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Heavy Metal Contamination around the Abandoned Au-Ag and Base Metal Mine Sites in Korea

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국내 전형적 금은 및 비(base)금속 폐광산지역의 중금속 오염특성

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이 연구의 목적은 국내 폐광산지역의 주변 환경오염 양상을 평가하고 독성 중금속 원소들의 거동에 대한 일반적인 결론을 도출하고자 함이다. 이를 위해 국내의 전형적인 비(base)금속 광산과 금은 광산 4개 지역을 각각 선정하여 환경오염 조사결과를 상호 비교, 검토하였다. 비금속광산으로서 삼보 Pb-Zn-중정석, 신예미 Pb-Zn-Fe, 거도 Cu-Fe 및 시흥 Cu-Pb-Zn 광산지역의 광미 및 슬래그 등 폐기물에서 유래된 토양에서 상당한 수준의 Cd, Cu, Pb 및 Zn의 함량이 나타났다. 또한 광산 하부지역 주변 농경지, 하상퇴적물 및 하천수에서도 지속적인 분산의 영향으로 심각한 오염양상이 나타났으며 이는 광산으로부터의 거리, 풍향, 지형 등에 의해 영향을 받고 있었다. 구봉, 삼광, 금왕 및 길곡 금은광산지역에서도 광미 및 광산 폐기토양에서 As, Cd, Cu, Pb 및 Zn의 높은 함량이 나타났으며 직접적인 하부유출로 하상퇴적물 및 하천수의 오염을 유발하고 있었다. 금은광산지역에서 비소가 특징적인 환경오염 원소로 나타났으며 중금속원소와 함께 황화광물에서 비롯되어 산화영향에 따라 그 이동도가 증진될 수 있다. 토양시료의 연속추출 분석결과 대부분의 중금속은 비잔류성 형태로 존재하며 주변 환경조건의 변화에 취약한 것으로 나타났다. 오염지수의 적용결과 폐광산 토양에서 1.0 이상으로 중금속원소들의 복합적 오염양상을 나타내었다.

주제어 : 폐광산, 비소, 중금속, 연속추출, 오염지수

The objectives of this study are to assess the extent and degree of environmental contamination and to draw general conclusions on the fate of toxic elements derived from mining activities in Korea. Eight abandoned mines with four base-metal mines and four Au-Ag mines were selected and the results of environmental surveys in those areas were discussed. In the base-metal mining areas, the Sambo Pb-Zn-barite, the Shinyemi Pb-Zn-Fe, the Geodo Cu-Fe and the Shiheung Cu-Pb-Zn mine, significant levels of Cd, Cu, Pb and Zn were found in mine dump soils developed over mine waste materials, tailings and slag. Furthermore, agricultural soils, stream sediments and stream water near the mines were severely contaminated by the metals mainly due to the continuing dispersion downstream and downslope from the sites, which was controlled by the feature of geography, prevailing wind directions and the distance from the mine. In the Au-Ag mining areas, the Kubong, the Samkwang, the Keumwang and the Kilkok mines, elevated levels of As, Cd, Cu, Pb and Zn were found in tailings and mine dump soils. These levels may have caused increased concentrations of those elements in stream sediments and waters due to direct discharge downstream from tailings and mine dumps. In the Au-Ag mines, As would be the most characteristic contaminant in the nearby environment. Arsenic and heavy metals were found to be mainly associated with sulfide gangue minerals, and mobility of these metals would be enhanced by the effect of oxidation. According to sequential extraction of metals in soils, most heavy metals were identified as non-residual chemical forms, and those are very susceptible to the change of ambient

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conditions of a nearby environment. As application of pollution index (PI), giving data on multi-element contamination in soils, over 1.0 value of the PI was found in soils sampled at and around the mining areas.
Key words : Abandoned mines, Arsenic, Heavy metals, Sequential extraction, Pollution index

INTRODUCTION

The metal industry can be an important source of trace elements in the environment owing to various mining activities including processing and transportation of ores, disposal of tailings and waste water around mines (Adriano, 1986). Thus, significant levels of toxic elements discharged from mine wastes can be found in the nearby streams, agricultural soils and food crops, and eventually, they may pose a potential health risk to residents in the vicinity of mines.

Korea has a long history of metal mining, and the most extensive activities occurred during the early twentieth century. At present, however, most of the mines are abandoned due to the exhaustion of ore minerals, and they become an important point source of trace elements including As, Cd, Cu, Pb and Zn. It is well known that the extent and degree of trace element contamination derived from the mining activities may vary depending upon the type of mineralization, composition of ore minerals, geology, topography, method of mining and smelting (Jung, 1995). Thus, many researchers have been investigated on environmental contamination in soils, plants, sediments and natural waters caused by these activities (Adriano, 1986; Merrington and Alloway, 1994; Jung and Thornton, 1996). In Korea, environmental surveys of abandoned mining districts have been also undertaken since the early 1990s, but further investigation is still needed to make comparison of the degree of metal pollution between sites or to draw general conclusions on the fate of toxic metals in different environments.

In this study, eight abandoned mines including four typical base-metal mines (the Sambo Pb-Zn-barite, the Shinyemi Pb-Zn-Fe, the Geodo Cu-Fe and the Shiheung Cu-Pb-Zn) and four Au-Ag mines (the Samkwang, the Kubong, the Keumwang and the Kilkok) were selected. The results of the environmental surveys in those areas previously conducted by the authors and co-workers were discussed and compared between sites. A previous review on the heavy metal contamination in the vicinity of base metal mines in Korea has been published elsewhere (Chon *et al.,* 1998).

SITE DESCRIPTION

Locations of the eight surveyed mines are shown in Fig. 1, and the brief descriptions of geology and site features of each mine are summarized in Table 1. The Sambo Pb-Zn-barite mine was opened in 1945 and stopped production in 1991. At the peak time of the 1980s, the mine has produced about 10% of the total Pb production and 10-20% of the total Zn production of Korea, processing up to 400 tons of ore a day. The geology of the mine is underlain by muscovite schist, granitic gneiss and two mica granite. The mineralization is classified as a hydrothermal vein type with ore minerals of galena, sphalerite and barite (Jung, 1995).

The Shinyemi mine produced Pb and Zn ores from 1967 to 1983, and then, it was redeveloped as an Fe-producing mine with 300,000 tons per year. The orebodies are classified as a replacement

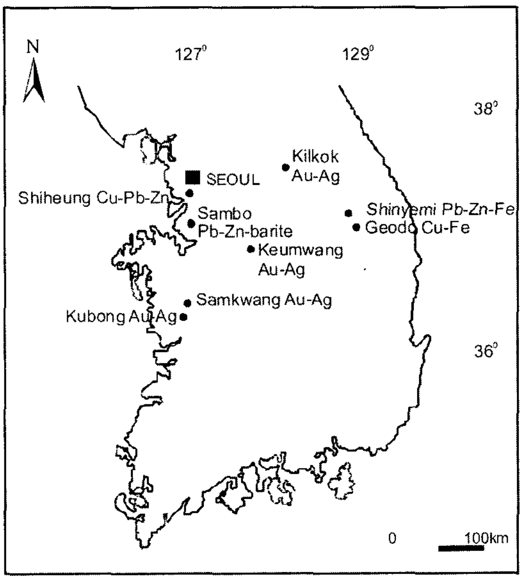

Fig. 1. Locations of study mines in Korea.

Table 1. Geology and site description of the study mines.

Mine	Main geology	Type of mineralization	Target metal	Working period	Topography and Land use	Main pollution sources	Reference
Sambo	muscovite schist, granite gneiss, two mica granite	hydrothermal vein	Pb, Zn, barite	1945 - 1991	low hilly, flat paddy field, household garden	tailings, leachate	Kim and Chon (1993a); Jung (1995)
Shinyemi	limestone	lens or pipe skarn	Zn, Pb Zn, Mo, Cu	1941 - present	hilly forest, farmland	tailings	Jeon *et al.* (1995)
Geodo	limestone, diorite porphyry	skarn	Fe, Cu	1921 - 1988	hilly forest, farmland	tailings	Jeon *et al.* (1995)
Shiheung	biotite banded gneiss, schist, lime-silicates	skarn	Pb, Zn, Cu	1912 - 1973	low hilly, flat paddy field	tailings	Hwang and Chon (1995)
Samkwang	granitic gneiss, metasediments	Au-bearing quartz vein	Au, Ag	1939 - 1995	hilly, forest, farmland	tailings	Chon *et al.* (1997)
Kubong	granitic gneiss, lime-silicate	Au-bearing quartz vein	Au, Ag	1908 - 1970	low hilly, flat paddy field	tailings, leachate	Chon *et al.* (1997)
Keumwang	biotite granite	Au-bearing quartz vein	Au, Ag	1913 - 1995	low hilly, flat paddy field	tailings	Park *et al.* (1997)
Kilkok	biotite gneiss	Au-bearing quartz vein	Au, Ag	? - 1973(?)	hilly, flat paddy field	tailings	KMPC (1987)

Table 2. Mean concentrations and ranges of Cd, Cu, Pb and Zn in tailings and soils from some base-metal mines in Korea (unit in mg/kg).

Mine	Sample	Cd	Cu	Pb	Zn
[a]Sambo Pb-Zn-barite	Tailings (N=5)	9.6 (3.9-23.1)	105 (35-299)	1,140 (13-3,540)	5,190 (2,120-13,500)
	paddy soil (N=47)	4.1 (1.8-7.9)	33 (13-115)	276 (122-552)	384 (52-2,730)
	farmland soil (N=30)	3.4 (2.1-5.0)	22 (14-39)	234(153-342)	87 (34-245)
	forest soil (N=71)	4.5 (2.3-13.7)	94 (15-2,230)	483 (132-2,880)	533 (52-7,420)
[b]Shinyemi Pb-Zn-Fe	Tailings (N=2)	28.5	267	1,630	5,940
	farmland soil (N=29)	6.2 (2.1-14.2)	89 (19-324)	128 (23-564)	802 (84-3,480)
	forest soil (N=21)	5.1 (0.8-21.2)	62 (17-286)	88 (31-301)	753 (65-4,690)
[b]Geodo Cu-Fe	Tailings (N=3)	5.6	952	112	312
	farmland soil (N=20)	2.9 (1.6-5.1)	142 (64-441)	40 (25-67)	96 (54-168)
	forest soil (N=15)	2.7 (1.7-5.4)	156 (77-432)	36 (21-59)	96 (52-201)
	pit soil (N=3)	4.9 (4.4-5.6)	11,000 (10,280-12,220)	43 (35-58)	197 (183-214)
[c]Shiheung Cu-Pb-Zn	Tailings (N=5)	96.6 (34-249)	5,820 (948-13,980)	10,410 (2,910-22,320)	14,960 (5,000-41,200)
	paddy soil (N=11)	11 (1.4-30)	233 (56-616)	742 (116-2,016)	1620 (196-3,960)
	forest soil (N=2)	4.2 (3.8-4.6)	101 (78-123)	336 (272-400)	475 (465-484)

N = No. of samples
[a]Kim and Chon(1993a), [b]Jeon *et al.*(1995), [c]Hwang and Chon(1995)

and skarn type with sulfide ore minerals. The Geodo mine, a skarn type deposits, initiated mining activity in 1921 and produced 1,300 tons of Fe, 130 tons of Cu, 2 kg of Au and 13 kg of Ag per month until closure in 1988 (Jeon *et al.*, 1995).

The Shiheung Cu-Pb-Zn mine has been the most famous sulfide-producing mine since 1912. Until closure in 1973, 250 tons/day of ore minerals were produced. The geology of the mine consists of biotite banded gneiss, biotite schist and lime-silicate rocks (Hwang and Chon, 1995). Tailings and waste materials were distributed without proper storage systems, and they became a major source of toxic metals nearby streams and paddy fields. As a result of previous environmental surveys, the heavy metal contamination in soils and higher Cd levels in residents' blood and food crops were identified. Thus, reclamation of this area including dumping out the waste materials and layering with unpolluted soils, was executed in 1996, and now a incineration facility is also constructed for other land-use.

The Samkwang and Kubong Au-Ag mines are located in mid-west of Korea. The mineralization of the Samkwang mine is a hydrothermal vein type, with As, Au and Ag bearing sulfides with average ore grades of 12 mg/kg of Au and 15 mg/kg of Ag (Lee *et al.*, 1995). The Kubong mine was one of the largest Au mines in Korea with production up to 4,500 tons of crude ore in a month. The geology of the mine consists of granitic gneiss, lime-silicate and sedimentary rocks. In Au-Ag bearing quartz vein, small amounts of pyrite, chalcopyrite, arsenopyrite, galena and sphalerite also occur as native state (Cheon and Oh, 1970). The mine ceased operation in 1970 due to worse economic condition, and tailings and waste materials with solid and sludge were discharged directly into downstream and lower land. The Keumwang Au-Ag mine, a hydrothermal type, has been worked until 1995. Its geology consists of biotite granite, leucocratic granite and sediments (Park *et al.*, 1997). The Kilkok mine is an Au-Ag bearing deposits in fissures of biotite granite, and its operation history is unknown exactly. Tailings and waste rock piles are left and become a source of toxic elements in nearby environment.

HEAVY METAL CONTAMINATION IN THE STUDY AREAS

Mean concentrations and ranges of trace elements in tailings and soil from base-metal mines and Au-Ag mines are shown in Table 2 and 3, respectively. In addition, average contents of trace elements in stream sediment and stream water are summarized in Table 4 and 5, respectively. Chemical decomposition of the soils and sediments were carried out by a mixture of concentrated acids with HNO_3-$HClO_4$ or HCl-HNO_3 (aqua regia). Con-

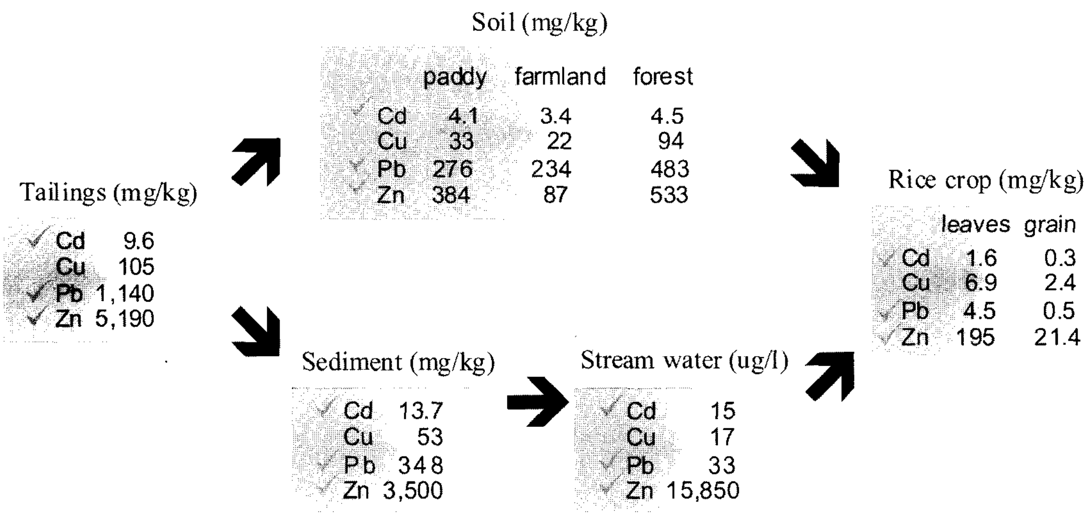

Fig. 2. Heavy metal concentrations around the Sambo Pb-Zn-barite mine.

Table 3. Mean concentrations and ranges of As, Cd, Cu, Pb and Zn in tailings and soils from some Au-Ag mines in Korea (unit in mg/kg).

Mine	Sample	As	Cd	Cu	Pb	Zn
[a]Samkwang	Tailings (N=2)	341 (328-354)	49.6 (45.4-53.8)	113 (49-177)	840 (502-1,178)	2,350 (2,000-2,700)
	mine surface soil (N=4)	820 (424-1,385)	68.0 (3.4-195.2)	226 (23-672)	5,410 (136-17,280)	2,370 (119-7,480)
	farmland soil (N=2)	779 (312-1,246)	5.2 (2.7-7.8)	71 (40-102)	361 (183-540)	274 (181-368)
	forest soil (N=3)	21 (2-51)	1.5 (0.8-2.0)	40 (29-45)	59 (36-76)	93 (64-116)
[a]Kubong	Tailings (N=4)	954 (282-1,310)	49.0 (13.8-85.1)	247 (116-528)	3,510 (10,82-5,900)	1,880 (440-2,650)
	mine surface soil (N=3)	1,470 (886-2,430)	27.7 (14.4-46.1)	173 (119-244)	2,040 (1,436-3,160)	1,080 (697-1,786)
	paddy soil (N=5)	66 (2-256)	1.3 (0.6-2.5)	39 (19-82)	106 (44-288)	95 (63-152)
	forest soil (N=2)	6* (1-55)	0.9* (0.4-1.9)	14* (7-26)	74* (44-127)	52* (27-100)
[a]Keumwang	Tailings (N=10)	40.9 (0.4-71.9)	0.8 (0.4-1.4)	21 (7-60)	58 (14-195)	84 (35-202)
	mine surface soil (N=18)	1,070 (0.1-9,629)	2.3 (0.6-17.1)	183 (9.1,479)	1,150 (21-10,078)	2,040 (39-18,396)
	farmland soil (N=53)	3.9 (0.1-11.3)	0.7 (0.2-1.4)	11 (3-35)	19 (1-38)	58 (28-81)
	forest soil (N=15)	15.4 (0.02-61.1)	0.8 (0.4-1.3)	9 (5-26)	20 (7-30)	60 (44-81)
[b]Kilkok	Tailings (N=3)	147 (1.4-332.5)	14 (1.4-39)	274 (84-620)	73 (42-121)	1,040 (44-2,860)
	paddy soil (N=17)	4.7 (1.3-18.8)	0.7 (0.05-1.1)	43 (30-62)	38 (30-50)	127 (95-162)
	farmland soil (N=14)	59.3 (0.6-435)	0.5 (0.1-1.3)	39 (29-60)	40 (25-80)	121 (86-166)
	forest soil (N-17)	61.4 (0.3-184)	0.6 (0.2-1.0)	44 (23-94)	41 (27-130)	107 (58-269)

N=No. of samples

[a]Chon *et al.*(1997); [b]on study; *geomean value

Table 4. Mean concentrations and ranges of As, Cd, Cu, Pb and Zn in stream sediments from some base-metal and Au-Ag mines in Korea (unit in mg/kg).

Mine	As	Cd	Cu	Pb	Zn
[a]Sambo Pb-Zn-barite (N=27)	-	13.7 (3.7-49.2)	53 (8-262)	348 (25-3,310)	3,500 (12-19,110)
[b]Shinyemi Pb-Zn-Fe (N=21)	-	7.9 (1.3-15.4)	77 (19-453)	132 (39-542)	1,220 (84-3,830)
[b]Geodo Cu-Fe (N=25)	-	3.3 (1.4-6.4)	398 (71-4,030)	43 (20-77)	115 (52-284)
[c]Shiheung Cu-Pb-Zn (N=9)	-	25.2 (6.6-41.6)	794 (180-1,930)	1,630 (424-4,020)	2,950 (781-5,280)
[d]Samkwang Au-Ag (N=4)	970 (90-2,264)	23.3 (1.8-60.9)	106 (13-209)	2,000 (115-6,060)	963 (82-2,268)
[d]Kubong Au-Ag (N=3)	1,830 (402-3,442)	22.5 (20.9-23.5)	160 (150-170)	1,660 (893-2,068)	860 (718-1,043)
[d]Keumwang Au-Ag (N=36)	10.4 (0.02-51.8)	0.5 (0.1-1.1)	8 (3-45)	19 (5-52)	52 (24-151)
[e]Kilkok Au-Ag (N=7)	-	2.1 (1.9-2.3)	35 (26-40)	28 (26-34)	88 (74-104)

N=No. of samples

[a]Kim and Chon(1993b), [b]Jeon *et al.*(1995), [c]Hwang and Chon(1995), [d]Chon *et al.*(1997); [e]on study

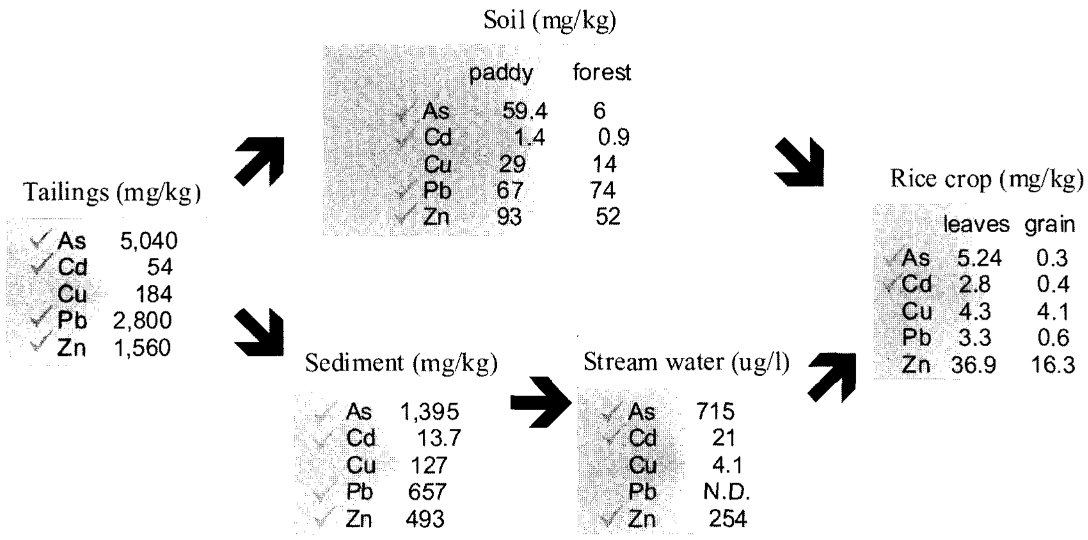

Fig. 3. Heavy metal concentrations around the Kubong Au-Ag mine.

centrations of Cd, Cu, Pb and Zn in soils, sediments and waters were undertaken by ICP-AES. For the analysis of As from Au-Ag mines, soils and sediments were decomposed by 1N HCl, and measured by ICP-AES using hydride generator, which is based on a Korean Standard Method for As analysis.

Base-metal mines

Mean concentrations of Cd, Cu, Pb and Zn in tailings and soils from 4 base-metal mines are summarized in Table 2. As shown in the table, significant levels of those metals were found in tailings and some agricultural lands. For the Sambo mine, elevated levels of heavy metals were found in tailings, especially for Cd, Pb and Zn. According to Jung and Thornton(1996), forest soils have been contaminated severely by Cd (max 13.7 mg/kg), Pb (max. 2,880 mg/kg) and Zn (max. 7,420 mg/kg) due to wind-blown input of tailings containing significant amounts of Pb and Zn. They also reported that the large amount of metals in the mine wastes and associated soils provided an important source for continuing dispersion downstream, and have led to a moderate degree of contamination of soils used for crop production. High contents of Cd, Pb and Zn were found in the tailings, and these high contents were also determined in soil, sediments, and stream water. Finally, the rice crops growing near the mine site contain high levels of Cd, Pb, and Zn (Fig. 2).

Like the Sambo mine, significant levels of Cd, Cu, Pb and Zn were found in tailings from the Shinyemi and Geodo mine. Although the two mine areas comprise hilly forest and farmland with relatively few residents, those enhanced concentrations of the metals can be influenced on farmland and forest soils (Table 2).

Among the four base-metal mines, most severely contaminated area is the Shiheung mine. As seen in Table 2, mean concentrations of Cd, Cu, Pb and Zn in tailings were up to 97 mg/kg, 5,820 mg/kg, 10,410 mg/kg and 14,960 mg/kg, respectively. These levels are ten to hundred times higher than those in uncontaminated soils. As a result, paddy soils and forest soils sampled in the vicinity of the tailings contained very high levels of the heavy metals. It can be also expected that those high amounts of heavy metals in tailings may be dispersed downstream and downslope from the mine by clastic movement through wind and water and tend to accumulate in food crops grown on soils in the vicinity of the mine.

Mean concentrations of As, Cd, Cu, Pb and Zn in stream sediments from the studied mines are shown in Table 4. Stream sediments were contaminated by waterborne transport of heavy metals inherent in tailings and mine waste materials. In the Sambo mine, the effluent waste waters had

Table 5. Mean concentrations and ranges of Cd, Cu, Pb and Zn in nearby stream water from some base-metal and Au-Ag mines in Korea (unit in μg/l).

Mine	Cd	Cu	Pb	Zn
[a]Sambo Pb-Zn-barite (N=15)	15 (1-89)	17 (1-138)	33 (1-183)	15,850 (20-96,500)
[b]Shinyemi Pb-Zn-Fe (N=7)	4 (1-7)	418 (346-512)	46 (24-69)	1,019 (93-1,512)
[b]Geodo Cu-Fe (N=5)	3 (2-6)	363 (24-654)	21 (11-32)	416 (124-753)
[c]Shiheung Cu-Pb-Zn (N=8)	6 (n.d.-10)	-	41 (10-130)	165 (30-310)
[d]Samkwang Au-Ag (N=5)	12 (8-16)	3 (2-3)	32 (10-50)	40 (10-130)
[d]Kubong Au-Ag (N=4)	44 (9-130)	6 (2-9)	53 (10-120)	190 (20-600)
[d]Keumwang Au-Ag (N=8)	10	10	130	10

N=No. of samples

[a]Jung(1995), [b]Jeon *et al.*(1995), [c]Hwang and Chon(1995), [d]Chon *et al.*(1997)

maximum contents of 89 μg/l of Cd, 138 μg/l of Cu, 183 μg/l of Pb and 96,500 μg/l of Zn (Jung, 1995). This sample also had a high S content of 273,000 μg/l, probably derived from sulfide minerals in the tailings and wastes of the mine. As a result, elevated levels of heavy metals were found in sediments sampled in the immediate vicinity of the mine, especially for Cd, Pb and Zn. In comparison with the Sambo mine, relatively low contents of the metals were found in sediments taken at the Shinyemi and Geodo mines. These may be due to the differences in the amount of the effluent of mine waste materials and tailings into nearby stream around the mines. Like soils in the Shiheung mine, the highest levels of metals were found in sediments with average values of 25.2 mg/kg of Cd, 794 mg/kg of Cu, 1,630 mg/kg of Pb and 2,950 mg/kg of Zn. In the Table 4, we can also find that Cu concentrations in sediments taken around the Geodo and Shiheung mines were relatively higher than those around the others due to their Cu mineralization. This result is strongly supported that the types of mineralization of each mine have a great influence on the species, the extent and degree of toxic element contamination in the surface environment.

It is well known that heavy metal concentrations in fresh or uncontaminated waters are normally very low. According to Bowen (1979), the median values of Cd, Cu, Pb and Zn in fresh waters are 0.1, 3.0, 3.0, 15 μg/l, respectively. However, many researchers have found significant levels of heavy metals in mine waste waters (Fergusson, 1990; Jung, 1995). In this study, high concentrations of heavy metals were also found in stream waters from base-metal mines, and to a lesser extent Au-Ag mines (Table 5). Because of its mineralization, relatively high contents of Zn in the stream waters are investigated at the Sambo and Shinyemi mines. In comparison with metal concentrations in soils and sediments, low concentrations of metals were found in waste waters from the Shiheung mine.

Gold-Silver mines

Mean concentrations of As, Cd, Cu, Pb and Zn in tailings and soils from the 4 studied Au-Ag mines are shown in Table 3. As shown in the table, significant levels of As were found in tailings and surface soils of mine dump sites. In comparison with the tailings, relatively high contents of As were found in the surface soils developed over the mine dump sites. It can be explained that surface soils of the mine dumps contain relatively large amount of As-bearing sulfide minerals such as arsenopyrite. However, the tailings have much lesser amount of the minerals due to removal in the process of mineral separation for Au and Ag. Like base-metal mines, enhanced concentrations of heavy metals were found in tailings and surface soils of mine dump sites. Both the Samkwang and Kubong mines, significant levels of Cd, Pb and Zn, to a less extent Cu, were found in soils sampled at mine dump and tailings sites. These high figures of the metals may be directly influenced by the weathering of sulfide minerals including galena, sphalerite and chalcopyrite existing in the tailings and mine dumps. Thus, these metals are continuously dispersed downstream and downslope from the mine by clastic movement through wind and water. Although enriched concentrations of As and heavy metals were found in surface soils of mine dump site in the Keumwang mine, rel-

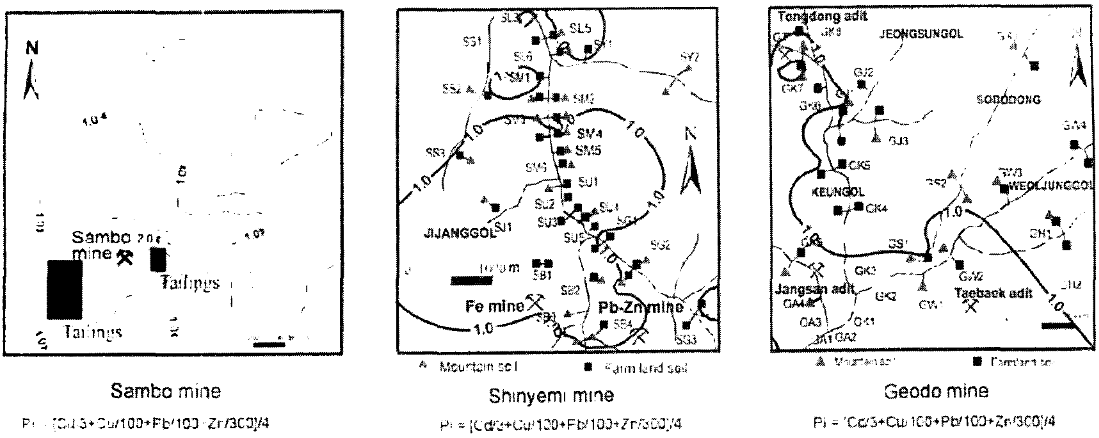

Fig. 4. Pollution index maps of soils in the vicinity of the Sambo Pb-Zn-barite, the Shinyemi Pb-Zn-Fe and the Geodo Cu-Fe mines (adapted from Kim and Chon, 1993a; Jeon *et al.*, 1995).

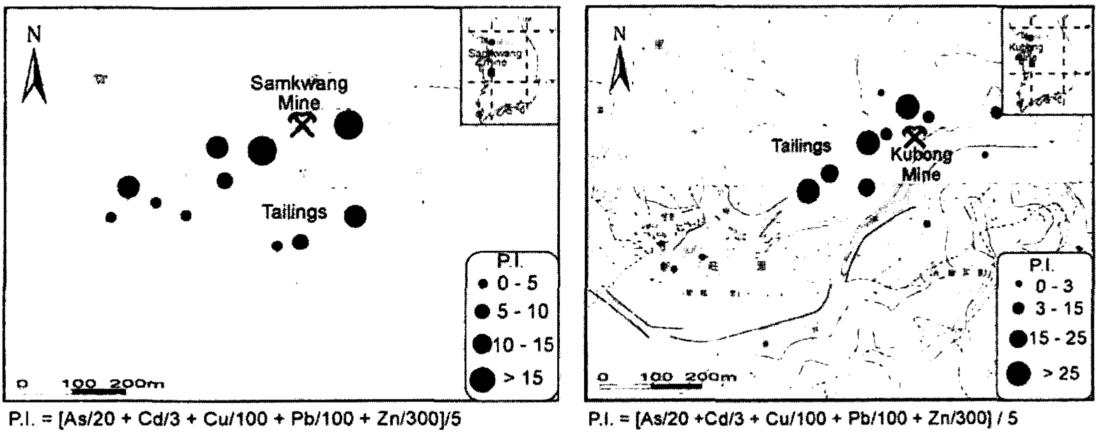

Fig. 5. Pollution index maps of soils from the Samkwang and the Kubong Au-Ag mines (Chon *et al.*, 1997).

atively low contents of As and heavy metals were determined in tailings due to the lack of sulfide minerals. Chon *et al.* (1997) also reported that very limited mineralization of sulfide mineralization occurred in the Keumwang mine. In comparison with the other Au-Ag mines, the concentrations of As and metals in soils from the Kilkok mine were much lower than those from the other mines.

Like element concentrations in soils, significant levels of As, Cd, Cu, Pb and Zn were found in stream sediments from Au-Ag mines, especially for the Samkwang and Kubong mines (Table 4). In the Kubong Au-Ag mine, soils and stream were contaminated by As and heavy metals, and the rice crops collected near the mine show high contents of As and Cd. This shows different uptake preference for As and Cd of rice crops (Fig. 3). These high contents of the elements can be originated from clastic movement through mine waste water. As mentioned, however, relatively low contents of the elements were found in sediments from the Keumwang and Kilkok mines due to a lack of sulfide mineralization of the mines. Similar trends with sediments were also found in element concentrations in stream water samples (Table 5).

Pollution index

It is well known that most of metal and metalloid contamination in the surface environment is associated with a cocktail effect of each contaminant rather than one element. Thus, a pollution

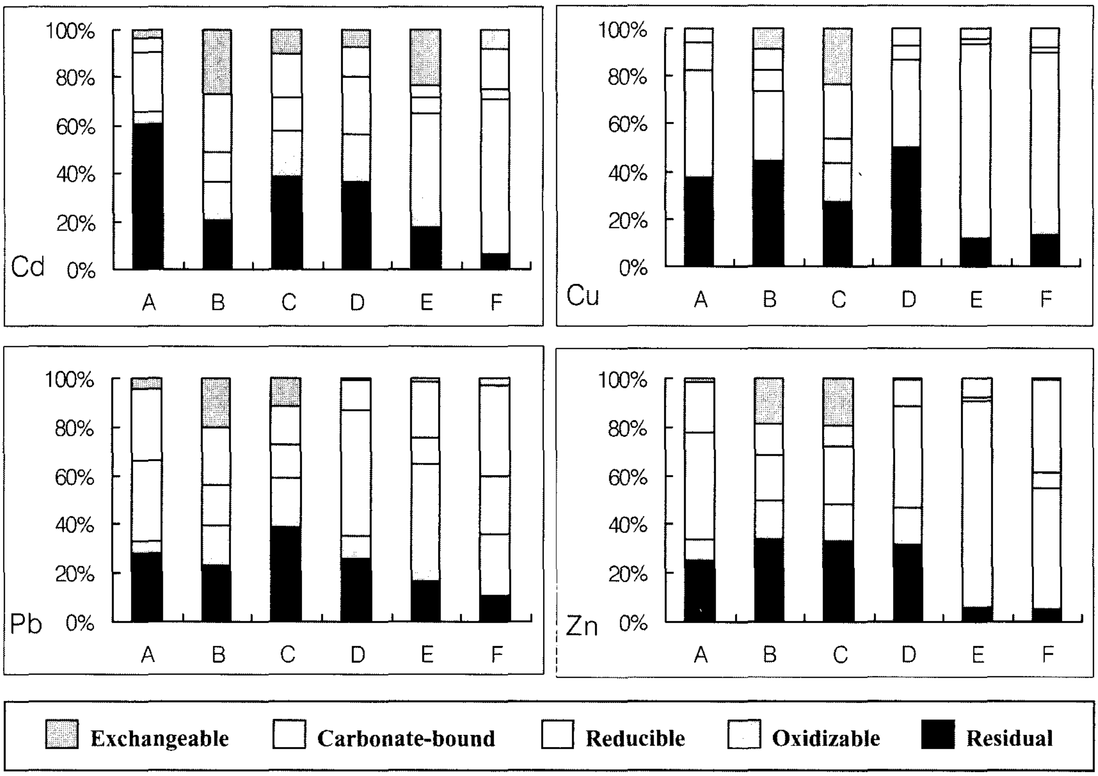

Fig. 6. Mean chemical partitionings of Cd, Cu, Pb and Zn in stream sediments from Sambo (A)[a], Shinyemi (B)[b] and Geodo (C)[c], soils from Shiheung (D)[d], and tailings from Samkwang (E)[e] and Kubong (F)[f].
[a]Kim and Chon (1993b), N=16; [b]Jeon *et al.* (1995), N=10; [c]Jeon *et al.* (1995), N=10; [d]Hwang and Chon (1995), N=6; [e]Chon *et al.* (1997), N=3, [f]Chon *et al.* (1997), N=4

index (PI) was introduced to identify multi-element contamination. This study also implemented the concept of the PI to examine an overall elemental toxicity in the study areas. The PI of soils is computed by average ratios of trace element concentrations in soils divided by the guideline values. When the PI values of soils exceed 1.0, the soils are considered as potentially contaminated by multi-elements and it may recommend a continuous environmental monitoring of the area.

For the Sambo, Shinyemi and Geodo mine areas, tolerable levels in soils (Kloke, 1979) were used as guideline values, and the contouring maps for computed PI values are illustrated in Fig. 4. In general, tolerable levels suggested by Kloke (1979) are the threshold values of trace element concentrations in soils based on total-content determination methods, which can produce crops being unsafe for human or animal consumption, if higher than those. The values of Cd, Cu, Pb and Zn are 3, 100, 100 and 300, respectively. Kloke (1979) calculated that if the content of metals in soil is not higher than the threshold values, it can be expected that the content of metals in human diets will not exceed weekly tolerable intakes established by FAO/WHO. Therefore, at the areas of high PI values (>1.0) shown in Fig. 4, agricultural activity should be forbidden.

In the Samkwang and Kubong Au-Ag mine areas, As was also included for PI calculation. For the guideline value of As, the warning standard for industrial sites from the Soil Environment Preservation Act of Korea (MOE, 1996; *i.e.* 20 mg/kg) was adopted due to the use of 1.0N HCl for the determination. The areas covered with tailings and soils at ore dressing plants have very high PI values (>10) due to direct influence of mining activities (Fig. 5). Thus, the PI values indicate that the tailings and mine surface soils can be an important source in the nearby environment as their high levels.

CHEMICAL FORMS OF HEAVY METALS

Sequentially extracted metals in several studies are shown as fractionation patterns in Fig. 6. Most extraction procedures in the study of base-metal mines were based on Tessier *et al.* (1979) with five different fractions of metals, such as exchangeable (1M $MgCl_2$), bound to carbonates (1 M NaOAc), bound to Fe-Mn oxides (0.04 M $NH_2OH \cdot HCl$ in 25% HOAc), bound to organic matter (0.02 M HNO_3, 30% H_2O_2) and residual (HF-$HClO_4$). In the Samkwang and Kubong Au-Ag mine areas, the procedure modified from Davidson *et al.* (1994) was applied, which fractionated as exchangeable (1 M $MgCl_2$), bound to carbonates (0.16 M HOAc), reducible (0.1 M $NH_2OH \cdot HCl$), oxidizable (30% H_2O_2, 1 M CH_3COONH_4) and residual(aqua regia).

At the Sambo mine, the chemical forms of Cd, Cu, Pb and Zn in stream sediment samples were investigated. Heavy metals in sediments with directly affected by tailings effluent were mainly present in non-residual forms, especially for Zn (75%), which was probably a consequence of the oxidation of tailings through the streams. This was well in accordance with high contents of Zn in stream water samples.

Heavy metals around the Shinyemi and the Geodo mines were present predominantly in ion-exchangeable forms (9-27%) within the heavily polluted sediments. Particularly, high proportions in exchangeable fraction of Pb in the Shinyemi (20%) and of Cu in the Geodo mine areas (24%) indicated easier release of the elements in the surface environment.

Contaminated soils around the Shiheung mine area shows relatively higher ion-exchangeable fraction of Cd (7%) than those of Cu, Pb and Zn. Most Cu was bound to organic matter and sulfide (37%), and Pb was mainly associated with Fe-Mn oxides (51%). Zinc was largely bound to Fe-Mn oxides (41%) and residual fraction (32%).

From the sequential extraction analysis for tailings samples in the Samkwang and Kubong Au-Ag mines, most of metals were present in the oxidizable fraction, which is well correspondent to the association of metals with sulfide gangue minerals (Fig. 6). Weathering and oxidation of the sulfide minerals may mobilize As and heavy metals into tailings leachate and stream water. In addition, Cd existed more in exchangeable phase than other elements, and high concentration of Cd was also found in stream water from the Samkwang and Kubong mine. Identification of the chemical forms of heavy metals as done in each study may be helpful to estimate the biological availability of metal contaminants and to determine the method of remediation and its operating conditions.

CONCLUSIONS

Heavy metal contamination in the areas of typical base-metal mines and Au-Ag mines in Korea was investigated, and the results of each study were compared between sites. In the base-metal mine areas, agricultural soil, stream sediment and stream water around each mine were severely contaminated by heavy metals that comprised the ore mineralogy. Although the degree and extent of contamination varied with each mine, the dispersion patterns of metals were mainly controlled by the feature of geography, the prevailing wind direction and the distance from the mine.

Elevated levels of As, Cd, Cu, Pb and Zn were found in soils developed over mine waste materials, tailings and slag sampled in the vicinity of the eight mines studied. The source of these elements is mainly the weathering of sulfide minerals associated with their mineralization. In stream sediments, significant contents of trace elements are found in the immediate vicinity of the effluent sites of mine waste materials and waters. Slightly low contents of Cd, Cu, Pb and Zn were found in waters mainly due to their low solubility under high pH of the waters.

In addition, the concept of the pollution index (PI) of soils gives important information on the extent and degree of multi-element contamination and can be applied to the evaluation of soils before their use for agriculture and production of food crops.

Most of chemical forms of metals identified by sequential extraction scheme were non-residual fractions, such as exchangeable, Fe-Mn oxides or organic matter bound forms. Those non-residual forms of metals are susceptible to the change of ambient conditions of a nearby environment and they have a high possibility on bioavailability. In general, Cd and Zn have a higher fraction in exchangeable form than other elements presenting the highest mobility in the soils or sediments.

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