

## Environmental Assessment of Contaminated Soils around Abandoned Mines using The Current Soil Quality Standards

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### 요 약

토양오염기준은 토지이용별 또는 오염노출경로별 오염토양의 조사, 평가 및 복구를 위한 유용한 지침으로 이용될 수 있다. 이 연구에서는 한국을 포함한 몇몇 국가의 토양오염기준을 특히 중금속에 주안점을 두고 검토하였다. 또한 국내 일부 폐광산 지역의 환경오염 조사결과를 토양오염기준과 비교하며 평가하였다. 영국, 네덜란드, 독일, 캐나다, 일본 등의 국가에서는 복구우선순위 선정과 인체건강 및 생태계 보전을 위한 오염토양의 선별수단으로 토양오염기준을 개발하여 왔다. 국내에서는 1996년 토양환경보전법(시행규칙)의 시행에 따라 토양오염기준 설정과 특정토양오염유발시설의 관리, 정기적 토양오염도 조사를 실시하고 있으며 이후 2001년 보완·개정되어 토양오염물질의 확대적용과 토양오염 조사, 관리 및 복원 방법의 보완이 이루어진 바 있다. 그럼에도 불구하고 현 중금속(Cd, Cu 및 Pb)의 오염기준을 적용할 때 폐광산 지역의 폐기물과 이에 오염된 토양의 경우 다량의 중금속을 함유하고 있지만 오염지역으로 규정되지 않을 수도 있다. 이 연구 결과, 0.1N 염산용출법은 중금속의 토양 내 화학적 형태 중 일부 교환성 및 환원성 형태만을 추출하며 황화물 형태를 충분히 용출하지 못하고 있는 것으로 나타났다. 또한 장기적인 환경조건 변화에 따른 토양 내 중금속의 용출성 변화를 평가하기 위해서는 강산추출법이 요구되어진다. 따라서 폐광산지역의 중금속에 의한 토양오염의 타당한 환경평가 결정을 위해 현 분석기법 외에 총함량 분석방법의 병행적용과 이에 따른 새로운 오염기준 설정 등이 필요한 것으로 제시되었다.

**Keywords** : soil quality guidelines, Soil Environment Preservation Act, environmental assessment, abandoned mines

## I. Introduction

Environmental contamination of soils can be aroused by organic and inorganic contaminants from various sources including mining and smelting processes, industrial use of chemicals, vehicle emissions, improper control of tailings, etc. Investigation and assessment of contaminated soils require a risk-based approach, and the risk assessment is based on site investigation to determine contaminant levels which could be compared with available guidelines and standard values. Guidelines are numerical values issued by an authoritative body and intended to assist in the assessment of risks (Petts *et al.*, 1997). In a qualitative risk assessment process, the sites which have the potential to present a significant risk can be identified from a group of sites through screening against guidelines. Regulatory guidelines are nationally or regionally acceptable levels of risks to certain targets assuming defined exposure scenarios, and are given by risk-based calculations to meet with a target level of acceptable residual risks combined with economic and technical feasibility. Alternatively, if information for the risk assessment is limited, the values are set by corresponding natural background levels or by detection limits in analysis.

Most countries with an active policy to deal with contaminated sites use generic criteria, and many countries have been revising these values either to broaden the basis of protection for including ecotoxicological as well as human health risks, or to extend the range of contaminants covered, or to present figures derived from a more risk-based model. Although most of the guidelines produced in different countries have used an approach based on risk assessment in their derivations so as to protect targets of concern, these different guidelines differ markedly in purpose and hence in design. Since the risk characteristics of a contaminated medium vary according to its use, different assumptions and uncertainty factors can be used to develop a range of generic values for different uses. Risk assessment of contaminated soils requires a detailed understanding of the basis of the generic guideline values and the assumptions inherent within them if robust decisions are to be made (Petts *et al.*, 1997).

In Korea, the warning and countermeasure standards were initially set up for eleven residual soil substances including heavy metals (Cd, Cu, As, Hg, Pb and Cr), organic phosphorus compound, petroleum products (BTEX), polychlorinated biphenyl (PCB), and other toxic substances (CN and phenol) based on the Soil Environment Preservation Act in 1996. Five more substances (Zn, Ni, F, TCE and PCE) were added in 2001, and the guidelines are currently under scrutiny for another substances. However, environmental scientists and engineers have pointed out relatively high target

levels of heavy metals despite dilute acid (0.1N HCl) extraction for their analyses, particularly when applied to contaminated areas around abandoned mines (Kim, 1997; Oh *et al.*, 2001). The partial extraction method was also questioned with regard to the suitability of application to soils with a high buffer capacity, and to the long-term environmental assessment. Oh *et al.* (2003) suggested that the partial extraction method is not suitable for an assessment of soil contamination in areas where buffer capacity of soil can be decreased or lost by a long-term exposure to environmental damage such as acidic rain. With increased concern for soil contamination from extended land uses, there is a need to examine current guideline levels and their analytical methods. In this paper, soil quality guidelines in different countries are reviewed with particular respect to inorganic contaminants such as heavy metals, and the current Korean guidelines are envisaged for application in environmental assessment of contaminated soils in mining areas. The results of site investigations around abandoned mine areas that are known to be contaminated with heavy metals were evaluated with guideline values, and the extraction characteristics of heavy metals by the dilute acid extraction method were examined against their chemical speciation.

## **II. Soil quality guidelines in other countries and Korea**

### **1. In other countries**

<Table 1> summarizes the regulatory criteria of some metals and metalloids in soils from the UK, the Netherlands, Germany, and Canada. They have substantially different values for each element and a different set of guidelines according to land uses except the Netherlands. In the UK, the criteria for concentrations of certain contaminants in soil were developed by the Interdepartmental Committee for the Redevelopment of Contaminated Land in the early 1980s (ICRCL, 1987). At this time, two criteria (threshold values and action values) were envisaged for 19 contaminants and pH to assist in the risk assessment for contaminated sites. However, the development of more extensive guidance covering a number of different aspects of risks in the assessment of land contamination was requested by the Government. New risk-based guideline values have been derived using the Contaminated Land Exposure Assessment (CLEA) model on the basis of a particular land-use (DEFRA and Environment Agency, 2002). There are three types of land-use for which guidance values have been developed: residential, allotments and

commercial/industrial. The CLEA model is a computer-based application that combines information on the toxicity of soil contaminants with estimates of potential exposure by adults and children living, working and/or playing on land affected by contamination, over long periods of time. The model was used to generate soil guidance values that establish a contaminant concentration in soil that is protective of human health (DEFRA and Environment Agency, 2002).

<Table 1> Summary of the regulatory criteria of some metals and metalloids (mg/kg)

| Country                  | Classification                             | As  | Cd             | Cu  | Pb    | Zn  | Cr    | Ni    | Hg  |
|--------------------------|--|-----|----------------|-----|-------|-----|-------|-------|-----|
| UK <sup>a</sup>          | Residential without plant uptake           | 20  | 30             | -   | 450   | -   | 200   | 75    | 15  |
|                          | Allotments (residential with plant uptake) | 20  | 2<br>(at pH 7) | -   | 450   | -   | 130   | 50    | 8   |
|                          | Commercial/Industrial                      | 500 | 1,400          | -   | 750   | -   | 5,000 | 5,000 | 480 |
| Netherlands <sup>b</sup> | Target values                              | 29  | 0.8            | 36  | 85    | 140 | 100   | 35    | 0.3 |
|                          | Intervention values                        | 55  | 12             | 190 | 530   | 720 | 380   | 210   | 10  |
| Germany <sup>c</sup>     | Playgrounds                                | 25  | 10             | -   | 200   | -   | 200   | 70    | 10  |
|                          | Residential                                | 50  | 20             | -   | 400   | -   | 400   | 140   | 20  |
|                          | Parks and Recreational                     | 125 | 50             | -   | 1,000 | -   | 1,000 | 350   | 50  |
|                          | Industrial/Commercial                      | 140 | 60             | -   | 2,000 | -   | 1,000 | 900   | 80  |
| Canada <sup>d</sup>      | Agricultural                               | 12  | 1.4            | 63  | 70    | 200 | 64    | 50    | 6.6 |
|                          | Residential/Park land                      | 12  | 10             | 63  | 140   | 200 | 64    | 50    | 6.6 |
|                          | Commercial                                 | 12  | 22             | 91  | 260   | 360 | 87    | 50    | 24  |
|                          | Industrial                                 | 12  | 22             | 91  | 600   | 360 | 87    | 50    | 50  |

<sup>a</sup> DEFRA and Environment Agency (2002)

<sup>b</sup> MHSPE (2000), for a standard soil (10% organic matter and 25% clay)

<sup>c</sup> FEM (1998), trigger values for soil-human health pathway

<sup>d</sup> CCME (1997)

In the Netherlands, the government sought to improve contaminated land, and it would be suitable for any potential use. This led to the development of guidance values for a range of 57 contaminants known as the 'ABC values'. These were subsequently refined to form the 'Target and Intervention values' for 67 contaminants. The target value is in the baseline concentration value with no risk for humans, plants, animals and ecological systems. The intervention value is the maximum tolerable concentration with a significant risk above which remediation is required. Target and intervention values of arsenic and heavy metals listed in <Table 1> are for a standard soil (10%

organic matter and 25% clay), and they can vary according to the composition of the soil. The relevant intervention values can be calculated with a soil type correction formula for the various contents of clay and organic matter (MHSPE, 2000).

Soil quality standards in Germany are defined in the Federal Soil Protection Act (FEM, 1998) and Soil Protection Ordinance (FEM, 1999). The purpose of the Act is to protect or restore the functions of the soil on a permanent sustainable basis. Trigger and action values as guidelines are defined with respect to soil use and pathways (soil-human being, soil-plant, and soil-groundwater). Precautionary values are also defined to have the objective of maintaining multi-functionality and therefore have to comprise all possible soil uses. A differentiation is performed with respect to chemical and physical soil properties. For heavy metals, different soil types and pH-values are considered. For organic chemicals the values are differentiated with respect to different humic contents (FEM, 1998).

In 1991, the Canadian Council of Ministers of the Environment (CCME) recommended interim environmental quality criteria for soil and water to address the immediate need for management tools to support the assessment and remediation of contaminated sites in Canada. New soil quality guidelines have been provided for the protection, maintenance and improvement of specific uses of land and water. Recommended soil quality guidelines were developed for different land uses with defined exposure scenarios: agricultural, residential/parkland, commercial and industrial (CCME 1997). Guidelines are applied in identifying and classifying sites, to assess the general degree of contamination at a site and to determine the need for further action, and as a basis for remediation objectives.

Soil pollution control measures have been established for agricultural land soil and urban type soil in Japan (<Table 2>). Maximum allowable limits of heavy metals in agricultural soils have been set for Cd, Cu and As. The requirements for the designation of agricultural land soil pollution policy areas under the Agricultural Land Soil Pollution Prevention Law are based on the maximum allowable limit of Cd of 1.0 mg/kg in unpolished rice grown on soil, on soil concentration of Cu of 125 mg/kg by 0.1N HCl extraction, and on soil concentration of As of 15 mg/kg by 1.0N HCl extraction. Since the relationship between the Cd concentration in rice and that in soil is affected by many factors, the maximum allowable limit of Cd in soil is determined by the concentration of Cd in rice grown in the paddy soil (Asami, 1997). Environmental Quality Standards (EQS) for urban type soils were issued in 1991 to deal with pollution problems in urban areas, and were revised in 1994 regulating 25 substances (EA, 1994). Administrative guidance is provided to

polluters to urge them to clean up polluted soil voluntarily under the guidelines. Notably, it is mentioned on the regulation that the standards listed in <Table 2> are not applicable to places where natural toxic substances exist such as near mineral veins, and places designated for storage of toxic materials such as waste disposal sites.

<Table 2> Environmental Quality Standards (EQS) for soil pollution in Japan <sup>a</sup>

| Substance     | Target level of soil quality examined through leaching test <sup>b</sup> and content test                                  |
|---------------|--|
| Arsenic       | 0.01 mg/l or less in sample solution, and less than 15 mg/kg <sup>c</sup> in soil for agricultural land (paddy field only) |
| Cadmium       | 0.01 mg/l in sample solution and less than 1 mg/kg in rice for agricultural land   |
| Lead          | 0.01 mg/l or less in sample solution   |
| Chromium (VI) | 0.05 mg/l or less in sample solution   |
| Copper        | less than 125 mg/kg <sup>d</sup> in soil for agricultural land (paddy field only)  |
| alkyl mercury | not detectable in sample solution  |
| total mercury | 0.0005 mg/l or less in sample solution   |

<sup>a</sup> Japan Environment Agency (EA, 1994)

<sup>b</sup> soil (1) : water (10) leaching

<sup>c</sup> 1.0N HCl extraction

<sup>d</sup> 0.1N HCl extraction

A setup for soil contamination assessment is based on the Soil Screening Guidance (SSG). The U.S. Environmental Protection Agency (EPA) has developed the SSG as a tool to help standardize and accelerate the evaluation and cleanup of contaminated soils at National Priorities List (NPL) sites. The guidance provides a methodology for environmental science/engineering professionals to calculate risk-based, site-specific, soil screening levels (SSLs) for contaminants in soil that may be used to identify areas for further study or investigation (EPA, 1996). The SSLs are not intended to be used as national cleanup standards but are risk-based concentrations derived from equations combining exposure information assumptions with EPA toxicity data. The soil screening process is a step-by-step approach that involves: developing a conceptual site model (CSM), comparing the CSM to the SSL scenario, defining data collection needs, sampling and analyzing soils at site, calculating site-specific SSLs, comparing site soil contaminant concentrations to calculated SSLs, and determining which areas of the site require further study (EPA, 1996).

## 2. In Korea

Regulatory criteria of arsenic and heavy metals in soils were set up based on the Soil Environment Preservation Act by the Ministry of Environment (MOE) in 1996, which was revised in 2001 augmenting regulations by more substances. Under the standards for soil contamination, lands are classified by their uses as either agricultural areas or factory/industrial areas, and a separate set of standards for soil contaminants applies to each. When soil contamination poses a real danger to human health or crops and animals and therefore requires the imposition of regulatory measures, including possible suspension of activities or injunctions on the construction of new facilities, warning and countermeasure standards depending on the degree of soil contamination will apply (<Table 3>). The warning standards are set forth at about 40% of the countermeasure standards for soil contamination, which is the degree of soil contamination requiring action to prevent further soil contamination (MOE, 1996).

<Table 3> Warning standards and countermeasure standards of heavy metals in the Soil Environment Preservation Act of Korea (mg/kg)

| Contaminants    | Warning standards     |                       | Countermeasure standards |                       |
|-----------------|-----------------------|-----------------------|--------------------------|-----------------------|
|                 | site "A" <sup>a</sup> | site "B" <sup>b</sup> | site "A" <sup>a</sup>    | site "B" <sup>b</sup> |
| Cd              | 1.5                   | 12                    | 4                        | 30                    |
| Cu              | 50                    | 200                   | 125                      | 500                   |
| As              | 6                     | 20                    | 15                       | 50                    |
| Hg              | 4                     | 16                    | 10                       | 40                    |
| Pb              | 100                   | 400                   | 300                      | 1,000                 |
| Cr (VI)         | 4                     | 12                    | 10                       | 30                    |
| Zn <sup>c</sup> | 300                   | 800                   | 700                      | 2,000                 |
| Ni <sup>c</sup> | 40                    | 160                   | 100                      | 400                   |

<sup>a</sup> Agricultural areas include rice paddies, orchards, pastures and recreational sites (limited to sites with trees or grass).

<sup>b</sup> Factory/industrial areas cover industrial sites and other miscellaneous sites.

<sup>c</sup> revised in 2001.

The MOE established two separate soil contamination monitoring networks: the nationwide network and the regional network, and has been monitoring soil contamination at specified locations of networks under the standards of soil contamination. Specific soil contaminating facilities are also

designated: manufacturing or storing facilities for petroleum products and for toxic chemicals, and oil pipeline facilities. These facilities must be registered at city, county and district offices, being subject to government controls, and should satisfy the applicable standards during regular inspections. Soil contamination prevention projects were carried out in the areas of closed mines located in water supply source protection zones where inspections revealed concentrations of heavy metals in excess of the warning standards of soil contamination. Prevention measures in mining areas entail closing of mine entrances to prevent the flow of mine water and slag, the installation of retaining walls to prevent rainwater and groundwater from flowing through mines, and the removal of pollutants accumulated in drainage pipes. The relevant authorities are notified of soil contaminated with hazardous heavy metals (MOE, 1996).

The guideline values are based on the Korean standard analytical method which is 0.1N HCl extraction for heavy metals (Cd, Cu and Pb), and 1.0N HCl for As. For Zn and Ni, which were added in the revised version in 2001, sub-total determination procedures are applied using aqua regia. In other countries listed in <Table 1>, mineral acids or their mixtures (HNO<sub>3</sub> + HClO<sub>4</sub>, aqua regia etc.) have been used for heavy metal determination from soils. Dilute acids such as 0.1N HCl are frequently used as extractants for estimating metals available for plant uptake, or as simulated gastric solutions for determining bioavailability (Gasser *et al.*, 1996). However, they may give doubtful values when applied to some soil and to other materials such as metalliferous mining wastes because of the variations in pH, mineral composition, weathering rates and metal speciation; hence care must be taken in the interpretation of results (Petts *et al.*, 1997). In Japan which also has a dilute-acid (0.1N or 1.0N HCl) determination method, the standards are provided not applicable to the place where natural toxic substances exist such as the vicinities of mineral veins (EA, 1994). The application of the current dilute-acid determination method needs to be evaluated with regard to the effective assessment of contaminated soils in abandoned mine areas.

### III. Materials and Methods

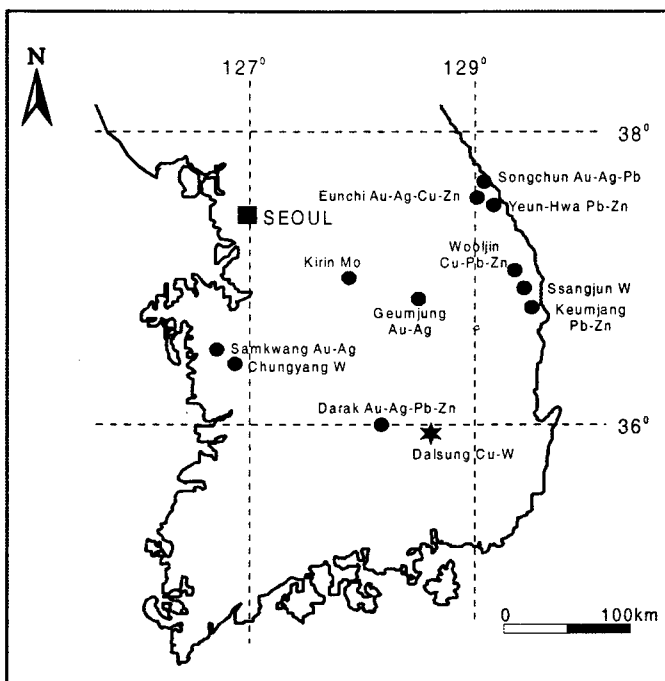
In order to investigate heavy metal contamination around inactive mine areas, mine tailings and associated soils were sampled in 11 metalliferous mines as shown in <Figure 1>. The mines produced gold, silver, tungsten and base metals depending on ore mineralogy, and were abandoned due to exhaustion of reserves about 10 to 30 years ago. In these mineral deposits, base metals occurred predominantly as galena (PbS), sphalerite (ZnS) and chalcopyrite (CuFeS<sub>2</sub>), and Au-Ag



bearing quartz vein also contained some sulphides such as pyrite ( $\text{FeS}_2$ ) and arsenopyrite ( $\text{FeAsS}$ ) (KMPC, 1987). The metals were extracted through pulverization and flotation processes, and large quantities of mine tailings were generated. Much of the wastes, including tailings, were abandoned without continuing management, and would be subject to wind and water erosion, resulting in wind and waterborne transport of the contaminants inherent in the wastes.

Each sample was a composite of sub-samples taken from the surface of mine dumps, tailings, and around ore-processing facilities. The collected samples were air-dried and sieved to less than 2 mm. For the chemical analysis, the samples were ground to pass an 80-mesh sieve ( $180 \mu\text{m}$ ), and sub-total concentrations of Cd, Cu, Pb, and Zn were determined by ICP-AES (inductively coupled plasma atomic emission spectrometry) of aqua regia-digested samples. Aqua regia digestion extracts between 70 and 90% of the total contents of heavy metals (Ure, 1995). The 0.1N HCl-extraction concentrations of heavy metals were also measured following the Korean standard analytical method. In the study, mixtures of 0.1N HCl (50ml) and tailings samples (10g) were shaken on a horizontal shaker (100rpm) at  $30^\circ\text{C}$  for 1 hour and the supernatants were filtered through a 0.45  $\mu\text{m}$  membrane filter for subsequent chemical analysis using ICP-AES. The paste pH of the samples was determined using a 2:1 ratio of sample to deionized water (Jung *et al.*, 1999).

Detailed geochemical surveys were undertaken in the Dalsung Cu-W mine area, which was located in southeastern Korea (<Figure 1>). The mine was closed in 1975, and acid drainage from old mine adits was found to be the source of the heavy metal contamination in the tributary system and nearby agricultural field (Kim, 1997). Surface and subsurface soils from orchards and upland fields were sampled in the vicinity of the mine, and different extraction methods for the determination of heavy metal concentrations were applied in order to investigate their influences on the assessment of contaminated soils. The air-dried samples were sieved to  $< 2 \text{ mm}$ , and were ground to pass an 80-mesh sieve ( $180 \mu\text{m}$ ). Concentrations of Cd, Cu, Pb and Zn were determined by sub-total extraction using  $\text{HNO}_3 + \text{HClO}_4$  (Thompson and Walsh, 1989) and aqua regia (Ure, 1995), and by a extraction method with 0.1N HCl. Heavy metal contamination of the area was assessed based on the result of each method. In addition, chemical speciation of heavy metals in soil samples was examined from a sequential extraction procedure recommended by Davidson *et al.* (1994). Sequentially extracted heavy metals were compared with the concentration data from the above methods.



<Figure 1> Locations of metalliferous mines of Korea in case studies

#### IV. Results and Discussion

Concentrations of heavy metals in the mine tailings extracted by aqua regia and 0.1N HCl are summarized in <Table 4>, organized in order of pH values. There is a great variation in pH values, ranging from 1.80 to 7.59, which may result from relative abundance of sulphide and carbonate minerals (Balistrieri *et al.*, 1999). The low pH values are a result of the oxidation of sulphide minerals such as pyrite, whereas the high pH may indicate some interactions with carbonate minerals in the tailings. In acidic mine tailings, the quantity or dissolution of carbonate minerals has been insufficient to buffer the acidity generated by sulphide mineral oxidation, and there is a potential to result in the mobilization of heavy metals into solution.

Heavy metal concentrations extracted by aqua regia vary among the mines, apparently depending on the product metals. The tailings of base metal mines contain relatively high contents of Pb and Zn, often including Cd. Among them, the Chungyang mine sample has the highest concentrations of Cd, Pb and Zn, which are derived from abundant sulphide mineral compositions (KMPC, 1987). Based on the results of sub-total concentrations of heavy metals, it can be suggested that most of

the mine tailings contain considerable amounts of heavy metals, exceeding the guideline values produced in other countries (<Table 1>). It is anticipated that environmental contamination by heavy metals in nearby tributaries and agricultural soils have been aroused from the erosion and weathering of mine tailings. However, the concentrations of metals extracted by 0.1N HCl are not directly related to those extracted by aqua regia, and in some tailings, they are less than the warning standards of Korea for an industry area, 12 mg/kg Cd, 200 mg/kg Cu and 400 mg/kg Pb. For example, although total concentrations of Pb in most of the mine tailings are significantly high, greater than 2,000 mg/kg of German guideline, the 0.1N HCl extractable concentrations are in all instances below the current Korean guideline. In reality, some mine tailings which have metal contaminants exceeding the guidelines based on total concentration may not be designated as a contamination source when assessed by the 0.1N HCl extraction method and its guidelines.

<Table 4> Values of pH and concentrations (mg/kg) of Cd, Cu, Pb and Zn in various mine tailings extracted by 0.1N HCl and aqua regia

| Mine               | pH   | 0.1N HCl |       |      |        | aqua regia |       |        |        | extractability (%)* |      |      |      |
|--------------------|------|----------|-------|------|--------|------------|-------|--------|--------|---------------------|------|------|------|
|                    |      | Cd       | Cu    | Pb   | Zn     | Cd         | Cu    | Pb     | Zn     | Cd                  | Cu   | Pb   | Zn   |
| Songchun Au-Ag-Pb  | 1.80 | 2.08     | 106   | 52   | 990    | 8.5        | 456   | 17,200 | 2,910  | 24.5                | 23.1 | 0.3  | 34.0 |
| Wooljin Cu-Pb-Zn   | 2.38 | 0.84     | 6.0   | 51   | 127    | 2.6        | 121   | 3,100  | 1,180  | 32.1                | 5.0  | 1.6  | 10.7 |
| Ssangjun W         | 2.47 | 0.08     | 69.5  | 7.1  | 10     | 0.68       | 1,124 | 58.4   | 25.2   | 11.0                | 6.2  | 12.1 | 39.7 |
| Darak Au-Ag-Pb-Zn  | 3.50 | 1.34     | 24.4  | 73.5 | 187    | 2.9        | 82.8  | 13,080 | 394    | 46.4                | 29.5 | 0.6  | 47.3 |
| Eunchi Au-Ag-Cu-Zn | 4.23 | 58.0     | 239   | 126  | 10,400 | 142        | 876   | 18,080 | 24,320 | 40.8                | 27.2 | 0.7  | 42.8 |
| Chungyang W        | 4.33 | 47.3     | 52    | 103  | 1,520  | 986        | 2,130 | 35,160 | 28,960 | 4.8                 | 2.4  | 0.3  | 5.2  |
| Yeunhwa Pb-Zn      | 5.66 | 3.96     | 0.1   | 4.3  | 97     | 84.4       | 404   | 7,480  | 9,640  | 4.7                 | 0.0  | 0.1  | 1.0  |
| Keumjang Pb-Zn     | 5.94 | 20.8     | 1,240 | 51   | 3,880  | 58.4       | 4,220 | 10,000 | 14,920 | 35.5                | 29.3 | 0.5  | 26.0 |
| Kirin Mo           | 7.00 | 0.13     | 0.2   | 1.0  | 2.0    | 0.44       | 10    | 11.2   | 116    | 28.4                | 1.5  | 8.9  | 1.7  |
| Geumjung Au-Ag     | 7.20 | 0.08     | 7.0   | 0.3  | 7.2    | 0.7        | 18.8  | 12.4   | 29     | 11.4                | 37.0 | 2.0  | 24.7 |
| Samkwang Au-Ag     | 7.59 | 13.2     | 7.6   | 510  | 500    | 27.4       | 34.8  | 720    | 1,050  | 48.2                | 21.7 | 70.8 | 47.5 |

\* extractability (%) = conc. by 0.1N HCl / conc. by aqua regia  $\times$  100(%)

Extractabilities of heavy metals by 0.1N HCl (conc. by 0.1N HCl divided by conc. by aqua regia) may indicate easily soluble fraction and weakly adsorbed phases which are relatively mobile and involved in chemical reactions. It is generally accepted that the leachable amount of metals increases with decreasing pH. However, calculated extractabilities have a poor relationship with pH values and yield very low values for Pb (0.1-12.1%) except one mine (<Table 4>). This is because the mobility and bioavailability of heavy metals are influenced not only by pH condition, but also

mineral compositions, weathering rates, and geochemical properties of metals. It is apparent that heavy metals become more mobile as the weathering and oxidation reaction of sulphide minerals in mine tailings proceeds. In this viewpoint, the 0.1N HCl extraction method may not be appropriate for a long-term risk assessment of heavy metal contamination.

<Table 5> Concentrations (mg/kg) of Cd, Cu, Pb and Zn in some soil samples in the Dalsung Cu-W mine area extracted by 0.1N HCl, HNO<sub>3</sub>-HClO<sub>4</sub> and aqua regia<sup>a</sup>

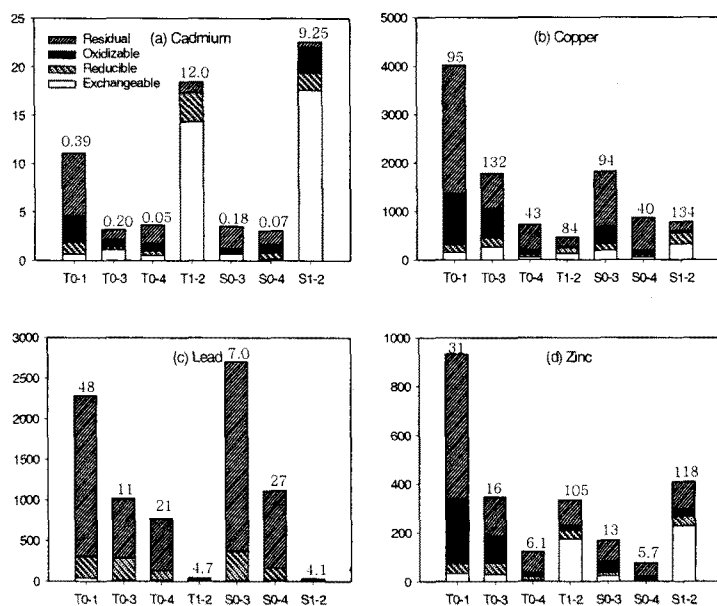
| Sample I.D. | 0.1N HCl |     |     |     | HNO <sub>3</sub> -HClO <sub>4</sub> |       |       |     | aqua regia |       |       |     |
|-------------|----------|-----|-----|-----|-------------------------------------|-------|-------|-----|------------|-------|-------|-----|
|             | Cd       | Cu  | Pb  | Zn  | Cd                                  | Cu    | Pb    | Zn  | Cd         | Cu    | Pb    | Zn  |
| T*0-1       | 0.39     | 95  | 48  | 31  | 9.5                                 | 5,000 | 2,390 | 930 | 10         | 5,050 | 2,790 | 965 |
| T*0-2       | 1.10     | 57  | 4.5 | 6.3 | 3.6                                 | 2,750 | 957   | 234 | -          | -     | -     | -   |
| S**0-2      | 0.32     | 40  | 2.5 | 4.8 | 2.0                                 | 1,340 | 2,410 | 110 | -          | -     | -     | -   |
| T*0-3       | 0.20     | 132 | 11  | 16  | 2.9                                 | 1,810 | 1,010 | 313 | 2.8        | 1,850 | 1,150 | 311 |
| S**0-3      | 0.18     | 94  | 7.0 | 13  | 3.1                                 | 1,870 | 2,920 | 124 | 2.5        | 1,920 | 3,200 | 140 |
| T*0-4       | 0.05     | 43  | 21  | 6.1 | 28                                  | 776   | 801   | 173 | 2.2        | 775   | 785   | 132 |
| S**0-4      | 0.07     | 40  | 27  | 5.7 | 2.0                                 | 956   | 1,140 | 105 | 3.0        | 920   | 1,200 | 82  |
| T*0-6       | 0.50     | 43  | 19  | 4.9 | 4.3                                 | 1,230 | 785   | 272 | -          | -     | -     | -   |
| S**0-6      | 0.14     | 55  | 14  | 4.8 | 2.8                                 | 880   | 821   | 237 | -          | -     | -     | -   |
| T*1-2       | 12.0     | 84  | 4.7 | 105 | 12                                  | 496   | 61    | 333 | 16         | 535   | 44    | 336 |
| S**1-2      | 9.25     | 134 | 4.1 | 118 | 16                                  | 868   | 61    | 371 | 17         | 875   | 42    | 450 |

<sup>a</sup> Kim (1997)

T\* : top soil, S\*\* : subsurface soil

In the Dalsung mine area, Kim (1997) reported that the concentrations of heavy metals in soil samples where mine wastewater have been discharged, were higher than average levels of non-polluted soils, ranging up to 28 mg/kg Cd, 5,000 mg/kg Cu, 2,390 mg/kg Pb and 930 mg/kg Zn. It was suggested that contamination of soils in the area was derived from acid mine drainage and weathering process of the parent rocks, particularly for Cu and associated elements (Kim, 1997). Soil pH was extremely acidic to 3.9, and under this condition, heavy metals are easily mobilized and accumulated in growing crops. The results of some soil samples around the mine adits in this study are given in <Table 5>, and sub-total concentrations of heavy metals extracted by mixed acids (HNO<sub>3</sub>+HClO<sub>4</sub>) and aqua regia, are higher than the normal background values reported in literature, such as 0.35 mg/kg Cd, 30 mg/kg Cu, 35 mg/kg Pb and 90 mg/kg Zn (Bowen, 1979). Some heavy metal concentrations also exceed the criteria for agricultural area of Canada (<Table 1>), requiring remediation of the areas. However, the concentrations extracted by

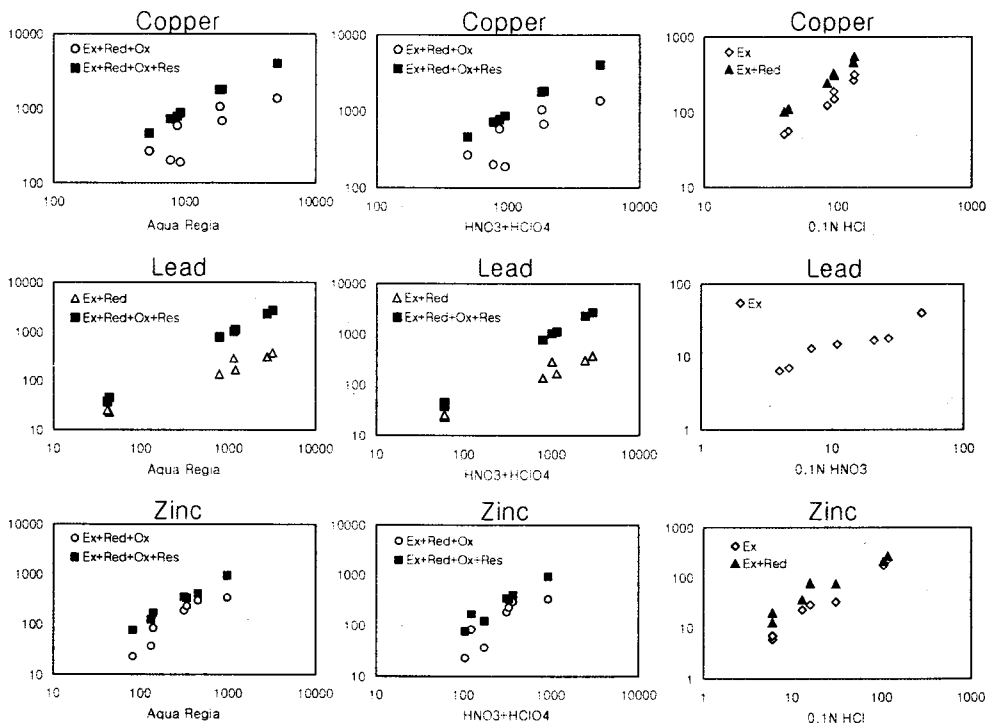
0.1N HCl are significantly low compared to the data from the other methods. When the results of the samples are evaluated with the warning standards of Korea (<Table 3>), heavy metal concentrations are lower than the values, and the study area can be assessed as uncontaminated. The current guideline values are set too high to assess the observed contamination of soils as shown in this case.



<Figure 2> Heavy metal concentrations (mg/kg) in soils by a sequential extraction method in the Dalsung mine area (Kim, 1997)  
 0.1N HCl extractable concentrations are given on top of each column.  
 T : top soil, S : subsurface soil

Sequentially extracted concentrations of heavy metals are illustrated as their chemical forms, such as exchangeable, reducible, oxidizable and residual forms (<Figure 2>). The exchangeable forms give the most easily available fraction of metals which are weakly adsorbed or coated on oxides and organic compounds, and in the procedure used, carbonate-bound fraction is also included. The reducible, oxidizable and residual fractions are equated with iron/manganese oxides, organic matter/sulphides and silicates/primary sulphide minerals, respectively (Ure and Davidson, 1995). Residual fractions are dominant for Cu and Pb indicating their origin of soil parent materials, and Cd and Zn are also associated with exchangeable and oxidizable phases. When the results of the Korean standard analytical method are compared with sequential extraction data, the 0.1N HCl extractable concentration of each element is less than the corresponding exchangeable

phase. Relationships between cumulative concentrations of sequential extraction steps and concentration data by single extractions are summarized in <Table 6> and graphically illustrated in <Figure 3>. Although it was hard to get statistical meaning in relationships for Cd due to two extremely high values (outliers), sub-total determination methods are correlated well with cumulative values to oxidizable or residual fractions in Cu and Zn. Extraction data by 0.1N HCl are related to exchangeable and reducible phases. However, the concentration of Pb by 0.1N HCl has a correlation with only exchangeable phase. In the 0.1N HCl extraction method, some amounts of heavy metals in easily soluble and exchangeable phases and bound to oxides of Fe and Mn can be extracted depending on the geochemical properties of metals, but the residual sulphide fraction is the least extractable. Relative low extractability of Pb may be due to geochemical characteristics and resistance to oxidation of Pb-containing sulphide minerals. Considering the sulphide minerals are predominant sources of heavy metals in metalliferous mine areas, the analytical method should evaluate the heavy metals associated with sulphides for a risk assessment of the area.



<Figure 3> Relationship between heavy metal concentrations (mg/kg) in soils by a sequential extraction method and single extraction analyses (Kim, 1997)

Ex : exchangeable, Red: reducible, Ox: oxidizable & Res: residual

<Table 6> Correlation coefficients between heavy metal concentrations in soils by sequential extraction method and total analysis<sup>a</sup>

(Ex : exchangeable, Red : reducible, Ox : oxidizable &amp; Res : residual)

| Cadmium                             |            |                                     |          |
|-------------------------------------|------------|-------------------------------------|----------|
|                                     | aqua regia | HNO <sub>3</sub> -HClO <sub>4</sub> | 0.1N HCl |
| Ex                                  | 0.91**     | 0.27                                | 0.96**   |
| Ex+Red                              | 0.93**     | 0.27                                | 0.97**   |
| Ex+Red+Ox                           | 0.95**     | 0.28                                | 0.95**   |
| Ex+Red+Ox+Res                       | 0.99**     | 0.28                                | 0.90**   |
| 0.1N HCl                            | 0.89**     | 0.23                                | 1.00     |
| HNO <sub>3</sub> -HClO <sub>4</sub> | 0.22       | 1.00                                |          |
| aqua regia                          | 1.00       |                                     |          |
| Copper                              |            |                                     |          |
|                                     | aqua regia | HNO <sub>3</sub> -HClO <sub>4</sub> | 0.1N HCl |
| Ex                                  | 0.09       | 0.08                                | 0.97**   |
| Ex+Red                              | 0.16       | 0.16                                | 0.98**   |
| Ex+Red+Ox                           | 0.88**     | 0.87*                               | 0.62     |
| Ex+Red+Ox+Res                       | 1.00**     | 0.99**                              | 0.25     |
| 0.1N HCl                            | 0.22       | 0.21                                | 1.00     |
| HNO <sub>3</sub> -HClO <sub>4</sub> | 1.00       | 1.00                                |          |
| aqua regia                          | 1.00       |                                     |          |
| Lead                                |            |                                     |          |
|                                     | aqua regia | HNO <sub>3</sub> -HClO <sub>4</sub> | 0.1N HCl |
| Ex                                  | 0.63       | 0.60                                | 0.96**   |
| Ex+Red                              | 0.92**     | 0.92**                              | 0.37     |
| Ex+Red+Ox                           | 0.93**     | 0.92**                              | 0.38     |
| Ex+Red+Ox+Res                       | 1.00**     | 1.00**                              | 0.48     |
| 0.1N HCl                            | 0.48       | 0.45                                | 1.00     |
| HNO <sub>3</sub> -HClO <sub>4</sub> | 1.00       | 1.00                                |          |
| aqua regia                          | 1.00       |                                     |          |
| Zinc                                |            |                                     |          |
|                                     | aqua regia | HNO <sub>3</sub> -HClO <sub>4</sub> | 0.1N HCl |
| Ex                                  | 0.21       | 0.12                                | 0.99**   |
| Ex+Red                              | 0.30       | 0.22                                | 0.99**   |
| Ex+Red+Ox                           | 0.88**     | 0.83*                               | 0.65     |
| Ex+Red+Ox+Res                       | 1.00**     | 0.99**                              | 0.24     |
| 0.1N HCl                            | 0.28       | 0.21                                | 1.00     |
| HNO <sub>3</sub> -HClO <sub>4</sub> | 0.99**     | 1.00                                |          |
| Aqua regia                          | 1.00       |                                     |          |

<sup>a</sup> Kim (1997)

\*Significant at P = 0.05, \*\*Significant at P = 0.01

As discussed in the above, it may be inadequate to assess heavy metal contamination of mine tailings and associated soils with the 0.1N HCl extraction method. It should also be noted that the extractability of 0.1N HCl on heavy metals may vary at different mine sites depending on the environmental conditions. For an appropriate assessment of contaminated soils in the area, extraction methods with strong extractants should be provided to evaluate all chemical forms of heavy metals present in soils, in addition to the partial extraction method. The obtained concentration data using strong extractants can cover the possible variations of leachability or mobility of heavy metals, which may be caused by long-term environmental changes. A different set of quality guideline values needs to be established which is based on total (or sub-total) extraction methods, and the risk assessment based result should be provided as supplementary data.

## V. Conclusion

Soil quality guidelines were reviewed in some other countries and Korea, and mine tailings and affected soils from various inactive mines in Korea were assessed with the guidelines. The mine tailings frequently contain significant concentrations of Cd, Cu, Pb and Zn exceeding the guideline values provided by other countries. It is evident that the adjacent soils and groundwater have been contaminated by mine tailings as primary sources of environmental contamination. However, the 0.1N HCl extraction suggested by the Korean standard analytical method has shown that only small fractions of heavy metals can be extracted in the tailings and the method is inappropriate to assess the long-term contamination by ongoing oxidation and weathering process.

Detailed geochemical study on the Dalsung Cu-W mine area, also revealed the heavy metal contamination by acid mine drainage in soils around the mine adits. The concentrations of Cd, Cu, Pb and Zn in soils extracted by mixed acids ( $\text{HNO}_3 + \text{HClO}_4$  and aqua regia) exceed the normal values and the guidelines based on total concentrations. When soil contamination of the area is assessed with the current guidelines of Korea, however, metal concentrations extracted by 0.1N HCl are lower than the values, and the area may be designated as uncontaminated. The 0.1N HCl extractable metals are related with exchangeable and iron/manganese oxide bound fractions in comparison with sequentially extracted phases. The metals associated with sulphides cannot be reflected with the method. It is recommended that the analytical method with strong reagents should be applied to the soils in addition to the 0.1N HCl extraction for an appropriate assessment of



contaminated soils in mining areas.

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