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In-situ electrochemical measurements of total concentration and speciation of heavy metals in acid mine drainage (AMD): assessment of the use of anodic stripping voltammetry

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Abstract

We assessed the use of anodic stripping voltammetry (ASV) for *in-situ* determinations of both total concentration and speciation of dissolved heavy metals (Cd, Cu, Pb and Zn) in acid mine drainage (AMD). In the Kwangyang Au–Ag mine area of South Korea, different sites with varying water chemistry within an AMD were studied with a field portable anodic stripping voltammeter. Anodic stripping voltammetry after wet oxidation (acidification) was very sensitive enough to determine total concentration of dissolved Cd because Cd was dominantly present as 'labile' species, whilst the technique was not so effective for determining total Cu especially in the downstream sites from the retention pond, due to its complexation with organic matter. For dissolved Pb, the concentrations determined by ASV after wet oxidation generally agreed with those by ICP-AES. In the downstream samples ($pH > 5$), however, ASV data after wet oxidation were lower than ICP-AES data because a significant fraction of dissolved Pb was present in those samples as 'inert' species associated with colloidal iron oxide particles. The determination of total dissolved Zn by ASV after wet oxidation appeared to be unsatisfactory for the samples with high Cu content, possibly due to the interference by the formation of Zn–Cu intermetallic compounds on the mercury coated electrode. In AMD samples with high dissolved iron, use of ultraviolet irradiation was not effective for determining total concentrations because humate destruction by UV irradiation possibly resulted in the removal of a part of dissolved heavy metals from waters through the precipitation of iron hydroxides.

Introduction

The chemical speciation measurements are needed for understanding both the metal toxicity to aquatic organisms and the metal transport in river and estuarine environments, as it is now well established that measurement of the total concentration of a heavy metal in water provides insufficient informations on its mobility and bioavailability or its interaction with sediments and suspended particulates. Many studies have reported that uptake and toxicity of dissolved heavy metals to aquatic organisms are proportional to the concentration of ‘labile’ species such as free metal ions (Florence & Batley 1980; Sunda 1994; Mota & Simoes 1996; Hudson 1998; Huang & Wang 2003).

Various techniques have been developed for measuring trace metal speciation in water, including anodic and cathodic stripping voltammetry, ion-selective electrode (ISE) analysis, ion-exchange chromatography, ultrafiltration and dialysis (Pickering 1995). However, any analytical procedure used in speciation measurements should be carefully designed to minimize contamination and adsorptive losses of the metals considered. Therefore, one ideal method to enhance data quality is the direct measurement of trace metals in the field. In this viewpoint, the application of anodic stripping voltammetry (ASV) is preferred, as this approach can be performed as soon as possible upon sampling without potential disturbance during sample storage and therefore may reduce the risk of contamination. In particular, acid mine drainage (AMD) water that contains a high concentration of iron may cause the significant loss of trace metals during transportation and storage because of the precipitation of hydrous iron oxide. ASV is also advantageous due to its selectivity, low detection limit, high accuracy and low cost, and has a high sensitivity particularly to common toxic metals such as cadmium, copper, lead and zinc (Florence 1982, 1986). The effectiveness of ASV technique for understanding chemical speciation and bioavailability of heavy metals in fresh and seawaters recently has been well documented (Nürnberg 1983; Kozelka *et al.* 1997; Kozelka & Bruland 1998; Rozan & Benoit 1999; Huang & Wang 2003). However, the capacity of ASV to determine the total dissolved metal concentration in freshwaters has been poorly validated. For example, Hall & Vaive (1992) compared the results obtained by ASV (model: PDV-2000) with those by AAS technique in determining Cd, Cu, Pb and Zn, and demonstrated that agreement between the two analytical techniques was excellent with the exception of Zn. Previous studies on the applicability of ASV to mine drainage are quite lacking, however (Yun *et al.* 2001; Achterberg *et al.* 2003; Alonso *et al.* 2004). The objectives of this study are to determine both total concentration and geochemical speciation of dissolved heavy metals (Cd, Cu, Pb and Zn) using ASV and to evaluate the applicability of ASV for *in-situ* monitoring and metal speciation studies for acid mine drainage.

Materials and methods

Site description

This study was undertaken for mine drainage samples collected from Chonam-ri Creek in an abandoned mine area at Kwangyang, South Korea (Figures 1 and 2). The Kwangyang mine was one of the most important gold–silver mines in Korea. Major ore minerals comprise about 10 vol% of the ore and consist of pyrite (FeS_2), chalcopyrite ($CuFeS_2$), pyrrhotite ($Fe_{1-x}S$), arsenopyrite (FeAsS), sphalerite (ZnS) and galena (PbS) (So *et al.* 1999). Waste rocks had been dumped in the upstream site of Chonam-ri Creek, acting as a significant source of AMD. Chonam-ri Creek is characterized by a single drainage system with a length of about 800 m flowing into Kwangyang Bay of the South Sea (Figure 2). A small retention pond had been constructed 440 m downstream from the waste dump to passively treat metal-contaminated water with limestone acting as a neutralizing agent (Yun *et al.* 2001). In that pond, yellow-brown precipitates were deposited and waterweeds were growing. The concentrations of dissolved organic matter (DOM) in Chonam-ri Creek were higher (average 1.26 mg L^{-1}) in the sites downstream from the retention pond than in those upstream (average 0.68 mg L^{-1}), possibly because of more abundant aquatic plants in retention pond.

Sampling and analysis

In July and October of 1997, May of 1998 and August of 1999, mine drainage samples were collected from Chonam-ri Creek (Figure 2). Each sample was pressure-filtered through a 0.45 μm membrane filter (acid washed) and transferred to a 1 L Nalgene bottle cleaned with acid. All collection bottles were cleansed using trace metal protocols by soaking in 10% (v/v) nitric acid (trace metal grade) for 1 week and rinsing in 18 MΩ water, then allowed to stand overnight in 18 MΩ

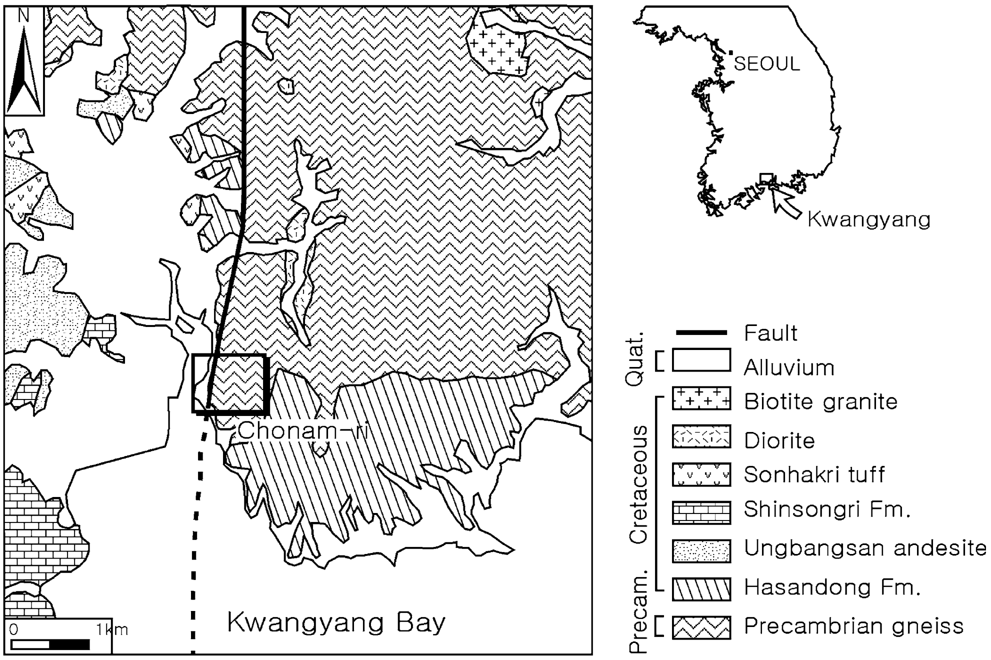

Fig. 1. Geologic map of Kwangyang area, Korea, showing the locality of Chonam-ri Creek.

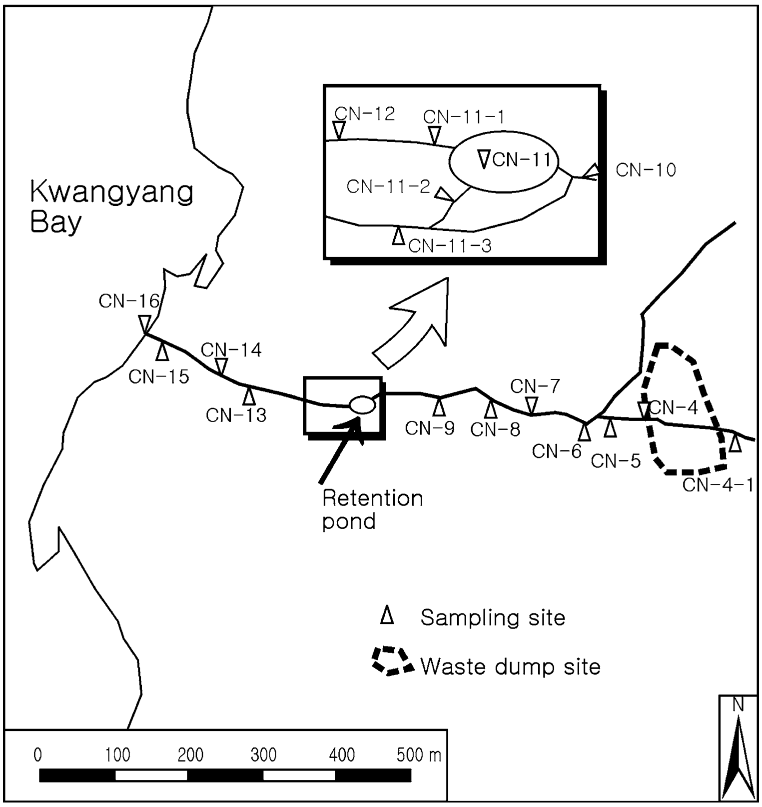

Fig. 2. Locality map showing Chonam-ri Creek sampling sites in the Kwangyang mine area.

water before sample collection. All containers were washed twice with field water before sampling. The samples were stored at 4 °C until analysis. A 50 mL aliquot of filtered sample was preserved for analysis for dissolved metals, by addition of 0.5 mL concentrated HNO_3. Water samples collected were packed in ice and transported immediately to the laboratory for chemical analyses. For the DOM analysis, total 7 samples were collected after filtration through a 0.45 μm membrane filter and analyzed by total organic carbon analyzer (model Shimadzu TOC-5000).

For all the water samples collected ($N = 38$), the concentration of 'labile' metals was determined by ASV at a natural pH. Among them, 21 water samples collected in May 1998 and August 1999 were also analyzed by ASV after wet oxidation (acidification) using concentrated nitric acid, in order to measure the concentration of 'total recoverable' dissolved metals. The inductively coupled plasma atomic emission spectrometer (ICP-AES; model Perkin-Elmer OPTIMA 3000XL) with an ultrasonic nebulizer (detection limit for Cd, Cu and Pb, Zn ≤ 1 μg L^{-1}) was also used for determining 'total' dissolved metals and for comparing the data with ASV data. In this study, 8 samples out of the total samples collected were also processed with ultraviolet (UV) irradiation after wet oxidation with concentrated HNO_3 and 0.1% H_2O_2 and then were analyzed by ASV for 'total recoverable' concentrations of heavy metals. Many organic compounds in water interfere with ASV analysis by blocking the working electrode or by binding the metals of interest in inactive compounds. The instrument used for UV irradiation was UVI-3000 (Chemtronics) designed to destroy organic compounds by ozone without diluting or denaturing the water samples.

The instrument used for all ASV measurements was a portable digital voltammeter (model TEA-3000) made by Chemtronics Co. The TEA-3000 is an electro-chemical instrument designed for trace element analysis at low levels utilizing solid and mercury-coated electrodes. The electrochemical cell consists of a glassy carbon working electrode, an Ag/AgCl reference electrode, and an auxiliary electrode. Analytical conditions used were as follows: stirrer speed, 2000 rpm; plating potential, −900 mV; plating time, 60 s; holding potential, −900 mV; holding time, 15 s; sweep rate, 375 mV s^{-1}; final potential, 100 mV; stripping time, 5 s; rest potential, −100 mV; and buffer, chloro-acetate. For a deposition time of 60 s, detection limits for Cd, Cu, Pb and Zn were 1 μg L^{-1} and the relative standard deviation (RSD) was below 5%.

Results and discussion

General water chemistry

Chonam-ri Creek water was characterized as a typical AMD with a minimum pH as low as 2.8 and very high concentrations of dissolved metals. The maximum concentrations of Cd, Cu, Pb and Zn were 590, 24,000, 109 and 64,400 μg L^{-1}, respectively (Table 1; All the metal concentration data in this table were obtained by ICP-AES with an ultrasonic nebulizer). Between site CN-4 (corresponding to the waste dump site) and site CN-10 (corresponding to the immediate upstream site from the retention pond; see Figure 2), there were progressive decreases of dissolved metal concentration with increasing pH. In particular, between CN-10 and CN-11 (retention pond site; see Figure 2), there were sudden drops of dissolved metal concentration due to pH increase resulting from the dissolution of limestone contained in the retention pond (Yun *et al.* 2001). There were two types of concentration variation within the pond (Table 1): most metals including Cd, Cu, Pb and Zn obviously decreased, whilst some constituents including Ca, Mg and HCO_3, originating from dissolution of limestone, increased.

Determination of 'total' dissolved metals

In order to evaluate the capacity of ASV for the determination of 'total recoverable' concentrations of dissolved heavy metals, wet oxidation of water samples by conc HNO_3 to the pH of 2 was performed before ASV analysis. Then, the acquired data were compared with 'total' concentrations obtained by ICP-AES analysis. The results for a total of 21 samples are summarized in Table 2. Figure 3 also shows the relationships between log 'total' dissolved metal concentrations measured by ICP-AES and those by ASV after wet oxidation.

Table 1. Physicochemical parameters, and major and trace element composition of Chonam-ri Creek water in the Kwangyang mine area, Korea.

Sample no.	Date	pH	EC (µS cm^{-1})	mg L^{-1}				µg L^{-1}						
				Ca	Mg	SO_4	HCO_3	Al	Cd	Cu	Fe	Mn	Pb	Zn
CN-4-1	Aug-99	4.2	356	35.6	nd	nd	0.0	2050	11	221	109	1110	10	2670
CN-4	Jul-97	3.4	621	43.4	24.5	314.5	0.0	5810	182	2810	2520	8130	109	22600
	Aug-99	2.8	2090	96.7	nd	nd	0.0	68500	590	24000	106000	22100	13	64400
CN-5	Jul-97	3.6	497	22.6	19.4	245.6	0.0	7490	129	2240	1240	4770	24	17000
	Oct-97	3.6	450	28.5	15.1	268.9	0.0	6630	101	2630	132	3240	16	11700
	May-98	3.3	361	27.4	10.7	145.5	0.0	5650	81	1830	570	2480	22	11200
	Aug-99	3.3	944	38.9	nd	nd	0.0	25000	158	6740	11400	6810	7	25000
CN-6	Jul-97	4.9	195	21.7	7.2	76.7	0.6	458	13	224	28	379	6	1930
	May-98	4.9	155	17.9	5.8	59.4	1.2	296	4	119	8	232	4	1310
	Aug-99	4.8	112	10.6	nd	nd	3.1	536	5	165	35	139	ND	1020
CN-7	Jul-97	4.2	366	35.9	15.4	174.8	0.0	4020	50	1030	75	2130	8	7070
	May-98	4.3	204	22.0	7.6	80.5	0.0	984	15	348	9	673	6	2890
CN-8	Jul-97	4.2	345	35.0	14.7	163.9	0.0	3260	44	908	33	1870	12	6290
	Aug-99	4.9	119	11.4	nd	nd	3.1	538	6	191	ND	175	ND	1120
CN-9	Jul-97	4.2	320	34.6	14.2	153.2	0.0	2820	40	854	49	1740	13	5800
CN-10	Oct-97	3.7	559	47.0	19.8	355.1	0.0	4260	69	1660	36	3280	27	9330
	May-98	4.5	235	23.1	7.7	90.1	0.0	980	16	397	5	701	10	2970
	Aug-99	4.8	131	12.3	nd	nd	2.3	673	6	259	7	275	ND	1400
CN-11-3	May-98	5.1	315	27.4	9.5	107.9	3.1	835	15	383	69	674	10	2840
	Aug-99	5.7	295	32.7	nd	nd	3.1	185	7	197	224	319	2	1210
CN-11	Jul-97	5.6	1085	186.0	68.0	764.4	39.7	314	9	179	10300	2130	4	1260
	Oct-97	5.4	1071	120.4	51.2	580.0	88.5	182	6	141	4240	1360	3	920
	May-98	5.8	864	112.0	40.2	442.8	42.8	245	10	222	3490	1550	7	1950
	Aug-99	6.0	688	120.0	nd	nd	25.9	142	6	150	1410	741	ND	956
CN-11-1	May-98	6.1	980	155.4	54.5	550.8	53.7	124	5	116	5220	1930	6	1270
	Aug-99	6.2	866	168.0	nd	nd	51.9	43	5	76	2230	839	ND	700
CN-11-2	Aug-99	6.4	857	166.0	nd	nd	48.8	25	5	55	1730	836	ND	660
CN-12	Jul-97	6.4	1024	169.5	62.5	673.5	44.5	43	8	77	4850	1690	3	1250
	Oct-97	6.5	1019	118.6	50.2	578.3	56.4	30	5	70	2250	1210	2	760
	May-98	6.4	1065	161.2	55.1	472.3	49.2	49	4	54	3360	1690	8	1120
CN-13	Jul-97	6.7	1002	168.0	62.5	661.6	28.7	35	7	5	993	1620	3	1100
CN-14	Jul-97	6.7	996	160.0	60.0	660.6	38.4	33	7	4	419	1620	3	1040
	Aug-99	6.5	611	111.0	nd	nd	30.5	18	6	87	830	628	ND	897
CN-15	Jul-97	7.0	995	165.0	61.5	661.0	25.6	45	6	2	47	1610	ND	918
	May-98	7.0	820	109.0	41.3	369.1	36.6	44	5	6	35	1130	5	1190
CN-16	Jul-97	7.0	1016	166.5	64.5	666.1	25.5	50	6	2	8	1590	1	819
	Oct-97	7.2	17530	426.7	1005.4	992.3	47.6	60	1	7	59	248	12	234
	Aug-99	7.0	581	102.0	nd	nd	25.9	18	5	1	ND	517	ND	717

nd = not determined, ND = below detection limits (1 µg L^{-1}).

Cadmium

Agreement between the two analytical techniques was excellent for Cd with the exceptions of a few sites (Table 2). The average ratio of ASV/ICP-AES for total water samples was 0.99. The average ASV/ICP-AES ratio (1.08) for water samples in the downstream sites from a retention pond was similar to that (0.92) for the sample from the upstream sites. The following regression equation was obtained for the relationship between log 'total' dissolved Cd concentrations measured by ICP-AES and those by ASV after wet oxidation (Figure 3A):

$$\text{Log`total' Cd (ASV)} = 0.97 \times \text{log`total' Cd (ICP-AES)}; \quad (95\%\ \text{confidence limits}: 0.94 < \text{X variance} < 1.01) \qquad (1)$$

The R^2 value for the regression was 0.973 ($N = 21$), suggesting that the ASV technique after

Table 2. Comparison of 'total' metal concentrations (μg L^{-1}) analyzed by ASV (after wet oxidation) with those by ICP for Chonam-ri Creek water samples.

Sample no.	Date	pH	Cd			Cu			Pb			Zn		
			ICP	ASV	ASV/ICP	ICP	ASV	ASV/ICP	ICP	ASV	ASV/ICP	ICP	ASV	ASV/ICP
CN-4-1	Aug-99	4.2	11	10	0.91	221	208	0.94	10	10	1.00	2670	1700	0.64
CN-4	Aug-99	2.8	590	500	0.85	24000	18400	0.77	13	11	0.85	64400	32000	0.50
CN-5	May-98	3.3	81	80	0.99	1830	1620	0.89	22	23	1.05	11200	7930	0.71
	Aug-99	3.3	158	100	0.63	6740	4800	0.71	7	5	0.71	25000	14400	0.58
CN-6	May-98	4.9	4	4	1.00	119	114	0.96	4	3	0.75	1310	930	0.71
	Aug-99	4.8	5	5	1.00	165	142	0.86	ND	ND	nd	1020	690	0.68
CN-7	May-98	4.3	15	14	0.93	348	280	0.80	6	4	0.67	2890	1690	0.58
CN-8	Aug-99	4.9	6	4	0.67	191	170	0.89	ND	ND	nd	1120	680	0.61
CN-10	May-98	4.5	16	16	1.00	397	360	0.91	10	10	1.00	2970	2100	0.71
	Aug-99	4.8	6	6	1.00	259	240	0.93	ND	ND	nd	1400	790	0.56
CN-11-3	May-98	5.1	15	13	0.87	383	282	0.74	10	11	1.10	2840	1860	0.65
	Aug-99	5.7	7	8	1.14	197	209	1.06	2	2	1.00	1210	800	0.66
CN-11	May-98	5.8	10	14	1.40	222	232	1.05	7	10	1.43	1950	2000	1.03
	Aug-99	6.0	6	6	1.00	150	142	0.95	ND	ND	nd	956	660	0.69
CN-11-1	May-98	6.1	5	6	1.20	116	46	0.40	6	4	0.67	1270	980	0.77
	Aug-99	6.2	5	4	0.80	76	20	0.26	ND	ND	nd	696	560	0.80
CN-11-2	Aug-99	6.4	5	4	0.80	55	7	0.13	ND	ND	nd	660	280	0.42
CN-12	May-98	6.4	4	6	1.50	54	12	0.22	8	ND	0.00	1120	900	0.80
CN-14	Aug-99	6.5	6	6	1.00	87	19	0.22	ND	ND	nd	897	710	0.79
CN-15	May-98	7.0	5	6	1.20	6	6	1.00	5	2	0.40	1190	920	0.77
CN-16	Aug-99	7.0	5	4	0.80	10	8	0.80	ND	ND	nd	717	570	0.79
Average (upstream from pond)					0.92			0.87			0.90			0.63
Average (downstream from pond)					1.08			0.56			0.62			0.76
Total average					0.99			0.74			0.82			0.69

nd = not determined, ND = below detection limits (1 μg L^{-1}).

wet oxidation was sufficiently sensitive for a direct determination of Cd in the field. However, the actual difference between ICP-AES and ASV analyses became wider (>50 μg L^{-1}) at concentrations higher than 100 μg L^{-1}. The optimistic calibration range for ASV analysis is below 100 μg L^{-1}. Therefore, we consider that if the concentration of Cd is less than 100 μg L^{-1}, ASV measurement for Cd in AMD samples in the field is more suitable than ICP-AES measurement because of the lower risk of contamination or trace element losses due to simpler analytical procedures.

Copper

The average ratio of ASV/ICP-AES for 'total' Cu concentration was 0.74 (Table 2). Agreement between the two analytical techniques for Cu was fairly good in the upstream sites from the retention pond (ratio = 0.87), but was not satisfactory in the downstream sites (ratio = 0.56) where dissolved organic matter (DOM) was relatively more abundant (1.26 mg L^{-1}, downstream; 0.68 mg L^{-1}, upstream). This result suggests that the ASV technique after wet oxidation is quite effective for direct determination of dissolved Cu in AMD waters with low pH and low DOM content, such as that found in the upstream sites from the retention pond. However, this technique is not effective and erroneous for AMD waters with high pH and high DOM content, as found in sites downstream sites, because wet oxidation is not capable of breaking down strong Cu-organic complexes. Sholkovitz (1978) also demonstrated that oxidation of fresh water samples can even considerably decrease the dissolved Cu because acidification for preservation may lead to the precipitation of humic materials. From the relationship between 'total' Cu concentrations measured by ICP-AES and those by ASV after wet oxidation, the following equation was obtained (Figure 3B):

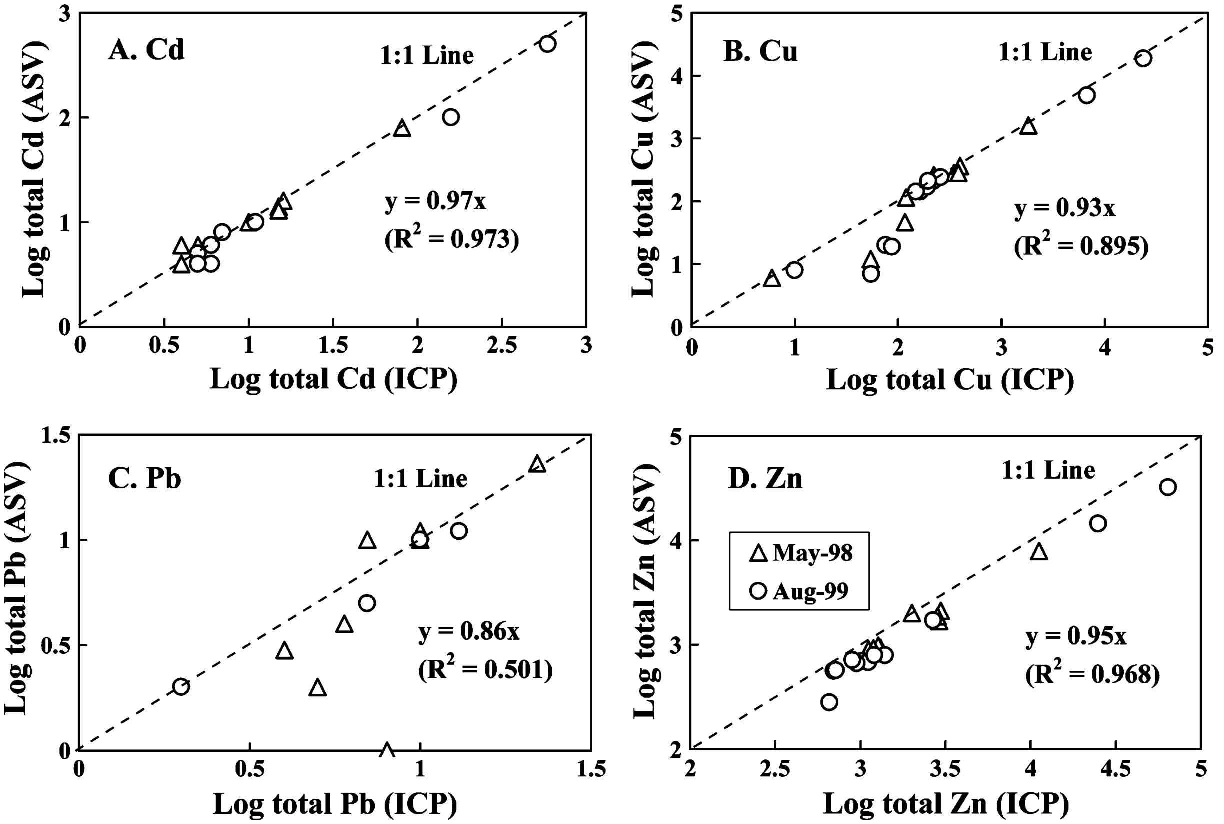

Fig. 3. Comparison of 'total' metal concentrations (μg L^{-1}) analyzed by ASV after wet oxidation (acidification) with those by ICP-AES for Chonam-ri Creek water samples.

$$\text{Log`total'Cu(ASV)} = 0.93 \times \text{log`total'Cu(ICP-AES)}; \quad (95\%\ \text{confidence limits}: 0.88 < X\ \text{variance} < 0.99) \tag{2}$$

The R^2 for the regression was 0.895 ($N = 21$). We consider that Cu's relatively lower slope than Cd resulted from the decrease of ASV peaks due to a high fraction of organic complexes in the downstream sites from the retention pond.

Among the samples collected from the upstream sites, however, the ASV/ICP-AES ratios appeared to be slightly lower (0.71–0.89) for the samples (CN-4, CN-5) with very high concentrations of 'total' dissolved Cu (>1830 μg L^{-1}) than those for the samples (CN-4-1 and CN-6 to CN-10) with a relatively low Cu content (<400 μg L^{-1}; Table 2). This possibly resulted from an analytical error caused by high dilution for the samples with high Cu concentrations. We also should note that the ratios for the samples with low ASV concentrations (<360 μg L^{-1}) were close to unity. Consequently ASV may be suitable only for samples with concentrations less than 360 μg L^{-1}.

Lead

The concentration of dissolved Pb in Chonam-ri Creek was much lower than those of other metals (Table 2). Agreement between the two analytical techniques (ICP-AES and ASV) was comparatively good for Pb (average ratio = 0.82). Figure 3C shows the relationship between log 'total' Pb concentrations measured by ICP-AES and those by ASV after wet oxidation. The following regression equation was obtained:

$$\text{Log`total'Pb(ASV)} = 0.86 \times \text{log`total'Pb(ICP-AES)}; \quad (95\%\ \text{confidence limits}: 0.68 < X\ \text{variance} < 1.05) \tag{3}$$

However, the R^2 for the regression was relatively low (0.501; $N = 13$). The average ASV/ICP-AES ratio was lower for the downstream samples (0.62; Table 2) than those for the upstream samples (0.90). These observations possibly indicate that a significant fraction of dissolved Pb was present as 'inert' species associated with colloidal iron oxide particles and/or occurring as organic complexes. However, we consider that colloidal iron oxide particles played more important role to control the behavior of dissolved Pb in the downstream sites, because (1) Pb generally has a strong tendency to be adsorbed onto colloidal Fe oxides and (2) however, dissolved iron cannot be effectively separated from colloidal iron by a routine filtration technique using a 0.45 μm membrane filter (Florence 1986; Fox 1988). Geochemical modeling (Yun *et al.* 2001) and field observations (Jung *et al.* 2005) also demonstrated that waters from the downstream sites from the retention pond in Chonam-ri Creek were supersaturated with respect to goethite, which was likely present as colloidal particles. Therefore, we consider that the use of a filter small (<0.45 μm) enough to eliminate colloidal Fe particles was necessary to determine the exact fraction of dissolved Pb, especially in an AMD environment with a high content of dissolved Fe.

Zinc

The relationship between 'total' dissolved Zn concentrations determined by ASV after wet oxidation and those by ICP-AES was represented by the regression equation (Figure 3D):

$$\begin{aligned}&\text{Log'total'Zn(ASV)} = 0.95\times\\&\text{log'total'Zn(ICP-AES);}\\&(95\%\,\text{confidence limits:}\,0.94 < \text{X variance} < 0.96)\end{aligned}\tag{4}$$

The R^2 for the regression was high (0.968; $N = 21$). The 'total' Zn concentrations determined by ASV after wet oxidation were consistently slightly lower than those by ICP-AES (Figure 3D). The average ratio of ASV/ICP-AES for 'total' Zn concentration was also relatively low (0.69), compared to the other metals examined (Table 2).

Two explanations are possible for the low ASV/ICP-AES ratio for Zn. Firstly, the lower ratio might have resulted from a greater analytical error potentially owing to higher degree of sample dilution, because very high concentrations of Zn (660–64,400 μg L^{-1} in ICP-AES data) required substantial dilution to its optimum detection level in ASV (below 100 μg L^{-1} in the cell). However, repeated experiments of dilution and analysis indicated that this possibility was negligible (if present) for Chonam-ri Creek AMD. Secondly, the formation of a Zn–Cu intermetallic compound could decrease the detection of Zn by ASV. It is noteworthy that agreement between the two analytical techniques for Zn was better for the downstream samples (ratio = 0.76) than for the upstream samples (ratio = 0.63; Table 2). The upstream samples were more enriched in dissolved Cu (from 119 to 24,000 μg L^{-1}). Thus, we consider that a relatively lower ASV/ICP-AES ratio for more Cu-rich upstream samples probably resulted from the interference caused by the formation of a Zn–Cu intermetallic compound on the mercury coated electrode. The intermetallic compound formation between Zn and Cu in ASV and other potentiometric stripping analyses has been recognized as a classic interference case by many researchers; Copeland *et al.* (1974) first recognized that the reduction of the Zn oxidation signal was due to the formation of a Zn–Cu intermetallic compound in the Hg film of the working electrode. The above result suggests that the ASV technique is not suitable for determining 'total' dissolved Zn in AMD with high concentrations of dissolved Zn and Cu. However, Copeland *et al.* (1974) and Obiols *et al.* (1988) suggested that the addition of Ga into such samples would negate the interference of Cu on Zn by preferential formation of the more stable Ga–Cu compounds on the mercury coated electrode.

Determination of the speciation of dissolved heavy metals

As described above, *in-situ* ASV technique may reduce the risk of disturbance of the chemical equilibria (and speciation) during sample storage. If the AMD sample was analyzed at a natural pH after simple pretreatments such as filtering and dilution in the field, therefore, the 'labile' fraction of metal could be easily determined. The

Table 3. Comparison of 'labile' metal concentrations analyzed by ASV (at a natural pH) with 'total' metal concentrations by ICP for water samples (unit: µg L^{-1}).

Sample no.	Date	pH	Cd			Cu			Pb			Zn		
			ICP	ASV	ASV/ICP	ICP	ASV	ASV/ICP	ICP	ASV	ASV/ICP	ICP	ASV	ASV/ICP
CN-4-1	Aug-99	4.2	11	10	0.91	221	208	0.94	10	8	0.80	2670	1700	0.64
CN-4	Jul-97	3.4	182	110	0.60	2810	2400	0.85	109	50	0.46	22600	18000	0.80
	Aug-99	2.8	590	500	0.85	24000	18200	0.76	13	ND	0.00	64400	29000	0.45
CN-5	Jul-97	3.6	129	110	0.85	2240	1900	0.85	24	9	0.38	17000	13400	0.79
	Oct-97	3.6	101	70	0.69	2630	1620	0.62	16	15	0.94	11700	10500	0.90
	May-98	3.3	81	80	0.99	1830	1630	0.89	22	22	1.00	11200	7930	0.71
	Aug-99	3.3	158	100	0.63	6740	4800	0.71	7	ND	0.00	25000	14300	0.57
CN-6	Jul-97	4.9	13	12	0.92	224	150	0.67	6	5	0.83	1930	1500	0.78
	May-98	4.9	4	4	1.00	119	82	0.69	4	ND	0.00	1310	910	0.69
	Aug-99	4.8	5	4	0.80	165	138	0.84	ND	ND	nd	1020	660	0.65
CN-7	Jul-97	4.2	50	32	0.64	1030	690	0.67	8	6	0.75	7070	5500	0.78
	May-98	4.3	15	10	0.67	348	220	0.63	6	ND	0.00	2890	1600	0.55
CN-8	Jul-97	4.2	44	30	0.68	908	710	0.78	12	10	0.83	6290	4800	0.76
	Aug-99	4.9	6	4	0.67	191	156	0.82	ND	ND	nd	1120	670	0.60
CN-9	Jul-97	4.2	40	36	0.90	854	740	0.87	13	13	1.00	5800	4500	0.78
CN-10	Oct-97	4.1	69	40	0.58	1660	990	0.60	27	5	0.19	9330	8450	0.91
	May-98	4.5	16	12	0.75	397	292	0.74	10	8	0.80	2970	2100	0.71
	Aug-99	4.8	6	6	1.00	259	234	0.90	ND	ND	nd	1400	790	0.56
CN-11-3	May-98	5.1	15	12	0.80	383	260	0.68	10	ND	0.00	2840	1830	0.64
	Aug-99	5.7	7	6	0.86	197	196	0.99	2	ND	0.00	1210	800	0.66
CN-11	Jul-97	5.6	9	9	1.00	179	2	0.01	4	2	0.50	1260	930	0.74
	Oct-97	5.4	6	6	1.00	141	ND	0.00	3	ND	0.00	920	920	1.00
	May-98	5.8	10	10	1.00	222	232	1.05	7	ND	0.00	1950	2000	1.03
	Aug-99	6.0	6	4	0.67	150	98	0.65	ND	ND	nd	956	690	0.72
CN-11-1	May-98	6.1	5	5	1.00	116	24	0.21	6	ND	0.00	1270	927	0.73
	Aug-99	6.2	5	4	0.80	76	16	0.21	ND	ND	nd	700	560	0.80
CN-11-2	Aug-99	6.4	5	2	0.40	55	ND	0.00	ND	ND	nd	660	280	0.42
CN-12	Jul-97	6.4	8	6	0.75	77	ND	0.00	3	ND	0.00	1250	910	0.73
	Oct-97	6.5	5	5	1.00	70	ND	0.00	2	ND	0.00	760	670	0.88
	May-98	6.4	4	4	1.00	54	ND	0.00	8	ND	0.00	1120	850	0.76
CN-13	Jul-97	6.7	7	6	0.86	5	ND	0.00	3	ND	0.00	1100	870	0.79
CN-14	Jul-97	6.7	7	6	0.86	4	ND	0.00	3	ND	0.00	1040	840	0.81
	Aug-99	6.5	6	4	0.67	87	14	0.16	ND	ND	nd	897	640	0.71
CN-15	Jul-97	7.0	6	5	0.83	2	ND	0.00	ND	ND	nd	918	750	0.82
	May-98	7.0	5	4	0.80	6	ND	0.00	5	ND	0.00	1190	880	0.74
CN-16	Jul-97	7.0	6	5	0.83	2	ND	0.00	1	ND	0.00	819	680	0.83
	Oct-97	7.2	1	1	1.00	7	ND	0.00	12	ND	0.00	234	34	0.15
	Aug-99	7.0	5	3	0.60	1	ND	0.00	ND	ND	nd	717	530	0.74
Average (upstream from pond)					0.79			0.77			0.47			0.70
Average (downstream from pond)					0.84			0.13			0.04			0.74
Total average					0.81			0.47			0.29			0.72

nd = not determined, ND = below detection limits (1 µg L^{-1}).

concentrations of dissolved 'labile' metals in Chonam-ri Creek AMD samples ($N = 38$) are summarized in Table 3. This table also shows the comparison of ASV data with ICP-AES data. Figure 4 shows the relationships between log 'total' dissolved metal concentrations measured by ICP-AES and log 'labile' metal concentrations measured by ASV at a natural pH (without wet oxidation).

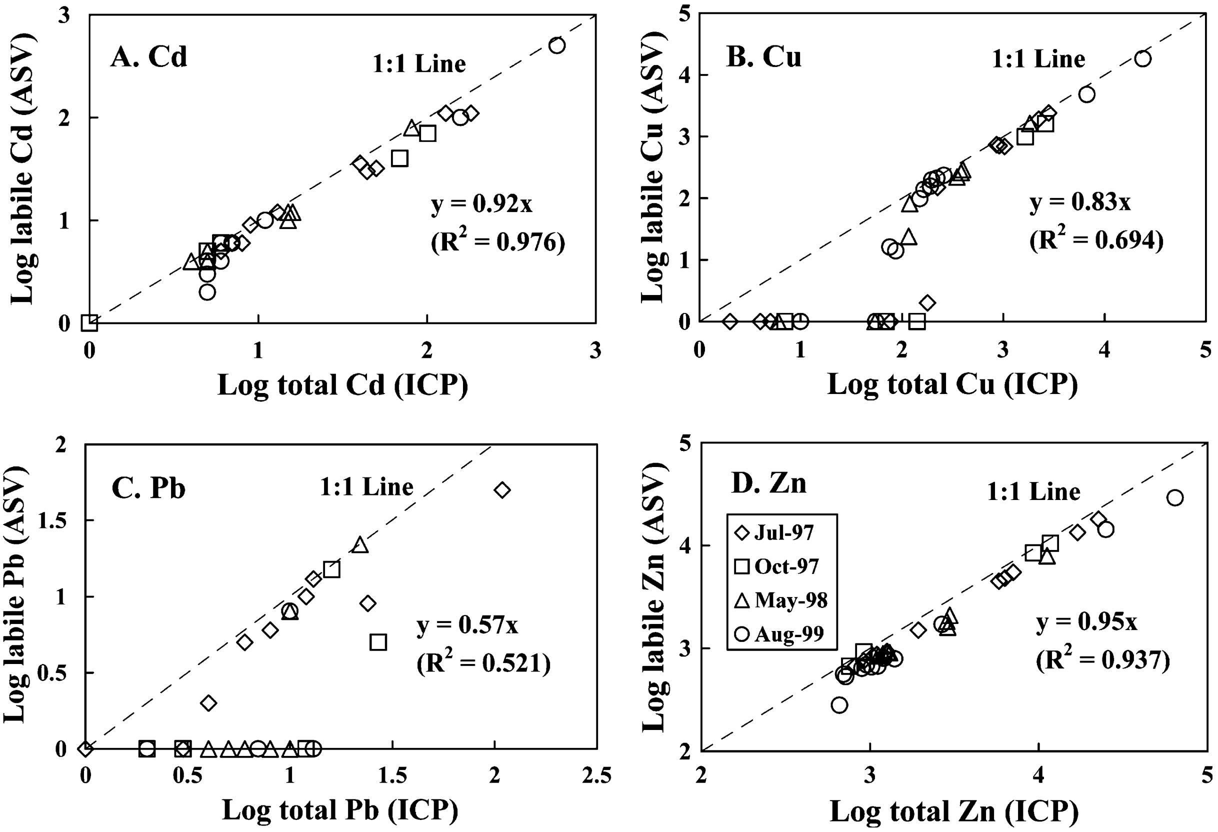

Fig. 4. Comparison of 'labile' metal concentrations (µg L^{-1}) analyzed by ASV (at a natural pH) with 'total' metal concentrations by ICP-AES for Chonam-ri Creek water samples.

Cadmium

The ratio of the 'labile' Cd concentration determined by ASV (at a natural pH) to 'total' Cd concentration determined by ICP-AES indicated that an average of 81% of Cd was present as 'labile' fractions in Chonam-ri Creek AMD samples (Table 3). From an experimental measurement of the speciation of Cd in fresh water, Florence (1977) also demonstrated that 70–90% Cd was present as free hydrated ions or other 'labile' complexes. It is also noteworthy that the fractions of 'labile' Cd (0.58–1.00, average = 0.81) are not significantly different from the ratios of ASV/ICP-AES for 'total' Cd concentration (0.63–1.50, average 0.99; Table 2). This may indicate that noncomplexed Cd ions dominated in the pH range observed in Chonam-ri Creek. We consider that less than 20% of dissolved Cd was present as 'non-labile' complexes. The following regression equation was obtained for the relationship between 'labile' Cd's concentration and 'total' Cd's concentration (Figure 4A):

$$\text{Log`labile'Cd(ASV)} = 0.92 \times \text{log`total'Cd(ICP-AES)}; \quad (95\% \text{ confidence limits}: 0.90 < X \text{variance} < 0.95) \qquad (5)$$

The R^2 for the regression was 0.976 ($N = 38$). This relationship clearly indicates that dissolved Cd was mostly present as 'labile' fractions in the whole range of Chonam-ri Creek.

Copper

Unlike Cd, a number of previous studies have demonstrated that more than 80% (and often as much as 99%) of dissolved Cu in surface waters is organically complexed (Florence, 1977; Donat *et al.* 1994; Rozan & Benoit 1999). In the whole range of Chonam-ri Creek, an average of 53% of dissolved Cu was likely present as electrochemically 'inert' species such as organic Cu complexes (Table 3). The average proportion of 'inert' species among dissolved Cu was 23% for the samples of the upstream sites from the retention pond, while the value was 87% for the samples from the downstream sites where the pH was neutral and dissolved organic matter was relatively abundant (1.26 mg L^{-1}, upstream; 0.68 mg L^{-1}, downstream). The following regression equation was obtained for the relationship between 'labile' concentration and 'total' concentration (Figure 4B):

$$\begin{aligned}&\text{Log 'labile' Cu (ASV)} = 0.83 \times\\&\text{log 'total' Cu (ICP-AES);}\\&(95\%\ \text{confidence limits: } 0.72 < \text{X variance} < 0.93)\end{aligned} \tag{6}$$

The R^2 for the regression was low (0.694; $N = 38$), however.

The slope and R^2 value for Equation (6) are smaller than those for the Equation (2) (0.93 and 0.895, respectively; Figure 3B) on the relationship between 'total' concentrations by ASV after wet oxidation and those by ICP-AES. Such smaller slope and R^2 values resulted from a substantial reduction of the 'labile' concentration of Cu in the downstream sites (Figure 4B), due to the formation of organically complexed, 'inert' Cu species preferentially in those sites. This explanation is also supported by the lower average value (0.13; Table 3) of 'labile' Cu/'total' Cu ratios observed for the downstream samples. In the upstream sites from the retention pond where pH was low (< 5), on the contrary, the average value of 'labile' Cu/'total' Cu ratios was higher (0.77; Table 3) and was similar to the average value (0.87; Table 2) of the 'total recoverable' Cu (by ASV after wet oxidation)/'total' Cu (by ICP-AES) ratios. Therefore, dissolved Cu in the upstream samples was dominated by 'labile' species.

Conclusively, the concentrations of 'inert' dissolved Cu were higher in the downstream sites of Chonam-ri Creek. However, we also should note that a large proportion of the 'inert' Cu species in the downstream samples could be easily converted to 'labile' species by wet oxidation, as suggested by the increased average value (0.56; Table 2) of the 'total recoverable' Cu (by ASV after wet oxidation)/'total' Cu (by ICP-AES) ratios compared to the average 'labile' Cu/'total' ratio (0.13; Table 3) for the downstream samples.

Lead

In case of Pb, no 'labile' fraction was detected by ASV in almost all the samples from the downstream sites with $pH > 5$ (Table 3), except in a sample CN-11 (Jul-97). As described above, this phenomenon was probably due to the strong affinity of dissolved Pb onto colloidal iron oxide particles (Batley & Gardner 1978; Florence 1986; Jensen *et al.* 1999). As was actually observed in Chonam-ri Creek, the calculation of saturation indices (SI) also predicted that goethite was slightly supersaturated with respect to the waters below the retention pond (Yun *et al.* 2001). On the other hand, an average of 47% of dissolved Pb was present as 'labile' species in the samples from the upstream sites where pH was typically acidic (Table 3). The following equation was obtained for the relationship between 'labile' concentration and 'total' concentration in the total samples examined (Figure 4C):

$$\begin{aligned}&\text{Log 'labile' Pb (ASV)} = 0.57 \times\\&\text{log 'total' Pb (ICP-AES);}\\&(95\%\ \text{confidence limits: } 0.43 < \text{X variance} < 0.71)\end{aligned} \tag{7}$$

The slope and R^2 values for the regression were very low (0.57 and 0.521, respectively), owing to a substantial reduction of the 'labile' concentration in the downstream sites.

Like Cu, however, wet oxidation easily could change the 'inert' Pb species (if present) to the 'labile' species, as indicated by a high average value (0.82; Table 2) of the 'total recoverable' Cu/'total' Cu ratios. We consider that for a Fe-rich AMD water, wet oxidation could dissolve even the Pb associated with small-sized (< 0.45 μm), colloidal iron oxide particles and therefore could result in excessive 'total recoverable' concentrations of Pb.

Zinc

The ASV measurement of Chonam-ri Creek waters showed that an average of 72% of Zn was present as 'labile' species (Table 3). Table 3 also shows that the average ASV/ICP ratio was not different between the upstream (0.70) and downstream samples (0.74). The average fraction of 'labile' Zn was slightly higher in Chonam-ri Creek than those generally reported in previous studies [e.g., about 50% in seawater and river water by Florence (1989); 26–68% with a mean of 45% in estuarine water by Baeyens *et al.* (1998)]. This could result from the lower pH (and thus the larger proportion of 'labile' Zn) in Chonam-ri AMD water. The relationship between 'labile' Zn by ASV and 'total' Zn by ICP-AES was (Figure 4D):

$$\text{Log 'labile' Zn (ASV)} = 0.95 \times \text{log 'total' Zn (ICP-AES)}; \quad (95\%\ \text{confidence limits}: 0.94 < \text{X variance} < 0.97) \tag{8}$$

The R^2 for the regression was 0.937 ($N = 38$). The slope of Equation (8) was identical to that (0.95) of Equation (3). The average value (0.72; Table 3) of 'labile' Zn/'total' Zn ratios was almost equal to that (0.69; Table 2) of the 'total recoverable' Zn (by ASV after wet oxidation)/'total' Zn (by ICP-AES) ratios. These results may indicate that even with wet oxidation used in this study, ASV did not give a reliable indication of the total concentration of Zn in Chonam-ri Creek.

Effectiveness of ultraviolet irradiation for determining 'total' dissolved metals

For the determination of organically-bound metals in natural water, only a limited number of methods have been generally used. These are ion exchange and solvent extraction, ozone oxidation, and ultraviolet (UV) oxidation. Among them, the destruction of organic matter by UV irradiation at a natural pH has been used most frequently (Donat & Bruland 1990; Gerringa *et al.* 1996). In this study, we tested the efficiency of UV irradiation to obtain 'total recoverable' metal concentrations in AMD samples. Our results showed that the ASV data before and after UV irradiation were not significantly different in most samples, except only two samples (CN-5 and CN-11-1), which showed somewhat higher metal concentrations after UV irradiation (Figure 5). Similarly, many other studies reported that UV irradiation is not capable of destroying all organic matters in natural water (Florence 1977; Laxen & Harrison 1981). Laxen and Harrison (1981) also demonstrated that in some cases, destruction of humate in natural water by UV irradiation may lead to the precipitation of hydrous iron oxides so that dissolved Cu, Pb, Cd and Zn can be rather underestimated. Therefore, the significant loss of dissolved metal by the enhanced precipitation of hydrous iron oxides after UV irradiation is expected especially for a sample containing abundant dissolved iron, like the Chonam-ri Creek AMD. We suggest that UV irradiation is not suitable for determining both total concentration and speciation of dissolved metals in Fe-rich AMD water.

Conclusions

By comparing the data obtained by ASV after wet oxidation with those by ICP-AES with an ultrasonic nebulizer, we found that the two analytical results for dissolved Cd agreed well each other. In case of Cu, agreement between the two techniques was relatively good for the samples of the upstream sites from the retention pond. However, the agreement for Cu was low in the downstream samples from the pond, probably due to the existence of strong Cu-organic complexes. For Zn, agreement between the two analytical results was unsatisfactory, possibly due to the interference in ASV measurement by the formation of a Zn–Cu intermetallic compound on the mercury coated electrode especially in Cu-rich water. The two analytical results generally agreed well each other for Pb concentration in the upstream sites from the pond. However, lower ASV/ICP-AES ratios were found in the downstream sites from the pond suggesting that in the downstream sites a significant fraction of Pb was associated with iron-oxide colloidal particles.

In order to determine 'labile' concentrations of heavy metals in mine drainage samples, we also performed ASV analysis at a natural pH. The 'labile' concentration data were compared to the 'total' concentration data obtained by ICP-AES, in order to estimate the chemical speciation of a heavy metal and to evaluate the efficiency of wet oxidation for destroying dissolved 'inert' species. Our results showed that an average of 81% of 'total' dissolved Cd was present as 'labile' species in Chonam-ri Creek; however, most of the 'inert' Cd species (less than 20%) were effectively destroyed by wet oxidation. For Cu, wet oxidation to determine total

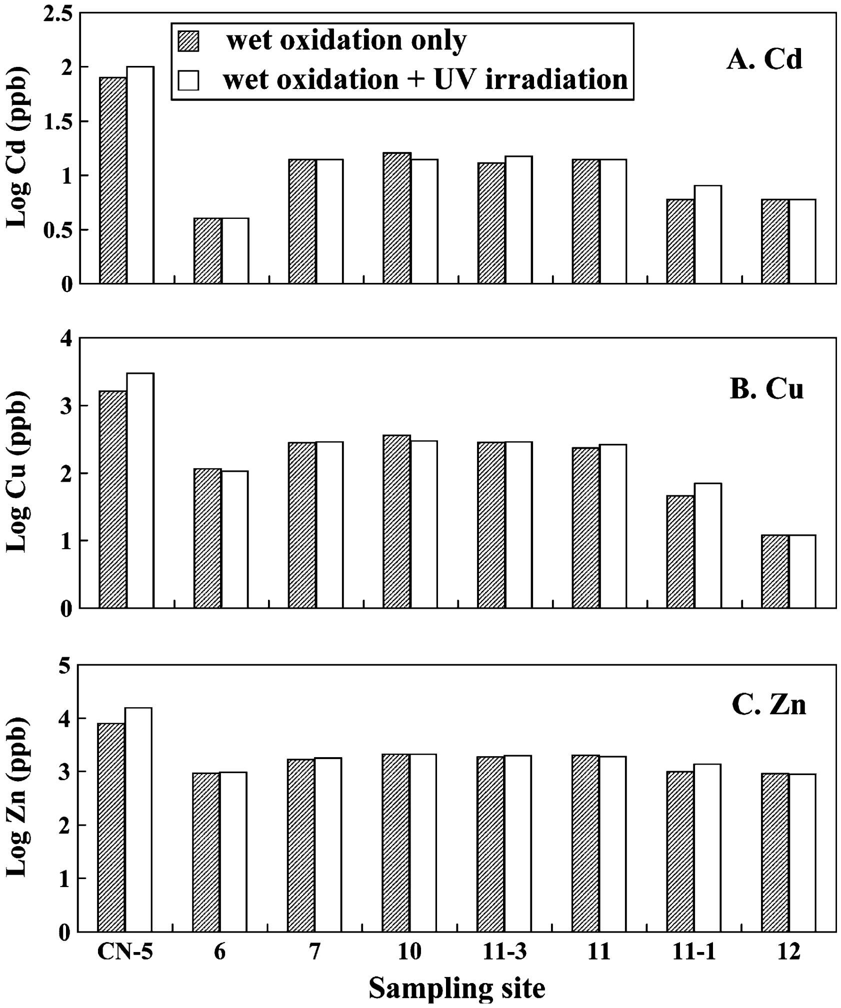

Fig. 5. Comparison of ASV data after wet oxidation with those after wet oxidation and successive UV irradiation.

concentration was effective for samples from the upstream sites where pH was typically low ($pH < 5$). On the other hand, less than 60% of the 'total' Cu concentration measured by ICP-AES was determined for the downstream samples by ASV after wet oxidation because more than 80% of dissolved Cu was present as 'inert' organic complexes in those waters. ASV measurement showed that an average of 72% of dissolved Zn was present as 'labile' species; however, the Zn concentration data obtained by ASV after wet oxidation were similar to those obtained by ASV at a natural pH, suggesting that wet oxidation was unsatisfactory to obtain 'total' Zn concentration. For Pb, 'labile' species were not detected by ASV in the downstream samples with $pH > 5$, probably because Pb existed as a form associated mainly with colloidal iron oxides particles in the downstream sites from the retention pond.

The application of UV irradiation before ASV analysis was shown to be not effective for determining 'total recoverable' metals in mine drainage samples, because UV irradiation possibly caused the loss of dissolved metals due to the destruction of humate accompanying the precipitation of hydrous iron oxide. We consider that for Fe-rich AMD samples like Chonam-ri Creek, UV irradiation is not adequate and should be used carefully.

Conclusively, we considered that ASV is generally suitable for *in-situ* determination of the total concentration and chemical speciation of heavy metals (Cd, Cu and Pb) with the exception of Zn in typical AMD samples, because of its low detection limits, modest cost, easy handling and portability.

However, we should be aware of a few limits of the instrument, which include the potential interferences by organic complexation (especially for Cu), formation of intermetallic Zn–Cu compounds (especially for Zn) on the mercury coated electrode, and formation of colloidal iron oxides particles (especially for Pb).

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