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# Determination of Cadmium and Zinc Contamination Source in Arable Soil in the Vicinity of a Zinc Smelting Factory

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**ABSTRACT: Agricultural area in the vicinity of the △△ smelting factory in Kyeongbuk province, the third largest zinc smelting factory in the world, was contaminated by high concentration of heavy metals. However, the heavy metals source was not yet directly traced and thus, resulted to a conflict between the factory and residents within its vicinity. In order to determine the level of heavy metal contamination in the arable lands located at the north eastern part of the factory, soils were sampled systematically. To find out the major reason for the occurrence of this problem, waters and aerosols were sampled with constant intervals to the upward and downward direction from the factory and were analyzed to find out the heavy metal concentrations. Cadmium (Cd) and zinc (Zn) of the heavy metals were highly accumulated more than the Korean warning criteria (Cd 1.5, Zn 300 mg kg$^{-1}$) with mean values 1.7 and 407 mg kg$^{-1}$, respectively, at the surface soils (0-20 cm), and heavy metal concentration significantly decreased with increasing soil depth. In addition, the concentration of both metals slightly decreased with increasing distance from the factory to the surface soils. Cadmium and Zn were detected in the upward stream water with low concentration and concentrations increased significantly in the downstream after passing across the factory. Aerosol samples also showed traces of Cd and Zn which could be attributed to the contamination of the water system and the surface soils. Conclusively, Cd and Zn emitted from the △△ smelting factory moved with the aerosol in the atmosphere and thus, contaminated the agricultural areas and the water system within its vicinity.**

**Key Words:** cadmium, zinc, smelting factory, aerosol

## INTRODUCTION

At present heavy metal contamination of soils through anthropogenic activities is a widespread and serious problem confronting scientists and regulators throughout the world[1)]. Emission of heavy metals to the environment occurs via a wide range of processes and pathways, including to the air, to surface waters and to the soil[2)]. In Korea, we have a long history of metalliferous mining and metal smelting process development. In South Korea, 21% of arable soil near mining and industrial areas were found to be contaminated by heavy metals from 1995-1997[3)]. A number of studies have been undertaken into trace element contamination derived from mining activities, in soils, plants, waters and sediments in Korea[4-6)], but few studies of heavy metal concentration derived from smelting activities have been carried out.

Of metal smelting factories in Korea, the △△ smelting factory is located in the southeastern part of Korean peninsula and the third largest zinc smelting factory in the world. This factory was founded in 1970 and nowadays produce 450,000 tons of sulfuric acid, 280,000 tons of Zn, 1,700 tons of cupric sulfate, and 900 tons of Cd per year. However, there were cases

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previously reported about its ill-health effects especially to the heavy metal exposed – workers, residents and adverse environmental problems in the mass media. The factory is located in the center of a valley community that is surrounded by a mountain range. A t around 20-hectare arable land located in a sloping area at the northeastern part of the factory is heavily contaminated with toxic metals. However, the source of the heavy metal contamination had not yet been traced resulting to a conflict between the factory and the living communities within that particular area.

Thus, the objectives of this study are mainly to; (1) investigate the extent and degree of trace element contamination of soils located nearby the △△ smelting factory; (2) find out the major reason for such occurrence in the agricultural areas.

## 2. Materials and methods

Sampling of soils, waters, and aerosols were carried out on 7 August, 2006 to examine concentration of heavy metals. Soils (0-20 cm, 40-60 cm, and 80-100 cm in depth) were sampled by hand auger (2.5 cm in diameter) in the arable lands nearby the smelting factory with an estimated land area at 20 hectares. Twenty samples were randomly collected from these sites mostly planted to corn and a little portion is grown into food crops like red pepper, radish and sesame plant. Eight stream water and five aerosol samples were collected randomly in the upstream and downstream of the large stream adjacent to the smelting factory.

After air-drying for 5 days, soil samples were disaggregated and sieved to < 2 mm for soil testing. The concentrations of heavy metals were analyzed following the standard method which was established by the Korean Soil Environmental Conservation Act[7]. For analysis of heavy metals concentrations like Cd, Cu, Cr, and Pb soil samples were extracted by 0.1 N HCl solution, for As were extracted by 1N HCl solution and for Ni and Zn (finely milled soil samples, < 180 ㎛) were digested in 3:1 concentrated HCl and $HNO_3$ (aqua regia). The pH of the soil samples were determined by 1:5 (soil : water) suspension (pH meter, Thermo Orion 3 star, Beverly USA). Meanwhile, water samples were filtered using a hand-pump on site through a 0.45 μm membrane filter paper and after acidification with concentrated $HNO_3$ were stored in a cooling box. The aerosol (dust, fume, and mist in atmosphere) samples that were collected by high volume air sampler for 24 hours and filtered through a 0.45 μm membrane filter paper were digested using 3:1 concentrated HCl and $HNO_3$. Finally, the extracted solutions produced from the soil, water and aerosol samples were analyzed for their heavy metal concentrations like As, Cd, Cr, Cu, Ni, Pb and Zn through ICP-OES (inductively coupled plasma-optical emission spectrophotometer Perkin Elmer Model OPTIMA 4300 DV, Shelton USA).

## 3. Results and Discussions

### 3.1. Soil properties

The mean and range of soil pH values are shown in Table 1. The pH of soils collected from different sampling sites ranged widely from 4.40 to 7.87. This wide range of soil pH results might be affected by the different agricultural activity such as crop planting, land use, and fertilization in each farm land. Trace elements like Cu, Pb and Ni which gave corresponding values of 4.0 ± 2.7, 10.1 ± and 11.4 ± 2.1 mg $kg^{-1}$ were lower than the warning criteria (Cu : 50, Pb : 100, and Ni : 40 mg $kg^{-1}$) as described in the Soil Environmental Conservation Act of Korea[7]. Herein, the warning criteria mean the permissible level to prevent an expansion of the heavy metal contamination in soil. In case of Cd and Zn, almost all the soil samples were over than the warning criteria (Cd 1.5, Zn

**Table 1. pH and heavy metal concentrations of soil samples collected in the targeted sites**

| Data | pH | 0.1 N HCl extractable (mg $kg^{-1}$) | | | Total (mg $kg^{-1}$) | |
|---|---|---|---|---|---|---|
| | (1:5, $H_2O$) | Cd | Cu | Pb | Ni | Zn |
| AM±SD* | 5.3 ± 0.8 | 1.7 ± 0.7 | 4.0 ± 2.7 | 10.1 ± 8.6 | 11.4 ± 2.1 | 407 ± 142 |
| Range | 4.4 - 7.9 | 0.3 - 2.8 | 0.3 - 11 | 0.1 - 29 | 6.2 - 15 | 105 - 641 |
| Warning criteria | - | 1.5 | 50 | 100 | 40 | 300 |

*AM ± SD., arithmetic mean ± standard deviation; **As and Cr was not detected

300 mg $kg^{-1}$). The average values for Cd and Zn concentration were 1.7 ± 0.7 and 407 ± 142 mg $kg^{-1}$, respectively. Likewise, 80% (Zn) and 65 % (Cd) out of total sampling sites gave content values greater than the warning level.

High concentration of Cd inhibited growth and induced visual phytotoxic symptom such as stunted growth and chlorosis of leaves for radish[8,9]. Quite often, zinc toxicity leads to chlorosis in young leaves induced deficiency of magnesium or iron because of the similar ion radius of $Zn^{2+}$ and $Fe^{2+}$[10] and $Zn^{2+}$ and $Mg^{2+}$[11]. Cadmium in plants can easily reach up human body through food chain. Elevated levels of Cd in humans can cause kidney damage, and low levels of Cd in the diet are linked renal dysfunction. Other diseases associated with Cd exposure are pulmonary emphysema and the notorious Itai-Itai ("ouch-ouch") disease[12]. In this study, Cd and Zn toxicity or specific damage to crop plants were not observed.

The farther the sampling site from the zinc smelting factory, the lesser Cd and Zn contents obtained from its samples. Using the linear equation model, Cd and Zn concentration were related to its sampling distance (d) from the zinc smelting factory as Cd concentration in soil = -4.28 x $10^{-3}$ (d) + 3.988, r = 0.382 and Zn concentration in soil = -0.973 (d) + 927, r = 0.423 (Fig. 1), where concentration is expressed in mg $kg^{-1}$ and distance as meter (m). The distance from the smelting factory to the sampling site significantly affected Cd and Zn concentration.

Higher concentration of Cd and Zn with the corresponding average values of 1.70 ± 0.70 and 407 ± 143 mg $kg^{-1}$ respectively were found at the sample surface soil collected at 0-20 cm than in the other layers of its soil profile (Table 2). In addition for Cd, average concentration decreased significantly at the increasing soil depth at 40-60 cm and 80-100 cm. The same distribution can be observed too in Zn which also decreased significantly at increasing soil depths. A higher Cd and Zn concentration at the surface soil than in the subsoil horizons may mean that the heavy metal sources doesn't come from the parent materials but from its external environment.

## 3.2. Water and aerosol properties

The range and mean concentrations of water pH and heavy metal concentration in stream waters are shown in Table 3. A narrow range of water pH was also observed among the sampling sites. In this study, water samples collected downstream contained very high amount of Zn. Perhaps the effluent or other waste materials disposed into the water system by the Zn smelting factory contains too high concentration of such metals after passing across the factory unto

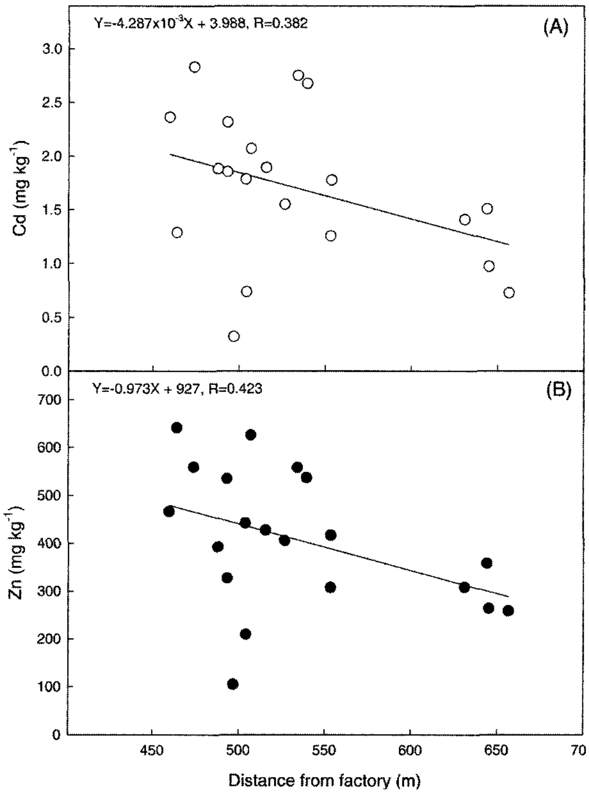


**Fig. 1. Relationship between Cd (A) and Zn (B) concentration in surface soil and distance of sampling site from the smelting factory.**

**Table 2. Cd and Zn concentration of soil samples by depth**

| Heavy metal | 0.1 N HCl extractable Cd (mg $kg^{-1}$) | | | Total Zn (mg $kg^{-1}$) | | |
|---|---|---|---|---|---|---|
| Soil depth (cm) | 0 - 20 | 40 - 60 | 80 - 100 | 0 - 20 | 40 - 60 | 80 - 100 |
| AM ± SD* | 1.70 ± 0.70 | 0.53 ± 0.44 | 0.20 ± 0.17 | 407 ± 143 | 149 ± 68 | 102 ± 31 |
| Range | 0.32 - 2.83 | 0.01 - 1.32 | 0.01 - 0.40 | 105 - 641 | 83 - 323 | 51 - 173 |

*AM ± SD means arithmetic mean±standard deviation.

the downstream through downward water movement. The presence of As, Cr, Cu, Ni, and Pb were not detected, however Cd was detected in the last two down stream sites (W7 and W8). Traces of Zn metals were also found in the upstream areas (W1-W5) as it is assumed that the dust particles that contained such metals were emitted and transported into these sites. The site which we investigated particularly the down stream contained appreciable levels of Cd and Zn. This water can be an important source of heavy metal contamination to arable soil and cultivated plants through irrigation water. Meanwhile, Bowen[13] reported that fresh water contains 0.1, 3.0, 3.0 and 15 μg/l of Cd, Cu, Pb and Zn, respectively. Cadmium concentrations in the last two sites were three and nine times higher compared to that of freshwater Cd content. The concentrations of Zn were high and were 10 and 20 times higher also in these two sites. Generally, Cd and Zn with higher mobility can be widely dispersed downstream from the source[6], which means that these two heavy metals can easily reach down to the ground water and possibly contaminate the drinking water too. Heavy metal pollution in river by industrial activity can affect on water ecosystem[14].

Range and average values of heavy metals in aerosols as sampled in the five targeted areas are also shown in Table 4. Except for Cd and Zn, other heavy metals were not detected. Zinc concentration found in all the sampling site were 30.2 mg $kg^{-1}$. However, Cd concentration in aerosol samples showed trace. The greater aerosol Zn levels play a significant factor in contaminating the water systems (upstream and downstream) and arable soil with high concentration as these metals can be carried upon through winds. Long range atmospheric transport can deposit appreciable levels of heavy metals in remote areas[15]. In the vicinity of industrial area, the large amount of particulate matter in the air is a matter for concern, especially the heavy metals associated with it that have serious health effects. Suspended particulate matter is considered to be a health hazard since it can be absorbed into human lung tissues during breathing. High atmospheric levels of heavy metal-bearing fine particulate matter could have a considerable impact on the environment and human health[16-19].

As a result, Cd and Zn emitted from the △△ smel-

**Table 3. Heavy metal concentration and pH of water samples collected in the targeted sites**

| Location from factory | Distance from factory (km) | pH | Total Cd (mg $L^{-1}$) | Total Zn (mg $L^{-1}$) |
|---|---|---|---|---|
| Upstream | 8.0 | 7.44 | ND* | 0.003 |
| Upstream | 7.0 | 7.05 | ND | 0.008 |
| Upstream | 4.5 | 7.27 | ND | 0.007 |
| Upstream | 4.5 | 6.87 | ND | 0.002 |
| Upstream | 1.0 | 7.01 | ND | 0.006 |
| Onsite | 0.5 | 7.27 | ND | 0.005 |
| Downstream | 5.0 | 6.93 | 0.003 | 0.153 |
| Downstream | 10 | 6.98 | 0.009 | 0.345 |

*ND means not detected; **As, Cr, Cu, Ni and Pb were not detected.

**Table 4. Heavy metal concentration of aerosol in targeted sites**

| Location from factory | Distance from factory (km) | Total Cd (mg $kg^{-1}$) | Total Zn (mg $kg^{-1}$) |
|---|---|---|---|
| Upstream | 8.0 | ND** | 26 |
| Upstream | 4.5 | ND | 30 |
| Upstream | 1.0 | Tr** | 32 |
| Onsite | 0.5 | Tr | 34 |
| Downstream | 5.0 | ND | 29 |
| AM ± SD* | | - | 30.2 ± 2.7 |

* AM ± SD., arithmetic mean ± standard deviation

** ND and Tr mean not detected and detected with < 0.0001 mg $kg^{-1}$, respectively

**** As, Cr, Cu, Ni and Pb were not detected.

ting factory moved with aerosol in the atmosphere and thus, contaminated the agricultural area on the hill side and upstream water within vicinity of the factory.

## 4. Conclusion

The present study has determined that the arable soils, water systems and aerosol samples in the vicinity of the △△ zinc smelting factory are indeed heavily contaminated with Cd and Zn. Cadmium (Cd) and Zn concentrations with the corresponding mean values of 1.7 and 407mg $kg^{-1}$ in the soil surface were greater than the warning criteria. Their concentrations significantly decreased with decreasing soil depths. The water from the upstream of the factory also contained low concentration of Cd and Zn but the concentration of these toxic metals increased significantly at downstream which might be due to the effluent and waste materials discharged by the factory into the water system. The aerosol samples also contained trace of Cd and Zn. Conclusively, the toxic metals particularly Cd and Zn released by atmospheric emission from the △△ zinc smelting factory is the major reason for Cd and Zn contamination within the agricultural areas on the hill side and upstream water of its vicinity.

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