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Reduction of As Mobility using Soil Amendments, and Its Impact on Soil Enzyme Activity and Phytotoxicity of the Former Au Mine Tailings

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Abstract

Understanding the efficiency of soil amendments for arsenic (As) stabilization, and its impacts on the soil biological toxicity, various soil amendments ($FeSO_4$, $FeSO_4/CaCO_3$, zero-valent Fe, furnace slag, red mud, red mud/$FeSO_4$, mushroom waste and by-product fertilizer) were applied to As-rich gold mine tailings (Kangwon, KW; Keumkey, KK; Chungryong, CR). Following their application, the sequential extraction test, evaluation of soil enzyme activities (dehydrogenase, β-glucosidase, acid phosphatase and urease) and phytotoxicity assay, using lettuce and Chinese cabbage seeds, were conducted. The As fractionation study demonstrated that water-soluble As (W-As) was strongly influenced by changes in pH and dissolve organic carbon content, as well as Fe and Al oxides, while the WNS-As fraction (water-soluble + non-specifically + specifically sorbed fractions) mainly corresponded to Fe and Al oxides. A study on soil biological toxicity revealed that soil enzyme activities were mostly associated with changes in W-As; whereas, the plant root growth was affected by WNS-As. Nonetheless, $FeSO_4$-treated KK and CR, possessing lower As mobility, caused increases in the biological toxicities, while the mushroom waste-treated KK, which showed a slight induction of As mobility, reduced the biological toxicities. In conclusion, the use of suitable soil amendments, coinciding with goals for remediation, whether only As immobilization or recovery in soil biological quality, should be required for successful As stabilization in soils via careful consideration of, not only their potential for As immobilization, but also their adverse effects on the soil pH and mobilities of other heavy metals.

Introduction

Arsenopyrite(FeAsS), an arsenic-bearing mineral commonly found in the bedrock associated with gold deposits

Arsenic (As) is a ubiquitous trace element in the environment. Although As is sometimes utilized for beneficial purposes, such as in herbicides and medicines, it is more commonly recognized as being toxic to animals and humans. Since gold (Au)-bearing ore minerals worldwide contain variable quantities of As compounds, it is widely known that there is a connection between Au mining activity and As pollution. In order to remediate As contaminated sites, the incorporation of various soil amendments into As contaminated soil has been recognized as a cost-effective and environment-friendly technique. Actually, chemical stabilization of As using soil amendments is considered for remediating As polluted soil, and possible amendments for reducing the availability of the toxic element and improving the soil quality have been reported in many investigations. Reducing the As mobility in soil by the addition of amendments has been mostly evaluated via the chemical distribution from sequential extraction tests. Although this approach has some advantages, such as simple and rapid decisions, it does not provide useful information on the toxicity of As with respect to the soil biological quality as a result of changes in the soil enzyme activity and plant growth, which have previously been used as good indicators for predicting the changes in soil quality and biological toxicity due to As. The objective of this study was to elucidate for the effects of agricultural and industrial by-products, such as mushroom waste, red mud and furnace slag, as well as conventional Fe amendments, like Fe (II) and zero-valent Fe, on the As stabilization and soil biological toxicity of As-rich gold mine tailings. The effects of various amendments on the mobility and bioavailability of As were determined via the chemical distribution of As in the soil, change in soil enzyme activity and phytotoxicity assay.

Materials and Methods

1. The mine tailings samples and soil amendments in the present study

1.1 Three former Au mine tailings samples

Surface mine tailings samples were taken from following sites

: **Kangwon mine** (KW; 37°19'19"N, 128°48'47"E), a former gold mine site
at Kangwon province, the Republic of Korea

: **Keumkye mine** (KK; 37°27'44"N, 127°45'53"E) and **Chungryong mine** (CR; 37°30'38"N,
127°46'07"E), former gold-polymetallic mines, including Cu, Ni and Zn,
at Kyunggi province, the Republic of Korea.

1.2 Selected soil amendments (application rate: 1 %, ageing period: 60 d)

: $FeSO_4$, Fe^{II}; $FeSO_4/CaCO_3$, Fe^{II} / L; zero-valent Fe, ZVI

: Furnace slag, FS; Red mud, RM; Red mud / $FeSO_4$, RM / F

: Mushroom waste (spent mushroom substrate), MW; by-product fertilizer, BPF

Table 1. Basic properties and trace element contents of mine tailings and soil amendments

		KW[a]	KK	CR	FS	RM	MW	BPF
pH		7.80	4.07	4.15	10.46	10.74	6.61	7.10
EC (µS cm^{-1})		116	320	77	201	469	160	215
Clay (%)		15.9	14.8	17.2	-[f]	-	-	-
Silt (%)		12.4	27.5	10.6	-	-	-	-
LOI[b] (%)		1.4	0.5	1.3	-	-	43.4	47.2
DOC[c] (g kg^{-1})		0.12	0.06	0.08	-	-	4.80	29.62
Al_{OX}[d] (g kg^{-1})		0.54	0.11	0.55	1.35	1.54	0.25	0.24
Fe_{OX} (g kg^{-1})		7.06	2.98	3.45	29.81	37.05	0.96	0.90
Al_{DCB} (g kg^{-1})		0.52	0.17	0.92	3.53	5.80	0.38	0.37
Fe_{DCB} (g kg^{-1})		11.63	5.89	30.70	73.23	125.51	3.25	3.04
Trace Elements (mg kg^{-1})	As	1357	1496	792	3	2	0.2	0.4
	Cu	38	13	14	8	9	103	65
	Ni	19	8	13	14	18	9	10
	Zn	94	15	40	38	25	308	424

[a] KW, Kangwon; KK, Keumkey; CR, Chungryong; FS, funance slag; RM, red mud; MW, spent mushroom waste; BPF, by-product fertilizer.
[b] Loss on ignition determined at 550 °C for 24 hr, [c] Dissolved organic carbon extracted with deioninzed water, [d] Oxalate and dithionite-citrate-bicarbonate extractable Al and Fe, [e] Total contents determined with *aqua regia* digestion, [f] Not determined.

2. As fractionation, soil biological toxicity in terms of soil enzyme activity and phytotoxicity

2.1 Chemical distiribution of As

Wenzel's sequential extraction (6-step) with minor modifications

Step	Fraction	Extraction
1	Water-soluble	deionized water extraction for 4 hr
2	Non-specifically sorbed	0.05 M $(NH_4)_2SO_4$ extraction for 4 hr
3	Specifically sorbed fraction	0.05 M $(NH_4)H_2PO_4$ extraction for 16 hr
4	Amorphous Fe-Al hydrous oxide	0.2 M NH_4-oxalate buffer extraction for 4 hr
5	Crystalline Fe-Al hydrous oxide	0.2 M NH_4-oxalate buffer/0.1 M ascorbic acid extraction at 96 °C for 0.5 hr
6	Residual	*aqua regia* digestion

2.2 Soil enzyme activity

: Dehydrogenase (DHA)

: β-glucosidase (GLU)

: Urease (URE)

: Acid phosphatase (APA)

2.3 The phytotoxicity assay with lettuce and Chinese cabbage

No. of seeds		20 seeds / Petri-dish
Wt. of soil		20 g / Petri-dish
Replicate		X 3
Test condition	Periods / Temp.	21 days / 25±0.5℃
	Light : dark	16 : 8 (h)
	Water content	40 % (based on soil weight)

Results & Discussion

1. The changes in soil properties following the application of soil amendments

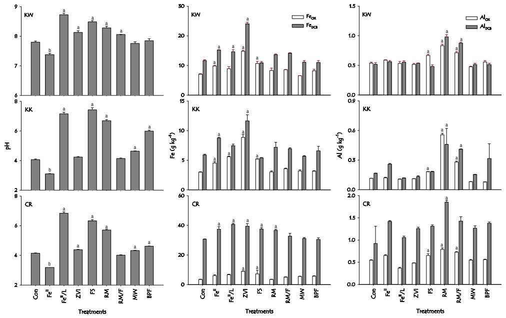


Fig 1. The changes in pH, oxalate (OX) and dithionite-citrate-bicarbonate (DCB) extractable Fe and Al contents of Kangwon (KW), Keumkey (KK) and Chungryong (CR) mine tailings samples after applications of amendments. Letter "a" represents a significant increase over the controls at $p < 0.05$, whilst letter "b" represents a significant decrease at $p < 0.05$, according to Dunnett's test. (Con, Control; Fe^{II}, $FeSO_4$; Fe^{II}/L, $FeSO_4/CaCO_3$; ZVI, zero-valent Fe; FS, furnace slag; RM, red mud; RM/F, red mud/$FeSO_4$; MW, spent mushroom waste; BPF, by-product fertilizer)

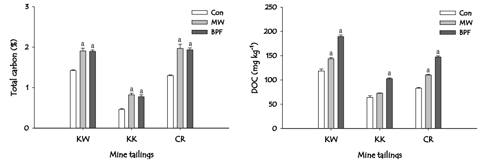
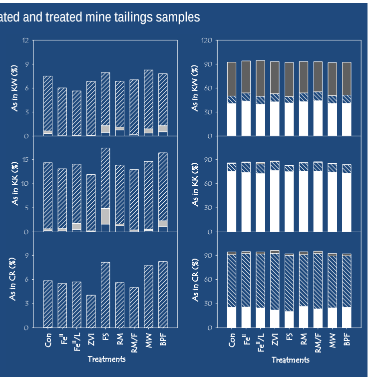


Fig 2. The changes in total carbon (LOI) and dissolved organic carbon (DOC) contents of Kangwon (KW), Keumkey (KK) and Chungryong (CR) mine tailings samples after applications of organic amendments. Letter "a" represents a significant increase over the controls at $p < 0.05$, according to Dunnett's test.

2. As fractionation in untreated and treated mine tailings samples

Fig 3. As fractionation, obtained from 6-step Wenzel sequential extraction, for Kangwon (KW), Keumkey (KK) and Chungryong (CR) untreated and treated mine tailings samples (Con, Control; Fe^{II}, $FeSO_4$; Fe^{II}/L, $FeSO_4/CaCO_3$; ZVI, zero-valent Fe; FS, furnace slag; RM, red mud; RM/F, red mud/$FeSO_4$; MW, spent mushroom waste; BPF, by-product fertilizer).



3. The soil biological toxicity assay

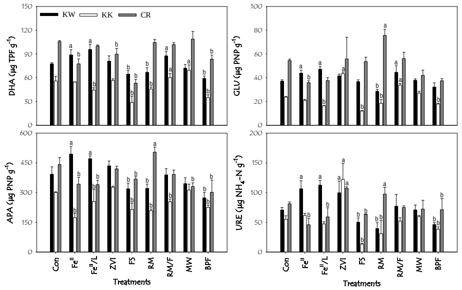


Fig 4. Soil enzyme activity (dehydrogenase, DHA; β-glucosidase, GLU; acid phosphatase, APA; and urease, URE) monitored of Kangwon (KW), Keumkey (KK) and Chungryong (CR) untreated and treated mine tailings samples (Con, Control; Fe^{II}, $FeSO_4$; Fe^{II}/L, $FeSO_4/CaCO_3$; ZVI, zero-valent Fe; FS, furnace slag; RM, red mud; RM/F, red mud/$FeSO_4$; MW, spent mushroom waste; BPF, by-product fertilizer). Letter "a" represents a significant increase over control, whilst letter "b" represents a significant decrease at $p < 0.05$, according to Dunnett's test.

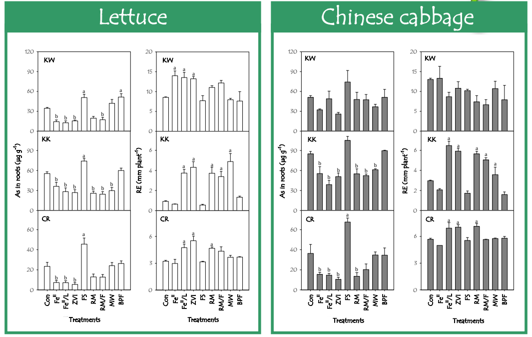


Fig 4. Arsenic concentrations and growth of lettuce and Chinese cabbage roots in Kangwon (KW), Keumkey (KK) and Chungryong (CR) untreated and treated mine tailings samples (Con, Control; Fe^{II}, $FeSO_4$; Fe^{II}/L, $FeSO_4/CaCO_3$; ZVI, zero-valent Fe; FS, furnace slag; RM, red mud; RM/F, red mud/$FeSO_4$; MW, spent mushroom waste; BPF, by-product fertilizer). Letter "a" represents a significant increase over control, whilst letter "b" represents a significant decrease at $p < 0.05$, according to Dunnett's test.

4. Changes in mobility and root uptake of heavy metals in mine tailings

Table 4. Water-soluble heavy metals (Cu, Ni and Zn) concentration in untreated (control) and $FeSO_4$ (Fe^{II})-treated Keumkey (KK) and Chungryong (CR) mine tailings samples, and total heavy metals concentrations of plant roots (lettuce and Chinese cabbage) grown in these treatments.

		Cu	Ni	Zn
Water-soluble heavy metals concentrations in mine tailings (mg kg^{-1})				
KK	Con[a]	0.48 ± 0.062	0.091 ± 0.009	0.33 ± 0.025
	Fe^{II}	3.08 ± 0.15a	1.05 ± 0.040a	1.17 ± 0.071a
CR	Con	0.08 ± 0.018	0.34 ± 0.14	0.44 ± 0.026
	Fe^{II}	1.38 ± 0.089a	3.15 ± 0.061a	4.05 ± 0.041a
Heavy metals concentrations in lettuce roots (µg g^{-1})				
KK	Con	41.57 ± 2.38	14.50 ± 2.99	69.95 ± 3.80
	Fe^{II}	67.90 ± 6.79a	24.97 ± 4.36	97.78 ± 9.16a
CR	Con	20.06 ± 2.39	5.11 ± 2.12	53.21 ± 4.53
	Fe^{II}	38.03 ± 6.07a	7.80 ± 1.13	79.84 ± 13.26a
Heavy metals concentrations in Chinese cabbage roots (µg g^{-1})				
KK	Con	28.82 ± 1.74	26.39 ± 2.70	86.91 ± 3.16
	Fe^{II}	61.15 ± 3.22a	23.85 ± 3.40	197.92 ± 23.18a
CR	Con	9.94 ± 1.34	14.83 ± 1.01	28.18 ± 4.60
	Fe^{II}	20.54 ± 2.63a	32.04 ± 6.80a	153.37 ± 41.89a

[a] Con, Control; and Fe^{II}, $FeSO_4$.
Data represent the mean values of three replicates ± one standard deviation.
Letter "a" represents a significant increase over each heavy metal concentration in control at $p < 0.05$, according to Dunnett's test.

5. The relationship between As mobility and soil biological toxicity

Table 3. Correlation coefficients (*r*) between soil enzyme activity, root growth and labile As fractions (W- As and WNS-As) in the amended Kangwon (KW), Keumkey (KK) and Chungryong (CR) mine tailings samples.

		Soil enzyme activity				Plant root growth	
		DHA[a]	GLU	APA	URE	LET	CAB
KW	W-As[b]	-0.870***	-0.895***	-0.860***	-0.942***	-0.688**	-0.279
	WNS-As	-0.747**	-0.468*	-0.728**	-0.626**	-0.804***	0.028
KK	W-As	-0.841***	-0.738**	-0.536*	-0.771**	-0.340	-0.319
	WNS-As	-0.651**	-0.661**	-0.259	-0.787**	-0.451*	-0.430*
CR	W-As	-0.091	-0.061	0.241	-0.026	-0.214	-0.257
	WNS-As	-0.327	-0.290	-0.460*	-0.399	-0.579*	-0.412*

[a] DHA, dehydrogenase; GLU, β-glucosidase; APA, acid phosphatase; URE, urease; LET, Lettuce; CAB, Chinese cabbage.
[b] W-As (water-soluble As) obtains from deioninzed water extraction of 6-step sequential extraction study, whilst WNS-As (mobile As) obtains summation of water-soluble, non-specifically sorbed and specifically sorbed fraction.
*, **, *** represent significant at $p < 0.05$, 0.01, and 0.001, respectively, according to Pearson correlation analysis.

Conclusion

- The applications of the Fe-rich amendments, particularly Fe^{II} and ZVI, were the most effective for the stabilization of As. However, despite the high Fe and Al oxide contents, FS and RM alone, applied without any pH control, led to marked increases in the mobility of As, particularly water-soluble As (W-As), indicating that the incorporation of alkaline amendments as As immobilizing agents requires particular caution with respect to changes in the equilibrium pH. Both the organic amendments also had no positive effects on the stabilization of As due to their elevated dissolved organic carbon (DOC) contents.
- Soil enzymes were significantly activated, with decreasing W-As, but the plant root growth was strongly increased with declining WNS-As (calculated by summation of water-soluble, non-specifically sorbed and specifically sorbed As fraction from 6-step sequential extraction study) rather than W-As. Conversely, some soil amendments, such as MW, RM and Fe^{II}, caused contrasting results under certain soil conditions, suggesting that the recovery in the soil biological quality via As stabilization could be related to other soil properties, such as other toxic metals, pH or DOC, as well as the mobility of As.
- In conclusion, the use of suitable soil amendments, coinciding with goals for remediation, whether only As immobilization or recovery in soil biological quality, should be required for successful As stabilization in soils via careful consideration of, not only their potential for As immobilization, but also their adverse effects on the soil pH and mobilities of other heavy metals.

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