The Mobility and Phytotoxicity of Trace Elements in Metalliferous Mine Tailings

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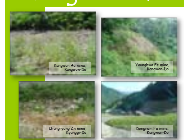
Abstract

Understanding the mobility of trace element, mostly bound to residual fraction, in mine tailings is essential to assess its environmental impacts. In the present study, the chemical distribution, leachability and phytotoxicity using lettuce (*Lactuca sativa*) root growth for Cd, Pb, Cu, Ni, Zn and As in mine tailings were determined. Furthermore, relationship among each characteristic was assessed. The results exhibited that despite all samples were considered as heavily contamination based on total contents of trace elements, they would be low mobility because they mainly associated with stable fraction. Likewise, synthetic precipitation leaching procedure (SPLP) contents for trace elements showed lower value (< 1% to total contents), and toxic characteristic leaching procedure (TCLP) and diethylene triamine pentaacetic acid (DTPA) extractable contents showed < 15% to total contents. Although simplified bioaccessibility extraction test (SBET) represented higher value than other extraction methods, they showed < 20% except for Cu (22%). There was significantly positive correlation between mobile fraction for trace element from sequential extraction procedure and their leachabilities from TCLP, SBET and DTPA extraction test except for SPLP. SPLP content for almost elements used was strongly correlated with water-soluble fraction. Also, mobile fraction of trace element provided well prediction for lettuce root growth than total content. Consequently, in the case of the residual fraction bound trace element-rich mine tailings used in this study, trace elements associated with mobile fraction would appear to play more effective role in their leachability.

Background



The mine tailings

Many metalliferous mines in Republic of Korea have been left to inactive without any other reclamation and restoration. According to Korea Ministry of Environment (KMoE), about thousands of abandoned metalliferous mine present on all side of the country. They also established that, since mining activity in Republic of Korea had done on a small-scale, a method to treat mine tailings, may contain a large amount of trace elements, had been unprepared. By this, plenty of mining tailings without treatment had been deposited into a valley and side of stream where located in the vicinity of mine, and have caused serious problem for environment and human health. For these mine tailings management, therefore, it is important to obtain better understandings of chemical distribution and leachability of trace element, affecting the environmental mobility and impact of them in mine tailings. Hence, the objectives of this study are to investigate trace element distribution and leachability in mine tailings, containing highly stable fraction of trace element, as well as the relationship between the results. And then the utility of the effective fractions was refined using result obtained from seed germination and root elongation.

Experimental

1. The characteristics of mine tailings samples used in the present study

MT	Ore	Silt (%)	Clay (%)	pH	OC (%)	TN (%)	TP (%)	Total contents of trace elements (mg kg^{-1}) Cd	Pb	Cu	Ni	Zn	As	IPI[a]
T1	Au	15	18	4.39	0.5	0.03	0.00	8	951	61	24	52	1,510	208.2
T2	Au	16	20	4.18	0.5	0.05	0.01	12	117	64	28	65	3,013	191.5
T3	Au	8	11	6.17	0.8	0.04	0.01	3	100	86	40	141	944	72.3
T4	Poly[b]	4	8	3.69	0.4	0.06	0.00	3	867	37	17	43	1,390	191.0
T5	Poly	11	24	4.66	1.2	0.03	0.01	3	88	42	15	167	867	62.1
T6	Au	22	38	5.04	0.9	0.08	0.00	1	71	9	4	62	24	11.8
T7	Poly	8	20	5.39	0.5	0.09	0.04	3	112	52	30	79	383	43.2
T8	Au	8	21	5.04	0.8	0.09	0.00	3	105	40	25	72	295	35.6
T9	Au	7	12	4.34	0.6	0.02	0.00	8	136	40	33	82	1,260	94.2
T10	Au	24	23	5.53	0.1	0.03	0.00	2	113	62	46	93	429	44.7
T11	Au	23	23	4.54	0.5	0.03	0.00	2	79	41	22	37	207	27.7
T12	Au	34	18	4.8	0.4	0.09	0.00	4	401	110	5	551	459	89.9
T13	Au	38	34	7.58	1.3	0.07	0.01	5	174	70	40	166	1,340	112.6
T14	Au	2	8	7.72	1.0	0.02	0.00	19	544	194	80	1,423	299	127.0
T15	Au	20	11	7.57	0.4	0.09	0.01	14	258	59	25	1,136	444	79.5
T16	Au	9	12	5.92	0.4	0.05	0.01	24	456	157	34	2,312	679	141.2
T17	Fe	13	17	7.48	0.5	0.01	0.03	23	601	455	61	3,155	186	172.2
T18	Au	15	13	4.56	0.6	0.03	0.03	10	529	663	51	1,088	109	165.0
T19	Au	9	16	6.92	0.8	0.01	0.00	9	495	375	66	1,951	164	107.4
T20	Poly	14	21	6.27	1.0	0.03	0.02	8	201	50	27	1,927	45	46.4
T21	Au	16	26	7.57	0.8	0.06	0.01	26	132	108	11	5,700	143	70.3

[a], Integrated pollution index, suggested by Chen et al. (2005), was a mean value of pollution index (PI) for each trace element. PI was calculated as the ratio of element contents in mine tailings to these in background soil (n = 21). According to classification of contamination for sample using IPI value, the case of IPI ≤ 1 considered as low contamination, mid for 1 < IPI ≤ 2 and high for IPI > 2, respectively. [b], Ore minerals of polymetallic mine include several elements such as Au, Cu, Pb, Zn, etc.

2. Trace elements contents

2.1. 6-step sequential extraction test

Step	Fraction	Extraction fluid	Conc. (M)	pH
1	Water-soluble	D.W.	-	6.50
2	Exchangeable	CH_3COOH	1	7.00
3	Bound to Carbonate	NaOAc	1	5.00
4	Bound to Fe-Mn oxide	HO-NH_3Cl (/25% HOAc)	0.04/1	-
5	Residual(OM, bound to silicate)	Aqua regia	-	-

2.2. Selective single extraction test

No.	Method	Extraction fluid	Reference	Remarks
1	TCLP #1	CH_3COOH	EPA method 1311	soil pH <5
	TCLP #2	CH_3COOH	EPA method 1311	soil pH >5
2	SPLP	HNO_3/H_2SO_4	EPA method 1312	-
3	SBET	Glycine	modified from PBET	-
4	DTPA	DTPA	Maiz et al., 2000	-

3. The phytotoxicity assay with lettuce

No. of seeds		10 seeds / petridish
Wt. of soil		20 g / petridish
Replicate		X 3
Test condition	Periods	28 days
	Temp.	25±0.5℃
	Light : dark	16 : 8 (h)
	Water content	40 % (based on soil weight)

Results & Discussion

1. The distribution and leachability of trace elements in the mine tailings

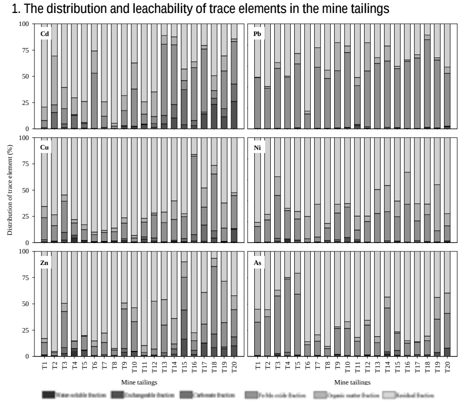


Fig 1. The trace element distribution, as % of the total content, in mine tailings samples through the 6-step sequential extraction test.

Table 1. Statistical results for trace element in mine tailings obtained from selective single extraction methods such as SPLP, TCLP, SBET and DTPA extraction test.

		pH[a]	Cd	Pb	Cu	Ni	Zn	As
SPLP (mg L^{-1})	Mean	5.56	0.000	0.002	0.009	0.006	0.044	0.077
	Median	5.09	0.000	0.000	0.004	0.003	0.026	0.033
	Min	3.64	0.000	0.000	0.000	0.000	0.000	0.000
	Max	7.82	0.003	0.024	0.075	0.035	0.169	0.388
	n.d.[b]	-[c]	6	12	5	-	2	2
TCLP (mg L^{-1})	Mean	-	0.055	0.040	0.175	0.054	3.091	0.112
	Median	-	0.006	0.010	0.062	0.025	1.268	0.028
	Min	-	0.000	0.000	0.007	0.003	0.024	0.000
	Max	-	0.285	0.548	0.737	0.217	18.449	0.750
	n.d.f	-	2	1	-	-	-	1
SBET (%)	Mean	-	18.9	10.1	22.2	7.8	16.8	12.9
	Median	-	10.1	9.6	17.3	5.6	10.2	7.0
	Min	-	0.9	1.5	7.9	2.1	1.2	1.5
	Max	-	74.0	27.3	56.4	29.2	83.4	68.8
DTPA (%)	Mean	-	9.7	2.9	9.1	1.4	6.8	0.4
	Median	-	1.5	2.4	7.0	0.9	5.2	0.0
	Min	-	0.1	0.4	1.7	0.2	0.7	0.0
	Max	-	50	7	36	5	29	6

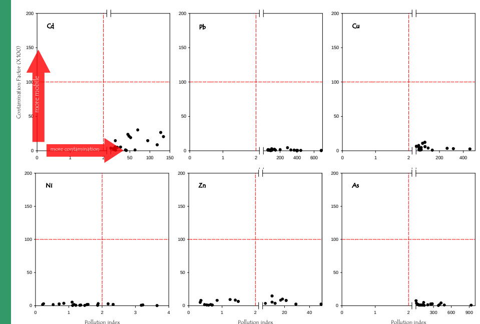
[a] Initial pH of extraction fluid for SPLP is 4.20 ± 0.05, [b] Number of sample not detected, [c] None.

2. The relationship between mobile fraction and leachability of trace elements

Table 2. Pearson correlation coefficients between trace element fractions from sequential extraction and selective single extraction methods.

		F1	F2	F3	F4	F5	F6	F1-3[a]	Total
Cd	SPLP	0.66**	0.33	-0.13	0.10	-0.07	-0.13	0.00	0.01
	TCLP	0.58**	0.72**	0.38	0.38	0.19	0.19	0.59**	0.55*
	SBET	0.51*	0.89***	0.15	0.71**	0.13	0.04	0.44*	0.66**
	DTPA	0.67**	0.52*	0.42	0.40	0.31	0.23	0.56**	0.58**
Pb	SPLP	0.19	-0.08	0.00	-0.14	-0.09	-0.15	-0.06	-0.16
	TCLP	0.60**	0.97***	0.60**	-0.05	0.29	0.07	0.94***	0.03
	SBET	0.44*	0.35	0.64**	0.68**	0.14	0.39	0.48*	0.60**
	DTPA	0.72**	0.61**	0.80***	0.49*	0.30	0.17	0.73***	0.38
Cu	SPLP	0.93***	0.03	-0.30	-0.25	-0.23	-0.04	-0.17	-0.20
	TCLP	-0.09	0.41	0.93***	0.58**	0.25	-0.07	0.95***	0.34
	SBET	-0.14	0.61**	0.78***	0.71**	0.25	-0.02	0.93***	0.44*
	DTPA	0.08	0.58**	0.75***	0.37	0.33	-0.14	0.90***	0.18
Ni	SPLP	0.66**	0.05	-0.27	-0.28	-0.01	-0.25	0.07	-0.23
	TCLP	-0.01	0.44*	0.87***	0.47*	0.06	0.20	0.83***	0.31
	SBET	-0.02	0.26	0.82***	0.45*	0.06	0.34	0.68**	0.37
	DTPA	0.44*	0.89***	0.22	0.15	-0.06	0.12	0.87***	0.12
Zn	SPLP	0.58**	0.17	-0.15	-0.18	-0.12	0.14	0.05	0.01
	TCLP	0.12	0.33	0.66**	0.25	0.04	0.23	0.56**	0.27
	SBET	-0.07	0.29	0.59**	0.51*	0.02	0.01	0.49*	0.19
	DTPA	0.01	0.49*	0.81***	0.56**	0.07	0.16	0.74***	0.33
As	SPLP	0.95***	0.73***	-0.09	0.20	0.09	0.07	0.35	0.15
	TCLP	0.35	0.41	0.63**	0.51*	0.10	-0.04	0.73***	0.23
	SBET	0.21	0.34	0.75***	0.89***	0.36	0.33	0.78***	0.64**
	DTPA	0.33	0.37	0.56**	0.39	-0.01	-0.11	0.65**	0.13

[a] Mobile fraction with summation of water-soluble (F1), exchangeable (F2) and carbonate fraction (F3) for each trace element. Probabilities for Pearson correlation represent *, at $p < 0.05$; **, at $p < 0.01$ and ***, at $p < 0.001$, respectively.

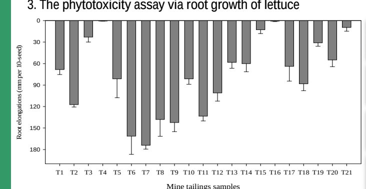


Pollution index (PI), suggested by Chen et al.(2005)
: was calculated as the ratio of element contents in mine tailings to that in background soil in the vicinity of area where mine tailings samples were taken.

Contamination factor (CF), suggested by Kazi etal.(2005)
: represents the ratio of the mobile fraction contents from sequential extraction to residual fraction contents.

Fig 2. Matrix of PI and Cf value for trace elements in the mine tailings

3. The phytotoxicity assay via root growth of lettuce



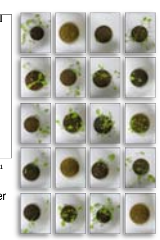


Fig 3. Germination percentages (GP) and root elongations (RE, mm per 10-seed) of lettuce seeds, obtained for phytotoxicity assay in mine tailings samples

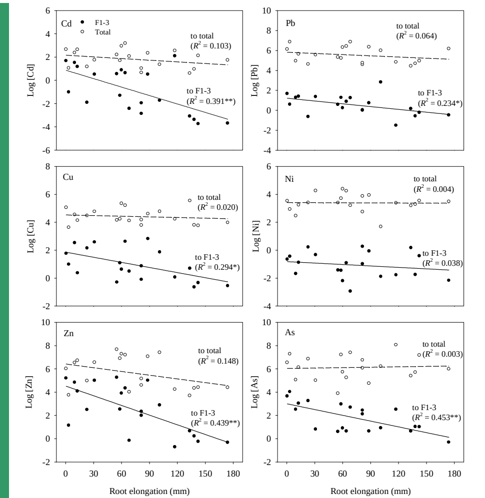


Fig 4. Linear regression analysis models between total (○, broken line), mobile fraction (●, solid line) content, summation of fraction 1 to 3 (F1-3), and root elongation from phytotoxicity assay with lettuce seeds. Trace element concentrations transformed into log scale were used. (*, $p < 0.05$ and **, $p < 0.01$, respectively)

Conclusion

The mine tailings samples, containing a large amount of trace elements (such as Cd, Pb, Cu, Ni, Zn and As), from old metalliferous mines used in this study. Total contents of trace elements in samples were too much higher and characterized as heavily contamination (IPI > 2) with them.

However, due to higher stable fraction, mobile fraction content was relatively lower (< 15%) for all trace elements monitored in the present study. In addition, SPLP contents for trace elements showed lower value (< 1% to total contents), and TCLP and DTPA extractable contents showed < 15%. Although SBET represented higher value than other extraction, they showed < 20% except for Cu (22%).

Comparing between distribution and leachability for trace elements, mobile fraction provided well prediction for leachability in diverse environmental condition than total concentration of trace element. In contrary, SPLP extractable content was not correlated with mobile fraction. It was affected by only F1.

It was verified through relation among mobile fraction of trace element and their phytotoxicity. Although total contents did not offer significant prediction capabilities for phytotoxicity of trace element, mobile fraction was strongly correlated with phytotoxicity impact of trace element except for Ni.

In conclusion, mobile fraction of trace element, which almost present binding to residual phase in mine tailings, would provide useful information on evaluation of leachability and phytotoxicity of them. However, despite new try to assess leachability and phytotoxicity of trace elements for mine tailings in Republic of Korea, the findings in this work were conducted using mine tailings, being heavily contamination of trace elements and containing most of them bound to stable phase, from 20 abandoned metalliferous mines. Hence it requires to be validated by study using wide range of mine tailings samples and distribution for trace elements.

Reference

Jordão, C.P., Fialho, L.L., Cecon, P.R., Matos, A.T., Neves, J.C.L., Mendonça, E.S., Fontes, R.L.F., 2006. Effects of Cu, Ni and Zn on Lettuce grown in metal-enriched vermicompost amended soil. Water Air Soil Poll. 172, 21-38.

Mercier, G., Duchesne, J., Carles-Gibergues, A., 2002. A simple and fast screening test to detect soils polluted by lead. Chemosphere 118, 285-296.

Rodríguez, L., Ruiz, E., Alonso-Azcárate, J., Rincón, J., 2009. Heavy metal distribution and chemical speciation in tailings and soils around a Pb–Zn mine in Spain. J. Environ. Manage. 90, 1106-1116.

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