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Acid Mine Drainage and Heavy Metal Contamination of Stream Sediments in the Okdongcheon Stream, Sangdong Area, South Korea

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ABSTRACT: Geochemical investigations based on measurements of water parameters and sampling of stream sediments have been carried out, in the Okdongcheon stream and its tributaries in the Sangdong area of South Korea. There are two main problems occurring in the Okdongcheon stream: an acid mine drainage in the upper reaches and toxic trace metal contamination of the stream sediments mainly in the lower reaches.

Acid mine water originating from coal mining was neutralized at the confluence of the Cheonpyongcheon stream whilst suspended solids due to flocculation of iron in water caused turbidity which was undesirable. Sediments in the Okdongcheon stream have been contaminated by mining activites. Iron was heavily concentrated in sediments in the upper Okdongcheon whilst toxic trace metals including Pb, Cu, Zn, Co, Cd, As and Bi were accumulated in sediments at stations draining metallic mining areas and near the tailings dam.

There is now a requrement to neutralise the acid mine drainage and to use site-specific analysis of biological communities to ensure the conservation and preservation of aquatic organisms.

INTRODUCTION

Mining activity can range from scarcely perceptible to highly obstructive and the nature of the impact can vary widely depending upon the mineral worked, the benificiation process, the method of mining and the characteristics of the mine site and its surrounding hydrogeology. Among the specific pollution problems arising from mining activity are heavy metal contamination, acid mine drainage (AMD), suspended solids, deoxygenation and eutrophication. These are recognised as the most serious water pollution situations to be associated with mining and are thought to of large risk to the aquatic environment (Koryak et al., 1972; Down and Stocks, 1978; Clark and Crawshaw, 1979; Kelly, 1988; UNEP, 1991).

It appears that a large portion of the metallic compounds discharged in effluents is ultimately incorporated into sediments. However metals are not necessarily fixed permanantly by sediments, but may be recycled via mechanical, biological and chemical processes, both within the sedimentary compartment and also back into the water column (Lion et al., 1982; Johnson, 1986; Tessier and Campbell, 1988). Therefore, sediments are important carriers of trace metals in the hydrological cycle and, depending on environmental conditions, can represent a sink or a source for trace metals in the fluvial system. In addition, they are an important component of aquatic ecosystems because of the niche they provide for benthic aquatic organisms. Contaminated sediments, from non point sources, are thought to be one of the largest risks to the aquatic environment, and they must be given serious consideration in the planning, design of any water quality study, as well as in the utilization and disposal of wastes (Baudo and Muntau 1990; Horowitz, 1991; Burton, 1992).

In the present study, stream sediments and suspended solids were sampled from a stream draining mineralised catchment areas with tungsten-molybdenum, copper-iron and tin mineralisation and a coal mining area in the Sangdong district located in the middle eastern part of South Korea. The study is focused upon the degree of contamination of sediments by toxic metals and water quality affected by AMD. The toxic metal contamination and the description of AMD provide information to establish programms for the prevention of contamination in aquatic environments and for the development of treatments for AMD.

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DESCRIPTION OF THE STUDY AREA

The study area in the Sangdong region is located

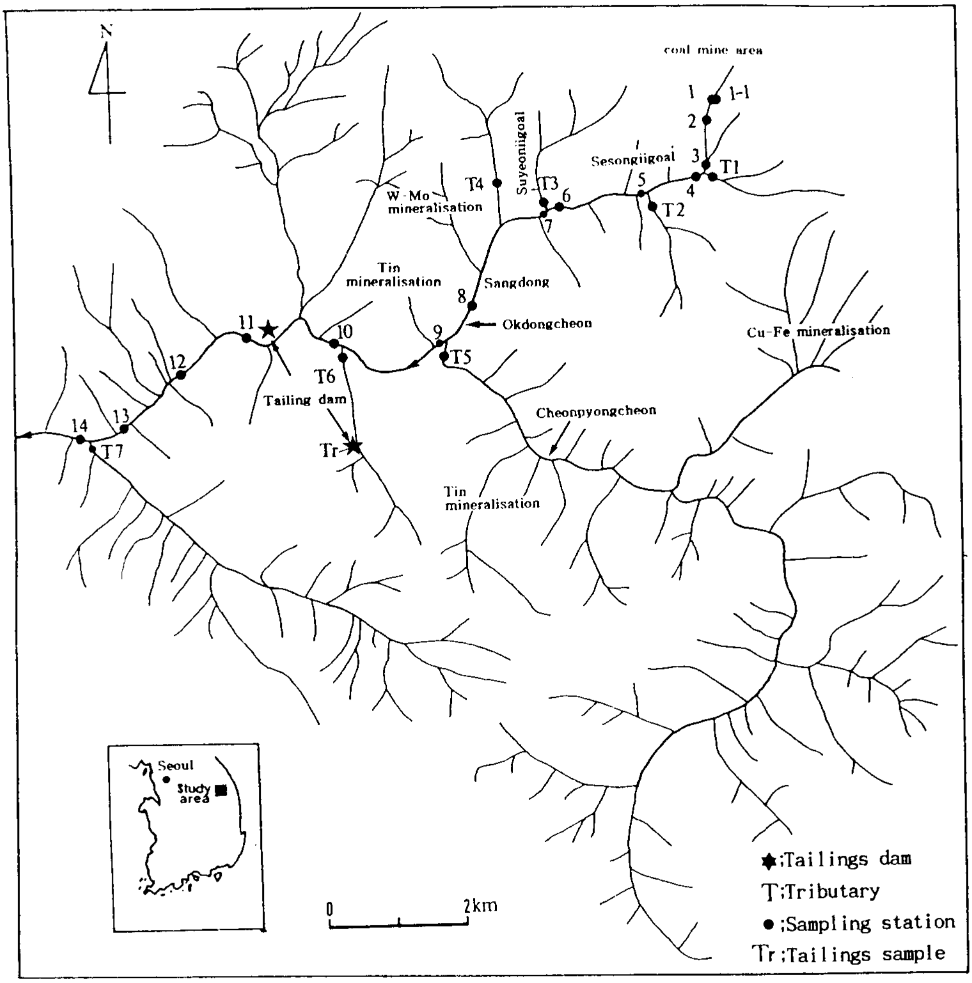

Fig. 1. Location of sampling stations in the Okdongcheon stream.

in the Taebaeksan metallogenic province, in the middle eastern part of South Korea where many productive base-metal ore deposits are concentrated.

The representative geology of the catchment area situated in the Sangdong region consists of Pre-Cambrian metasediments, granites (south part) overlying the Choseon Supergroup of Cambro-ordovician age (middle part) and the Hongjom formation upper Carboniferous (northern part) (Kim et al., 1988; Kim et al., 1989). Tributaries to the north drain largely the Carboniferous rock as well as several coal mining areas. The middle part of the catchment area mainly consists of Jangsan quartzite, Myobong slate and the great limestone series, the latter within which the tungsten-molybdenum mineralisation occurrs (Sangdong mine). Middle Cretaceous Eopyong granodiorite, with copper-iron mineralisation (Geodo mine), is situated to the south-east and is drained by the Cheonpyongcheon stream. Pegmatites which are spacially close to Pre-Cambrian granites in the lower part of the study area, contain tin mineralisation (Soonkyoung tin mine and Seongdoeg tin mine). These areas are drained by the Cheonpyongcheon and Okdongcheon streams, respectively (Fig. 1).

Since 1940 the Sangdong mine, which is the most largest metal mine in this area has been an important world tungsten producer maintaining an annual production of scheelite concentrates from between several hundred to about 5000 metric tons of 70 percent WO_3 in grade. In addition to tungsten, approximately 300 metric tons of molybdenum with 90 percent MoS_2 and the byproducts of bismuth and gold were also recovered annually. Ore minerals of the Sangdong mine consist mainly of scheelite, powellite, molybdenite and a minor amount of bismuthinite. Major gangue minerals include wollastonite, garnet and some sulphides such as pyrrhotite and pyrite (Kim et al., 1988). The grain sizes of tailings produced after ore processing from this mine varied from clay to sand, with the latter coarse fraction in predominance. Cassiterite, columbite, tantalite and rutile were produced from the Soonkyoung tin-bearing pegmatite (Kim et al., 1989). Ore minerals of the Geodo mine consist of chalcopyrite, pyrrotite, bornite and pyrite.

The main Okdongcheon stream has a long, narrow shape extending in a south-westly direction, connecting many complicated tributaries. Two tributaries from the Sesongiigoal and Suyeoniigoal valleys originate from the same area of coal mines. Water from the Sesongiigoal and Suyeoniigoal valleys flows upstream of the Okdongcheon stream and then drains mineralised areas which include tungsten-molybdenum, tin and copper-iron mineralisation (Fig. 1). Upper reaches of Okdongcheon stream are well oxygenated as a result of rapid and turbulent flow above station 8, where the slope of stream was rather high. Stream beds in these sites are covered with yellowish concretions of iron hydroxides. Fine yellowish sediments were observed on the top of sediments betweens stations 9 to 14. On the Okdongcheon stream the colour of stream water in the Sesongiigoal and Suyeoniigoal valleys and the Okdongcheon stream was dull and turbid which was aesthetically objectionable. With the exception of T3, tributaries had a low suspended solid content and were fairly clear. There are two tailings dams containing slurry from the Sangdong tungsten-molybdenum ore processing plant located on the Okdongcheon stream. Although the distance between stations 1 and 1-1 is only a few metres, the water at station 1 flowed from the access road to the coal mine and its volume was small whilst that at station 1-1 passed through coal mine spoil and the amount of the water was much larger than that at station 1.

For purposes of discussion, that part of the Okdongcheon stream before its confluence with the Cheonpyongcheon stream has been termed the upper Okdongcheon and the lower part the lower Okdongcheon.

MATERIALS AND METHODS

Sampling and Field Measurements

Samples of sediments were taken at selected stations along the Okdongcheon stream, its tributaries and from the tailings dam in August, 1992. Suspended solids were determined by filtration (0.45 μm) of water from the selected stream. Oxidation potential (Eh) and pH were measured with a portable pH/Eh meter in situ. Total numbers of samples were 23 including a tailing waste sample collected from a tailings dam. Sediment samples were placed in polyethylene bottles and oven-dried at 60℃.

Analysis

Stream sediments were disaggregated and the portion passing through an −80 mesh (180 μm) nylon sieve was retained. Samples were then digested in concentrated HNO_3 and $HClO_4$ (in a ratio of 4 : 1) and taken to dryness on a hot block. The residue was then leached with 5M HCl, diluted to 1M HCl with deionized water, and analysed for Al, Fe, Mg, Ca, K, Na, Mn, P, Sr, Ba, V, Cd, Pb, Zn, Cu, Cr, Ni, and Co by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) (Thompson and Walsh, 1988). A sub-sample from each of the sediment samples was ashed with 1.0 m*l* saturated magnesium nitrate at 450℃ in a furnace for 6 hours, digested in 0.2% potassium iodide and analysed for As, Sb, and Bi by hydride generator-ICP (after modified Pahlavanpour et al., method, 1981).

Adquate standard, reagent, replicate and blank tests were carried out for all analytical techniques (a minimum of 10% of each randomly distributed).

RESULTS

pH-Eh and Suspended Solids in Stream Water

Measurements of Eh-pH and suspended solids showed that the water quality of the Okdongcheon stream was poor, reflecting the impact of AMD. The water pH values range from 2.7 at station 1 in which the water flowed from the road around the coal mine to 7.9 in uncontaminated surface waters such as those at stations T1 and T2. Water Eh ranged from 513 mV in water near the coal mine area to 40 mV in water at station T7 (Table 1). Water Eh-pH measured at stations 1, 2, 3, 4, 5, 6, 7, 8 and T3 indicated the presence of acid mine water, but at the other stations the water appeared unaffected (Brookins, 1988).

The major source of acid mine drainage was the tributary at stations 1 and 1-1. In addition, another source was found at station T3 of the Suyeoniigoal valley. Two tributaries were linked to the same aban-

Table. 1. Summary of water parameters measured in the Okdongcheon and tributaries.

	upper Okdongcheon		lower Okdongcheon		tributaries	
	mean	range	mean	range	mean	range
SS (mg/l)	31	0.6~88	26	12~34	3	2~4
Eh (mV)	432	305~513	128	57~320	176	40~336
pH	3.6	2.7~4.9	6.8	6.4~7.6	7.3	6.0~7.9

Numbers and stations of measurements are shown on Fig. 2. Mean; arithmetic mean.

doned coal mine area (Fig. 1). Although the acid water at stations 1, 1-1 and T3 was mixed with natural water in several tributaries including those at stations T1, T2 and T4 in the upper Okdongcheon stream, the water pH value in the upper Okdongcheon, above station 8, was still very low (Table 1). As acid water of the Okdongcheon stream mixed with water from the larger Cheonpyongcheon stream from station T5, the pH of the Okdongcheon water then changed from 3.7 at station 8 to 7.6 at station 9 (Fig. 2). It is believed that this might be attributed to the variable discharge/acid mine drainage volume relationship and that contents of neutralising agents such as bicarbonate might influence the variation of water pH as well (Barnes and Romberger, 1968; Chapman et al., 1983).

Suspended solids were present in concentrations that ranged from 0.6~88 mg/l (Table 1). The amount of suspended solids in water at stations 1 and 1-1 was only a few mg/l, but this increased abruptly downstream as a result of mixing from other tributaries. This result is similar to those reported by Karlsson et al., (1988) and Kelly (1988). After the stream passed through station 8 and then mixed with the Cheonpyongcheon stream from station T5, the amount of suspended solids decreased gradually, probably because of dilution and settlement due to an increase in water volume and reduced velocity of the stream respectively (Fig. 2). The coaser A certain size fraction of the suspended solids is likely to settle on the base of the stream where the water velocity is low.

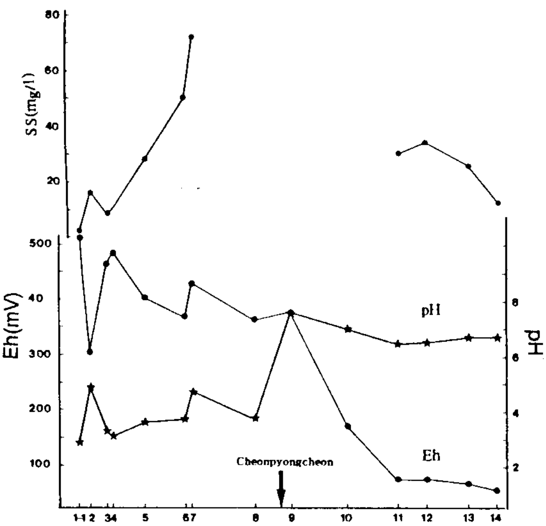

Fig. 2. Variation of pH, Eh and suspended solid (SS) with the distance of the Okdongcheon stream. A arrow indicates the position of the confluence of the Cheonpyongcheon stream.

Metal Contents in Stream Sediments.

The major and trace metal contents in sediments vary appreciably from station to station (Tables 2 and 3). A comparison of heavy metal contents in the upper Okdongcheon (from station 1 to station 8) and those in the lower Okdongcheon (from station 9 to station 14) highlighted some marked differences (Tables 4 and 5). The major soluble elements in acid water such as Mn, Na, Ca and Mg and most of the toxic elements except chromium were somewhat enriched in the lower Okdongcheon whilst Fe, Al, P, and K concentrations in stream sediments were more concentrated in the upper Okdongcheon (Figs. 3 and 4). It is interesting that all toxic trace elements except chromium exibit a peak at station 10 where the main stream mixes with the effluent from the tailings dam for slurry wastes of the tungsten-molybdenum ore processsing plant (Figs. 5, 6 and 7). No ready explanation is apparent but it does correspond to the input from the tributary (T6) draining the tailings dam. Concentrations of 450 μg/g As, 265 μg/g Bi and 1μg/g Cd were found at station T6 in the watercourse downstream from the tailings dam. Sediments collected from the tributary at station T4 draining the tungsten-molybdenum mineralized area contained higher concentrations of Cu, Zn, Cd, Pb, As and Bi with values up to 229 μg/g Cu, 228 μg/g Zn, 2 μg/g Cd, 81 μg/g Pb, 299 μg/g As and 250 μg/g Bi. High concentrations of As and Bi were found in sediments at stations T4, T6 and Tr, associated with the W-Mo mineralisation or its mining activities. Sediments collected from the Cheonpyongcheon stream draining the copper-iron and tin mineralized area contained concentrations of 229 μg/g Cu, 228 μg/g Zn, 299 μg/g As and 213 μg/g Bi.

Table 2. Major element concentration (μg/g in the minus 80 mesh fraction) in the stream sediments taken from the Okdongcheon stream and its tributaries.

No	Na	K	Mg	Ca	Sr	Ba	Al	V	Mn	Fe	P
1	370	14500	2280	940	71	123	49000	44	233	97300	1700
1-1	243	14100	5180	8910	64	147	48800	54	574	131000	737
2	88	1100	444	664	6	22	118000	4	69	136000	186
3	363	15100	2380	1200	71	110	48000	42	211	104000	1340
4	380	15700	2320	1200	76	196	51600	42	211	94000	1070
5	278	12800	3570	2440	60	152	47700	48	478	88900	989
6	337	15200	4360	5160	72	207	56000	47	513	72700	822
7	230	11900	4550	5040	49	163	50600	43	709	141000	1290
8	216	9690	6750	11700	38	212	35900	47	514	46400	602
T3	147	9880	5200	1540	31	114	33400	45	562	183000	1610
Samples taken from acid mine drainage											
9	246	9880	6510	15500	40	198	36300	48	668	51000	651
10	598	6950	5780	38200	42	113	28500	41	2330	68600	839
11	297	11000	8990	17700	50	222	45300	53	1440	50300	862
12	408	7790	6970	38000	48	119	31100	42	1570	49300	830
13	392	6990	6350	43100	45	104	28800	41	1490	57000	795
14	393	8570	7750	35400	49	137	34300	45	1650	50100	819
Samples taken from the stream contaminated by AMD											
T1	187	14800	17800	38100	123	171	41600	55	863	38900	938
T2	130	13000	11900	24000	40	181	49700	78	1820	51900	882
T4	185	6620	6610	78800	92	97	24000	31	1800	40600	707
T5	324	10900	5660	22300	59	175	42600	42	1060	52900	778
T6	442	6500	5680	39900	41	84	26100	35	1500	49200	698
T7	160	9250	7630	2270	28	241	38600	44	422	28200	490
Samples taken from tributaries not associated with AMD											
Tr	762	8820	7570	63100	54	80	28200	47	2610	54300	672

Table 3. Trace element concentration (μg/g in the minus 80 mesh fraction) in the stream sediments taken from the Okdongcheon stream and its tributaries.

	Co	Ni	Cu	Cr	Zn	Cd	Pb	As	Sb	Bi
1	5	15	19	10	43	<0.2	13	77	0.67	11
1-1	13	30	61	17	93	<0.2	28	128	3.12	29
2	2	5	78	104	12	<0.2	28	5	0.80	3
3	5	16	20	8	35	<0.2	13	64	1.08	22
4	5	16	22	6	32	<0.2	18	45	0.97	23
5	12	25	48	15	52	<0.2	26	43	2.73	7
6	16	30	68	11	84	<0.2	30	43	1.75	14
7	19	31	87	19	84	<0.2	12	49	1.42	15
8	13	39	87	16	78	<0.2	13	38	2.73	3
T3	14	23	44	27	41	<0.2	9	58	2.16	7
Samples taken from acid mine drainage										
9	15	47	116	17	104	<0.2	18	65	2.15	48
10	33	185	806	45	902	20.7	446	942	14.12	1179
11	25	119	225	22	250	3.2	100	203	4.13	213
12	19	67	239	22	212	4.0	66	235	3.13	361
13	21	58	249	23	211	3.8	88	299	4.34	422
14	22	73	241	23	219	3.6	62	226	3.95	267
Samples taken from the stream contaminated by AMD										
T1	18	35	38	32	58	<0.2	10	39	2.88	7
T2	21	41	52	26	54	<0.2	17	53	12.27	1
T4	11	21	217	15	130	2.0	78	248	3.01	250
T5	22	77	229	21	228	2.2	81	299	5.94	213
T6	9	26	99	15	83	1.0	21	405	2.27	265
T7	11	35	21	23	59	<0.2	10	20	0.79	1
Samples taken from tributaries not associated with AMD										
Tr	18	192	212	23	14	3.8	94	249	4.5	525

Multivariate Analysis (Discriminant Analysis)

The objectives of the multivariate anayses are to identify the important factors (compared with the total number of elements analysed) which explain the majority of the spatial variability, and the understanding of differences in geochemical characteristics

Table 4. Arithmetic mean and ranges of major elements in the stream sediments (Unit in μg/g).

	upper Okdongcheon (N=10)		lower Okdongcheon (N=6)		tributaries (N=6)	
	mean	range	mean	range	mean	range
Na	265	88~380	389	246~598	238	130~324
K	11997	1100~15700	8530	6950~11000	10178	6500~14800
Mg	3703	444~6750	7058	5780~8990	9213	5660~17800
Ca	3879	664~11700	31316	15500~43100	34228	2270~78800
Sr	54	6~76	46	40~50	64	28~123
Ba	145	22~212	132	104~222	158	84~241
Al	53900	33400~118000	34050	28500~45300	37100	26100~49700
V	42	4~54	45	41~53	47	31~78
Mn	224	69~709	1525	668~2330	1244	422~1820
Fe	109430	46400~183000	54383	49300~68600	43617	28200~52900
P	1035	186~1700	799	651~862	748	490~938

N; Number of samples.

Table. 5. Arithmetic mean and ranges of trace elements in the stream sediments (Unit in μg/g).

	upper Okdongcheon (N=10)		lower Okdongcheon (N=6)		tributaries (N=6)	
	mean	range	mean	range	mean	range
Co	10	5~19	23	15~33	16	9~22
Ni	23	5~39	92	47~185	39	21~77
Cu	53	19~87	313	116~806	109	21~229
Cr	23	6~104	26	17~45	22	15~32
Zn	55	12~93	316	211~902	102	54~228
Cd	<0.2	<0.2	3.7	<0.2~20.7	1.0	<0.2~2.2
Pb	19	9~30	130	18~446	36	10~81
As	55	5~128	328	65~942	177	20~405
Sb	1.74	0.80~3.12	5.3	2.15~14.12	4.5	0.79~12.27
Bi	13	3~29	416	48~1179	123	1~265

N; Number of samples.

among training sets(e.g. the upper, lower Okdongcheon and its tributaries) (Davis, 1986).

Cadmium was not considered in multivariate analysis because concentrations were below the detection limit and thus a comparison of Cd concentration with sampling stations was obvious. No preliminary transformations were applied.

Discriminant Analysis

The linear combination of the discriminating variables was used to discriminate whether significant characteristics of the elements were among the groups defined by pH values and drainage systems, and also to determine the potential for the tailing wastes to influence to or associate with the distribution of elements in the sediments.

Sediment samples were grouped into three classes based on water pH and the drainage pattern in which the samples were collected:

Group 1 : sediment samples taken from stations 1, 1-1, 3, 4, 5, 6, 7, 8, and T3 (Upper Okdongcheon). Waters were acid and turbid, with the exception of those at stations 1 and 1-1 (number of cases=9);

Group 2 : sediment samples taken from stations 9, 10, 11, 12, 13, and 14. These water were contaminated by AMD, and were also turbid, but neutralized by the Cheonpyongcheon stream (number of cases=6), and

Group 3 : sediment samples taken from stations T1, T2, T4, T5, T6 and T7. The water in this group was not associated with AMD and was clear (number of cases=6).

One sample (Tr) taken from the tailings dam was not included because it was non-stream sediment whilst another sediment collected from station 2 also was not included because the sample was very different in colour and chemical composition in the rest of group 1. Therefore, the total number of cases (sediment samples) included in the discriminant analysis was 21.

Since there were three groups, only two discriminant functions were calculated and only two positive eigen values were found. Two discriminant functions were statistically significant ($p_{disc.1}=0.000$, $p_{disc.2}=0.0001$). The first of these, $\lambda_1=19.20$, accounts for 68.50 % of the between-group variance and the second, $\lambda_2=8.83$, accounts for the remaining 31.5% (Table 6). Fig. 8 shows two discriminant function axes, with the discriminant scores and centroids (large symbols) for the three groups plotted.

The first discriminant function separates significan-

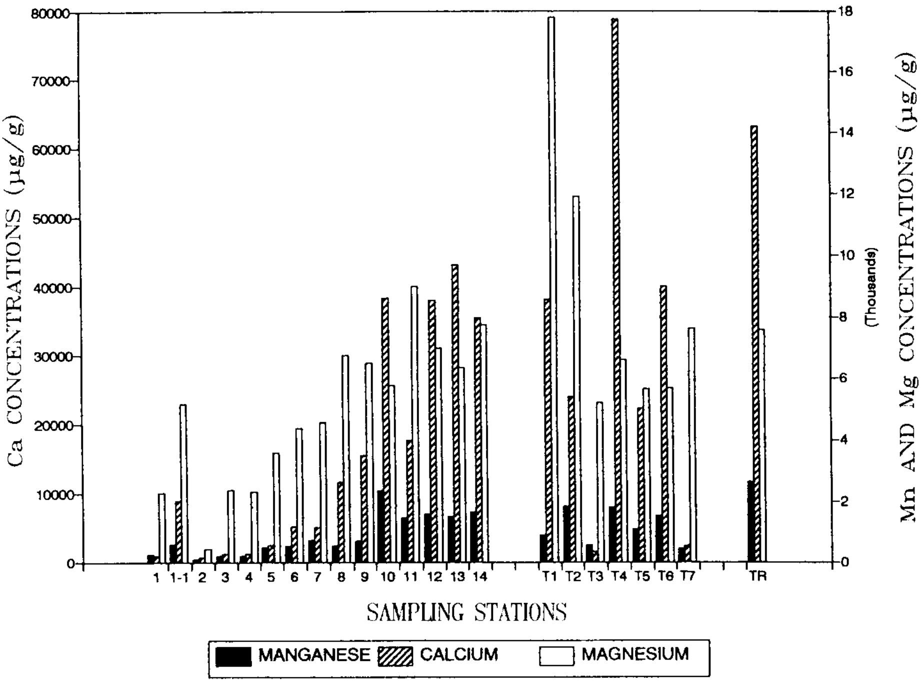

Fig. 3. Comparison of maganese, calcium and magnesium abundances in stream sediments.

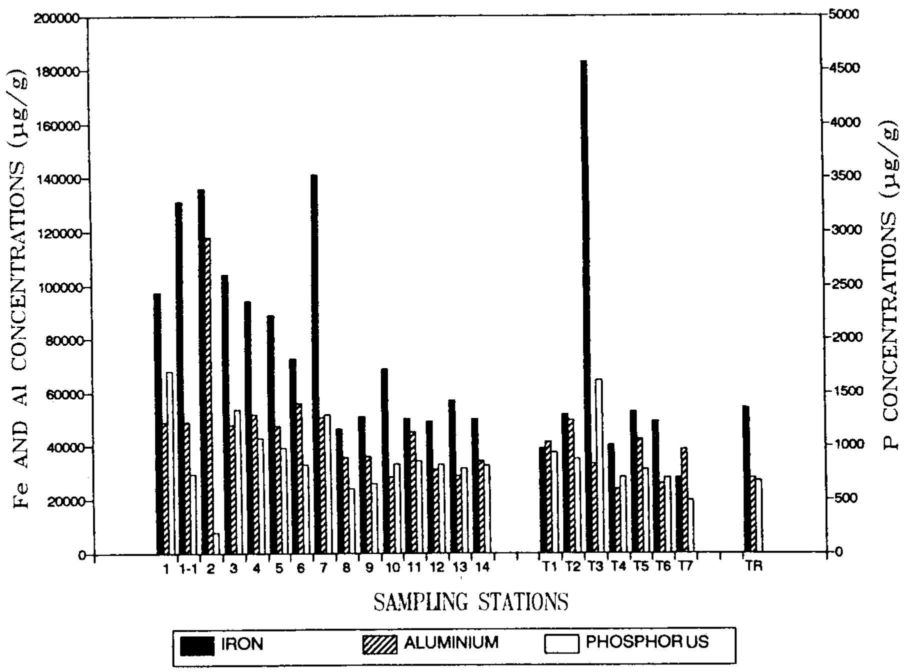

Fig. 4. Comparison of iron, aluminium and phosphorus abundances in stream sediments.

tly between group 2 and groups 1-3, especially in terms of As, Bi and Ni which have large coefficients on the first discriminant function (Table 6). Distinctions along the second discriminant function are less

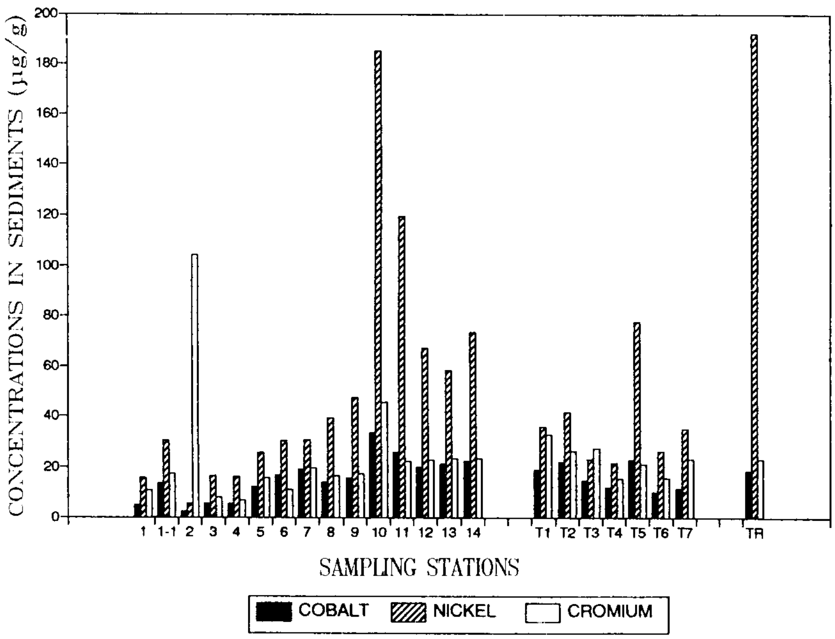

Fig. 5. Comparison of cobalt, nickel and chromium abundances in stream sediments.

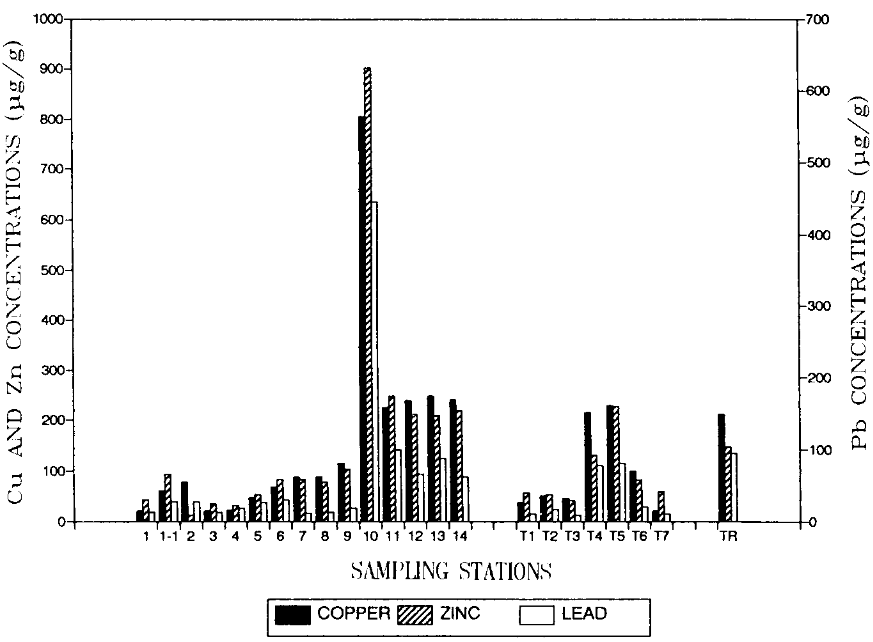

Fig. 6. Comparison of copper, zinc and lead abundances in stream sediments.

clear mainly in terms of Pb, As, Bi and Na, with some overlap among groups 1, 2 and 3. However, when viewed together, both functions are adequate to separate the three groups. This result suggests that the chemical characteristics of group 2 are considerably different to groups 1 and 3, and stream sediments collected from streams having a similar pH value may remain rather unique, with relatively homoge-

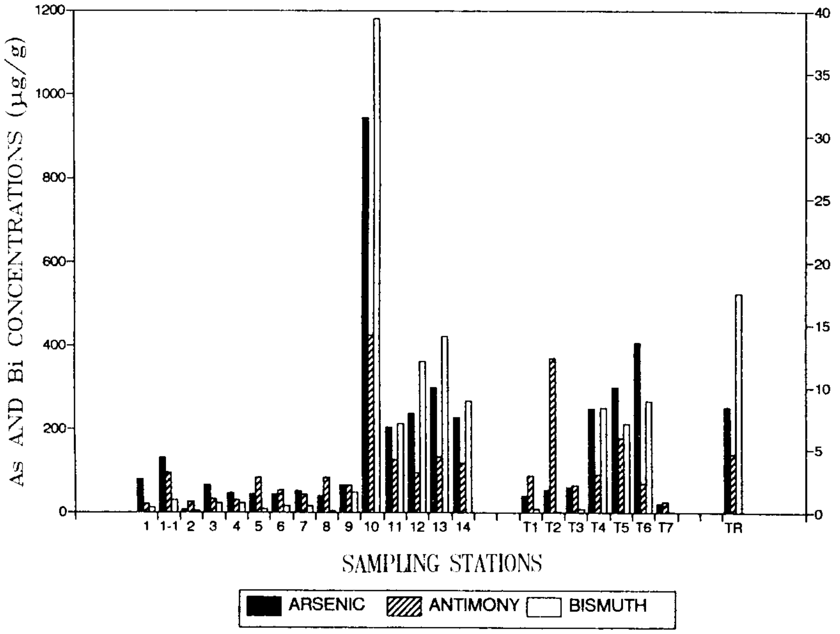

Fig. 7. Comparison of arsenic, antimony and bismuth abundances in stream sediments.

Table 6. Standardized discriminant function coefficients and statistics.

	Function 1	Function 2
Na	−1.86	−3.16
K	0.69	1.14
Ba	2.49	0.29
Fe	−0.33	−1.69
P	0.94	0.67
Ni	−4.41	0.15
Pb	1.58	−5.50
As	8.44	5.16
Bi	−4.42	3.09
eigenvalue	19.20	8.83
percent of variance	68.50	31.50
significance	0.0000	0.0001

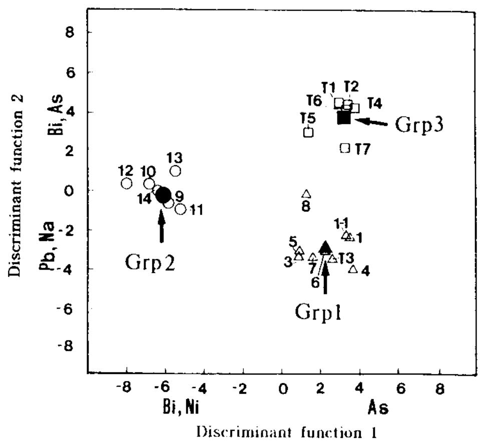

Fig. 8. Plots of scores from standardized discriminant functions on first and second discriminant functions. Numbers or alphabets on the figure indicate the sampling stations. Large solid symbols are group centroids (means).

neous characteristics. Lead, Bi and As mentioned above are enriched in stream sediment in lower Okdongcheon(stations 10, 11, 12, 13 and 14) and some tributaries (T4, T5 and T6) draining mineralised areas (Table 5). After the discriminate functions were calculated, the chemical data of the tailings sample (Tr) was substituted into the standardized discriminant functions to obtain discriminant scores. This result showed that the discriminant scores ($-37.40_{disc.1}$, $-9.17_{disc.2}$) of the tailings sample could be plotted near the discriminant scores' field of group 2. This result probably means that distribution of elements of group 2 may be influenced by or associated with the tailing effluents or their wastes.

DISCUSSION

Ocurrence of Acid Mine Drainage and Turbidity

In the process of mining, acid mine drainage was-

Table 7. Some sediment quality criteria (column A, B and C; unit in $\mu g/g$) and sampling stations (column D) exceeding three criteria.

	A	B	C	D
As	33	10	17	All stations except st. 2 and T7
Cd	10	1	2.5	st. 10
Cr	111	100	100	
Cu	114	100	85	st. 9, 10, 11, 12, 13, 14, T4 and T5
Fe	4	5.9	–	st. 1, 1-1, 2, 3, 4, 5, 6, 7, T3 and 10
Pb	250	50	55	st. 10
Mn	1110	–	1200	st. 10, 11, 12, 13, 14, T2 and T6
Ni	90	100	92	st. 10, 11
Zn	800	100	143	st. 10

St.; Sampling Station.

tes result from the passage of water through mines and mine spoils where iron sulphides, usually pyrites, are exposed to the oxidising action of air and water. As a result of the oxidation of sulphide minerals, iron ions are bonded to water molecules or to other stronger bases. Hydrated ferric ions lose protons in aqueous solution causing acid mine water and ferric hydroxides to be produced. According to the stoichiometry of oxidation of pyrite, one mole of FeS_2 can oxidize in the presence of excess Fe^{3+} in solution with water and further hydrolyse to form 16 moles of H^+ (Caruccio et al., 1976). There is also a lot of evidence that bacterial catalysis plays an important role in acid formation (Nemerow, 1978; Murr, 1980).

Hdroxide, (OH^-), bonded to an iron ion, may function as a bridging group to join two or more iron ions together through the subsequent dehydration-dimerisation. If the process continues, colloidal hydroxyl polymers (flocs) are formed, and finally precipitates coat the stream beds (Manahan, 1979; Hahn and Stumm, 1970). The size of colloidal hydrous iron particles varies with pH and can be as small as 100Å (Clark and Crawshaw, 1979; Leckie, 1988). These flocs form as the acid mine water becomes neutralized; at very low pH values the metal ions are soluble but as the pH rises some begin to precipitate out. It is well known that the minimum pH value for precipitation of metal as hydroxide is different for each element. The critical pH values of flocculation in water are about 2.5~4.3 for iron (III) and 5~5.2 for aluminium (Snoeyink and Jenkins, 1980; Wangen and Williams, 1982; Kelly, 1988).

Numerous studies on the classic orange-coloured precipitates associated with AMD have revealed that they are mainly composed of various partially hydrolysed iron oxide forms and that other flocs may form from aluminium oxide and hydroxides, as well as occasionally from other salts such as barium (Clark and Crawshaw, 1979; Kelly, 1988). White precipitates were found on the stream beds at station 2 and were very different in colour from other sediments within the the upper Okdongcheon.

From a geochemical point of view, Fe^{3+} and Al^{3+} may be flocculated as a hydroxide in the upper Okdongcheon, in which AMD mixed with tributaries showing a natural range of pH values (6-7). However Fe^{+2} and other soluble ions such as Zn, Cd, Mn and Pb, could be dissolved and remained in solution due to the presence of acid water. Analysis of suspended solids on filters shows that major components are iron and aluminum. It was observed that considerable amounts of flocs remained as suspended solids of iron and aluminum hydroxides and that there were transported downstream due to the velocity of the Okdongcheon stream. The processes of the flocculation are thought to be important in regulating trace metal concentrations in the Okdongcheon stream depending upon pH-adsorption edges for metals (Benjamine et al., 1982).

The occurrence of flocculation of iron hydroxide and its precipitation can be harmful to aquatic organisms in the Okdongcheon stream, in that oxidation of pyrite causing AMD results in depletion of dissolved oxygen in stream water. In addition, the growth of plant life which depends on photosynthesis can be greatly impaired due to the interference in light energy penetration through the body of water by suspended solids formed (Koryak et al., 1972; Herricks and Cairns, 1974; Cline and Balla, 1976).

Aquatic Sediments and Their Contamination

A major process governing the mobility of trace metals in the aquatic environment is adsorption onto particles and ion exchange. Some hydrated metal oxides, such as manganese (IV) and iron (III) oxide and other precipitate solids with surface areas as large as several hundred square metres per gram (e.g. up to 300 m^2/g for MnO_2 and 230 to 320 m^2/g for FeOOH; Förstner and Wittann, 1979), efficiently sorb various species from aqueous solution, or limit solubilities of metals in sediments (Drever, 1982; Johnson, 1986). The Zero Point of Charge (ZPC) of hydrous MnO_2 is 2.8~4.5 whilst that of iron is 6.5~8.5 (Manahan, 1979; Rose et al., 1979). In the present study area the water pH in the upper Okdongcheon ranged from 2.7~4.9 whilst that in the lower Okdongcheon ranged from 6.4~7.6 (Table 1). Therefore it is inferred that iron hydroxide could absorb negative charge of ions such as phosphate anions in the acid water of the upper Okdongcheon, but that manganese oxide could behave effectively as a metal scavenger or absorbant in the lower Okdongcheon (Figs. 3 and 4). However, organic substrates could also be absorbing materials. In addition ligands such as SO_4^{2-} in acid mine wastes or OH^- or CO_3^{2-} in natural water will complex with some metals to form quantities of solid phases such as sulphates, hydroxides and carbonates, depending on competitive effects of several ligands and the pH status of the Okdongcheon stream.

A major fraction of the toxic trace metals introduced into the aquatic environment is found in association with the bottom sediments, where they consititute a potential danger for aquatic organisms. The toxic trace metals in sediments are bound in various components, the most important being clay minerals, Fe-Mn hydroxides, carbonates, sulphides, organic substances. However it is very difficult to determine whether an element detected in a sediment is a component of a true amorphous solid or whether it is simply adsorbed on to a host precipitate. The specific bonding forms in all these phases determine the mobilization behaviour of heavy metals. Changes in chemical speciation due to variations in the hydrochemical conditions (e.g. pH) will have great impacts on solubilities, sorption phenomena, transport properties and the distribution of dissolved metals within an aquatic environment (Wangen and Williams, 1982). It is well known that the environmental behaviour and toxicity of an element can only be understood in terms of its actual molecular form. Total metal concentrations themselves do not account for toxicity or bioavailability. Some sediments can differ by a factor of 10 or more in terms of toxicity whilst sharing the same total metal concentration (Burton, 1992).

Recently several agencies have developed global numerical sediment quality criteria. A number of procedures, based on both chemical and biological analyses, have been proposed for the development of these criteria. The need to classify the cause and intensity of the toxic effects of sediments is important for the following reasons; 1) to regulate the release of chemicals to the aquatic system, 2) to determine the causes of observed effects and identify sources of effects, 3) to determine which sediments exhibit unacceptable effects on benthic and pelagic organisms, 4) to set priorities for remedial action , and 5) to determine the most appropriate remedial action (Giesy and Hoke, 1990). Sediment quality criteria for some toxic elements in sediments suggested by the OME (Ontario Ministry of Environment), Wisconsin Department of Natural Resources and Beak Consultants Ltd. (Giesy and Hoke, 1990) are cited in Table 7. Comparing the metal contents analyzed in the present study with these criteria, concentrations of arsenic exceed sediment quality criteria in many sampling stations. Manganese and copper are highly enriched, especially, in the the lower Okdongcheon. Most of metals in sediments collected from station 10 exceed these criteria. Analysis of energy dispersive spectrum shows that sediment at station 10 contain small grains of ore minerals such as arsenopyrite, bismuthinite, molybdenite, pyrrhotite and coal.

CONCLUSIONS

This study surveyed water parameters such as Eh-pH and suspended solid contents and concentrations of Al, Fe, Mg, Ca, K, Na, Mn, P, Cd, Pb, Zn, Cu, Cr, Ni, Co, As, Sb and Bi in sediments in the Okdongcheon stream within the Sangdong area of South Korea. There are two main problems occurring in the Okdongcheon stream: (a) acid mine drainage in the upper reaches and tributaries and (b) toxic trace metal contamination of stream sediments mainly in the lower reaches.

Acid mine water originating from a coal mine area was discharging into the Okdongcheon stream. As acid water from the Sesongiigoal and Suyeoniigoal valleys mixed with fresh water from tributaries draining other catchment areas, the ferrous iron in the water is oxidized to ferric hydroxide. In other words, irons in the water were removed by oxidation or aeration, a naturally occurring waste water treatment. Some amounts of hydroxides (flocs) however still remained in the water due to stream velocities and caused undesirable turbidity. The upper Okdongcheon, showing a low pH (2.7~4.9) range, especially, is not suitable for aquatic organisms which need oxygen. This is because the oxidation of pyrite causing AMD has resulted in a depletion of dissolved oxygen in the stream water. It is believed that the main factor reducing the acidity of mine water may be dilution within the Cheonpyongcheon stream, the biggest stream in this area. In addition, water containing bicarbonate or that passing through carbonate rocks may be much more efficient in neutralizing acid water than bicarbonate-free water.

Considerable geochemical variations have been demonstrated from station to station, with extremely high concentrations of some metals such as Mn, Fe, Ni, Cu, Zn, Cd, Pb, As, and Bi in sediments contaminated from past metallic mining and by AMD. It was observed that high concentration of toxic trace metals were mainly found in sediments collected from streams at stations T4, T5 and 10, which drained metallic mine areas, especially, at locations near the tailings dam. Although speciation and partitioning of trace elements were not determined, it may be presumed that there will be potential unfavourable effects of heavy metals in sediments in the Okdongcheon stream on aquatic organisms and on water quality.

Since AMD and the presence of contaminated sediments have been found in the Okdongcheon, more detailed studies such as site-specific biological based analysis, should now be used to estimate the bioavailable fraction of the total metals present for the protection of the benthic communities. Based on the assessment of sediment quality, it is possible that the areas and the volumes of fractions potentially harmful to aquatic organisms can be calculated and possibly removed from the Okdongcheon as a first step in remediation, with the aim of improving the quality of the benthic habitat. In addition AMD ruins the quality of fisheries and streams, damages concrete structures, and increases the cost of municipal water treatment (Ziemkiewicz et al., 1990). Therefore it is recommanded that AMD should be neutralized in order to enhance the water quality and to preserve the ecology of the Okdongcheon stream.

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강원도 상동지역 옥동천의 광산 산성수 및 하상퇴적물의 중금속 오염

정영욱 · Iain Thornton

요 약: 강원도 상동지역의 옥동천 및 그 지류들을 대상으로 수질 파라메터(Eh-pH, 부유물질)의 측정과 하상퇴적물의 화학분석을 통하여 석탄광 및 금속 광산활동에 의한 옥동천의 수성 환경의 오염정도를 조사하였다.

옥동천의 조사유역을 상부와 하부 옥동천으로 구분할 때 상부 유역은 석탄광의 개발로 인한 황화물의 산화작용으로 인하여 수질은 매우 낮은 pH를 나타내 광산 산성수(Acid Mine Drainage)로 심하게 오염된 것으로 조사되었다. 또한 상부 옥동천에 용존된 철이 지류들의 유입과 하천의 aeration으로 철 산화물(floc)의 발생과 이의 침전으로 하천 바닥은 황갈색의 철산화물이 퇴적되어 있다. 그러나 상부 옥동천의 유속에 의해 일부 철 산화물이 침전되지 못한채 부유되어 옥동천은 매우 탁하게 보인다. 상부 옥동천은 천평천의 유입으로 인하여 낮은 pH의 산성수는 중화되지만 부유물질의 존재로 인하여 하부 옥동천은 계속 탁하여 광산 산성수의 영향이 지속되고 있다. sediment quality criteria와 비교해 볼 때 하부 옥동천의 하상퇴적물, 특히 상동 텅스텐-모리브덴늄 광미 저장댐과 인접된 지점의 하상퇴적물은 Pb, Cu, Zn, Co, Cd, As 및 Bi 등의 유해금속에 의해 농축되어 있어 퇴적물의 질이 상당히 악화되어 있다.

수중 및 저서 생물에 대한 서식처 및 수질을 개선하기 위해서 옥동천 상부에는 산성수를 중화시킬 수 있는 경제성 있는 수처리 장치의 도입과 중금속의 speciation의 연구가 필요할 것으로 사료된다.