Environmental Geochemistry and Health (2005) 27: 289–300
DOI: 10.1007/s10653-004-5977-5

Stabilization of metals in acidic mine spoil with amendments and red fescue (*Festuca rubra* L.) growth*

László Simon
College of Nyíregyháza, Technical and Agricultural Faculty, Department of Land and Environmental Management, H-4401 Nyíregyháza, P.O. Box 166, Hungary (e-mail: simonl@nyf.hu)

Received 3 June 2004; Accepted 9 November 2004

Key words: amendments, heavy metal stabilization, mine spoil, phytostabilization, red fescue

Abstract

Stabilization of metals with amendments and red fescue (*Festuca rubra*, cv. Keszthelyi 2) growth was studied on an acidic and phytotoxic mine spoil (pH_{KCl} 3.20–3.26; Cd 7.1 mg kg^{-1}, Cu 120 mg kg^{-1}, Pb 2154 mg kg^{-1} and Zn 605 mg kg^{-1}) from Gyöngyösoroszi, Hungary in a pot experiment. Raising the pH above 5.0 by lime ($CaCO_3$), and supplementing with 40 mg kg^{-1} nitrogen (NH_4NO_3) made this material suitable for plant growth. All cultures were limed with 0.5% (m/m) $CaCO_3$ (treatment 1), which was combined with 5% (m/m) municipal sewage sludge compost (treatment 2), 5% (m/m) peat (treatment 3), 7.5% (m/m) natural zeolite (clinoptilolite) (treatment 4), and 0.5% (m/m) KH_2PO_4 (treatment 5). Treatments 1–5 were combined with each other (treatment 6). After 60 days of red fescue growth, pH of the limed mine spoil decreased in all cultures units. Application of peat caused the highest pH decrease (1.15), while decrease of pH was less than 0.23 in treatments 2, 5 or 6. Application of lime significantly reduced concentrations of metals in the 'plant available' fraction of mine spoil compared to non-limed mine spoil. Amendments added to limed mine spoil changed variously the ratio of Cd, Cu, Pb and Zn in exchangeable or 'plant available' fractions, differently influencing the phytoavailability of these metals. Most of the metals were captured in the roots of test plants. Treatment 2 caused the appearance of less Cd in shoots (<0.1 µg g^{-1}) or roots (3.11 µg g^{-1}), while treatment 5 resulted in the highest Cd concentration (2.13 µg g^{-1}) in shoots. Treatments did not influence significantly the Cu accumulation in shoots. The Pb accumulation of roots (44.7 µg g^{-1}) was most effectively inhibited by combined treatment, while the highest value (136 µg g^{-1}) was found in the culture treated with potassium phosphate. Pb concentration in shoots was below the detection limit, except for treatments 5 and 6. Peat application resulted in higher Zn concentration (448 µg g^{-1}) in shoots than other amendments, where these values were around 100 µg g^{-1}. All amendments influenced positively the dry matter yield of red fescue grown in limed mine spoil, however the application of 0.5% phosphate was less favourable. Liming, application of amendments and growth of red fescue can stabilize metals in acidic and phytotoxic mine spoil, and by phytostabilization they can reduce the risk of metal contamination of the food chain.

Introduction

Energy and mineral consumption by man is the main cause of trace element pollution in the biosphere. As a consequence of industrialization, traffic, mining, metal processing, burning of fossil fuels, disposal of wastes, etc., soil and water resources have been contaminated with heavy

* This paper was presented at the 20th European Conference of the Society for Environmental Geochemistry and Health 'Heavy Metal Contamination and the Quality of Life' in Debrecen, Hungary, 4–6 September 2002.

metals all over the world, including Hungary (Simon 1999; Kabata-Pendias & Pendias 2001). This becomes of environmental concern when the toxic concentration of metals (i.e., Pb, Cd, Zn, Cu, Cr, Ni and Hg) in soils and waters begins to affect human health.

Current remediation methods to clean the soils degraded with metals are expensive and environmentally invasive. These techniques (i.e., soil flushing, washing, vitrification) not only destroy the physical structure of the soils and stop their biological activity, but also generate secondary pollutants which needs further handling (Simon 1999). Instead of metal removal as an alternative *in situ* metal immobilization (inactivation, stabilization) could be more advantageous in many cases. During *in situ* metal stabilization various amendments and additives (i.e., liming agents, organic materials, aluminosilicates, phosphates, iron and manganese oxides) are mixed with contaminated soils or mine spoils to reduce the bioavailability of metals (Berti *et al.* 1998; Mench *et al.* 1998; Berti & Cunningham 2000; Mench *et al.* 2000).

Liming agents ($CaCO_3$, $CaCO_3 + MgCO_3$, $Ca(OH)_2$, CaO) are often used in traditional agricultural practises and in mine spoil revegetation to raise soil pH for plant growth. Liming materials may also be used to immobilize metals in waste products (sludges, composts, slags, fly ashes), or in contaminated sludge-amended soils and sediments. Generally, an increase in soil pH ionizes pH-dependent exchange sites, raising cation exchange capacity (CEC). This may result in greater metal sorption to soil particles. Addition of lime and alkaline pH also favours the formation of insoluble compounds such as $PbCO_3$ (Albasel & Cottenie 1985; Berti *et al.* 1998).

Organic materials such as composts, sludges, manures, biosolids, and peat are also prospects for use in *in situ* stabilization of metal contaminated soils or mine spoils (Berti *et al.* 1998; Berti & Cunningham 2000). Organic matter often has high CEC and may adsorb metals on pH-dependent exchange sites. Organic matter forms strong complexes with Pb, Cu, or Zn present in contaminated soils or mine spoils. Some organic amendments that contain high levels of P or Fe or have a high pH may have additional capacity to inactivate soil metals. Many organic materials (e.g., composts, sludges, manures) are inexpensive by-products or waste products; however their quantity could be limited and their properties may vary. Organic amendments may also benefit plant growth by increasing soil moisture retaining capacity, improving soil texture, stimulating biological activity and providing plant nutrients such as nitrogen and phosphorus (Berti *et al.* 1998; Vangronsveld & Cunningham 1998).

Aluminosilicates (clays, aluminium pillared clays, by-products from burning of coal refuse, natural and synthetic zeolites etc.) are also used for metal immobilization in contaminated soil or mine spoil (Mench *et al.* 1998; Simon 2001). Zeolites are crystalline, hydrated aluminosilicates of alkali and alkaline earth cations that possess infinitive three-dimensional crystal structure. The use of zeolites for pollution control primarily depends on their ion-exchange capabilities. These result from substitution of Al^{3+} for Si^{4+} in the silicate tetrahedra, creating fixed negatively-charged sites throughout the structure. The negative charges are balanced by an equivalent number of mobile cations loosely bonded in the crystal structure and free to exchange with other cations in solution. Zeolites also possess ion-sieve properties. The internal structure consists in a series of interconnecting channels and cages with specific dimensions. These either trap or exclude ions depending on size. Consequently, zeolites show selectivity properties at trapping certain metals (Mench *et al.* 1998; Mench *et al.* 2000; Friesl *et al.* 2003).

Phosphate minerals have the potential to sorb and/or co-precipitate trace metals. Phosphates may be added to contaminated soil or mine spoil as phosphoric acid, di- and tri-basic potassium phosphate, calcium phosphates, sodium phosphate, mono- and diammonium phosphate, and rock phosphate or apatite (Berti *et al.* 1998; Mench *et al.* 1998; Hettiarchchi *et al.* 2000). In case of Pb contamination a stable and highly insoluble pyromorphite is forming (Laperche *et al.* 1997). Zn and Cd sorption to hydroxyapatite is explained by surface complexation and co-precipitation, presumably combined with ion exchange and solid diffusion (Mench *et al.* 1998).

During *phytostabilization* not only amendments and additives are applied to metal-contaminated soil but also a vegetation (grass, bush, or tree) cover is established in the area to be remediated (Berti *et al.* 1998; Mench *et al.* 1998; Berti & Cunningham 2000). Plants must physically stabilize the soil to prevent erosion and deflation and may also help to reduce water percolation through the soil to minimize the leaching of contaminants to groundwater. Plants should be tolerant of site conditions (e.g., low pH, high metal concentration, salinity), grow quickly and produce sufficient biomass to provide complete coverage of the soil. Plants should have relatively dense root systems for stabilization, and not accumulate metals in above-ground plant tissues that could be consumed by humans or animals. Plant roots may provide some additional surface area for metal precipitation or adsorption to occur (Berti *et al.* 1998). Red fescue (*Festuca rubra* L.) and other grass species meet most of these requirements. Red fescue is a metal-tolerant plant that is frequently utilized to establish vegetative cover in mine spoil heaps or contaminated soils previously treated with stabilization amendments (Vangronsveld & Cunningham 1998, Li *et al.* 2000).

Similarly to well-developed countries an environmental remediation programme had started by 1996 in Hungary to clean-up the most critical contaminated sites of the country (Simon 1999). North of the village Gyöngyösoroszi (located in the Mátra Mountains, North Hungary) a flotation plant had been operating for 40 years (until 1985) near a sphalerite and galenite mine. The mine spoil (flotation mud) generated here was placed in large quantities without any further treatment in tailing dumps located between the Toka and Száraz stream. Careless handling of this mine spoil caused serious heavy metal pollution of the local environment (Horváth & Gruiz 1996; Kovács & Tamás 2002). Analysis of 61 mine spoil samples collected from this area revealed that the median concentration for Cd, Cu, Pb and Zn is 12.8, 173, 1073 and 1506 mg kg^{-1}, respectively (Kovács and Tamás 2002).

Considering these preliminaries, the objectives of our study was to evaluate:

- heavy metal (Cd, Cu, Pb and Zn) immobilization effect of different amendments (lime, municipal sewage sludge compost, peat, natural zeolite, potassium phosphate and their combination) added to the acidic mine spoil from Gyöngyösoroszi,
- phytoavailability, accumulation and translocation of heavy metals in red fescue grown in limed mine spoil treated with these amendments
- effect of these amendments on the dry matter accumulation of red fescue.

Materials and methods

Mine spoil collection, liming and extraction of heavy metals

Mine spoil samples were collected north of Gyöngyösoroszi from one terrace of tailing dumps of a former mine (coordinates: longitude 19° 52.727′ E, latitude 47° 50.557′N, 352 m above the Baltic sea level) (Lakatos *et al.* 2002). From a 10 m wide and 10 m long plot 20 mine spoil subsamples were taken randomly with stainless steel gauge auger from 0 to 25 cm depth. The yellow-coloured mine spoil samples were thoroughly mixed, air dried in the laboratory and screened on a 2-mm sieve. To determine the exchangeable or ‘plant available’ fraction of heavy metals, 5 g of mine spoil samples were extracted with 50 cm^3 of 0.01 $CaCl_2$ or Lakanen–Erviö solution (0.02 M H_4EDTA in ammonium acetate buffer, pH 4.65), respectively. To extract ‘total’ amount of heavy metals, 2 g samples were digested with conc. HNO_3 and H_2O_2 (3 M HNO_3 final concentration) prior to elemental analysis. Samples were shaken for 2 h. To determine pH, 5 g air dried mine spoil samples were shaken with 12.5 cm^3 of 1 M KCl in triplicate. Samples had been standing for 18 h, then pH of supernatants was determined with digital WTW pH320 type (Weilheim, Germany) pH meter.

To determine the amount of lime necessary to reach pH $>$ 5.5 (which is favourable for plant growth), 5 g mine spoil samples were mixed with 0.25, 0.5, 0.75% and 1.5% (m/m) of $CaCO_3$ (*puriss.*, Reanal Ltd., Hungary). Samples were saturated with distilled water to reach field moisture holding capacity (20%) of the mine spoil. During one week of incubation, samples were daily moisturized with distilled water. The pH of the mine spoil was found to be strongly acidic with pH_{KCl} 3.20–3.26. Addition of 0.5% $CaCO_3$ to this acidic mine spoil raised the pH above 6.3, which is suitable for plant growth.

Origin and characterization of amendments

Powdered *lime* ($CaCO_3$ *puriss.*) was produced by Reanal Ltd., Hungary.

Municipal sewage sludge compost originated from the Water and Canalization Works Enterprise of Nyíregyháza City and region. Preparation of sewage sludge compost and sampling of compost piles has been described elsewhere (Simon *et al.* 1997). The samples were air-dried, milled and screened on a 1-mm sieve before mixing with the mine spoil. Elemental analysis of samples in triplicate revealed (see the method later) that this municipal sewage sludge compost is relatively uncontaminated with heavy metals (see also Simon *et al.* 1997). Besides 31.7 g kg^{-1} Ca, 2.22 g kg^{-1} K and 9.81 g kg^{-1} P, 3.96 μg g^{-1}Cd, 158 μg g^{-1}Cu, 135 μg g^{-1} Pb and 1278 μg g^{-1} Zn was found in samples.

Peat moss originated from Joint Stock Company (Lithuania). Peat samples were ground to <1 mm particles. To determine its pH, 5 g peat samples were shaken in triplicate for 18 h by 180 rpm with 50 cm^3 of distilled water. The pH_{KCl} was determined in supernatants as described above and was found to be 3.88.

Natural zeolite (RBZ clinoptilolitic rhyolite tuff) samples originated from Healing Minerals Geoproduct Ltd. (Mád, Hungary) and were mined in the Zemplén Hills, Hungary. The RBZ type is a medium-hard microporous zeolite with ≈50% clinoptilolite, 0–10% mordenite, 20–30% altered volcanic glass, 10–15% montmorillonite, 0–5% quartz, 0–5% feldspar and 1–2% limonite composition. Its density is ≈2.05 g/cm^{-3}, wet surface pH is 7.8, NH_4^+-ion exchange capacity is 118 meq/100 g, and Ag^+-ion binding capacity is 177 meq/100 g (Simon, 2001).

Potassium phosphate (KH_2PO_4 *puriss.*) was purchased from Reanal Ltd., Hungary.

Growth chamber pot experiment with red fescue

Air-dried, homogenized and screened mine spoil (4500 g) was thoroughly mixed with 0.5% (m/m) $CaCO_3$ using mortar and pestle. The limed mine spoil was then divided to 750 g subsamples, which were mixed with different amendments and additives. The treatments were the following:

1. 0.5% $CaCO_3$
2. 1 + 5% (m/m) municipial sewage sludge compost
3. 1 + 5% (m/m) peat
4. 1 + 7.5% zeolite
5. 1 + 0.5% KH_2PO_4
6. 1 + 2 + 3 + 4 + 5 (combined treatment)

Since it was not possible to grow plants on the original non-limed mine spoil, the experiment did not contain a control without lime.

Treated subsamples were divided into 250 g portion and placed in plastic pots of 10 cm diameter and 7.5 cm height. The 250 g mixture in every pot was moisturized with 50 cm^3 distilled water. Each pot received with this water 40 mg kg^{-1} nitrogen as NH_4NO_3. Limed mine spoil was thereafter incubated for 62 days at room temperature receiving distilled water weekly to reach a constant weight (330 g). Before seeding, 5 g mine spoil samples were taken from every pot with a plastic tube in triplicate to determine pH.

The pot experiment was conducted with red fescue (*Festuca rubra* L. cv. Keszthelyi 2) from September to November 2001 in a light chamber of the College of Nyíregyháza, Hungary. In every pot 1.71 g red fescue seeds were planted. A randomized experimental design with three replicates was used. Light (350 μmol m^{-2} s^{-1}), temperature (23 ± 4 °C), and humidity (40~50%) were controlled. The plants were watered every 3–4 days with distilled water to reach a constant weight (field water holding capacity) of the mine spoil.

After 4 weeks of growth, shoots of red fescue were harvested (1st cut). Shoots were cut at a height of 1.5–2 cm, washed in three times changed distilled water, and dried at 70 °C for 8 h. This time, mine spoil in each pot was fertilized with 40 mg kg^{-1} nitrogen (NH_4NO_3) with the irrigation water. Eight weeks after planting, the shoots were harvested (2nd cut) as described above. Roots were thoroughly washed with running tap water, and in three-times-changed distilled water. After determination of dry weights (70 °C, 8 h), plant samples were ground (<1 mm), and digested with 3:1 v/v 65% HNO_3 and 30% H_2O_2 (3 M HNO_3 final concentration) prior to elemental analysis (Kovács *et al.* 1996).

Mine spoil samples were taken from every pot in three replicates at the end of the pot experiment. The samples were air-dried and sieved (<0.5 mm) to remove root debris prior to extraction. Extraction of exchangeable, 'plant available', and 'total' fraction of heavy metals was done as detailed formerly.

Elemental analysis of mine spoil and plant samples

Elemental composition of mine spoil and plant samples was determined by the inductively-coupled argon plasma emission spectrometry (ICAP, model Perkin-Elmer Optima 3300 DV) technique in triplicate at Debrecen University, Centre for Agricultural Sciences, Hungary. For validation of plant analysis CRM 281 rye grass (Commission of the European Communities, Community Bureau of Reference, Brussels, Belgium) certified reference material was used.

Statistics

Data processing of the experimental data was done with Excel XP software. Statistical analysis was performed with SPSS 11.0 software, using analysis of variance followed by Tukey's *b*-test.

Results and discussion

Effect of amendments on the pH of limed mine spoil

Figure 1 demonstrates the rate of pH_{KCl} decrease in limed mine spoil (treated with various amendments) after 2 months of red fescue growth. The decrease of pH can be explained by the oxidation of pyrite present in high quantities in mine spoils (Vangronsveld & Cunningham 1998). From the viewpoint of stabilization of metals in mine spoil, the least decrease in pH is the most advantageous, since the lower the pH the higher the mobility of the studied heavy metals (Cd, Cu, Pb and Zn) in the soil–plant system (Kabata-Pendias & Pendias 2001). Application of peat caused the highest decrease (>1.0) in pH, which predicts the highest mobility of metals in mine spoil and the highest accumulation of metals in red fescue. Our results confirm the findings of Albasel and Cottenie (1985) who found a similar pH decrease when barley, perennial ryegrass and Italian ryegrass were grown in metal-contaminated soil treated with peat. The pH was most stable in cultures receiving municipal sewage sludge compost (treatment 2) or potassium phosphate (treatment 5), which was also manifested in combined treatment (treatment 6).

After 60 days of red fescue growth the pH_{KCl} in mine spoil was 5.72 for treatment 1 (lime application only), 6.09 for treatment 2 (lime + municipal sewage sludge), 4.78 for treatment 3 (lime + peat), 5.69 for treatment 4 (lime + zeolite), 5.36 for treatment 5 (lime + potassium phosphate), and 5.07 for treatment 6 (combining all amendments).

Metals in mine spoil extracts and in red fescue

Elemental composition of limed mine spoil treated with various amendments is shown in Table 1. Application of calcium carbonate (liming in all treatments) raised calcium concentration in all mine spoil samples above 10 g kg^{-1}, while in the original mine spoil this value was only 5.2 g kg^{-1}. Amendment of limed mine spoil with municipal sewage sludge compost (treatment 2) resulted in the highest Ca concentration (Table 1), which was also manifested in red fescue shoots or roots (Table 2). Some by-products and wastes (e.g., sludges and manures) utilized in mine spoil stabilization may contain heavy metals that could contribute to the contamination levels already present in the site (Berti *et al.* 1998). From this point of view, it is advantageous that the metal concentration of the applied municipal sewage sludge compost is low, and will not enhance the metal concentration in limed mine spoil (Table 1).

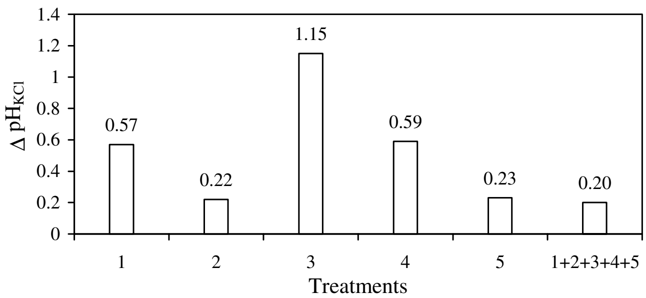

Fig. 1. Rate of pH decrease in limed mine spoil from Gyöngyösoroszi (Hungary) after 60 days of red fescue growth (pot experiment, Nyíregyháza, Hungary, 2001). The treatments were the following: 0.5% $CaCO_3$ (1); 1 + 5% municipal sewage sludge compost (2); 1 + 5% peat (3); 1 + 7.5% zeolite (4); 1 + 0.5% KH_2PO_4 (5); 1 + 2 + 3 + 4 + 5 (combined).

Table 1. Elemental composition of limed mine spoil from Gyöngyösoroszi (Hungary) treated with various amendments (determined in conc. HNO_3–H_2O_2 extracts at the end of the pot experiment, Nyíregyháza, Hungary, 2001).

Treatments	Ca	K	P	Cd	Cu	Pb	Zn
	g kg^{-1}			mg kg^{-1}			
0.5% $CaCO_3$ (1)	11.1^{ab}	1.42^{a}	0.19^{a}	7.31^{a}	126^{a}	2354^{a}	613^{c}
1 + 5% municipal sewage sludge compost (2)	12.6^{c}	1.44^{a}	0.40^{a}	7.09^{ab}	127^{a}	2299^{a}	526^{a}
1 + 5% peat (3)	10.7^{ab}	1.31^{a}	0.23^{a}	7.07^{ab}	118^{a}	2017^{ab}	638^{c}
1 + 7.5% zeolite (4)	12.0^{bc}	2.05^{b}	0.21^{a}	7.45^{a}	124^{a}	2196^{a}	723^{d}
1 + 0.5% KH_2PO_4 (5)	10.0^{a}	4.11^{c}	7.54^{c}	7.12^{a}	122^{a}	2260^{a}	541^{ab}
Combined (1 + 2 + 3 + 4 + 5)	10.2^{a}	4.94^{d}	6.08^{b}	6.49^{b}	102^{b}	1775^{b}	590^{bc}
Average	11.1	2.55	2.44	7.08	120	2150	605

Statistical analysis was done by Tukey's *b*-test. Data are means of three replications. Means within the columns followed by the same letter are not statistically significant at $p = 0.05$.

Table 2. Elemental composition of red fescue after 30 or 60 days of growth in limed mine spoil from Gyöngyösoroszi (Hungary) treated with amendments (pot experiment, Nyíregyháza, Hungary, 2001).

Treatments	Ca	K	P	Cd	Cu	Pb	Zn
	mg g^{-1}			μg g^{-1}			
30 days old shoots (1st cut)							
0.5% $CaCO_3$ (1)	8.45^{b}	36.9^{abc}	29.8^{a}	udl	18.7^{ab}	udl	86.4^{a}
1 + 5% municipal sewage sludge compost (2)	10.1^{c}	33.0^{ab}	27.5^{a}	udl	16.1^{ab}	udl	87.1^{a}
1 + 5% peat (3)	8.29^{b}	28.7^{a}	25.7^{a}	0.11	15.0^{a}	udl	355^{c}
1 + 7.5% zeolite (4)	7.97^{b}	48.0^{bcd}	30.4^{a}	0.11	15.8^{ab}	udl	121^{b}
1 + 0.5% KH_2PO_4 (5)	3.92^{a}	62.3^{d}	97.8^{b}	udl	23.0^{c}	udl	80.6^{a}
1 + 2 + 3 + 4 + 5 (combined)	4.64^{a}	54.0^{cd}	102^{b}	udl	19.5^{b}	11.0	98.0^{ab}
Average	7.23	43.8	5.2	–	18.0	–	138
60 days old shoots (2nd cut)							
0.5% $CaCO_3$ (1)	6.87^{b}	24.7^{a}	1.89^{a}	0.27^{a}	13.2^{a}	udl	129^{a}
1 + 5% municipal sewage sludge compost (2)	8.56^{c}	17.8^{a}	1.65^{a}	udl	11.8^{a}	udl	84.2^{a}
1 + 5% peat (3)	7.37^{bc}	19.7^{a}	1.43^{a}	0.76^{a}	12.4^{a}	udl	448^{b}
1 + 7.5% zeolite (4)	6.72^{b}	33.3^{b}	2.07^{a}	0.44^{a}	12.3^{a}	udl	125^{a}
1 + 0.5% KH_2PO_4 (5)	3.26^{a}	50.1^{c}	10.8^{c}	2.13^{b}	17.4^{a}	28.5	90.4^{a}
1 + 2 + 3 + 4 + 5 (combined))	3.55^{a}	36.7^{b}	7.64^{b}	0.93^{a}	11.7^{a}	17.8	97.2^{a}
Average	6.06	30.4	4.24	0.91	13.1	23.2	162
60 days old roots (2nd cut)							
0.5% $CaCO_3$ (1)	6.86^{bc}	9.16^{a}	1.42^{a}	4.13^{b}	104^{bc}	79.5^{ab}	350^{b}
1 + 5% municipal sewage sludge compost (2)	8.45^{c}	7.82^{a}	1.71^{a}	3.11^{a}	88.0^{b}	102^{ab}	183^{a}
1 + 5% peat (3)	4.96^{ab}	6.71^{a}	1.26^{a}	4.91^{cb}	63.4^{a}	92.2^{ab}	943^{c}
1 + 7.5% zeolite (4)	7.97^{c}	10.4^{a}	1.46^{a}	6.48^{d}	104^{bc}	125^{b}	363^{b}
1 + 0.5% KH_2PO_4 (5)	6.28^{abc}	15.8^{b}	4.34^{b}	4.73^{bc}	163^{d}	136^{b}	202^{a}
1 + 2 + 3 + 4 + 5 (combined)	4.05^{a}	15.3^{b}	4.58^{b}	5.29^{c}	126^{c}	44.7^{a}	265^{ab}
Average	6.43	10.9	2.46	4.78	108	96.7	384

Statistical analysis was done by Tukey's *b*-test. Data are means of three replications. Means within the columns followed by the same letter are not statistically significant at $p = 0.05$.
Abbreviation: udl = under detection limit.

Application of peat (treatment 3) did not significantly altere the elemental composition of limed mine spoil. According to Berti *et al.* (1998) aluminosilicates do not degrade or readily dissolve and do not increase metal or plant nutrient levels in limed mine spoils as do other amendments (e.g., sludges or manures). In our case, zeolite mixed with the limed mine spoil (treatment 4) slightly enhanced its zinc concentration (Table 1), although enhanced bioavailability and accumulation of this metal was not observed in this case in red fescue (Table 2). As could be supposed, the addition of 0.5% KH_2PO_4 to limed mine spoil (treatment 5 and 6) significantly raised its K and P concentration, and similarly higher potassium and phosphorus concentrations were measured in shoots or roots of red fescue test plants improving K and P nutrition (Table 2). High rates of phosphates, which are many times greater than those used in agriculture, may produce excess phosphorus that may reach water systems, causing nutrient enrichment and eutrophication (Berti *et al.* 1998). Regarding cadmium, copper and lead in limed mine spoil, the lowest concentrations of these metals were measured in the combined treatment (treatment 6). This could be attributed to a higher mass ratio (dilution effect) of applied amendments in mine spoil.

Table 2 presents the elemental composition of red fescue grown for 30 or 60 days in limed mine spoil, which was treated with various amendments. In spite of the high amounts of metals present in limed and amended mine spoil (Table 1), accumulation of cadmium, copper and lead was relatively low in red fescue shoots, while zinc concentrations were high in shoots and roots of peat-amended cultures. One reason for this could be the highest shift in pH of peat-amended and limed mine spoil during 60 days of red fescue growth (Figure 1). The normal range for zinc concentration in plant leaves is from 25 to 150 $\mu g\ g^{-1}$ (Kabata-Pendias & Pendias 2001) and above 400 $\mu g\ g^{-1}$ phytotoxicity symptoms occur in most plants. Although zinc concentrations were close to this value in peat-treated cultures, no phytotoxicity symptoms (or reduction in dry matter, Figure 7) were observed in 30 or 60 days old red fescue shoots. Since cadmium mobility in soil-plant system is high (Kabata-Pendias & Pendias 2001), it is advantageous that its concentration was below the detection limit or low in 30 or 60 days old shoots. Only potassium phosphate application (treatment 5) enhanced significantly the cadmium concentration in 60 days old shoots. The highest Pb concentration in roots was measured in cultures which were treated with potassium phosphate (Table 2). Presumably, lead phosphate (pyromorphite) formed and precipitated in the surface of roots (Laperche *et al.* 1997) and this influenced Pb accumulation.

All metals were accumulated prevalently in the roots of red fescue (Table 2). This indicates good functioning of the 'root trap', which is advantageous in the case of the mine spoil phytostabilization with grasses. It was confirmed that red fescue is a metal-tolerant plant when grown in limed and amended (stabilized) mine spoil (see also Figure 7) and its roots may provide surfaces for sorption or precipitation of metal contaminants. Plants chosen for phytostabilization should be poor translocators of metal contaminants to above ground plant tissues that could be consumed by animals or humans (Berti & Cunningham 2000) – red fescue meets this requirement.

Figure 2 demonstrates the percentual (%) ratio of heavy metals in the 'plant available' fraction compared to 'total' (HNO_3/H_2O_2) concentrations in unlimed or limed mine spoil from Gyöngyösoroszi. Unlimed mine spoil was sampled without plant growth, while limed mine spoil samples were taken after 60 days of red fescue growth, at the end of the pot experiment. From the data it is obvious that application of $CaCO_3$ and longer interaction of limed mine spoil with plant roots definitively reduced the ratio of Cd, Cu, Pb and Zn in the 'plant available' fraction. Concentrations of these metals in the exchangeable (most mobile) fraction were under the detection limits in limed mine spoil (data not shown). Liming (rise of pH), and application of amendments reduced metal availability, which made the originally acid and toxic mine spoil suitable for plant cultivation. The red fescue grew well in this limed and amended medium (see Figure 7).

Figures 3–4 demonstrate the relative percentual ratio of Cd, Cu, Pb and Zn in the exchangeable fraction of limed mine spoil amended with municipal sewage sludge compost, peat, zeolite, potassium phosphate and their combination. Metal concentrations in the exchangeable fraction were compared to 'total' concentration of these metals to calculate relative percentual ratios at the end of the pot experiment. Since it was not possible to grow

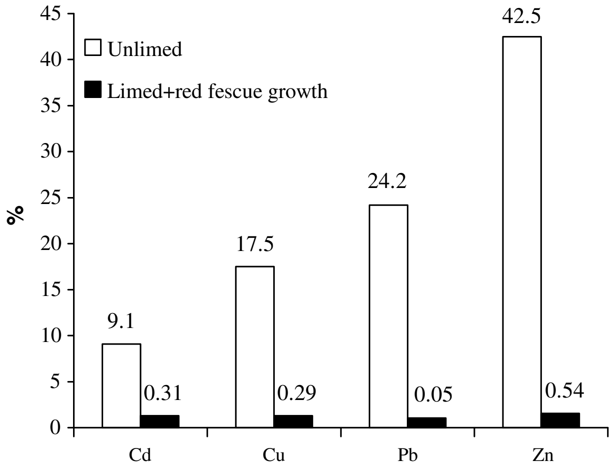

Fig. 2. Percentual (%) ratio of heavy metals in the 'plant available' fraction (extracted by H_4EDTA in ammonium acetate buffer according to Lakanen and Erviö) of non-limed (without plants) and of limed (after 60 days of red fescue growth) mine spoil from Gyöngyösoroszi compared to 'total' (HNO_3/H_2O_2) concentration of metals (pot experiment, Nyíregyháza, Hungary, 2001).

plants on the original non-limed mine spoil, it was not possible to distinguish the metal immobilizing effects of amendments or plant growth.

The highest ratio of exchangeable Cd and Zn was detected in peat-amended cultures (Figures 3 and 4). These data suggest that application of peat is the least suitable among amendments tested to immobilize Cd and Zn in limed mine spoil. This explains why we detected the highest Zn accumulation in shoots or roots of red fescue grown in peat amended and limed mine spoil (Table 2). The ratio of Cu in the exchangeable fraction was similar in all cultures; none of the amendments had a significant immobilizing effect in this case (Figure 3). Compared to other metals, the relative percentage of Pb in the exchangeable fraction (and also in the 'plant available fraction') was very low in all treatments (Figures 4 and 6). Mobility of Pb is usually low in the soil–plant system since lead is strongly bound to soil particles. Plants accumulate lead prevalently in roots and translocation of this metal to shoots is low (Kabata-Pendias & Pendias 2001). We observed the same phenomenon in red fescue cultures (Table 2).

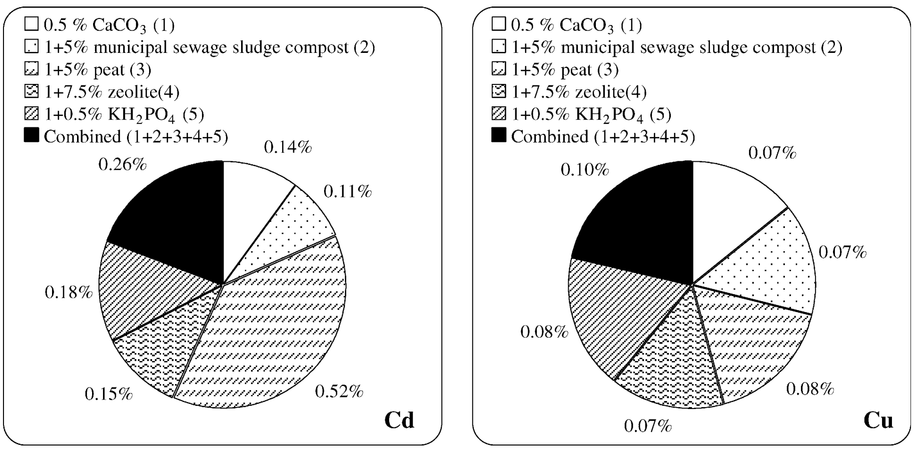

Fig. 3. Relative percentage of Cd and Cu in the exchangeable fraction (extracted by $CaCl_2$ solution) of variously treated mine spoil from Gyöngyösoroszi (Hungary) at the end of the pot experiment compared to 'total' (HNO_3/H_2O_2 extracted) concentration of these metals (Nyíregyháza, Hungary, 2001).

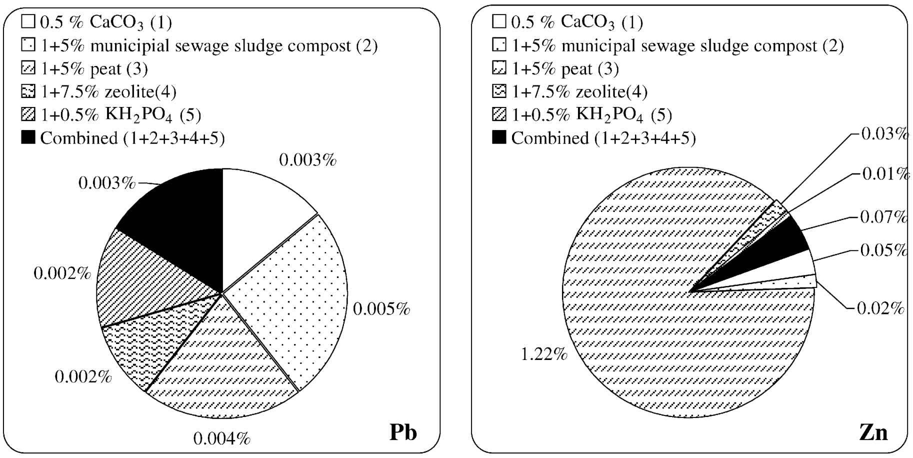

Fig. 4. Relative percentage of Pb and Zn in the exchangeable fraction (extracted by $CaCl_2$ solution) of variously treated mine spoil from Gyöngyösoroszi (Hungary) at the end of the pot experiment compared to 'total' (HNO_3/H_2O_2 extracted) concentration of these metals (Nyíregyháza, Hungary, 2001).

In Figures 5 and 6, relative percentage of Cd, Cu, Pb and Zn concentrations are shown in the 'plant available' fraction in limed and amended mine spoil compared to 'total' concentration of these metals. Least Cd was measured in limed ($CaCO_3$ application by itself) or municipal sewage sludge-amended limed mine spoil, and almost double concentrations were found in peat, potassium phosphate and combined treatments. Percentual ratios of 'plant available' Cu to 'total' Cu were similar to Cd. In this case, the least concentrations were measured in limed ($CaCO_3$ application by itself) and in zeolite-amended cultures. The amendments have not significantly changed the 'plant available' Pb; its ratio was equally low in all treatments. Differences in metal immobilizing of amendments were more pronounced in the case of Zn; the highest 'plant available' Zn was found in combined and also in potassium phosphate treatments, while the lowest was found when $CaCO_3$ was applied by itself or in combination with municipal sewage sludge compost (Figure 6).

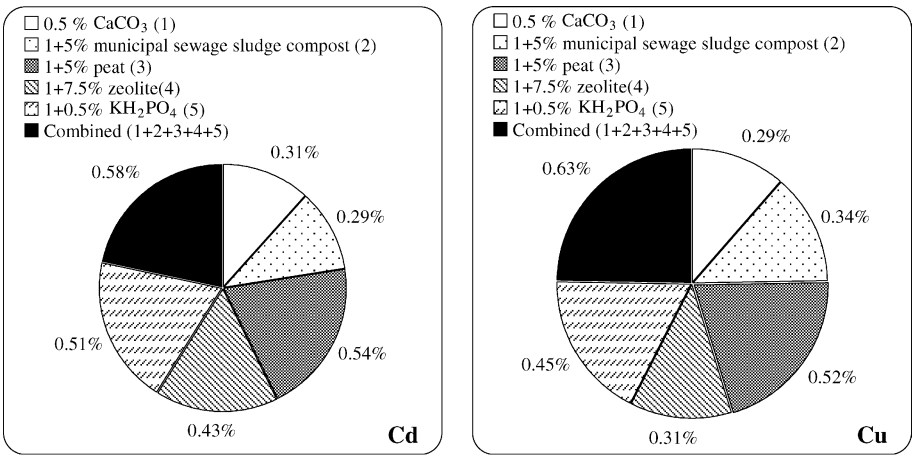

Fig. 5. Relative percentage of Cd and Cu in 'plant available' fraction (extracted by H_4EDTA in ammonium acetate buffer according to Lakanen and Erviö) of variously treated mine spoil from Gyöngyösoroszi (Hungary) at the end of the pot experiment (Nyíregyháza, Hungary, 2001) compared to 'total' (HNO_3/H_2O_2 extracted) concentration of these metals (Nyíregyháza, Hungary, 2001).

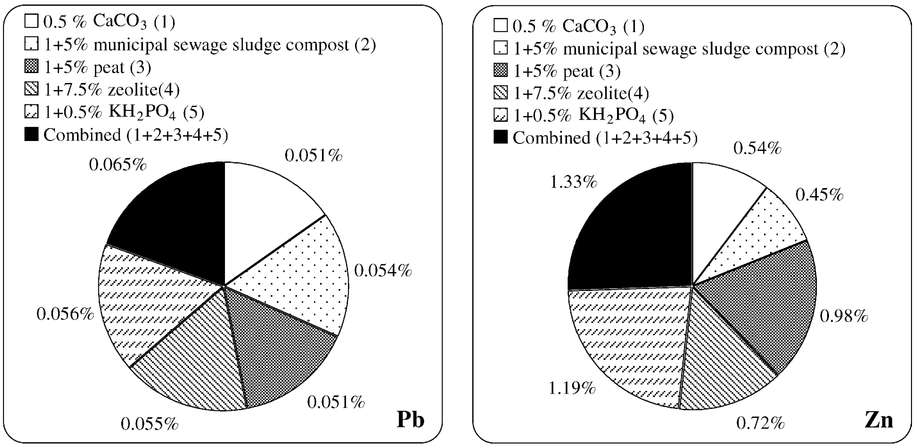

Fig. 6. Relative percentage of Pb and Zn in the 'plant available' fraction (extracted by H_4EDTA in ammonium acetate buffer according to Lakanen and Erviö) of variously treated mine spoil from Gyöngyösoroszi (Hungary) at the end of the pot experiment (Nyíregyháza, Hungary, 2001) compared to 'total' (HNO_3/H_2O_2 extracted) concentration of these metals (Nyíregyháza, Hungary, 2001).

From our data and from previous findings of other authors (Berti *et al.* 1998; Mench *et al.* 1998; Berti & Cunningham 2000; Mench *et al.* 2000; Friesl *et al.*, 2003), it is obvious that amendments added to the metal-contaminated mine spoil can change variously the mobility and phytoavailability of Cd, Cu, Pb and Zn during plant growth. To choose the most suitable amendment and plant to immobilize metals in mine spoil, it is recommended to test these factors.

Dry matter yield of red fescue

Figure 7 shows the dry matter yield of red fescue shoots and roots after 30 or 60 days of growth in limed mine spoil treated with various amendments. All treatments made the mine spoil fertile. The shoots of cultures receiving municipal sewage sludge compost (treatment 2) and combined treatment (treatment 6) were the tallest at the end of the experiment (data not shown), and here was

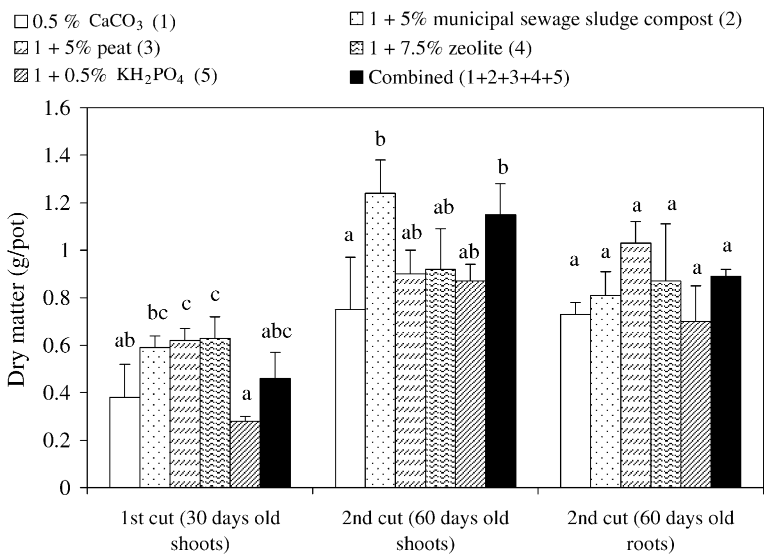

Fig. 7. Dry matter yield of red fescue after 30 or 60 days of growth in limed mine spoil from Gyöngyösoroszi (Hungary) treated with various amendments (pot experiment, Nyíregyháza, Hungary, 2001). Statistical analysis was done by Tukey's *b*-test. Data are means of three replications. Means within the columns followed by the same letter are not statistically significant at $p = 0.05$.

detected the highest dry matter yield in shoots (Figure 7). The blades and tips of leaves were in this case green and healthy, without any senescence. In treatments 1, 3, 4 and 5, however, several senescent older (lower positioned) leaf blades and dried leaf tips were observed. Harvested roots were yellow-brownish with a medium number of root tips, this indicates excess of metals in the root zone.

After 30 days of growth (1st cut) the dry matter of shoots, on the basis of treatment 1 (100%), was 155% for treatment 2, 163% for treatment 3, 166% for treatment 4, 74% for treatment 5, and 121% for treatment 6. After 60 days of growth (2nd cut) these values were modified; on the basis of treatment 1 (100%) the dry matter of shoots was 165% for treatment 2, 120% for treatment 3, 123% for treatment 4, 116% for treatment 5, and 153% for combined treatment 6. In case of roots' dry matter yield these values were 100%, 111, 141, 119, 96 and 122% for yield the 6 treatments, although differences were not statistically significant (Figure 7).

Conclusions

Liming of an acidic mine spoil with high Cd, Cu, Pb and Zn concentrations to pH higher than 5.0, amendment with municipal sewage sludge compost, peat, zeolite, or potassium phosphate, and fertilization with nitrogen made this material suitable for plant growth. After 60 days of red fescue growth peat caused the largest decrease in limed mine spoil pH, while pH was most the stable in cultures receiving municipal sewage sludge compost, potassium phosphate or combined treatment. Liming considerably reduced the phytoavailability of heavy metals in the mine spoil. Amendments added to limed mine spoil changed variously the ratio of Cd, Cu, Pb and Zn in the exchangeable or 'plant available' fraction, influencing the phytoavailability of these metals. Most of the heavy metals were captured in the roots of test plants, except phosphate treatment when enhanced Cd and Pb accumulation, and peat treatment when enhanced Zn yield was observed in shoots. All amendments influenced positively the dry matter yield (biomass production) of red fescue, but application of 0.5% potassium phosphate was, however, from this point of view less favourable. Liming, application of amendments and growth of red fescue can stabilize metals in acidic and phytotoxic mine spoil, and by phytostabilization they can reduce the risk of metal toxicity to the food chain.

Acknowledgements

This research was sponsored by the Hungarian National Scientific Research Fund (projects OTKA T030230 and OTKA T043479), by János Bolyai Scientific Scholarship and István Széchenyi Scholarship awarded to Dr László Simon. The author wishes to thank Mr Károly Iványi (University of Veszprém, Georgikon Agricultural Faculty from Keszthely, Hungary) for providing seeds of red fescue, and Dr Gyula Lakatos (University of Debrecen, Department of Applied Ecology, Hungary) for providing samples of mine spoil. The valuable help of Dr Béla Kovács and Dr Zoltán Győri with elemental analysis is appreciated.

References cited

Albasel N, Cottenie A. 1985 Heavy metals uptake from contaminated soils as affected by peat, lime and chelate. *Soil Sci Soc Am J* **49**, 386–390.

Berti WR, Cunningham SC, Cooper E.M. 1998 Case studies in the field – in-place inactivation and phytorestoration of Pb-containated sites. In Vangronsveld J, Cunningham SC. eds. *Metal-Contaminated Soils: In Situ Inactivation and Phytorestoration*. Heidelberg, Berlin: Springer-Verlag pp. 235–248.

Berti WR, Cunningham SC. 2000 Phytostabilization of metals. In: Raskin I, Ensley BD eds. *Phytoremediation of Toxic Metals: Using Plants to Clean up the Environment*. New York: John Wiley and Sons, Inc., pp. 71–88.

Friesl W, Lombi E, Horak O, Wenzel WW. 2003 Immobilization of heavy metals in soils using inorganic amendments in a greenhouse study. *J Plant Nutr Soil Sci* **166**, 191–196.

Hettiarachchi GM, Pierzynski GM, Ransom MD. 2000 *In situ* metal stabilization of soil lead using phosphorus. *J Environ Qual* **30**, 1214–1221.

Horváth B, Gruiz K. 1996 Impact of metalliferous ore mining activity on the environment in Gyongyosoroszi, Hungary. *Sci Total Environ* **184**, 215–227.

Kabata-Pendias A, Pendias H. 2001 *Trace Elements in Soils and Plants,* (3rd edn) Boca Raton, London, New York, Washington DC: CRC Press LLC 413 pp.

Kovács B, Győri Z, Prokisch J, Loch J, Dániel P. 1996 A study of plant sample preparation and inductively coupled plasma emission spectrometry parameters. *Commun Soil Sci Plant Anal* **27**, 1177–1198.

Kovács E, Tamás J. 2002 Support of phytoremediation technology by using geographic information system for fields contaminated with metals. In *Acta Agraria Debrecenіensis*. Hungary: University of Debrecen, 51–56. (in Hungarian).

Lakatos G, Mészáros I, Tóth A, Keresztúri P, Galicz É, Paksi V. 2002 Study on phytostabilization and phytoextraction in Hungarian practice. In Mench M., Mocqout B. eds. *Risk Assessment and Sustainable Land Management Using Plants in Trace Element-Contaminated Soils*. COST Action 837. 4th WG2 Workshop, Bordeaux'2002. Villenave d'Omon, France: Institut National de la Recherche Agronomiqeu, pp. 144–145.

Laperche V, Logan TJ, Gaddam P, Traina SJ. 1997 Effect of apatite amendments on plant uptake of lead from contaminated soil. *Environ Sci Technol* **31**, 2745–2753.

Li YM, Chaney RL, Siebielec G, Kerschner BA. 2000 Response of four turfgrass cultivars to limestone and biosolids-compost amendment of a zinc and cadmium contaminated soil at Palmerton, Pennsylvania. *J Environ Qual* **29**, 1440–1447.

Mench M, Vangronsveld J, Clijsters H, Lepp NW, Edwards R. 2000 *In situ* metal immobilization and phytostabilization of contaminated soils. In Terry N, Bañuelos G. eds. *Phytoremediation of Contaminated Soil and Water*. Boca Raton, London, New York, Washington DC: Lewis Publishers, pp. 323–358.

Mench M, Vangronsveld J, Lepp NW, Edwards R. 1998 Physico-chemical aspects and efficiency of trace element immobilization by soil amendments. In Vangronsveld J, Cunningham SC. eds. *Metal-Contaminated Soils: In situ Inactivation and Phytorestoration*. Heidelberg, Berlin: Springer-Verlag pp. 151–182.

Simon L, ed. 1999 *Soil Pollution, Soil Remediation*. Budapest: Környezetgazdálkodási Intézet (Environmental Management Institute), 221 pp. (in Hungarian).

Simon L. 2001 Effects of natural zeolite and bentonite on the phytoavailability of heavy metals in chicory. In Iskandar IK ed. *Environmental Restoration of Metals Contaminated Soil*. Boca Raton: Lewis Publishers, pp. 261–271.

Simon L., Prokisch J, Kovács B. 1997 Chicory (*Cichorium intybus* L.) as bioindicator of heavy metal contamination. In Prost R, ed. Contaminated Soils: Third International Conference on the Biogeochemistry of Trace Elements, Paris, May 15–19 1995. Paris, France: INRA Editions, (CD-ROM\data\communic\066.PDF, Colloque n°85).

Vangronsveld J, Cunningham SC, eds. 1998 *Metal-Contaminated Soils: In Situ Inactivation and Phytorestoration*. Heidelberg, Berlin: Springer-Verlag, 265 pp.