Characteristics of soil heavy metal contents in the agricultural areas near closed mine in Korea

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Abstract
There is an increasing concern over heavy metal contamination of soil in agricultural areas. This study was carried out for monitoring the status and long term trend of heavy metal contents in agricultural fields near closed metal mines on a regular basis. Six hundred soil samples were collected in 58 paddy fields near mine sites nationwide in 2000, 2004 and 2008, respectively. Six heavy metals including cadmium (Cd), copper (Cu), lead (Pb), arsenic (As), zinc (Zn) and nickel (Ni) were analysed and the data were used for further statistical data analysis such as correlation analysis. Average concentrations of cadmium, copper, and lead in the soil samples were 0.4, 13.3 and 14.0 mg/kg, respectively. It indicated that the concentration of the heavy metals in the soil were higher in the paddy fields located at closed mine areas than that in the conventional paddy fields. There were 120 sampling points which exceeded the threshold level (TL) and 57 points which showed the corrective action level (CL) according to the Soil Environment Conservation Act enacted by Ministry of Environment (ME) out of 600 sampling points in 2000. The heavy metal concentrations of cadmium, copper, lead, and arsenic have gradually decreased intervals of every four years since the monitoring started in 2000. The highest correlations (R^2=0.79**) exist between zinc and cadmium concentrations and the regression model estimating zinc from cadmium exhibited high R^2 value of 0.69**.

Key Words
Paddy fields, soil heavy metals, mine, monitoring, data analysis.

Introduction
Research on soil heavy metals, which are known harmful and residual substances affecting food safety have been becoming popular in recent years. Some mine tailings have been left without proper management in closed metal mines and have become the source of heavy metal contamination in adjacent agricultural soils and crops (Jung *et al.* 2005). Exchangeable cadmium in the soil correlates to cadmium content increments in polished rice (Kim *et al.* 2008). We have monitored soil heavy metals and chemical properties in agricultural fields as well as in the vulnerable agricultural paddy fields such as the wastewater flowing area, closed metal mines area, an industrial complex area, and around of highway on a regular basis since 1999 as a nationwide agri-environmental project carried by Rural Development Administration (RDA), Korea to grasp the spatial and temporal changes over the country. In this study, we analysed soil heavy metal data collected in 2000, 2004, and 2008 from vulnerable agricultural paddy fields which were near closed metal mines to understand the characteristic heavy metal contents of vulnerable paddy fields in terms of concentration levels and correlations.

Methods
Soil sampling
In the agricultural paddy fields near closed metal mines, 600 soil samples of a nationwide paddy field surveying of 58 sites were collected at fixed sites in 2000, 2004 and 2008.

Chemical analysis
The heavy metal contents were analysed by using ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometer) after 0.1N-HCl extraction, and arsenic was analysed by the above same method after 1N-HCl extraction (Guide book of ME 2002). Zinc and nickel were extracted using a microwave oven (Mars-x, CEM Co. Ltd., USA) according to EPA 3051 method (US Environmental Protection Agency 1996).

Statistical Analysis
The data were analysed for correlation between heavy metal concentrations in the soil samples using the statistical software, SPSS 12.0(SPSS Inc.; Chicago).

Results

The distribution of the 58 sites for nationwide monitoring of soil heavy metals in agricultural fields located at near closed metal mines every four years since 2000 are shown in Figure 1. The 600 sampling points and the chemical data were established as a spatial database for spatial and temporal analysis.

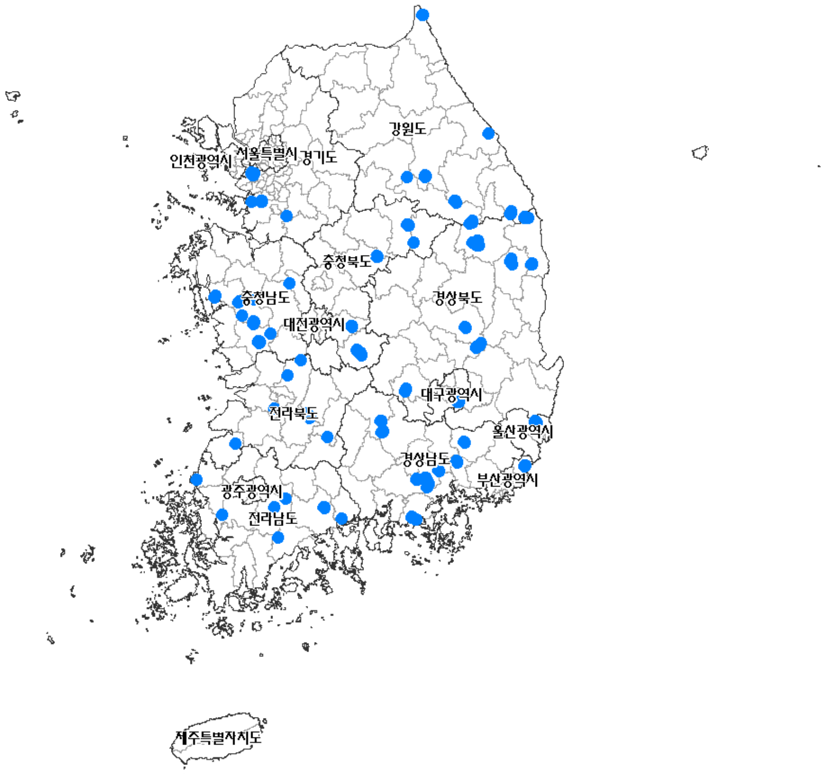

Figure 1. Nationwide monitoring sites and sampling points for soil heavy metals in agricultural fields located at near closed metal mines.

Mean value and the range of soil heavy metal concentrations in paddy field samples collected in 2000, 2004, and 2008 near closed mines as well as the threshold level (TL) and the corrective action level (CL) are shown in Table 1. Some of heavy metal concentrations from soil samples which were collected in the paddy fields near the closed mine are above TL and CL for 2000, 2004, and 2008 (Table 1). Mean value of cadmium, copper, and lead in the soil samples were 0.4, 13.3 and 14.0 mg/kg, respectively. Concentrations of the heavy metals in the soil samples were remarkably higher than those in conventional farmland investigated by our research group in 2007(Kim *et al.* 2007).

Table 1. Mean value and the range of soil heavy metal concentrations in paddy fields near closed mines. (unit : mg/kg)

Year	Cd	Cu	Pb	As	Zn	Ni
2000	0.6	17.9	22.6	3.7	-	-
	(0.01~8.6)	(0.1~305.8)	(tr~557. 5)	(tr~62.0)		
2004	0.46	13.9	14.8	1.9	-	-
	(tr~5.6)	(tr~292.0)	(tr~402.9)	(tr~43.4)		
2008	0.4	13.3	14.0	1.9	132.4	22.0
	(tr~7.7)	(tr~284.0)	(tr~329.7)	(tr~29.5)	(17.4~1548)	(18.4~1157)
Mean of conventional paddy fields [x]	0.1	3.3	4.8	0.02	-	-
Threshold level (TL)	1.5	50	100	6	300	40
Corrective action level(CL)	4	125	300	15	700	100

x : Average concentrations of heavy metal in paddy fields in Korea (Kim *et al.* 2007)

The number of points which exceeded TL and CL are shown in Table 2. Analyses of Ni and Zn were only conducted in 2008. There were 120 sampling points which exceeded TL and 57 points which showed CL according to the Soil Environment Conservation Act enacted by Ministry of Environment (ME) out of 600 sampling points in 2000 (Table 2). The concentrations of cadmium, copper, lead, and arsenic have gradually decreased for an interval of every four year since monitoring started in 2000. Our institute, Rural Development Administration(RDA), has suggested soil remediation for the sites around closed mines which showed the TL and CL to Ministry for Food, Agriculture, Forestry and Fisheries (MIFAFF) of Korea. MIFAFF conducted soil remediation for those sites.

Table 2. The number of exceeding points on the threshold level (TL) and the corrective action level (CL).

Year	Cd	Cu	Pb	As	Zn	Ni	Total
2000	54^x (7^y)	38 (13)	25 (3)	61 (40)	-	-	120 $(57)^z$
2004	31 (1)	26 (10)	13 (1)	26 (10)	-	-	74 (20)
2008	17 (2)	19 (11)	11 (1)	20 (14)	26 (9)	33 (3)	100 (39)

x, y: Number of exceeding points on TL and CL, respectively. z : Some of soil samples were observed more than two metals exceeded on TL and CL per sample.

Table 3 is the result of correlation analysis among heavy metals collected in paddy fields near closed mines. The highest correlation was observed between zinc and cadmium concentrations (R^2=0.788**), the next highest correlation was found between zinc and arsenic (R^2=0.409**). Figure 2 shows a linear relationship between zinc and cadmium concentrations collected in paddy fields near closed mine in 2008. The regression model for estimating zinc content from cadmium content has a R^2 value of 0.69**.

Table 3. Correlation analysis among heavy metal concentrations for soils collected in paddy fields near closed mine.

Heavy metal	Cd	Cu	Pb	Zn	As	Ni
Cd	1.000					
Cu	0.286**	1.000				
Pb	0.143*	0.266**	1.000			
Zn	0.788**	NS	NS	1.000		
As	0.358**	NS	NS	0.409**	1.000	
Ni	NS	NS	NS	NS	0.150*	1.000

*, ** Significant at the 0.05, 0.01 probability level
NS : Not Significant

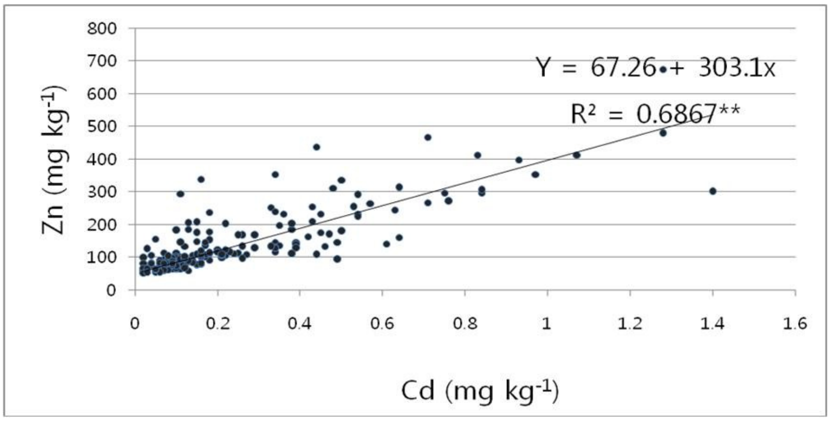

Figure 2. A linear relationship between zinc and cadmium concentrations for soils collected in paddy field near closed mines in 2008.

Conclusion

The result shows that the heavy metal concentrations were higher for the closed mine areas than for conventional paddy field, and some of samples exceed the TL and CL according to the Soil Environment Conservation Act. The highest correlation (R^2=0.79**) was between zinc and cadmium concentrations and the regression model estimating zinc from cadmium exhibited the high R^2 value of 0.69**. During the experimental period, soil remediation of the farmlands around closed mine areas has been conducted by the Korea Ministry for Food, Agriculture, Forestry and Fisheries (MIFAFF). Critical decreasing of the heavy metal concentration was due to the remediation as shown in the above results. However, several reports indicate that farmlands around closed mines are still affected by the heavy metals exceeding the TL and CL based on the prescription of the Soil Environment Conservation Act in Korea. Continuous monitoring related to heavy metal flows in the soil-water-plant system are done by our research group for maintaining of food safety.

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