Environment Protection Engineering

Vol. 41 2015 No. 3

DOI: 10.5277/epe150305

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CONTAMINATION OF SOIL WITH HEAVY METALS DRAINED OUT FROM ABANDONED MINES IN THE SOUTH-WEST REGION OF KOREA

Contamination of soil with heavy metals drained out from twenty eight abandoned mines in the southwest regions of Korea has been investigated. Utilizing various statistical techniques, the goal was to evaluate and analyze pH and the contamination with Arsenic, and the following six heavy metals: cadmium, hydrargyrum, lead, nickel, chromium, and zinc. Contamination levels of heavy metals were determined depending on the depth of the soil. Results indicated that the subsoil and the surface soil both were strongly contaminated with lead and arsenic. Furthermore, the subsoil also contained much nickel. In forest regions, high levels of lead and arsenic, whereas in all regions high levels of zinc have been detected.

1. INTRODUCTION

The most severe problem among environmental issues is the accumulation of mine wastes and tailings at abandoned mine sites due to lack of remediation. There are two types of abandoned mines: metallic and nonmetallic. Metallic mines contaminate the surrounding lands and rivers more than nonmetallic, as they are composed of sulfide minerals easily oxidizing during weathering. Oxidized sulfide minerals cause the pH of the soil to decrease. Sulfide minerals containing heavy metals can be leached out of the soil with ease depending on pH and concentration [1].

Mine drainage consists of mine water that flow from abandoned caverns and waste impoundments. Mine drainage is highly acidic ($pH < 4$) as great quantities of heavy metals are included [2], causing severe contamination of the surrounding environment. If the contaminated soils surrounding the abandoned mines encounter the surrounding

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river system, than wide dispersion of pollutant substances could affect the environment. As a result, cultivated farmlands, surrounding water systems, groundwater, and soil are at risk [3]. Waste mine impoundments and their mine drainages contain high amounts of heavy metals (e.g. Cu, Pb, Cd, and As). Contaminated crops after consumption can accumulate within the organs and thus cause terminal diseases. In order to reduce the risk of contamination with heavy metals from mine wastes, two processes must occur. First, mine drainage must decrease to block the contaminated soil. Secondly, the mine drainage must be treated by biological, chemical, and physical purification [4].

Many researchers studied the behavior of heavy metals from abandoned mines and evaluated the environmental pollution. They conducted geochemical research on minerals containing heavy metals [6], on diminishing oxidation of pyrites by performing successive alkalinity producing system (SAPS) wetlands, and anoxic limestone drainage (ALD) [7], the contaminating distribution properties [5, 7], the statistical analysis [4, 8], and the risks of hazardous effects on the human body. However, the concentrations of heavy metals greatly differ. Even if the metals are detected in the same mine, it is difficult to accurately analyze and thus making the countermeasure for contamination insufficient.

This study focused on gathering data of the contaminated soils found in the abandoned mines located in the southwest region of Korea to analyze the pollution degrees with heavy metals using various statistical techniques. Also, the correlation between the heavy metal components was investigated; and the relationship between its contamination and the distance from the abandoned mine was evaluated.

2. THE STUDY AREA

The selected study area focused on 28 different abandoned mines located in the southwest region of Korea. In each mine, thirty-eight to eighty different samples were

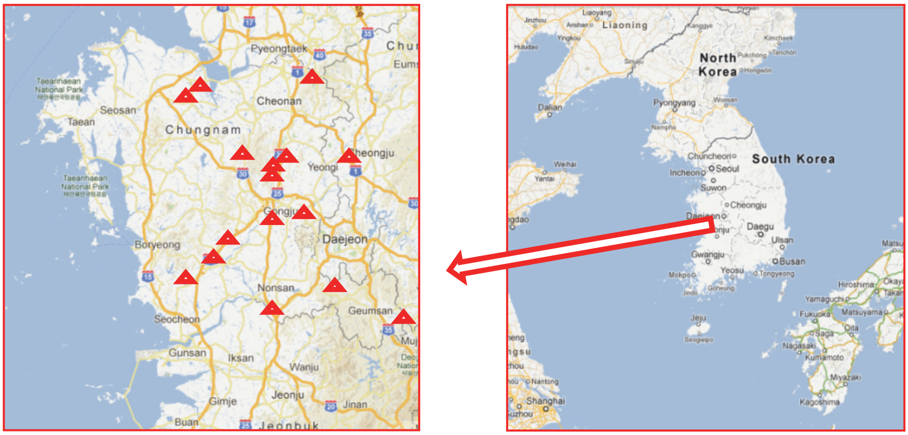

Fig. 1. Selected study area

obtained from the subsoil, the soil beneath the surface, and the surface soil using hand auger and hand shovel. Surface samples ranged between zero and ten centimeters and subsoil samples ranged between 30 and 100 centimeters. A total of 1496 samples were collected, 1218 of them being surface and 278 – subsoil samples. This study was performed between 1997 and 2007 by the Ministry of the Korean Environment through general research and detailed investigation [9]. Figure 1 shows the location of the investigated abandoned mines in the southwest region of Korea [10].

3. ANALYSIS AND RESULTS

This study was performed using statistical methods to evaluate pH and the contamination levels of the following elements within the polluted soil surroundings: As, and the following six heavy metals – Cd, Hg, Pb, Ni, Cr^{6+}, and Zn.

The mean dispersion, standard deviation (*SD*), and the coefficient of variation (*CV*) were calculated, and it was found that out of the heavy metals, Zn was the most detected element. The coefficients of variation can be ranked as follows As > Pb > Hg > Cr^{6+} > Cd > Zn > Cu > Ni > pH; the difference of variation is greatly high. As, Pb, Cd, and Cr^{6+} have very high coefficients of variation in comparison their mean values (Table 1).

Table 1

Summary of statistics for element's mean concentrations of heavy metals in soil [mg·kg^{-1} of soil]

Variable	Minimum	Median	Mean	Maximum	*SD*	*CV* [%]
pH	3.00	5.88	5.95	8.10	0.61	10.26
As	0.00	0.38	13.96	4510.77	141.49	1013.24
Cd	0.00	0.15	0.45	74.04	2.66	587.51
Cu	0.00	3.89	5.80	230.98	13.84	238.59
Ni	0.00	7.24	12.10	107.22	14.78	122.15
Pb	0.00	6.50	39.91	9531.98	398.93	999.56
Zn	0.00	81.72	126.56	5782.49	303.50	239.81
Hg	0.00	0.00	0.00	0.26	0.01	919.78
Cr^{6+}	0.00	0.00	0.00	0.17	0.01	842.67

Table 2 shows the contamination degrees with heavy metals depending on the soil depth of the selected areas using descriptive statistics and test of normality. As results from the descriptive statistics of subsoil and surface soil, the mean values of Pb and Zn content are relatively high compared to those of the other elements. This means that all land containing subsoil and surface soil is contaminated with Pb and Zn. According to the Shapiro–Wilk (S–P) test of normality, as the *p* values for all the heavy metals are lower than 0.05, the distributions of contamination degree of heavy metals obey normal distributions under 5% of significance level.

Table 2

Descriptive statistics for soil contamination data by the types of soil depth [mg·kg^{-1} of soil]

Variable	Soil	n^a	Minimum	Mean	Maximum	*SD*	*CV* [%]	S–W *p* value
pH	surface	1218	3.00	5.94	8.10	0.61	10.28	0.970502
	subsoil	278	4.50	5.97	7.70	0.61	10.18	0.983172
As	surface	1218	0.00	13.13	4510.77	148.18	1128.35	0.056187
	subsoil	278	0.00	17.61	1025.13	107.51	610.62	0.149981
Cd	surface	1218	0.00	0.42	74.04	2.63	624.31	0.095519
	subsoil	278	0.00	0.59	40.23	2.77	471.47	0.165189
Cu	surface	1218	0.00	5.46	230.98	13.48	246.70	0.303801
	subsoil	278	0.00	7.28	191.50	15.27	209.71	0.391945
Ni	surface	1218	0.00	11.50	79.31	14.40	125.22	0.790059
	subsoil	278	0.00	14.73	107.22	16.10	109.35	0.828138
Pb	surface	1218	0.00	36.63	9531.98	379.03	1034.85	0.051193
	subsoil	278	0.00	54.30	7797.50	476.97	878.36	0.072742
Zn	surface	1218	0.00	118.62	5742.99	262.96	221.68	0.230503
	subsoil	278	0.00	161.33	5782.49	438.01	271.50	0.231027
Hg	surface	1218	0.00	0.00	0.26	0.01	1013.42	0.073827
	subsoil	278	0.00	0.00	0.11	0.01	638.03	0.147054
Cr^{6+}	surface	1218	0.00	0.00	0.16	0.01	899.89	0.08884
	subsoil	278	0.00	0.00	0.17	0.02	672.15	0.136708

[a]*n* is the number of samples.

Table 3 shows the results of two sample *t*-test conducted to check whether the mean contamination degrees differ depending on soil depth; *F* test investigates similarity of dispersion. As results from the *t*-test, the subsoil is more contaminated with Ni than the surface soil. while soil and subsoil are greatly contaminated with As, Pb, and Zn without striking differences. Once the abandoned mine of this selected area is restored, the plan to countermeasure the contamination will be set up to treat the subsoil for Ni and both types of soil for As, Pb, and Zn.

Table 4 shows the results of the tests of normality depending on land use; for the forest regions the contamination mean values of Pb, Zn, and As are greatly high compared to those of the other elements. As for the rice and farm regions, the mean value of Zn comes out the highest, with the mean values of Ni and Pb following Zn. This shows that Zn is widely dispersed in the rice and farm regions, and therefore the crops from these cultivated regions have a higher exposure risk to Zn. Also, the subsoil and surface soil of the forest regions are mainly contaminated by Pb and Zn.

Table 3

Two sample *t*-tests of the equality of two mean concentrations for two soil depths

Variable	Soil	n^a	Mean	*SD*	*F* test		*t*-test	
					F	*p*	*t*	*p*
pH	surface subsoil	1218 278	5.94 5.97	0.61 0.61	1.01	0.9175	–0.63	0.5316
As	surface subsoil	1218 278	13.13 17.61	148.18 107.51	1.90	0.0001	–0.58	0.5624
Cd	surface subsoil	1218 278	0.42 0.59	74.04 40.23	1.11	0.2680	–0.94	0.3484
Cu	surface subsoil	1218 278	5.46 7.28	13.48 15.27	1.28	0.0064	–1.83	0.0686
Ni	surface subsoil	1218 278	11.50 14.73	14.40 16.10	1.25	0.0145	–3.07	0.0023
Pb	surface subsoil	1218 278	36.63 54.30	379.03 476.97	1.58	0.0001	–0.58	0.5639
Zn	surface subsoil	1218 278	118.62 161.33	262.96 438.01	2.77	0.0001	–1.56	0.1191
Hg	surface subsoil	1218 278	0.00 0.00	0.01 0.01	1.18	0.0893	–0.70	0.4860
Cr^{6+}	surface subsoil	1218 278	0.00 0.00	0.01 0.02	2.45	0.0001	–1.24	0.2156

[a]*n* is the number of samples.

Table 4

Descriptive statistics data for soil contamination depending on land use [mg·kg^{-1} of soil]

Variable	Usage	n^a	Minimum	Mean	Maximum	*SD*	*CV* [%]	S–W *p* value
pH	forest rice farm other	249 362 856 29	3.90 3.00 4.21 4.40	5.81 6.23 5.84 6.50	7.80 8.10 8.00 7.90	0.67 0.70 0.48 0.78	11.45 11.28 8.26 11.97	0.961732 0.987706 0.972216 0.970277
As	forest rice farm other	249 362 856 29	0.00 0.00 0.00 0.00	64.42 7.07 2.62 1.68	4510.77 342.85 392.20 12.43	339.21 26.94 20.67 2.98	526.54 381.14 789.42 176.85	0.183841 0.254919 0.085692 0.582709
Cd	forest rice farm other	249 362 856 29	0.00 0.00 0.00 0.00	1.48 0.19 0.28 0.06	74.04 2.42 8.39 0.29	6.29 0.35 0.69 0.07	424.88 178.98 247.84 107.07	0.213830 0.555569 0.321564 0.766839
Cu	forest rice farm other	249 362 856 29	0.00 0.00 0.00 0.00	10.34 4.11 5.39 0.14	230.98 53.91 77.49 2.12	29.90 6.89 6.87 0.47	289.30 167.72 127.47 327.30	0.319264 0.620492 0.652108 0.352021

Table 4

Descriptive statistics data for soil contamination depending on land use [mg·kg^{-1} of soil]

Ni	forest	249	0.00	19.51	70.90	14.41	73.83	0.935613
	rice	362	0.00	7.64	64.73	11.29	147.75	0.722477
	farm	856	0.00	12.24	107.22	15.45	126.27	0.781450
	other	29	0.00	0.14	1.71	0.44	304.38	0.781450
Pb	forest	249	0.00	165.05	9531.98	963.41	583.72	0.151881
	rice	362	0.25	16.37	459.43	38.18	233.22	0.358824
	farm	856	0.00	14.51	1067.36	54.36	374.73	0.152826
	other	29	0.83	9.22	73.08	14.67	159.08	0.557171
Zn	Forest	249	11.19	258.38	5782.49	673.47	260.65	0.295273
	Rice	362	0.00	114.90	542.88	72.09	62.74	0.875345
	Farm	856	0.00	93.68	1889.82	144.87	154.65	0.376613
	Etc	29	24.58	110.80	257.94	59.35	53.56	0.932708
Hg	Forest	249	0.00	0.00	0.11	0.02	440.96	0.235429
	Rice	362	0.00	0.00	0.00	0.00	–	–
	Farm	856	0.00	0.00	0.26	0.01	1175.95	0.059106
	Other	29	0.00	0.00	0.00	0.00	–	–
Cr^{6+}	Forest	249	0.00	0.00	0.16	0.02	591.53	0.164593
	Rice	362	0.00	0.00	0.00	0.00	–	–
	Farm	856	0.00	0.00	0.17	0.01	779.64	0.109670
	Other	29	0.00	0.00	0.00	0.00	–	–

[a]*n* is the number of samples.

Table 5 shows the results of the *F* test analysis of variance considering the land use. Under the signification level under 0.05, regardless of land, use the null hypothesis that the population of heavy metal is equal to the mean contamination level can be dismissed. Thus, the differences of the contamination degree with all heavy metal also exist. However, depending on the three types of land, differences of the concentrations of heavy metals were present. In order to distinguish the differences between certain regions among the three types of land, the Duncan's multiple comparisons test was performed.

Table 6 shows the results of the Duncan's multiple comparisons test. For the case of pH, differences are present between the farm and rice regions, whereas in the case of Pb and As, differences exist between the forest and rice regions. The contamination levels of Pb and As in the forest regions are ten times greater than in the rice and farm regions. In the case of Zn, there are no great differences between the contamination levels for rice and farm regions. However the mean value of contamination level of the forest is 2.5 times greater than that of the rice and farm regions.

In addition, according to Duncan's test, Cu, Cd, and Hg in both the rice and farm regions under the 5% significance level show no difference; however, differences are evident between the forest region and the rice and farm regions combined. Therefore, for Zn Pb, As, Cu, Cd, and Hg the forest regions display mean contamination levels higher than the rice and farm regions. For Zn, Pb, and As especially, the forest regions exhibit extremely high mean levels compared to the rice and farm regions.

Table 5

ANOVA table data for soil contamination depending on land use [mg·kg^{-1} of soil]

Variable	Source	Sum of squares	Degrees of freedom	Mean squares	*F* ratio	*p* value
pH	treatment	2	42.96	21.48	64.50	<0.0001
	error	1464	487.62	0.33		
	total	1466	530.58			
As	treatment	2	761 304.69	380 652.34	19.11	<0.0001
	error	1464	29 163 815.48	19 920.64		
	total	1466	29 925 120.17			
Cd	treatment	2	313.84	156.92	22.39	<0.0001
	error	1464	10 259.57	7.01		
	total	1466	10 573.41			
Cu	treatment	2	6283.17	3141.5867	16.47	<0.0001
	error	1464	279 260.66	190.7518		
	total	1466	285 543.83			
Ni	treatment	2	20 817.71	10 408.85	50.52	<0.0001
	error	1464	301 641.68	206.04		
	total	1466	322 459.39			
Pb	treatment	2	4 651 623.7	2 325 811.9	14.60	<0.0001
	error	1464	233 238 141.7	159 315.7		
	total	1466	237 889 765.5			
Zn	treatment	2	5 301 163.7	2 650 581.8	29.33	<0.0001
	error	1464	132 303 569.2	90 371.3		
	total	1466	137 604 732.8			
Hg	treatment	2	0.00288916	0.00144458	10.51	<0.0001
	error	1464	0.20126806	0.00013748		
	total	1466	0.20415721			
Cr^{6+}	treatment	2	0.00109247	0.00054623	4.14	0.0162
	error	1464	0.19332562	0.00013205		
	total	1466	0.19441809			

According to the Duncan's test, the Cr^{6+} in both the rice and farm regions under the 5% significance level exhibit a difference; however, differences are absent between the rice and farm regions. As a result of Duncan's test, only Ni shows differences of contamination levels depending on the three types of land use below the 5% of significance level. Therefore, we can conclude that Ni evenly contaminated the three different regions.

Table 6

Results of Duncan's multiple comparisons test

Variable	Grouping	Mean	*N*	Usage
pH	A	6.23	362	2 rice
	B	5.84	856	3 farm
	B	5.81		
	B		248	1 forest
As	A	64.42	249	1 forest
	B	7.07	362	2 rice
	B			
	B	2.62	856	3 farm
Cd	A	1.48	249	1 forest
	B	0.28	856	3 farm
	B			
	B	0.19	362	2 rice
Cu	A	10.34	249	1 forest
	B	5.39	856	3 farm
	B			
	B	4.11	362	2 rice
Ni	A	19.51	249	1 forest
	B	12.24	856	3 farm
	C	7.64	362	2 rice
Pb	A	165.05	249	1 forest
	B	16.37	362	2 rice
	B			
	B	14.51	856	3 farm
Zn	A	258.38	249	1 forest
	B	114.90	362	2 rice
	B			
	B	93.68	856	3 farm
Hg	A	0.0042	249	1 forest
	B	0.0010	856	3 farm
	B			
	B	0.0000	362	2 rice
Cr^{6+}	A	0.0026	249	1 forest
	A			
	B A	0.0016	856	3 farm
	B			
	B	0.0000	362	2 rice

The box plot in Fig. 2 is used to explain the differences of land use for Ni. In the box plot, 1 on the *x*-axis represents forest, 2 represents rice, and 3 represents farm region. The median value of contamination level for Ni is greatest in the forest and lowest in the rice region. The contamination level is scattered the most in the forest and the least in the rice region.

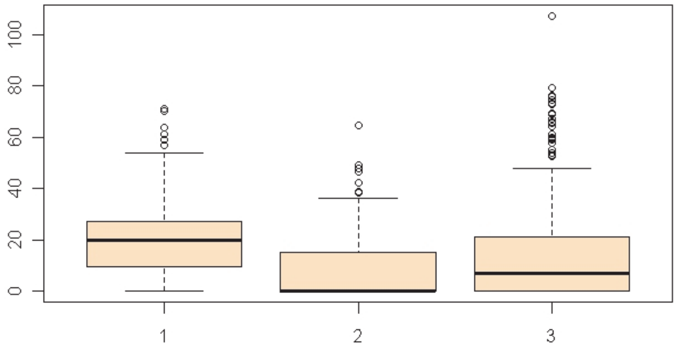

Fig. 2. Box plot of N_i depending on land use

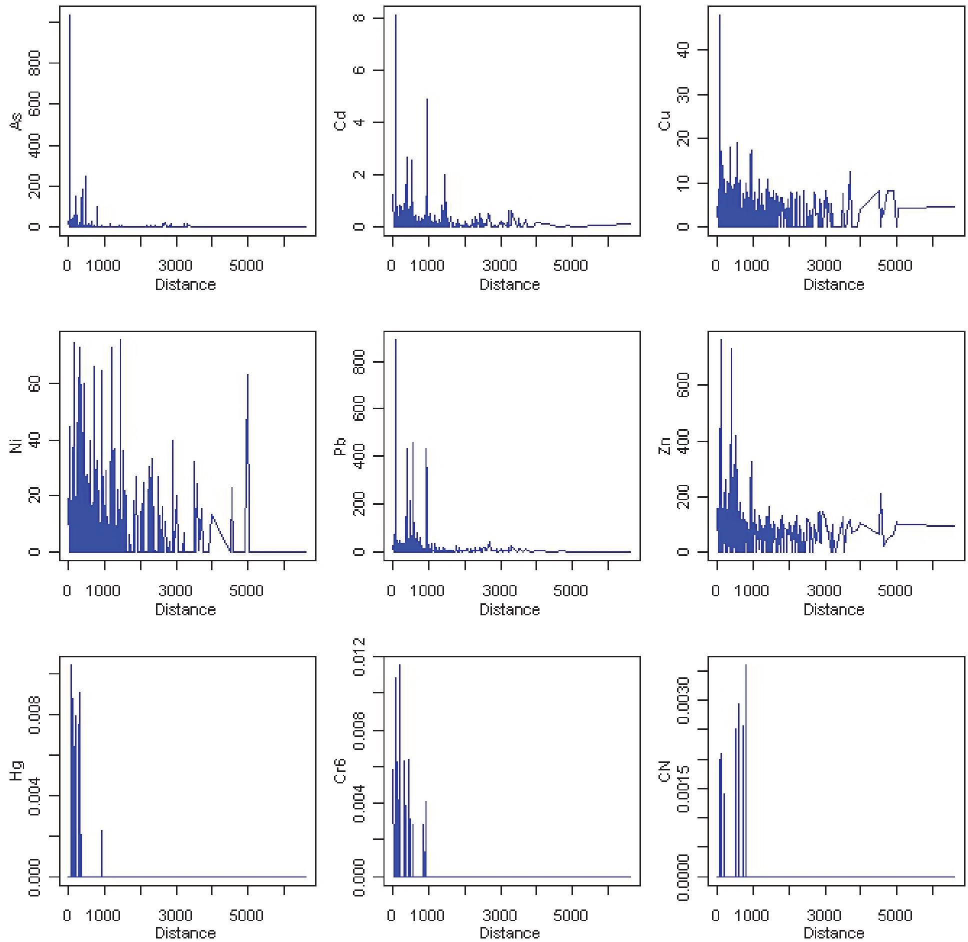

Fig. 3. Contamination level of heavy metals depending
on the distance from the abandoned mine (subsoil + surface soil)

Figure 3 shows the contamination levels of heavy metals depending on the distance from the abandoned mine. As, Pb and Zn were generally found within the radius of 1000 m. However, Zn is vastly dispersed around the selected area, it was also detected 3000 and 5000 m away. Similarly, Ni was also detected at far distances from the mines at greater amounts. The selected area consisted of ultrabasic rocks agglomerated within mineral deposit layers, thus allowing Ni to exist in vast amounts [11]. Immense amounts of Cd were found at a 1000 m radius from the abandoned mine. Cd ions existing in the soil with high pH are more mobile than the other elements.

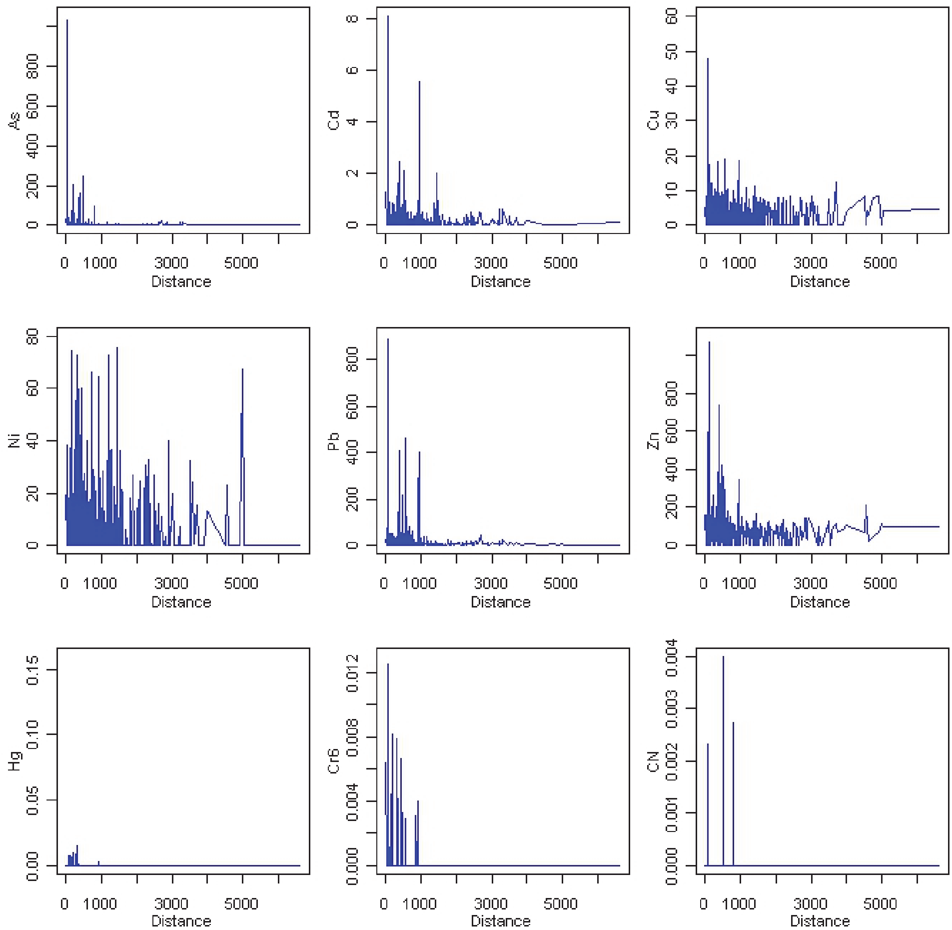

Fig. 4. Contamination level of surface soil with heavy metals vs. the distance from the abandoned mine

Figure 4 shows the contamination levels of surface soils depending on the distances from the abandoned mines, whereas Fig. 5 shows the contamination levels of subsoil. The results for overall soil (Fig. 3) are similar to those for surface soils (Fig. 4).

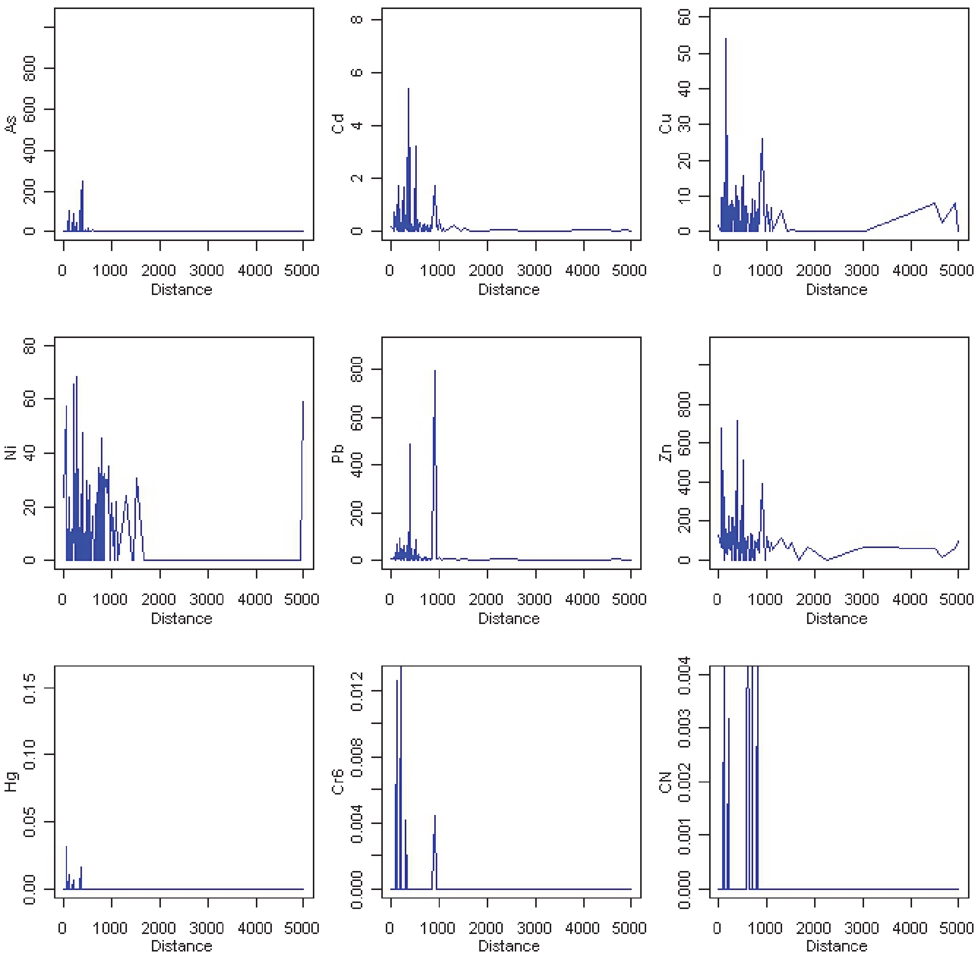

Fig. 5. Contamination level of subsoil with heavy metals vs. the distance from the abandoned mine

As shown in Fig. 5, most of the heavy metals were detected within the radius of 500 m in the subsoil. However, significant amounts of Cu, Ni, Zn, and Pb were also found within the radius of 1000 m. It is critical to understand the main source of pollution caused by heavy metals for environmental restoration of abandoned mines. This may be done based on hydraulic and hydrological factors such as the weather, flooding, groundwater, river tributary streams, etc.

4. CONCLUSION

Statistical analysis was applied with the sole purpose to investigate the contamination of heavy metals in twenty-eight different abandoned mines located in Korea. The results show that both the subsoil and the surface soil showed relatively high contamination levels with Pb and As. Only in the case of Ni the subsoil was more contaminated than the surface soil. The contamination mean values varied depending on the use of the selected land. The concentrations of Pb, Zn, and As in the soil of forest regions were very high and as in the rice and farm regions, the mean concentration of Zn came out the highest and widely dispersed.

From the results of the analysis of variance and Duncan's multiple comparisons test, for Pb and As differences were present between the forest and rice regions; the contamination levels in the forest regions were ten times greater than those in the rice and farm regions. Only Ni showed differences in the contamination levels in all the three types of land use, and thus it can be inferred that Ni evenly contaminated the three different regions. The box plot was used to explain the differences of land use for Ni, showing that the contamination was scattered the widest in the forest region.

Most of the heavy metals were detected within the radius of 500 m in the subsoil. However, amounts of Cu, Ni, Zn, and Pb were also found within the radius of 1000 m. Both As and Pb were generally found within the radius of 1000 m and Zn was vastly dispersed around the selected area. The results of this study may give information about the establishments of countermeasures and the plans of restoration concerning the contamination from the abandoned mines and the environments surrounding them.

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