.02	22.5±3.0	42±2.3	43.7±2.4	95.2±2.9	6.7	Clay loam (29, 41, 30)
Myungbong mine	MB-T	Tailing	5,769±23	1.3±0.02	16.7±1.7	1.1±0.02	160±9.8	2.1±0.02	3.5	Sandy loam (64, 20, 16)
	MB-S	Control soil	0.3±0.02	nd	nd	3±0.02	0.3±0.02	4.1±0.02	6.6	Clay loam (35.5, 34.5, 35)
	MB-ST	Sediment	254±0.1	0.8±0.02	22±1.8	18±1.2	130±13	1.2±0.02	6.6	Silty clay (15.3, 44.7, 40)

* Concentration unit, mg kg^{-1}.

** 1 : 10 H$_2$O mixture.

*** Soil particle size distribution (sand, silt, clay) unit, %.

**** nd, not detected.

Table 2. Organic fraction and mean molecular weight of humic and non-humic substances extracted from soil, sediment and mine tailing samples

Sampling site	Sample	Soil type	Soil organic matter (wt%)	Percentage of each organic fraction (%)				Average molecular weight (kilo-dalton)			
				Humic substance		Non-humic substance		Humic substance		Non-humic substance	
				Humic SOM	Fulvic SOM	Transphillic SOM	Hydrophilic SOM	Humic SOM	Fulvic SOM	Transphillic SOM	Hydrophilic SOM
Dongil mine	DI-T	Tailing	0.75	63.9±5.3	11.1±1.2	16.2±2.3	8.9±0.4	23.4	2.7	3	3.2
	DI-S	Control soil	5.33	51.5±3.1	16.7±2.3	20.1±2.8	11.8±1.1	34.1	3.2	3.1	2.8
	DI-PS1	Paddy soil	7.31	15.2±2.2	15.9±1.9	24.1±1.9	44.9±5.9	43.2	8.3	6.3	5.4
	DI-PS2	Paddy soil	6.85	49.9±4.9	6.7±0.5	11.6±2.4	31.7±3.4	35.1	5.3	5.1	4.6
Okdong mine	OD-T	Tailing	0.91	67.3±5.8	8.1±1.1	15.6±2.7	9.1±1.5	49.3	2.9	3.2	3.2
	OD-S	Control soil	7.42	70.7±6.1	7.0±0.6	16.3±3.2	6.0±0.4	45.3	1.6	1.5	1.8
	OD-ST	Sediment	15.28	65.6±5.8	10.4±0.3	16.3±1.5	7.7±0.6	28.4	2.3	2.2	2.4
	OD-PS1	Paddy soil	8.13	54.6±6.4	15.7±1.5	20.7±0.9	9.1±1.2	34.6	2.9	2.6	2.5
	OD-PS2	Paddy soil	6.96	15.5±2.9	14.9±2.8	19.8±2.4	49.9±6.9	50.2	8.2	7.6	7.1
	OD-FS	Farmland soil	9.88	68.8±7.2	8.7±0.9	16.0±2.1	6.6±0.3	47.2	3.2	2.5	1.9
Myungbong mine	MB-T	Tailing	0.96	66.3±5.5	8.8±0.9	15.5±1.8	9.5±0.8	18.3	2	2.1	3.2
	MB-S	Control soil	6.02	69.3±6.4	11.3±2.4	15.2±3.5	4.2±0.6	44.1	3.4	1.4	4.1
	MB-ST	Sediment	10.46	71.2±6.9	7.1±1.1	15.9±1.9	5.8±0.3	38.2	2.4	2.5	2.2

Table 3. Carbon-bonding concentration and bulk fraction of organic As species with respect to each organic fraction

Sampling site	Sample	Soil type	Alkali extractable As (% fraction)			
			Humic associated As (mg kg⁻¹ C)*	Fulvic associated As (mg kg⁻¹ C)	Transphillic associated As (mg kg⁻¹ C)	Hydrophilic associated As (mg kg⁻¹ C)
Dongil mine	DI-T	Tailing	2.42±1.1 (4.4)**	23.98±4.3 (43.3)	14.84±1.3 (26.8)	14.17±0.4 (25.6)
	DI-S	Control soil	0.70±0.6 (13.3)	1.53±0.2 (29.1)	2.02±0.03 (38.5)	1.01±0.2 (19.2)
	DI-PS1	Paddy soil	26.33±2.9 (67.8)	0.15±0.1 (0.4)	7.93±0.6 (20.4)	4.45±0.7 (11.4)
	DI-PS2	Paddy soil	0.18±0.12 (1.1)	0.64±0.2 (3.9)	14.53±1.4 (89.7)	0.85±0.05 (5.2)
Okdong mine	OD-T	Tailing	0.01±0.01 (0.0)	0.78±0.3 (1.8)	8.92±1.8 (20.3)	34.17±4.5 (77.9)
	OD-S	Control soil	0.01±0.01 (0.1)	0.42±0.1 (1.0)	22.04±2.4 (53.7)	18.56±2.8 (45.2)
	OD-ST	Sediment	0.09±0.06 (0.2)	0.34±0.08 (0.7)	6.15±1.1 (12.6)	42.25±6.1 (86.5)
	OD-PS1	Paddy soil	0.55±0.1 (6.9)	1.95±0.1 (24.4)	3.73±0.2 (46.5)	1.78±0.05 (22.2)
	OD-PS2	Paddy soil	0.06±0.02 (0.2)	0.20±0.1 (0.6)	2.22±0.05 (7.2)	28.39±2.9 (92.0)
	OD-FS	Farmland soil	1.21±0.4 (2.4)	12.54±2.5 (25.1)	24.41±3.7 (48.8)	11.83±1.7 (23.7)
Myungbong mine	MB-T	Tailing	1.02±0.1 (2.3)	5.91±1.2 (13.5)	12.36±2.1 (28.2)	24.51±2.6 (56.0)
	MB-S	Control soil	0.01±0.01 (0.0)	1.20±0.9 (10.7)	5.51±0.08 (49.3)	4.46±0.3 (39.9)
	MB-ST	Sediment	0.11±0.05 (0.1)	0.56±0.1 (0.8)	8.11±0.1 (12.1)	58.21±8.9 (86.9)

* Arsenic concentration per unit carbon in each organic As species.
** % fraction of each organic As fraction.

values. In this study, the average values of molecular weight were chosen, considering the range of polydispersity values of 1.1 to 1.4. From many literatures, molecular weights of humic SOM vary from a few thousand to a few hundred thousand Daltons [Thurman, 1985; Stevenson, 1994; Sposito, 1994]. There is also general agreement that fulvic SOM has molecular weights of at most a few thousand Daltons. Furthermore, hydrophillic SOM has less molecular weight than hydrophobic humic substances. This indicates that soil samples collected in this study may also have typical SOM properties.

Organic As speciation in the SOM fractionation. As shown in Table 3, As associated with SOM was a very small part of the total As concentration in the soil samples analyzed in Table 1. Organic As species were calculated on the basis of the concentration of As binding per unit organic carbon ($C_{SOM\text{-associated As}}$, mgAs kg^{-1}C) with respect to each SOM fraction using the below relationship;

$$C_{SOM-associatedAs} = \frac{C_{OAs}}{C_{OC}} \times \frac{1,000}{(g/mg)}$$

where C_{OAs} is the maximum concentration in each As form (mg As/L), and C_{OC} is the organic carbon in each SOM fraction (mg C/L).

In the results, some samples (DI-T, DI-S, DI-PS1, OD-PS1, and OD-FS) had more than 30% of the total sum of both humic- and fulvic-associated As. However, both transphillic and hydrophillic SOM for most of the soil samples were associated dominantly with organic As species up to about 90% of both transphillic- and hydrophillic-associated As. It evidently shows that As also has affinity to hydrophillic SOM in addition to hydrophobic organic molecules. Some researchers have consistently reported that in a smelter-polluted soil horizon, transphillic SOM, as XAD absorbable fraction, was more enriched with As species when compared to hydrophobic acids like humic and fulvic SOM [Gustafsson and Jacks, 1995]. Our study shows high contents of transphillic-associated As in soil samples, together with hydrophillic-associated As. We can therefore conclude that transphillic and hydrophillic SOM fractions play a significant role in As binding with SOM.

The interpretation of both organic and inorganic As species can not be properly understood in the bulk extractant solutions, due to the oxidation of As(III) and the change of the organic molecules by addition of acid and base solutions. This study investigated the effects of solution pH on the extractability of inorganic As from
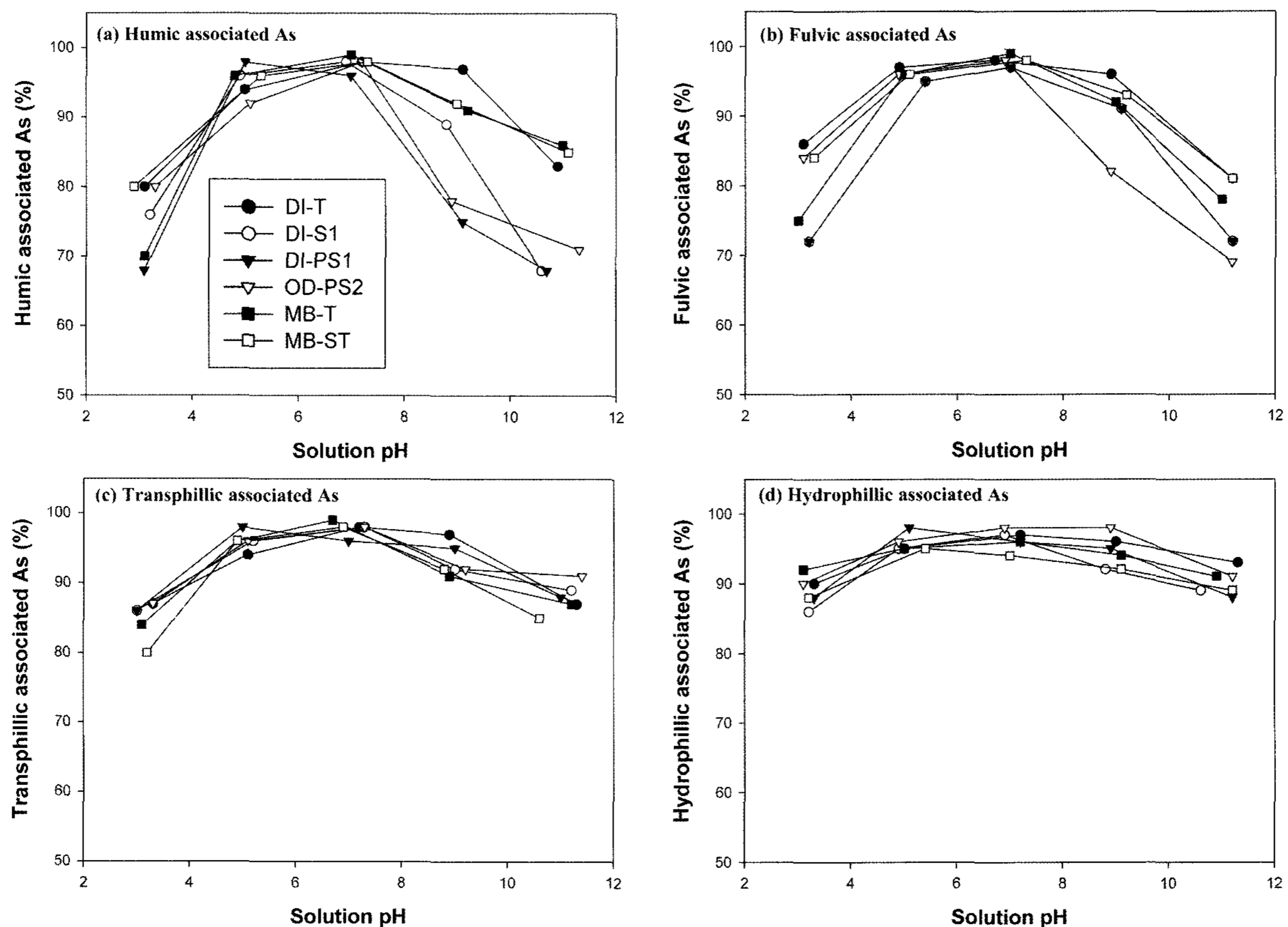

Fig. 3. The percent fraction of (a) humic-associated As, (b) fulvic-associated As, (c) transphillic-associated As, and (d) hydrophilic-associated As with respect to various solution pHs (about 3 to 11 as final equilibrium pH).

organic As species. The organic As species in each organic extractant solution varied with pHs of 3 to 11. As shown in Fig. 3, the content of humic-associated As was the highest in the intermediate pHs, and reduced to about 70% at both low and high pH regions. The stability of both humic- and fulvic-associated As was also shown in the same way. On the other hand, the amount of both transphillic- and hydrophilic-associated As changed little, compared with the behavior of humic- and fulvic-associated As, with respect to the varying solution pHs. It seemed that As had affinity towards hydrophilic organics in addition to hydrophobic organics.

Mechanism of organic As complexation. Organic As complexation has been reported in two reaction models; (1) bridging metal model, forming the ternary complexes linking As species through metal ions with organic molecules [Redman *et al.*, 2002; Ko *et al.*, 2004], and (2) ligand exchange model, interchanging As species with ligands, such as hydrated inorganic anions or organic ligands [Thanabalasingam and Pickering, 1986; Gustafsson and Jacks, 1995]. Qualls and Haines [1991] have suggested that the binding mechanism related with the chemical interaction for the transphillic and hydrophilic components of SOM, like ligand, exchange with nitrate and phosphate. They also explained that the ligand exchange reaction is related with the complexation between the weak organic ligand and oxyanions like the following reactions:

$$NH_2 + HX \leftrightarrow NH_3X$$
$$NH_3Y + X^- \leftrightarrow NH_3X + Y^-$$
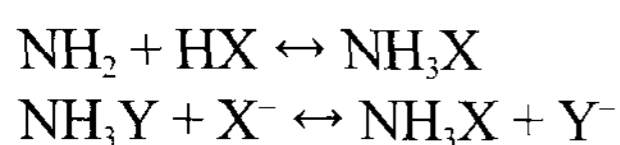
where X is inorganic As like As(III) or As(V), and Y is the organic ligand of SOM.

These reactions indicate that the As binding should decline with increasing pH, due to the enhanced deprotonation and anionic competition from OH⁻ for ligand exchange sites. In this study, both hydrophobic and hydrophillic-associated As were also enriched in the intermediate pH ranges rather than high pH ranges. Furthermore, other researchers explained that the anion exchangers usually contain the amino functional groups, which is basic and then interacts with acids, or exchange anions [Thanabalasingam and Pickering, 1986]. The ligand exchange model seems to be suitable for the explanation of hydrophillic affinity of As species like transphillic- and hydrophillic-associated As. Consistently, our experimental results support the notion that As binds with the transphillic and hydrophilic components of SOM. The mobility of As depends significantly on binding strength with organic species [Huang and Matzner, 2007]. Therefore, the organic form of As should be investigated with both spectroscopic and chemical experimental information.

References

Aiken GR, McKnight DM, Thorn KA, and Thurman EM (1992) Isolation of hydrophilic organic acids from water using nonionic macroporous resins. *Org Geochem* **18**, 567-573.

Chen SL, Dzeng SR, and Yang MH (1994) Arsenic species in groundwater of the blackfoot disease area, Taiwan. *Environ Sci Technol* **28**, 877-888.

Christl I and Kretzschmar R (2001) Relating ion binding by fulvic and humic acids to chemical composition and molecular size. 1. Proton binding. *Environ Sci Technol* **35**, 2505-2511.

Cullen WR and Reimer KJ (1989) Arsenic speciation in the environment. *Chem Rev* **89**, 713-764.

Datta R, Sarkar D, Sharma S, and Sand K (2006) Arsenic biogeochemistry and human health risk assessment in organo-arsenical pesticide-applied acidic and alkaline soils: An incubation study. *Sci Total Environ*, **372**, 39-48.

Davis JA (1984) Complexation of trace metals by adsorbed natural organic matter. *Geochim Cosmochim Acta* **48**, 679-691.

Del Razo LN, Arellano MA, Cebrian ME (1990) The oxidation states of arsenic in well-water from a chronic arsenic area of Northern Mexico. *Environ Pollut* **64**, 143-153.

Gustafsson JP and Jacks G (1995) Arsenic geochemistry in forested soil profiles as revealed by solid-phase studies. *Appl Geochem* **10**, 307-315.

Huang JH and Matzner E (2007) Mobile arsenic species in unpolluted and polluted soils. *Sci Total Environ* **377**, 308-318.

Impellitteri CA (2004) Effects of pH and competing anions on the speciation of arsenic in fixed ionic strength solutions by solid phase extraction cartridges. *Water Res* **38**, 1207-1214.

Kim JY, Davis AP, and Kim KW (2003) Stabilization of available arsenic in highly contaminated mine tailings using iron. *Environ Sci Technol* **37**, 189-195.

Ko I, Lee SW, Kim JY, Kim KW, Lee JS, Chon HT, and Jung MC (2003) Potential impact of arsenic and heavy metals in the vicinity of the closed Au-Ag mining areas and its remediation priority. *J of Geosystem Eng* **40** (**5**), 367-378.

Ko I, Kim JY, and Kim KW (2004) Interaction in a system of arsenic, hematite and humic acid: Arsenic speciation and sorption kinetics. *Colloids Surfaces A* **234**, 43-50.

Ko I, Kim JY, and Kim KW (2005) Adsorption and size

fractionation of soil humic and fulvic acids by hematite. *Chem Spec Bioavailab* **17(2)**, 41-48.

Ko I, Davis AP, Kim JY, and Kim KW (2006) Effect of contact order on the adsorption of inorganic arsenic species onto hematite in the presence of humic acid. *J Hazard Mater* **A141(1)**, 53-60.

Laxen DPH (1985) Trace-metal adsorption coprecipitation on hydrous ferric-oxide under realistic conditions - the role of humic substances. *Water Res* **19**, 1229-1236.

Le XC, Yalcin S, and Ma M (2000) Speciation of submicrogram per liter levels of arsenic in water: on-site species separation integrated with samples collection. *Environ Sci Technol* **34**, 2342-2347.

Leenheer JA (1981) Comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural waters and wastewaters. *Environ Sci Technol* **15**, 578-587.

Malcolm RL and McCarchy P (1992) Quantitative evaluation of XAD-8 and XAD-4 resins used in tandem for removing organic solutes from water. *Environ Int* **18**, 597-608.

Manning BA and Martens DA (1997) Speciation of arsenic(III) and arsenic(V) in sediment extracts by high-performance liquid chromatography-hydride generation atomic absorption spectrophotometry. *Environ Sci Technol* **31**, 171-177.

Nickson RT, McArthur JM, Ravenscroft P, Burgess WG, and Ahmed KM (2000) Mechanism of arsenic release to groundwater, Bangladesh and West Bengal. *Appl Geochem* **15**, 403-413.

Qualls RG and Haines BL (1991) Geochemistry of dissolved organic nutrients in water percolating through a forest ecosystem. *Soil Sci Soc Am J* **55**, 1112-1123.

Redman AD, Macalady DL and Ahmann D (2002) Natural organic matter affects arsenic speciation and sorption onto hematite. *Environ Sci Technol* **36**, 2889-2896.

Seby F, Potin Gautier M, Lespès G, Astruc M (1997) Selenium speciation in soils after alkaline extraction. *Sci Total Environ* **207**, 81-90.

Smedley PS and Kinniburgh DG (2002) A review of the source, behavior and distribution of arsenic in natural waters. *Appl Geochem* **17**, 517-568.

Sposito G (1984) The surface chemistry of soils, pp. 234, Oxford Univ. Press, New York.

Stevenson FJ (1994) Humus chemistry: Genesis, composition, reactions, pp. 512, Wiley.

Thanabalasgam P and Pickering WF (1986) Arsenic sorption by humic acid. *Environ Pollut* **12**, 233-246.

Thurman EM (1985) Organic geochemistry of natural waters, pp. 497, Martinus Nijhoff/Dr W. Junk Publishers.

Yalcin S and Le XC (2001) Speciation of arsenic using solid phase extraction cartridges. *J Environ Monit* **3**, 81-85.

Yi JM, Lee JS, and Chon HT (2003) Environmental contamination and chemical speciation of arsenic in the water system from some abandoned Au-Ag mines, Korea. *J Phys IV* **107**, 761-763.