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**GROWTH OF LETTUCE (*Lactuca sativa*)
AT MINE TAILINGS FROM SHIHEUNG/KOREA,
AND THE EFFECT OF ADDED ORGANIC COMPLEXANTS
ON METAL MOBILITIES**

**WZROST SAŁATY (*Lactuca sativa*) NA HAŁDACH KOPALNI
W POBLIŻU SHIHEUNG (KOREA)
ORAZ WPŁYW DODATKU ORGANICZNEGO
CZYNNIKA KOMPLEKSUJĄCEGO NA MOBILNOŚĆ METALI**

Abstract: In a series of pot experiments, lettuce seedlings (*Lactuca sativa*) were grown at tailings left from the abandoned mine at Shiheung/Korea, to test possible remediation strategies of the site. The test substrate contained far too much As, Cd, Cu, Pb, and Zn for agricultural use, available K and Mg were sufficient, but organic carbon, P, and N were low. About 1/3 to 1/2 of the original sulphidic material was already weathered to yield carbonates and hydroxides. At the base of the experimental pots, moderately contaminated soil was put to monitor downward migration. NaCl, as well as complexants EDTA, NTA, citrate, and malate were added together with the irrigation water to influence plant uptake. Addition of 20 % compost to the tailings, as well as plants growth in an artificially Pb/Cd-contaminated farmland soil, were run within further experimental series. Bulk soils, root soils, and base soils were sampled before the experiment, and after 5, 10 and 15 days of plant growth. All solids were submitted to a Tessier-like sequential leaching procedure, to yield exchangeables, carbonaceous, Mn-oxide, Fe-oxide, sulphidic, and residual fractions, and the resulting extracts finally were analyzed by ICP-OES and AAS methods.

The effect of plant growth on speciation shifts in root and bulk soils as well the effects of added complexants thereof is discussed. Exchangeable amounts were significantly higher in root soils than in bulk soils, but Fe-oxide bound fractions were lower. Complexant addition increased exchangeable contaminants in bulk soil, but decreased them in root soil. Washout led to increase of exchangeables in base soils, particularly after 15 days. Citrate caused the most effective washouts. Complexant addition also tended to shift contaminants from the carbonaceous to the exchangeable fraction. Concentrations in carbonaceous (weak acid-releasable) fractions from the mine tailings passed a flat maximum versus time of plant growth. During plant growth, the total amount of the Mn-oxide fraction increased, and the Fe-oxide fraction decreased. The uptake of Pb and Cd from the tailings was less than from artificially polluted farmland soils, like predicted from the mobility of these contaminants in sequential leaching. EDTA, citrate and compost addition increased

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most elemental concentrations in lettuce leaves with respect to the untreated samples, whereas malate and NaCl were largely ineffective.

Keywords: soil sequential leaching, mobility changes during plant growth, mine tailings, complexing agents addition, *Lactuca sativa*

In Korea, tailings deposited from past mining activities, have led to environmental concerns with respect to groundwater pollution, dust formation, and agricultural production [1–3]. In order to establish a suitable and natural soil life again, phyto-remediation with general accumulator plants has to be considered, which is a soft, cheap, but long-term strategy. Green plants should grow at contaminated sites, accumulate the toxicants in harvestable parts, and finally have to be ashed as hazardous waste after harvest. But tailings of abandoned mine sites are very low in nutrients, which are essential for the growth of green plants, like nitrogen, phosphorus and magnesium. A major disadvantage of phytoextraction might be the long-term scale needed to achieve levels tolerable for consumption. Therefore, within this study, it was investigated how to accelerate the extractions and to reduce the number of necessary extractions.

Mine tailings may contain parts of the original sulphidic ores, as well as weathered layers thereof, and also silicates and carbonates. During phytoextraction, mobile phases should get rapidly exhausted, but dissolution of sulphidic residues inside the tailings as well as washout to the groundwater should be rather avoided. Second, the transport inside the green plant from the roots to the harvestable leaves, should be high.

Root exudates are mainly low molecular organic compounds with complexation capabilities, which feed the microbial biomass at the rhizosphere [4], and also increase phosphate as well as metal availability by dissolution of carbonates and pedogenic oxides. Experiments were needed to test, whether complexant addition from outside would accelerate the soil to plant transfer by dissolution of carbonates and pedogenic oxides (without touching the residual sulphides), or if complexants may even mask free metal ions versus uptake. Formation of soluble complexes may increase the transport inside the green plants towards the leaves, provided there is an uptake of the complexants, but also increase the transport down to the groundwater. Sequential leaching of the solid substrates sampled during plant growth should indicate, if plant growth and addition of complexants induce speciation changes in the test substrate.

EDTA and NTA were chosen as hardly degradable synthetic chelating agents. Contrary to these, citric and malic acid were chosen as natural chelators, readily available to soil bacteria and the rhizosphere, which might increase soil biomass. Though arsenic does not yield such complexes, its availability is expected to be influenced by dissolution of pedogenic oxides, where it has got adsorbed after weathering of the original minerals.

Within a series of pot experiments, lettuce seedlings (*Lactuca sativa* L.) were selected to grow at material sampled from tailings at the abandoned mine site at Shiheung/Korea, because lettuce seedlings are known as universal accumulator plants [5], and to withstand a wide variety of nutrient and toxicant levels. Almost all plants survived for 15 days, but these crops, however, contained toxic levels of Pb and Cd, and

their consumption has to be prohibited. The metal transfer to the plant leaves was less than from a farmland soil soaked with Pb-Cd solution. Fertilization with compost was beneficial with respect to N and Mg supply, whereas addition of complexants like EDTA, citric acid or malic acid induced even more depletion in these essential nutrient elements in the plant tissues. Beneath an N-source, compost also adds a variety of natural microorganisms to the initially dead substrate. The effect of EDTA and NTA as an N-source, however, seemed marginal.

In order to monitor possible speciation changes of metals, As and P from plant growth and complexant addition, bulk soils, root soils, and base soils were sampled initially, and after 5, 10, and 15 days. They were submitted to a Tessier type sequential leaching procedure [6], to yield exchangeables, carbonaceous, Mn-oxides, Fe-oxides, sulphides, and residuals.

Material and methods

The test substrates were collected from the Shiheung Cu-Pb-Zn abandoned mine tailings. Artificially polluted soils were made by mixing the soil with Cd and Pb solution in a ratio 9:1, shaken for 2 hours, and washed 3 times with deionised water. In order to check whether mobile metals were discharged into non-polluted soils, non-polluted soils were put at the bottom of each pot. Each 40 cm³ of chelating agent solution (EDTA, NTA, citric acid, malic acid) were added into the pots every three days. On the other days, 40 cm³ of distilled water was added. Eluates from the pots were returned again. In order to evaluate nutrient effects, a series of tailings mixed with 20 % of compost was run.

Seedlings were grown in a greenhouse equipped with supplementary lighting for 14 hours per day, at 24–28 °C. 10 day-old seedlings were transplanted in sets of three into soil equivalent to 1 kg of dry mass, placed in 15 plastic pots of 15 cm diameter. Transplanted seedlings were well watered for 3 day before chelating agent application. After 5, 10 and 15 days, the plants were harvested.

For *aqua regia* digestion of soil samples, 2.00 g of solid sample were weighed into long-necked glass vessels, 21 cm³ conc. HCl and 7 cm³ conc. HNO₃ were added, and a reflux condenser was put on top. After some hours break, the sample was heated for 1/2 hour to 60° and for 1 1/2 hours to 140°, filtered, and made up to 100 cm³.

For sequential leaching, 1.00 g solid sample was weighed into centrifuge vessels, shaken for 2 hours with 20 cm³ 1 M magnesium chloride, centrifuged and filtered to yield the exchangeable fraction. After washing with water, subsequent extractions with 20 cm³ 0.16 M acetic acid overnight, 20 cm³ 0.5 M hydroxylamine pH 2 overnight, and 20 cm³ 0.2 M oxalate buffer pH 3 overnight, were done. Fraction V was obtained after two times oxidation with 3 cm³ H₂O₂ and 2 cm³ dil. HNO₃ (35 cm³ in 1 dm³) till almost evaporation in a heating block, and final uptake into 20 cm³ 0.16 M acetic acid (from step II). The residue was treated with *aqua regia* like the original sample (modified after [6]).

Reagent solutions for sequential leaching:

– 0.5 M magnesium chloride = 101.5 g MgCl₂ · 6H₂O in 1 dm³ H₂O, adjusted to pH 7 with approximately 7 cm³ 1 + 1 NH₃;

- 0.16 M acetic acid = 9.1 cm³ conc. acetic acid in 1 dm³;
- 0.5 M hydroxylamine pH 2 = 31.75 g NH₂OH · HCl + 3.1 cm³ HNO₃ in 1 dm³;
- 0.2 M oxalate buffer pH 3 = 12.6 g oxalic acid + 14.2 g ammonium oxalate in 1 dm³;
- diluted HNO₃ = 35 cm³ conc. HNO₃ in 1 dm³.

In order to simulate the effect of leachate spills of soluble salts on farmland soils, a sample was artificially polluted with Cd-solution (100 mg/kg Cd) and Pb-solution (30000 mg/kg Pb). The soil was shaken with the pollutant solution for 2 hours, and finally washed 3 times with deionised water.

Bulk soil, root soil, and base soil, as well as plant roots and plant leaves have been separately analysed by ICP-OES multielement spectrometry. The elements Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sr, V and Zn were read in fractions II to VI of sequential leaching, as well as in the *aqua regia* soil extracts. For the exchangeable fraction of sequential leaching (fraction I), neutralized magnesium chloride was preferred over ammonium nitrate(V), ammonium acetate or others. The investigated substrate was poor in nitrogen, not far away from the seaside, and the pH of this extract would be close to natural conditions. In ICP-OES, however, the high Mg levels encountered in the exchangeable fraction, yield some spectral interferences (mainly increased background noise). Therefore, the exchangeable fraction was only read for Cd, Cr, Cu, Fe, Mn, Na, P, and also S. Exchangeable Pb was determined by flame-AAS. Exchangeable sulphur (presumably sulphate) is a reasonable parameter, whereas sulphur losses might occur in other fractions and in the *aqua regia* digestion. In addition, in the fractions III and IV, Ge, Sn and Sb were read, which are not mobile in fractions I and II due to their chemical properties. But Ge is volatile in the *aqua regia* digestion, and no total element contents could be obtained from this procedure. In spite of high arsenic, the Ge, Sn and Sb data were quite low and at the limits of detection, therefore they were not considered for further evaluations.

In the nitric(V)/chloric(VII) acid digest of lettuce plants and lettuce roots, the elements Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sr, V, and Zn were determined.

Results and discussion

Main phases of the substrate

Tailings from an abandoned mine site at Shiheung/Korea, near Seoul capital city, were analysed by *aqua regia* extraction, as well as by sequential leaching. The farmland soil sampled nearby, was much higher in K than the tailings, and slightly enriched in Ba, Cr, Ni and V with respect to usual farmland soils, but extraordinary low in Ca and P. It was polluted with soluble Pb and Cd salts in the laboratory, in order to show possible contrasts in mobility and soil to plant transfer. High Pb, Zn, Cd, Cu and As met in the tailings are known to be hazardous to soil life and to agricultural use (Table 1). The pH of the substrate has been classified as weakly acid, but the sulphides in the mine tailings have a great potential of acidification, when they get oxidized. With respect to intended agricultural use, the action levels for As, Cd, Cu, Pb, and Zn, are superseded,

whereas in case of Ba, Be, Co, Cr, Cu, Mo, Ni, and V, no action is needed. The action level is the concentration which is sufficient to provoke toxic effects.

Table 1

Composition ranges of the mine tailing test substrate and the artificially polluted farmland soil found in *aqua regia*, with respect to target and action levels for agricultural use, proposed by Eikmann and Kloke 1993 [8]

	Test substrates	Polluted farmland soil	Target of remediation	Need of action
pH	5.5–6.9	5.7	—	—
Loss on ignition	1.08–2.90 %	3.42 %	—	—
Organic carbon	0.09–0.93 %	1.17 %	—	—
Main elements:				
Al	1.80–2.31 %	4.62 %	—	—
Ca	3.67–4.83 %	0.13 %	—	—
Fe	5.46–7.39 %	4.78 %	—	—
K	0.066–0.084 %	1.16 %	—	—
Mg	0.63–0.81 %	1.08 %	—	—
Mn	0.104–0.132 %	0.042 %	—	—
Na	0.008–0.014 %	0.015 %	—	—
P	0.060–0.083 %	0.051 %	—	—
Hazardous to soil life:				
As	31–423 mg/kg	4.4 mg/kg	40	50
Cd	97–164	22.9	2	5
Cu	2678–4334	67	50	200
Pb	2.09–2.93 %	1.01 %	0.05 %	0.10 %
Zn	1.17–2.41 %	0.041 %	0.030 %	0.060 %
Others, ambient levels:				
Ba	22–51 mg/kg	200 mg/kg	300	1500
Be	0.85–1.07	2.1	2	5
Co	32–39	14	200	1000
Cr	33–45	158	200	500
Li	7–9	28	—	—
Mo	< 0.2	0.8	20	100
Ni	21–38	51	100	200
Sr	58–73	10	—	—
V	22–32	56	100	400

Sequential leaching roughly helps to assign the amounts bound to carbonates, hydroxides, sulphides, organics and the almost insoluble silicate matrix (Table 2).

The test substrate contains some rests of sulphidic minerals, which are partially weathered to yield carbonates and oxides. About 2 thirds was material insoluble in *aqua regia*, or at least not found. In *aqua regia*, among main elements, silicon and titanium were not determined.

Table 2

Main elements found in *aqua regia*, expressed as main phases due to sequential leaching

	Main phases due to sequential leaching	
Al	0.43–0.59 % Al(OH) ₃	3.49–3.93 % Al ₂ O ₃
Ca	5.99–8.96 % CaCO ₃	1.72–1.83 % CaO
Cu	0.58–0.65 % CuS	
Fe	2.85–3.40 % Fe(OH) ₃	9.75– 10.60 % FeS ₂
K	0.08–0.10 % K ₂ O	
Mg	0.17–0.60 % MgCO ₃	1.03–1.16 % MgO
Mn	0.06–0.07 % MnOOH	0.09–0.13 % MnO
P	0.14–0.19 % P ₂ O ₅	
Pb	1.06–1.94 % PbCO ₃	1.97–3.83 % PbS
Zn	1.26–2.34 % ZnCO ₃	0.59–1.42 % ZnS
Insoluble	62–65.4 %	

The range of main elements given in Tables 1 and 2 has been taken from 5 subsamples, used before the start of the pot experiments. Some inhomogeneity with respect to the oxidation of the subsamples was noticed. It is well known, however, that ZnS and CdS are much easier oxidizable than PbS and CuS.

Fractions I+II+III have been assigned to carbonate minerals CaCO₃, MgCO₃, PbCO₃, and ZnCO₃. Fractions III+IV contain Fe(OH)₃, Al(OH)₃ and MnOOH, which are hardly seen in X-ray diffraction because they are partly amorphous. As organic carbon is very low, fractions V and VI may be attributed to be sulphides. In fraction VI, some silicates also begin to dissolve, but as K and Na are low, silicate dissolution may be limited. In case of Al, Ca, Mg, and Mn, the rest has been termed as “oxides” in the geochemical traditional way, which may be in reality also organics, phosphates or silicates.

The sulphide bound metals, mainly Pb, Zn and Cu, are not immediately available, but impose a great risk of metal intoxication and acidification after aeration.

Similar results had been found in the tailings at a historical Pb mining site in Northern England, appreciable Pb and Zn was found residual, and major parts of Zn was bound to the Mn/Fe-oxides, whereas Cd was highly exchangeable (7–52 %) [9]. In Pb-Zn mine tailings from the “old lead belt” in Missouri/USA, sequential extraction showed that major parts were still bound to the residual and oxidizable fractions [10].

Predicted effects of complexants upon main phases

Among the main components of the mine tailings, Fe is supposed to form the strongest complexes. Addition of complexants should first of all dissolve the pedogenic oxides and liberate all the traces bound therein.

In Table 3, solubilities of assumed main phases present in the test substrate in presence of EDTA, citrate and oxalate, have been calculated. EDTA and citrate have been added during the pot experiments, and oxalate has been used in sequential leaching. For calculations, total soluble sulphide was estimated as 0.1 mol/dm³.

The added complexants, as well as steps I–IV in sequential leaching, mainly attack the weathered phases, like $\text{Fe}(\text{OH})_3$, PbCO_3 , ZnCO_3 and PbSO_4 , whereas the original sulphidic ore minerals are left untouched. (Data for FeS_2 were not available).

Table 3

Calculations from solubility products and complex formation constants

pH = 5–7	EDTA	Citrate	Oxalate	Remarks
$\text{Fe}(\text{OH})_3$	Soluble	Soluble	Soluble pH < 6–7	Soluble in MgCl_2 -extract
Fe_2S_3	Insoluble	Soluble pH < 6	Insoluble	
PbSO_4	Soluble	Partially soluble	Oxalate precipitation	
PbCO_3	Soluble	Insoluble	Oxalate precipitation	
PbS	Insoluble	Insoluble	Insoluble	
CdS	Insoluble	—	—	
CuS	Insoluble	—	—	
ZnS	Partially soluble	—	—	
MnS	Soluble	—	Oxalate precipitation	

Exchangeable fraction

The exchangeable fraction is regarded to be immediately plant mobile and plant available. Readily soluble as well as amounts adsorbed upon various surfaces (humics, clay minerals) as well as the soluble contents of living cells are found here. The sum of the equivalents exchangeable versus neutral BaCl_2 -solution is termed the cation exchange capacity, which is known as a common parameter to characterize soils (Table 4).

Table 4

Sum of exchanged equivalents (meq/kg) versus Mg^{2+}

	Soil + Cd/Pb	Tailing	Tailing + compost	Soil + Cd/Pb	Tailing	Tailing + compost
	meq(Ca-Cd-Cr-Cu-Fe-Mn-Pb-Zn)/kg			meq (Cd-Cu-Fe-Zn)/kg		
Before plant growth	72	42	69	1.87	3.90	8.09
Bulk soil, 5 days	77	34	54	1.52	3.69	3.97
Bulk soil, 10 days	66	34	47	1.52	4.53	4.07
Bulk soil, 15 days	81	38	57	3.27	4.70	6.10
Base soil, 5 days	124	212	226	0.12	0.63	0.52
Base soil, 10 days	122	221	161	0.12	0.54	0.76
Base soil, 15 days	276	366	407	10.2	29.6	61.2
Root soil, 5 days	180	769	784	34.1	212	211
Root soil, 10 days	183	785	159*	33.0	206	9.6*
Root soil, 15 days	185	514	509	26.0	146	139

* Flyer, mainly from fixation of Zn.

Table 4 contains the calculated sum of milli-equivalents exchanged versus Mg in the first step of sequential leaching (Na and K were not determined in this extract). From this, the cation exchange capacity seems rather low in the mere tailings, but approached usual values in base soils, and extraordinary high values in the root soils of the tailings. Differences in exchanged cations were less for the artificially contaminated farmland soil than for the tailings.

Transport of exchangeables to the base soil is remarkably seen after 15 days (see below). Within Tables 5 and 6, the effect of added complexants is illustrated from differences in exchanged milliequivalents with respect to the untreated tailings. Complexants and compost increased exchangeable cations from bulk soil (Ca-Cd-Cr-Cu-Fe-Mn-Pb-Zn) in all cases. In the base soil, however, a decrease of exchangeable equivalents was noted for EDTA and NTA, whereas it was variable for the other cases. In the root soil, all exchangeables decreased with respect to the untreated sample.

Table 5

Milliequivalents (Ca-Cd-Cr-Cu-Fe-Mn-Pb-Zn) exchanged versus Mg^{2+} in fraction I

	Compost	EDTA	NTA	Citrate	Malate	NaCl	Citrate + NaCl
Before plant growth	26.7	-0.3	-13.9	-5.1		32.3	
Bulk soil, 5 days	20.3	19.2	14.8	15.6	13.2	32.1	23.0
Bulk soil, 10 days	12.5	12.8	11.8	7.3	7.5	15.3	16.6
Bulk soil, 15 days	19.8	29.3	17.7	16.6	0.4	33.9	25.8
Base soil, 5 days	14.7	-45.8	-80.1	-68.1	-69.3	-49.5	-69.2
Base soil, 10 days	-60.1	-87.5	-163.2	118.2	95.2		131.6
Base soil, 15 days	40.7	-24.8	-78.7	172.0	-73.4	93.3	14.8
Root soil, 5 days	14.5	-2.0	-624	12.0	4.5	48.1	41.7
Root soil, 10 days	-626	-276	-278	-285	-279	-280	-269
Root soil, 15 days	-5.0	-17.0	-25.8	-20.9	41.4	18.9	66.0

Table 6

Milliequivalents Cd-Cu-Fe-Zn exchanged versus Mg^{2+} in fraction I

	Compost	EDTA	NTA	Citrate	Malate	NaCl	Citrate + NaCl
Before plant growth	4.19	-0.21	-1.02	-0.68		3.94	
Bulk soil, 5 days	0.28	3.24	3.75	2.90	0.38	1.04	0.91
Bulk soil, 10 days	-0.45	3.18	4.19	0.65	-0.93	-0.39	-0.30
Bulk soil, 15 days	1.40	9.24	8.20	5.50	-0.67	3.88	3.35
Base soil, 5 days	-0.11	6.42	1.58	1.24	-0.07	0.24	-0.31
Base soil, 10 days	0.23	9.02	0.63	47.8	16.6		26.8
Base soil, 15 days	31.6	14.2	-7.9	44.9	-10.0	34.2	11.9
Root soil, 5 days	-0.12	-39.4	-195	-49.9	-54.4	-35.6	-35.6
Root soil, 10 days	-196	-79.5	-86.2	-87.9	-78.7	-80.6	-78.5
Root soil, 15 days	-6.28	-18.7	-23.0	-31.0	0.81	-21.9	-8.3

If just Cd-Cu-Fe-Zn are considered (main component = Zn), which give significantly more stable complexes with any of the added complexants than Mg, a similar increase of exchangeables was noted for EDTA, NTA, and citric acid from the bulk samples, whereas conditions varied for the rest. In the base soil, exchangeable Cd-Cu-Fe-Zn increased in most cases, but strongly decreased in the root soil. The difference between the data in Tables 5 and 6 is mainly due to Ca+Pb.

The added chelators are supposed to be released into the exchangeable fraction with $MgCl_2$, unless they have been degraded. Anglesite ($PbSO_4$), which might have been possibly formed from PbS within the tailings, is also sufficiently soluble to appear in the exchangeable fraction. Decrease of exchangeables in the root soil diminishes the difference between bulk and root soil. Differences due to different degradation rates of the added chelators during plant growth were not apparent.

From the artificially polluted farmland soil, which had been prepared by soaking with Cd- or Pb-solution, release of exchangeable Ca, Cu, Zn and S was higher from bulk soil, but lower from root and base soil, with respect to the mine tailings (Table 4).

Carbonaceous fraction

In the second step of sequential leaching, weak acid is applied to dissolve carbonates and the mobile fractions of those cations, which are likely to yield hydroxides in step one, or which are exchangeable against H^+ . Usually, buffer pH 5 is applied. In the Korean mine tailings, however, Ca is low, and slightly more acid conditions (0,16M acetic acid) were chosen to ensure possible dissolution of $PbCO_3$ (cerussite and dolomite).

Within the artificially polluted farmland soil, released matter in fraction II was lower in Ca-Cd-Cu-K-Mn-P-S-Sr-Zn, but higher in Mg. In both cases, the release versus time curves passed a flat maximum. The release of As-Be-Cr-Li-Mo-V into fraction II was negligible. A look at the proportions of released matter in the exchangeable over the carbonaceous fraction will show possible shifts of mobilities due to the addition of complexants.

In the artificially polluted soil, exchangeable Cd, Pb, Mn and Cr were significantly higher than for the carbonaceous fraction. In the tailings, exchangeable Cd and Cr was higher, and exchangeable Ca, Cu, Fe, Mn, Pb, and Zn was lower than for the carbonaceous fraction. As predicted, addition of complexants resulted in shifts from the carbonaceous to the exchangeable fraction. EDTA was the most effective, mobilizing Ca, Cd, Cu, Mn, and Zn. NTA mobilized Cd-Cu-Zn, citric acid mobilized Cd and Zn, and malic acid Cu and Mn.

During plant growth in the untreated tailings, the equivalents of weak-acid-mobile heavy metals (Pb-Cd-Zn), alkaline earths (Ca-Mg-Sr), nutrients (K+P), and Fe+Mn all pass a maximum, possibly at maximum growth rate. The Cd-Pb-treated soil showed the same effects at a lower level (Table 8). The proportion of concentrations of root soil over bulk soil released from the mine tailings during plant growth, however, steadily increased for a lot of elements (contaminants Cd-Pb-Zn, mains Al-Ca-K-Mn-S, traces Co-Li-Sr). Addition of complexants interrupted these trends, except for Cd. Na, which had been added together with the complexants, got steadily enriched in the root soil during plant growth.

Table 7

Results for the second fraction of sequential leaching

	Tailings before		Polluted farmland soil	
	Min.	Max	Min.	Max
Al	0.5	3.1	2.6	7.1
Ba	3.4	13.3	5.8	11.8
Ca	8467	9086	84	701
Cd	13.2	26.1	0.41	1.31
Co	0.97	1.64	<	0.69
Cu	48.4	94.7	0.17	4.07
Fe	1.21	5.81	0.60	2.11
K	35.1	62.4	<	22.6
Mg	292	625	1467	1977
Mn	81.9	95.3	3.5	19.9
Na	16.1	29.9	6.1	26.0
Ni	0.67	0.89	<	0.43
P	2.92	5.02	<	1.22
Pb	1000	2041	1152	3893
S	32.3	48.9	<	3.9
Sr	5.90	6.83	0.15	0.75
Zn	2368	3611	19.8	81.9

Table 8

Milliequivalents released in the carbonaceous fraction during plant growth
(equivalents of physiologically similar elements have been added for simplification)

Concentration [meq]	Mine tailing				Cd-Pb-pretreated soil			
	before	5 days	10 days	15 days	before	5 days	10 days	15 days
Ca + Mg + Sr	475	1081	1156	285	165	194	169	126
Fe + Mn	3.64	8.56	8.63	3.56	0.63	1.29	1.13	0.44
Pb + Zn + Cd	121	258	186	66	22.8	39.3	34.2	11.7
K ₂ O + P ₂ O ₅	59.2	92.0	98.8	0.44	30.0	29.0	26.9	<

Addition of compost immobilised Cu-Cd-P-Sr-Zn in bulk soil, and Al-Ba-Ca-Mn in root soil. More Cd-Pb-Zn was mobilised from base soil, and more Zn from root soil. Maybe, the nutrient input increased biomass, which is not fully attacked in this step, but also increased weathering of the base soil.

Fractions III and IV – the “pedogenic oxides”

In the weathering of primary minerals, Fe-Al-Mn hydroxides are formed, which scavenge a lot of other ions from the soil solution. Sequential leaching with acidified hydroxylamine (fraction III) and oxalate buffer (fraction IV) should discriminate

a Mn-rich phase and an Fe-rich phase (reviewed eg [11]). The load of these “pedogenic oxides” is usually homogenous, whereas the amount of pedogenics may vary within a soil profile. In soils, they may be also formed from degradation of humics, or oxidation of soluble Fe^{2+} . They get dissolved by complexants, like root exudates (see Table 3).

40 cm³ of 20 mM chelating agent in aqueous solutions have been added every 3 days to 1 kg of soil in each pot, starting on the 4th day; this means 3.2 mmole. Al and Fe form the strongest complexes with all chelators added. Added complexants are much less than all pedogenic oxides, present in the test substrates. The pedogenic oxides shifted from fraction III to fraction IV.

Growing roots release considerable amounts of organic carbon into the rhizosphere. This leads to the reduction of MnO_2 by organic acids, reduction/chelation of Fe^{3+} by phenolics, or phosphate mobilization from Al/Fe-phosphates by citric acid [12].

During plant growth, the pedogenic oxides increased in fraction III, and decreased in fraction IV, the sum remained surprisingly constant. For the Mn-oxides (fraction III), EDTA, NTA and citrate increased this effect, whereas Pb^{2+} pretreatment and compost retarded it. For the Fe-oxides (fraction IV), all followed this trend, except NaCl and malate. In the base soils, pedogenic oxides may be formed from washout and precipitation of divalent iron; there were the same trends, but less pronounced (Tables 9 and 10).

In root soils, decrease of pedogenics in fraction IV occurred in all cases. Fraction III increased again, except for compost treatment, and for the Cd-Pb treated farmland soil. Similar effects were noted at other mine tailing sites [13].

In the Mn-rich hydroxide fraction (fraction III), at the untreated tailings, enrichment for the root soils occurred just for Cd-Co-Cu-V, whereas the root soil contained less Al-As-B-Ni-Zn. But almost all additions (all except citrate) caused enrichment of Al and As in the root soil.

Within this fraction, Cu got the most strongly enriched element the in root soil, but this enrichment was lowered during plant growth from compost and NaCl addition. At the artificially polluted soil sample, root soil got also depleted in Al-As-Cu-Ni-Pb. When the action of various additives is compared with conditions at the untreated tailings,

EDTA and NTA addition lowered the differences of already initially depleted Al-Cr-Cu between root and bulk soil, but they increased the differences for Cd-Mn-Ni-Zn. NTA and citrate addition increased contaminant Cd in the root soils; and EDTA treatment lowered Co-Mn-Fe-Ni-Zn in root soil. The excess of Mn-oxide bound V in root soil was further increased by NaCl addition.

In the Fe-rich hydroxide fraction (fraction IV) of root soils from the untreated tailings, less As-B-Fe-Ni-Sb-Sn-Zn was found, but no element got enriched with respect to the corresponding bulk samples. A lot of similar root soil depletions were noted for various treatments also. Compared with the conditions met in the untreated tailings, EDTA even enlarged the root soil depletions for Cd-Co-Mn-Pb, NTA for Co-Mo-Pb, malate for Co-Cu-Mn, and NaCl for Zn.

Table 9
Pedogenic oxides in bulk soils during plant growth; sum of milli-equivalents Fe+Al+Mn

Hydroxyl-amine, pH = 2	Untreated tailings	Tailing + EDTA	Tailing + NTA	Tailing + citrate	Tailing + malate	Tailing + NaCl	Tailing + citrate + NaCl	Tailing + compost	Cd/Pb-treated soil
Before	161	139	164	158		241		185	219
5 days	253	203	194	190	199	308	300	227	285
10 days	200	363	366	285	389	429	554	195	253
15 days	565	573	502	478	142	198	160	543	657
Oxalate pH = 3									
Before	1036	1008	1023	1024		899		1012	915
5 days	724	932	754	814	1006	667	599	678	576
10 days	620	429	384	400	438	347	374	596	583
15 days	360	406	423	500	1016	1018	1012	402	448

Table 10
Pedogenic oxides in base soils during plant growth; sum of milli-equivalents Fe+Al+Mn

Hydroxyl-amine pH = 2	Untreated tailings	Tailing + EDTA	Tailing + NTA	Tailing + citrate	Tailing + malate	Tailing + NaCl	Tailing + citrate + NaCl	Tailing + compost	Cd/Pb-treated soil
Before	161	139	164	158		241		185	219
5 days	173	230	283	228	257	199	249	196	264
10 days	99	223	309	238	376		329	208	213
15 days	271	352	347	479	368	347	366	365	369
Oxalate pH = 3									
Before	1036	1008	1023	1024	×	899	×	1012	915
5 days	560	505	481	510	565	439	485	562	472
10 days	449	553	1031	214	263	×	323	603	432
15 days	295	366	359	524	307	362	296	364	221

Table 11
Pedogenic oxides in root soils during plant growth; sum of milli-equivalents Fe+Al+Mn

Hydroxyl-amine pH = 2	Untreated tailings	Tailing + EDTA	Tailing + NTA	Tailing + citrate	Tailing + malate	Tailing + NaCl	Tailing + citrate + NaCl	Tailing + compost	Cd/Pb treated soil
Before	161	139	164	158		241		185	219
5 days	321	290	295	266	307	331	337	383	72
10 days	362	426	393	371	402	429	408	184	77
15 days	367	386	399	393	421	451	414	370	116
Oxalate pH = 3									
Before	1036	1008	1023	1024	×	899	×	1012	915
5 days	533	611	668	667	558	600	617	574	609
10 days	479	456	561	372	357	344	351	527	531
15 days	354	441	421	451	414	434	436	380	559

The oxidizable fraction

After extraction of the pedogenic oxides, oxidation of the samples was performed to destruct organics and sulphides, and the resulting solubles were extracted like in fraction II. As the organic carbon content of the test substrates was very low, mainly sulphides were found here, just from the root soils some rests of the rhizosphere might have contributed. This was a main fraction for the contaminants met in the tailings, and represented unweathered parts. With respect to the sum of leached amounts, median Cu was 43.9 %, median Cd was 25.4 %, median Pb was 23.7 %, median Zn was 19.2 % and median Mn was 10.2 % found here. Just Fe and As were low, with a median of 0.21 % As and 0.24 % of totally leached, because they were got mainly as residuals.

In the root soils from the untreated tailings, less As-Ca-Cd-Cu-Fe-Mg-Mn-Pb-Sr-Zn than in the bulk soils was found, but none got enriched. From the artificially contaminated soil sample, depletion of Cu-P-Pb, as well as enrichment of Zn was noted.

Addition of compost and complexants to the tailings mainly increased the proportion of root over bulk soil in this organic/sulphidic fraction, thus decreasing the differences between root and bulk soil. Each case was different, and the significance of the effects should be proven in more experiments. For example, Cd and Zn in the root soils got enriched from compost, NTA, citrate, malate, and NaCl, Cu got enriched from EDTA, NTA, malate, and NaCl, and Pb just from compost and citrate. K-Li-Mg-P-S were increased in the root soil by compost-NTA-citrate-malate addition during plant growth.

Mobile sulphur

Aerobic bacterial oxidation of sulphides present in the tailings may lead to elution of sulphate, mobilization of metals and significant acidification of the drainage waters. Soil micro-organisms steadily mineralize organically-bound sulphur to yield sulphate, which is either readily consumed by higher plants, or rapidly washed out [14]. Sulphur (presumably sulphate) found in the exchangeable fraction, has been found within a range expectable for arable soils (Table 12). Arable soils (of Central Europe) contain 200–800 mg/kg of total sulphur, of which 60–90 % are organically-bound. The addition of compost was no significant source of mobile S.

Addition of NaCl, and NaCl + citric acid did not change the level of exchangeable sulphur, whereas the complexants lowered exchangeable sulphate to about half. The artificially polluted sample yielded drastically less sulphate. Root soil was slightly higher, and washout to base soil was not seen in the soluble fraction. Plant growth and respective sulphate uptake were of negligible effect. Reasons may be changes of sulphatase activities, or uptake by soil microbes.

Within the subsequently eluted “carbonaceous fraction”, the sulphur eluted from the tailings before plant growth, was in about the same range than the exchangeable. During plant growth, “carbonaceous” sulphur passed a strong maximum after 5–10 days, then went down to zero, and might approach the original values again. Complexants seemed to accelerate this wave, whereas compost addition had no significant effect on sulphur mobility. In the root soils, exchangeable sulphur was higher than in the corresponding

Table 12
Effect of various treatments on exchangeable sulphur

	Untreated tailings	Tailing + EDTA	Tailing + NTA	Tailing + citrate	Tailing + malate	Tailing + NaCl	Tailing + citrate + NaCl	Tailing + compost	Cd/Pb treated soil
Before	51.5	27.6	22.7	24.6		86.1		55.1	3.8
Soil:									
5 days	44.3	26.7	25.8	18.5	24.4	69.0	59.1	50.6	4.8
10 days	33.7	20.6	26.6	19.0	18.8	49.1	52.9	40.2	4.3
15 days	43.7	30.6	24.7	15.2	22.7	49.7	50.7	51.3	7.0
Base soil:									
5 days	53.8	28.2	21.3	25.6	24.1	44.4	26.4	56.6	4.0
10 days	22.2	19.5	42.8					68.1	3.8
Root soil:									
5 days	67.2	40.1	33.0	35.0	34.5	82.0	82.2	72.2	6.5
10 days	54.1							66.6	6.0

bulk soils, whereas for the “carbonaceous” fraction, this was reverse; the sum of both fractions, however, was always smaller for the root soils, indicating plant uptake.

Potassium

According to the Austrian guidelines for correct fertilization [15], supply of mobile K for medium soils within 113–212 mg/kg is classified as sufficient. Potassium in the weak-acid leachable fraction at the start of the experiments was about 40 mg/kg, but usually exchangeable K is more than weak-acid-leachable. Though exchangeable K had not been measured, it can be concluded from fraction II and the differences between *aqua regia* and the sum of fractions II+V+VI that the K supply in the mine tailings is sufficient, and it is high in the root and base soils. The compost addition did not increase mobile K. The base soil was generally higher, and the root soil was generally lower in mobile K.

Effects on the soil-plant transfer

The primary goal of this experimental series was to increase the soil to plant transfer of contaminant metals [7]. Chelates increase metal solubility in soil, overcome the diffusional limitation of metal in the rhizosphere, and facilitate translocation from roots to shoots. Inside the plant, formation of metal complexes may facilitate the transport to the shoots, and change toxicity effects.

In the lettuce leaves grown at the artificially contaminated farmland soil, Pb, Cd, and surprisingly Ba, were significantly higher than from the tailings (Table 13). This matches the predictions of sequential leaching, in which added Cd was largely recovered as exchangeable, and added Pb mainly as exchangeable + carbonaceous. On the other hand, high levels in the tailings caused higher Cu and Zn in lettuce leaves from the mine soils. Decreasing K, Mg, and P during plant growth might indicate the toxic effects of the metals.

Table 13

Selected element contents of lettuce leaves grown at mine tailings and at the artificially contaminated farmland soil

Contents [mg/kg]	After 5 days at tailings	After 10 days at tailings	After 15 days at tailings	After 5 days at contaminated soil	After 10 days at contaminated soil	After 15 days at contaminated soil
Cd	19.8	24.3	19.0	67.8	70.1	36.5
Pb	48.5	57.2	37.4	1323	2411	805
Ba	9.6	11.1	5.3	50.9	50.8	32.3
Cu	12.9	20.8	12.8	8.1	9.3	8.8
Zn	284	465	309	76	64	111
% K	2.51	3.50	3.19	2.60	1.63	1.86
% Na	0.284	0.467	0.433	0.231	0.104	0.154
% Mg	0.145	0.181	0.139	0.159	0.095	0.097
% P	0.178	0.221	0.236	0.225	0.215	0.150

Table 14
Concentrations in lettuce leaves grown at treated mine tailings over those grown at untreated mine tailings, after 5 days, 10 days, and 15 days of growth

	EDTA			NTA			Citrate			Malate			NaCl			NaCl + Citrate		
	after 5d	after 10d	after 15d	after 5d	after 10d	after 15d	after 5d	after 10d	after 15d	after 5d	after 10d	after 15d	after 5d	after 10d	after 15d	after 5d	after 10d	after 15d
Al	1.47	12.8	0.86	0.66	5.41	1.13	1.41	1.05	1.50	1.25	0.70	0.70	1.62	1.21	0.92	1.62	1.21	0.92
Ba	0.90	1.74	0.90	0.21	1.41	1.21	0.91	0.89	1.27	1.42	0.48	1.06	1.37	1.02	1.84	1.37	1.02	1.84
Ca	1.13	1.26	1.07	0.30	0.65	0.81	1.13	0.57	0.81	1.04	0.64	0.83	1.19	0.81	0.96	1.19	0.81	0.96
Cd	3.35	2.42	5.38	0.23	0.57	0.88	0.82	0.48	1.15	0.93	1.26	1.83	1.05	1.29	1.99	1.05	1.29	1.99
Co	2.65	16.1	5.17	0.78	5.11	2.18	1.50	1.25	1.83	0.98	0.75	1.14	1.29	1.27	1.49	1.29	1.27	1.49
Cr	1.07	3.16	0.43	0.37	1.25	0.74	0.97	0.41	0.78	1.59	0.33	0.49	1.29	0.86	0.45	1.29	0.86	0.45
Cu	7.39	22.2	7.54	2.25	6.79	1.34	1.32	0.73	1.37	1.16	0.65	0.81	2.41	1.11	1.04	2.41	1.11	1.04
Fe	1.38	19.9	0.71	0.70	6.14	1.09	1.01	1.11	1.48	1.31	0.72	0.71	1.61	1.16	0.73	1.61	1.16	0.73
K	1.34	0.71	0.82	0.46	0.46	0.69	1.04	0.51	0.74	1.35	0.76	0.90	1.26	0.72	0.80	1.26	0.72	0.80
Li	1.10	7.52	1.03	0.45	3.12	0.89	1.13	0.63	1.01	1.17	0.67	0.71	1.32	0.92	0.77	1.32	0.92	0.77
Mg	1.56	1.67	1.57	0.37	0.74	1.19	1.13	0.56	0.79	1.53	0.82	1.24	1.43	1.12	1.25	1.43	1.12	1.25
Mn	6.02	5.18	9.41	0.61	1.64	3.83	2.90	1.17	2.19	2.96	1.92	2.35	3.18	3.28	3.40	3.18	3.28	3.40
Mo	1.23	1.68	0.73	0.14	1.21	0.67	0.62	0.35	0.35	0.50	0.58	0.64	0.73	0.49	0.28	0.73	0.49	0.28
Na	5.29	3.01	4.74	2.38	1.73	2.05	1.35	0.55	0.72	3.78	2.33	3.09	2.75	1.85	2.25	2.75	1.85	2.25
Ni	1.14	6.54	1.12	0.92	3.04	1.15	1.60	0.84	0.80	1.16	0.59	0.76	1.04	0.98	0.59	1.04	0.98	0.59
P	1.12	0.82	0.65	0.63	0.74	1.00	1.09	0.67	0.66	1.10	0.66	0.60	0.86	0.74	0.51	0.86	0.74	0.51
Pb	13.6	48.2	14.2	3.97	19.0	1.99	2.23	1.58	2.84	1.14	0.93	1.01	1.58	2.92	1.13	1.58	2.92	1.13
Sr	1.18	1.44	1.12	0.31	0.88	1.02	1.15	0.62	0.84	1.14	0.62	0.91	1.12	0.84	0.96	1.12	0.84	0.96
Zn	5.29	9.82	6.94	1.52	2.50	1.84	2.53	1.17	1.48	1.18	0.75	1.05	1.50	1.16	1.37	1.50	1.16	1.37

When the concentrations encountered in the lettuce plant leaves grown at the mere tailings, are divided over the respective concentrations met in treated tailings, values > 1 mean an increased extraction effect (Table 14). From this, EDTA and compost addition were the most effective. EDTA increased Cd-Co-Cu-Mn-Pb-Zn concentrations in the leaves, but also Al-Li-Mg-Na-Ni-Sr. Citrate acted like EDTA, but is more moderate. NTA worked just for Cu-Na-Pb-Zn, and malate addition caused just moderate increase of Al-Co-Mn-Pb-Zn. Addition of NaCl had +/- no effect, except for higher Na and Mn levels. When NaCl and citrate were applied simultaneously, the action of citrate was just lowered. Compost admixture with the test substrate increased almost all elements, except Ca-Mo-P, which are essential for plant growth, possibly due to a competition effect with introduced soil bacteria.

Transfer to the base soil

Without the addition of complexants, the washout of metal cations (Cu, Pb, Cr) from columns of bare non-contaminated soil to deeper layers was marginal, even if addition of CuSO_4 to vineyard soils had occurred some years before. Similarly, added soluble Mo, V, and Se got rapidly fixed within upper layers [16]. To the contrary, complexing agents effectively washed out heavy metal contaminations from soils polluted with soluble salts, within 20 pore volumes in 10–15 hours [17]. Equilibrium conditions can be estimated from constants given in table 15, but there is no equilibrium during plant growth at all. Citrate, tartrate and oxalate were applied as a model for plant root exudates, and EDTA and DTPA as artificial and hardly-degradable substances. All were effective in removing contaminations of soluble Cd, Pb, Cr, and Cu, but the amount depended on the soil type. EDTA and DTPA leached 4–5 times more macronutrients, such as Ca, Mg, and Fe [17]. Mobility in the soil column has to be considered with respect to groundwater protection. Transfer from bulk soil to base soil may indicate washout reactions. In particular, objections exist against hardly degradable man-made complexants. EDTA is readily leachable, and 50–60 % of added EDTA could be recovered in aqueous soil extracts [18].

Complexants like root exudates, or added chelators, are supposed to increase metal mobility by dissolution of Fe-oxides and various sulphides. In order to monitor downward migration during the experiment, each pot contained a layer of base soil, which was submitted to *aqua regia* digestion and sequential leaching also. This base soil was contaminated with Cd, Cu, Zn, and above all, with Pb, and in addition to the tailings, also with Cr and Ni. Below the lettuce plants grown on untreated tailings, most of the fractions of main and contaminant elements steadily declined, like Mn-Cd-Pb-Zn in fractions II, III, and IV (carbonaceous, Mn-hydroxides, Fe-hydroxides), Fe-Cu in fraction IV (Fe-hydroxides), as well as Fe-Pb in fraction VI (residuals). High amounts of the main contaminants Cd-Cu-Pb-Zn, as well as Fe and Mn had moved to the exchangeable fraction after 15 days, which indicates a load readily adsorbed from the soil solution.

Table 15

Equilibrium constants (pK) and solubility products (pLp) used for calculations Ox = oxalate;
Pb forms its complex with H-citrate

	EDTA	Citrates	Oxalates	Sulphides	Others
H ⁺	2.0/2.67/6.16/10.26	3.13/4.76/6.40	1.27/4.27	7.04/14.92	—
Fe ³⁺	25.1	25	25	Fe ₂ S ₃ : 88	Fe(OH) ₃ : 37.4
Mn	14.04		14.96	MnS: 15.2	
Ca	10.69		8.4	—	CaCO ₃ : 8.32
Pb	18.04	PbH: 6.5	PbOx: 9.32	PbS: 29.0	PbCO ₃ : 12.82 PbSO ₄ : 7.74
Cu	18.8		CuOx: 7.64	CuS: 37.4	
Zn	16.5		ZnOx: 7.56	ZnS: 23.0	ZnCO ₃ : 10.2
Cd	16.46		CdOx: 7.04	CdS: 28.0	

Remark: from this, the solubility of PbSO₄ would be 28 mg Pb/dm³. Extraction in the exchangeable fraction was performed for 1 g in 20 cm³, which means 0.56 mg Pb, in 1 g means 560 mg/kg. Maximum 90 mg/kg have been found.

Both EDTA and compost addition during plant growth slightly increased exchangeable soil fractions, and lowered the decrease of the moderately mobiles. NaCl addition increased the washout of contaminants, but not of Fe and Mn. The most significant effects, however were noted from citrate addition – almost all fractions of contaminant Cd-Cu-Pb-Zn steadily increased during plant growth. This means a high downward flux. Citrate strongly complexed Fe, which seems to be mobilized from the test substrates, and reprecipitated in the base soils, whereas EDTA and NTA also react with Ca and Mg. On the other hand, citrate addition had low effects on the plant soil transfer.

EDTA was shown to be slowly biodegraded to CO₂ in soils and sediments under aerobic conditions [19], but there is probably no degradation of added EDTA and NTA during this experiment. Degradation of citrate and malate is possibly done by soil bacteria, but it is at least slow enough to increase transport to the base soils. In metal polluted substrates, respiration and enzyme activities are significantly lowered, but activities involved in the N-, P- and S-cycling are much more involved than those in the C-cycle [20].

Conclusions

Lettuce plants grown at mine tailings from Shiheung/Korea were capable to transfer a lot of contaminant elements to their harvestable leaves. When EDTA or citrate solutions, or compost, were added, both the trace element concentration in the lettuce leaves as well as downward migration was increased. Whereas EDTA caused the strongest effects for the plant tissues, citrate was the most effective to promote downward migration, and adsorption in deeper soil layers.

Speciation changes due to the action of complexants and plant growth can be monitored by a Tessier-type sequential leaching procedure. Exchangeable sulphur was

rather constant, but weak acid mobile (“carbonaceous”) sulphur at first increased, and then was depleted at the probable maximum growth rate of the roots. In the root soils, increase of Mn-oxide bound fractions (hydroxylamine leachable) occurred, and simultaneous decrease of Fe-oxide bound fractions (oxalate leachable). Intoxications from complexants might be indicated by wiping away the differences between root and bulk soils, whereas intense consumption enlarges these differences.

Beneath beneficial effects in nutrient supply [7] to promote plant growth and microbial activities, compost addition favoured the transfer of contaminant metals to the harvestable parts of the lettuce plants. Thus, fixation of contaminants could not be achieved, but phytoremediation with lettuce seedlings in presence of compost would be promising. Simultaneous addition of compost and complexants might be tried within further experiments.

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**WZROST SAŁATY (*Lactuca sativa*) NA HAŁDACH KOPALNI
W POBLIŻU SHIHEUNG (KOREA)
ORAZ WPŁYW DODATKU ORGANICZNEGO CZYNNIKA KOMPLEKSUJĄCEGO
NA MOBILNOŚĆ METALI**

Abstrakt: Przedmiotem badań były sadzonki sałaty (*Lactuca sativa*), uprawiane na hałdach opuszczonej kopalni w pobliżu Shiheung (Korea) w celu oceny możliwości ich wykorzystania w rekultywacji terenu. Badane podłoże zawierało zbyt dużo As, Cd, Cu, Pb i Zn, aby mogło być wykorzystane do celów rolniczych. Zawartości K i Mg były wystarczające, ale stężenie węgla organicznego P i N było małe. Około 1/3 do 1/2 wcześniej istniejących związków siarczkowych uległo zwietrzeniu oraz przekształceniu w węglany i wodorotlenki. W celu śledzenia migracji zanieczyszczeń w pojemnikach umieszczono średnio zanieczyszczoną glebę. Do wody, którą podlewano rośliny, dodawano NaCl, jak również kompleksotwórcze EDTA, NTA, cytryniany i jabłczany. Badano wzrost roślin na glebie zawierającej 20 % kompostu z odpadów oraz sztucznie zanieczyszczonej Pb / Cd. Próbkę gleby, w której rosły rośliny, próbkę gleby pobranej z obszarów przy korzeniu oraz próbki głębszych warstw gleby, były badane przed i po 5, 10 15 dniach wzrostu roślin. Wszystkie próbki gleby były poddane ekstrakcji zgodnie z procedurą sekwencyjną Tessiera. Pozwoliło to na wyodrębnienie frakcji wymiennej, węglanowej, tlenku Mn, tlenku Fe, siarczkowej oraz pozostałych frakcji. Roztwory po ekstrakcji analizowano za pomocą ICP-OES i metody AAS.

Omówiono wpływ zmian specyjalnych w warstwie korzeniowej i w całej glebie na wzrost roślin, a także wpływ związków kompleksujących. Frakcje wymienne były znacznie większe w warstwie korzeniowej niż w całej glebie, ale frakcje związane tlenków Fe były mniejsze. Dodanie związków kompleksujących spowodowało wzrost zanieczyszczeń w wymiennej frakcji gleby, ale ich zmniejszenie w warstwie korzeniowej. Wymywanie doprowadziło do wzrostu frakcji wymiennej w głębszych warstwach gleby, w szczególności po 15 dniach. Cytrynian był najskuteczniejszy w procesie wymywania. Ponadto związki kompleksujące powodowały tendencję do przenoszenia zanieczyszczeń z frakcji węglowych do frakcji wymiennej. Zależność stężenia we frakcjach węglanowych (uwalnianych przez słabe kwasy) od czasu wzrostu rośliny wykazywała płaskie maksimum. Podczas wzrostu roślin łączna liczba frakcji tlenków Mn rosła, a frakcja tlenków Fe malała. Pobieranie Pb i Cd z odpadów był mniejszy niż z gleb zanieczyszczonych sztucznie, co było zgodne z informacjami o ruchliwości tych zanieczyszczeń otrzymanymi doświadczalnie. Dodanie EDTA, cytrynianu i kompostu powodowało wzrost stężenia większości pierwiastków w liściach w porównaniu do próbek kontrolnych. Dodanie jabłczanów i NaCl przeważnie było mało skuteczne.

Słowa kluczowe: ługowanie gleby, zmiany mobilności podczas wzrostu roślin, odpady kopalniane, dodawanie związków kompleksujących, *Lactuca sativa*