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Citation for the original published paper (version of record):

Brännvall, E., Nilsson, M., Sjöblom, R., Skoglund, N., Kumpiene, J. (2014)
Effect of residue combinations on plant uptake of nutrients and potentially toxic
elements
Journal of Environmental Management, 132: 287-295
<https://doi.org/10.1016/j.jenvman.2013.11.024>

Access to the published version may require subscription.

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Effect of residue combinations on plant uptake of nutrients and potentially toxic elements

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A B S T R A C T

The aim of the plant pot experiment was to evaluate potential environmental impacts of combined industrial residues to be used as soil fertilisers by analysing i) element availability in fly ash and biosolids mixed with soil both individual and in combination, ii) changes in element phytoavailability in soil fertilised with these materials and iii) impact of the fertilisers on plant growth and element uptake.

Plant pot experiments were carried out, using soil to which fresh residue mixtures had been added. Results showed that element availability did not correlate with the plant growth in the fertilised soil. The largest concentrations of K (3534 mg/l), Mg (184 mg/l), P (1.8 mg/l), S (760 mg/l), Cu (0.39 mg/l) and Zn (0.58 mg/l) in soil pore water were found in the soil mixture with biosolids and MSWI fly ashes; however plants did not grow at all in mixtures containing the latter, most likely due to the high concentration of chlorides (82 g/kg in the leachate) in this ash. It is known that high salinity of soil can reduce germination by e.g. limiting water absorption by the seeds. Concentrations of As, Cd and Pb in grown plants in most of the soils were negligible being below the instrument detection limit values. The proportions of biofuel fly ash and biosolids can be adjusted in order to balance the amount and availability of macronutrients, while the possible increase of potentially toxic elements in biomass is negligible seeing as the plant uptake of such elements was low.

Keywords: Residues, phytoavailability, pore water, sequential extraction.

1. Introduction

Taking into account the global phosphorus (P) depletion, the use of alternative nutrient-rich materials is important in order to save natural resources. The Swedish Government's goal is that by 2015, at least 60 % of P originating from treated sewage sludge (biosolids) should be recycled to soil (Swedish EPA, 2010). However, conflicting information exists on e.g. migration of heavy metals in soil amended with biosolids.

Several studies showed that heavy metal migration in acidic soils amended with sewage sludge is negligible (He and Singh, 1994; McBride et al., 2004; Schiradoe et al., 1986) or even the leachability and toxicity of e.g. Pb, Zn and Cd may be reduced (Theodorathos et al., 2000). However there are studies showing significant increase of readily soluble amounts of Zn, Cr, Cu and Cd (Bramryd, 2013; Keller et al., 2002). In number of other studies in Sweden, where various sewage sludges were investigated (Eriksson, 2001; Henriksson et al., 2012; Lindberg et al., 2010) showed that in order to apply sewage sludge on soil, the rule of the right sludge for the right application should be followed (Henriksson et al., 2012). That can be done by detail investigation of sludge to be used as soil amendment.

The Swedish Forest Agency strongly recommends recycling of fly ash from combustion of wood-based fuel by applying it on forest soil (Skogsstyrelsen, 2008). The purpose of such recycling is to counteract acidification and nutrient depletion of forest soil after extraction of tree tops and branches (Olsson and Westling 2006). Nitrogen is often the limiting nutrient for the biomass growth. Although ash may have some positive influence on N availability in soil by increasing soil pH and facilitating the formation of nitrate instead of N_2 and NO_2 , it does not contribute N to soil. Additional sources are therefore needed in order to maintain productivity of the plants.

The balance between the major nutrients (N, P, K) can be improved by combining fly ash with biosolids. Moreover, mixing of these residues may also induce such chemical reactions that lead to the reduction of the phytoavailability of certain potentially harmful elements such as Cd and Pb. The term availability (phytoavailability) in this study refers to the readily soluble fraction of element that is taken up by plant.

Experimental studies of combining different residues are ample (Rautaray et al., 2003, Neuschütz et al., 2006). Studies about the combination of the industrial residues used as forest soil amendments are incomplete; therefore the need of research showing the advantages and disadvantages of industrial residues combinations use on soil is urgent.

The aim of the plant pot experiment was to evaluate potential environmental impacts of combined industrial residues to be used as soil fertilisers by analysing i) element availability in fly ash and biosolids mixed with soil both individual and in combination, ii) changes in element phytoavailability in soil fertilised with these materials and iii) impact of the fertilisers on plant growth and element uptake.

2. Materials and Methods

2.1 Materials

Fresh and dry (without added water) biofuel fly ash (BFA) from tree bark combustion was collected from a fluidised bed incinerator. Also a municipal solid waste incineration (MSWI) fly ash was collected. It was fresh and contained about 50 % lime. The fuel comprised household waste, animal by-products, recycled wood chips, and sleepers containing creosote and certain other hazardous substances. Dewatered, anaerobically digested biosolids were collected from the storage pile at a wastewater treatment plant. All residues originate from

Northern Sweden. Synthetic $\text{CaK}_2\text{P}_2\text{O}_7$ and CaKPO_4 were prepared at Umeå University, Sweden (Sandström and Boström, 2008), and were used for comparison reasons.

2.2 Preparation of soil mixtures

Materials were added to soil and homogenized thoroughly; no prior ageing of residue mixtures (ash-biosolids) was done. Proportions of soil and residues were chosen based on the results of a screening experiment in which a large number of residue combinations were tested. The selection of the proportions in this study was motivated by the pH of the mixtures. The material combinations with the pH values closest to neutral were selected in order to avoid N volatilization. The amount of synthetic chemicals in soil was chosen based on the amount of P in biosolids, which resulted in 5.033 g of $\text{CaK}_2\text{P}_2\text{O}_7$ and 1.5 g of CaKPO_4 per kg of dry soil.

2.3 Soil, plants and soil pore water

Forest soil collected in Luleå, Sweden, was air dried, homogenized and sieved to a <4mm fraction. The soil mixed with the selected material mixtures are shown in Figure 1.

Figure 1. Residues and their proportions used in soil mixtures.

One kg of each of the final mixtures was placed in plastic pots in triplicates (24 pots in total) and sown with 1.5 g of a grass seed mixture supplied by Veg Tech AB, Vislanda, Sweden. The seed mixture was composed of 90% grass and 10% herb species and is intended for re-vegetation of sandy, nutrient deficient soils. The pots were stored in the laboratory next to a window in natural light, holding constant soil moisture level by manual irrigation with distilled water during April through May months. Soil pore water was collected right before harvesting the plants using the Rhizon soil moisture samplers (Eijkelkamp, the Netherlands) in acid-washed, vacuumed 100 ml glass bottles and used for pH, EC and elemental analysis. The plant shoots were harvested after 7 weeks for biomass measurements and metal concentration analysis. The plants were washed with double distilled water, dried for 72 h at 60°C, weighed for dry mass determination, then ground using a stainless steel grinder and analysed for chemical elements by the accredited laboratory ALS Scandinavia. Bulk soil was carefully separated from the rhizosphere for further analyses.

2.4 Leaching and sequential extraction

Batch leaching test. A standard one-stage compliance batch leaching test (SS-EN 12457-4) at a liquid to solid ratio of 10 l/kg (L/S 10) was applied to estimate leachable concentrations of constituents in ashes, biosolids and soil. Samples (90 g) were mixed with deionised water and shaken for 24 h using a rotating device. The eluate was filtered through a 0.45 µm membrane filter using a vacuum filtration device and an aliquot was immediately used for electrical conductivity (EC) and pH measurements. The rest was stored at +4°C prior to analysis of major and trace elements, Cl⁻, DOC and total N.

Sequential extraction test. Six steps were applied for element fractionation in 1 g of the bulk and rhizosphere soil samples according to the following procedure which has been adjusted to this study. After each step, residues were centrifugation at 10 000 (rpm) for 15 min,

washing with 10 mL deionized water (except Fraction III), centrifuged and eluate discarded, while the residues were used in the subsequent steps:

Fraction (I): Exchangeable metals (the most soluble). Extraction was done with 40 ml of 1 mol/l NH_4OAc (adjusted to pH 6.5 acetic acid (HOAc)) by shaking 16 h (Bódog et al., 1996).

Fraction (II): Bound to Carbonates. Extraction was done with 8 mL of 1 M NaOAc adjusted to pH 5.0 by agitating for 5 h (Tessier et. al., 1979).

Fraction (III): poorly crystalline Fe(III) oxyhydroxide fraction. Extraction was done with 25 ml of 0.2 M NH_4 -oxalate adjusted to pH 3.0 for 2 h at ambient temperature in darkness, then additional 12.5 ml of solution was added again (Wenzel et al., 2001).

Fraction (IV): crystalline Fe-Mn oxide fraction. Extraction was done with 20 ml 0.04 M $\text{NH}_2\text{OH-HCl}$ in 25% (v/v) HOAc adjusted to pH 2 in a water bath at 96°C for 6 h (Tessier et. al., 1979).

Fraction (V): Organic matter and secondary sulphide fraction. Extraction was done with 25 ml of 35% H_2O_2 at 85°C for 1 h (Tessier et. al., 1979).

Fraction (VI): Residual fraction. Extraction was done with 15 ml aqua regia ($\text{HNO}_3\text{:HCl}$, 1:3 v/v), in a microwave digester (CEM Microwave Sample Preparation System, Model MARS 5) at 195 °C for 10 min.

2.5. Analytical and statistical methods

The content of total solids (TS) in the materials was determined according to Swedish standard SS 028113 (SIS, 1981). Concentrations of elements in the solutions were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin Elemer Otima 2000 DV). Dissolved organic carbon (DOC) and total carbon (TC) contents were analysed using a TOC-VCPH/CPN instrument (Shimadzu Corporation) according to European

standard for water analysis of TOC and DOC (SS-EN 1484). Chloride (Cl^-) content was determined spectrophotometrically (AACE Quattro, Bran+Luebbe, Germany). Total N was analysed according to the standard ASTM D5373 by the accredited laboratory ALS Scandinavia. The total composition of element concentrations was calculated from the sequential extraction analysis by summing all 6 fractions of each element. A two-sample t-test procedure ($p < 0.05$) was applied to discriminate among the sample means at 95% confidence level.

3. Results

3.1 Element availability in individual residues and soil

The most available elements in all ashes were K, Ca, S, Cl, Na, Pb, Ba, Al, As and Cd, while the least available were Cu, Ni and Mn (Table 1). MFA had by far the highest concentrations of soluble Pb and differed by 2-4 orders of magnitude from the other materials. Biosolids had the highest concentration of soluble N, DOC and Al, while the Cr was the least soluble element.

The least available element in all materials was Cd, followed by Pb in biosolids and soil, while As in ashes.

Table 1. Leached concentrations of elements and compounds, pH and EC in leachates of biofuel fly ash (BFA) and MSWI fly ash used in granules (MFAG) and pellets (MFAP), biosolids (BioS), peat (P), peat residues (Pr) and gypsum board waste (Gbw). Elements are sorted in ascending order after their concentrations.

	BFA	MFA	BioS	Soil
pH	12.8±0.1	11.2±0.01	7.9±0.01	7.2±0.3
EC, mS/cm	15.6 ±0.7	21.7±0.1	5.1±0.02	0.4±0.002
Macronutrients, mg/kg				

P <0.11	P <0.11	P 19	N n.d.
Mg <0.9	Mg <1.6	Mg 325	DOC n.d.
N 53	DOC 10	K 695	P 0.35
DOC 122	N 346	Ca 1 043	K 52
S 1 356	S 8 930	DOC 3 550	Mg 101
Ca 6 784	Ca 16 606	S 5 551	S 358
K 14 795	K 30 707	N 5 921	Ca 385
	Micronutrients, mg/kg		
Ni <0.01	Mn <0.07	Cr <0.01	Cl n.d.
Cu 0.01	Ni <0.19	Cu 0.10	Mo n.d.
Mn 0.05	Fe <0.30	Zn 0.10	Cr <0.003
Fe 0.15	Cu 0.14	Mo 0.60	Ni <0.03
Mo 2.82	Mo 4.21	Ni 0.80	Zn <0.03
Zn 3.50	Cr 4.71	Mn 3.80	Cu 0.035
Cr 3.93	Zn 8.22	Fe 24.50	Mn 0.05
Cl- 1 342	Na 29 330	Cl- 196	Fe 6.1
Na 1 696	Cl- 82 273	Na 399	Na 53.4
	Potentially toxic elements, mg/kg		
Cd <0.001	Cd 0.04	Cd <0.001	Ba n.d.
As 0.01	As 0.2	Pb <0.06	Cd <0.001
Al 0.2	Al 0.79	Ba 0.1	Pb <0.06
Pb 0.5	Ba 3.1	As 0.2	As <0.06
Ba 5	Pb 6.9	Al 2.1	Al 1.8

Relative standard deviation for macronutrients was 0-132%, micronutrients 0-139% and for potentially toxic elements 0-138%.

3.2 Element availability in soil pore water

Calcium, K, S and Na were among the most available elements in soil pore water of all the samples, and especially in soil containing MSWI ashes (Table 2). Dissolved P concentrations were highest in soils containing both fly ashes and biosolids, as well as in the soil amended with synthetic chemicals (Table 2).

Table 2. Composition of pore water (mg/l) of soil and soil mixtures from the pot experiment with plants. Elements are sorted in ascending order after their concentrations. n=3. Relative standard deviation for macronutrients was 3.5-39%, micronutrients 2.8-75% except for Fe (17.3-161%) and for potentially toxic elements 2.8-127%.

	Soil	Soil + BioS	Soil + BFA	Soil + BioS + BFA	Soil + MFA	Soil + BioS + MFA	Soil + CaK ₂ P ₂ O ₇	Soil + CaKPO ₄
pH	7.3±0.1	7.3±0.	8.5±0.1	7.9±0.04	8.1±0.1	7.8±0.1	8.0±0.1	7.7±0.1

EC, mS/cm	2.1±0.4	1 3.5±0.5	6.3±1.7	7.5±1.1	58.8±16	32±5	2.4±0.2	2.5±0.3
Macronutrients								
P	0.2	P 0.8	P 0.6	P 1.4	P 0.2	P 1.8	P 10	P 7
K	26	K 44	M 105	M 183	Mg 125	Mg 184	M 42	M 79
Mg	70	M 156	Ca 447	S 549	S 701	S 760	Ca 123	K 178
S	208	S 448	S 615	Ca 573	Ca 1938	Ca 1527	S 200	Ca 279
Ca	219	Ca 591	K 686	K 638	K 6184	K 3534	K 280	S 310
Micronutrients								
Cr	<0.001	Cr <0.001	Fe <0.03	Cr <0.001	Fe <0.03	Cr 0.01	Cr <0.001	Cr <0.001
Ni	0.002	Cu 0.04	Zn 0.01	Fe <0.03	Ni 0.006	Fe <0.03	Fe <0.03	Fe <0.03
Mn	0.02	Ni 0.04	Ni 0.02	Zn 0.04	Zn 0.07	Ni 0.04	Zn 0.03	Ni 0.003
Cu	0.03	Zn 0.12	Cr 0.05	Ni 0.07	Mn 0.09	Cu 0.39	M 0.04	Zn 0.02
Zn	0.05	Fe 0.8	Cu 0.1	Cu 0.11	Cu 0.13	Zn 0.58	Cu 0.04	Cu 0.03
Fe	0.06	M 3.7	M 0.2	M 0.41	Cr 0.22	Mn 1.3	Ni 0.04	M 0.05
Na	94	n 122	n 227	Na 212	Na 7057	Na 3905	Na 115	Na 138
Potentially toxic elements								
Cd	<0.0004	<0.00 Cd 04	<0.000 Cd 4	Cd <0.0004	<0.01 As 6	Pb <0.001	Cd <0.0004	Cd <0.0004
As	<0.016	Al <0.015	Pb <0.001	Al 0.01	Al 0.03	Al <0.015	Pb <0.001	Pb <0.001
Pb	<0.001	Pb <0.001	As 0.03	Pb 0.02	<0.00 Pb 1	As 0.07	Al <0.015	Al <0.015
Al	0.05	As 0.03	Al 0.4	As 0.07	Cd 0.22	Cd 0.19	As 0.03	As 0.05

Cadmium was the least available elements in all soil pore water samples except those containing MSWI fly ashes. The highest As and Al availability was found in soil containing biofuel fly ashes.

3.3 Element availability for plants

The highest concentrations of K, Mg, P, Cu, Na and Zn were found in plants that had grown in the soil mixtures with biosolids and biofuel fly ashes (Table 3). The concentrations of Ca, Cr, Fe and Al were largest in the plants that had grown in the pots with mixtures of soil and biosolids. Concentrations of As, Cd and Pb in most cases were negligible in plants being below the instrument detection limit values.

Table 3. Concentrations of elements (mg/kg) in plants (dry biomass). Elements are sorted in ascending order after their concentrations. n=3.

Soil	Soil+BFA	Soil+BioS	Soil+BioS+BFA	Soil+CaK ₂ P ₂ O ₇	Soil+CaKPO ₄
Cd <0.04	Cd 0.08	Cd 0.05	Cd 0.09	Cd <0.04	Cd <0.04
Pb <0.3	Pb <0.3	Pb <0.3	Pb <0.3	Pb <0.3	As <0.5
As <0.5	As <0.5	As <0.5	As <0.5	As 0.9	Pb <0.3
Cr 1.4	Cr 1.6	Ni 2.3	Cr 0.97	Cr 1.2	Cr 1.1
Ni 1.7	Ni 3.2	Cr 3.1	Ni 2.2	Ni 2.4	Ni 1.6
Mo 4.7	Mo 8.8	Mo 4.9	Mo 6.8	Mo 2.7	Mo 4.1
Cu 6.0	Cu 9.4	Cu 13	Cu 14	Cu 9.8	Cu 7.0
Zn 21	Zn 40.5	Zn 35	Zn 59	Zn 22	Zn 17
Al 119	Al 167	Al 174	Al 117	Mn 67	Al 101
Mn 163	Fe 294	Mn 189	Mn 189	Al 235	Mn 229
Fe 240	Mn 355	Fe 408	Fe 305	Fe 577	Fe 253
Na 1082	Na 1463	Na 2873	Na 3133	Mg 2780	Na 1033
Mg 1750	Mg 2070	P 3297	Mg 3877	Na 3104	Mg 1510
P 1883	P 2317	Mg 3607	P 4380	P 4093	P 3667
Ca 4477	Ca 4670	Ca 8063	Ca 5080	Ca 6923	Ca 5187
K 22667	K 33200	K 32133	K 35400	K 25833	K 26000

Relative standard deviation for macronutrients was 2.4-31%, micronutrients 3.2-55% and for potentially toxic elements 4.6-80%.

Soil fertilisation with biofuel fly ash and biosolids, in general, did not enhance the biomass production as compared to the unfertilised soil, although in some pots a notable improvement of plant growth was observed for soils containing biosolids (Figure 2). MSWI ash and its mixture with biosolids caused severe soil phytotoxicity. Seeds did not germinate and hence no biomass was produced in these two mixtures (Figure 2).

Figure 2. Biomass of the plants per pot of soil and soil mixtures. Error bars represent standard deviation, n=3.

3.4 Element fractionation in bulk and rhizosphere soil

Macronutrients

Calcium, K, P, Cu, Mn, Zn, Cd and Pb fractionation in soil depended mostly on amendment type (Figure 3).

Calcium and Mg were mainly bound to the reducible Fraction (IV) followed by the non-soluble Fraction (VI) in the rhizosphere in all samples (Figure 3). In Soil+BioS+BFA this pattern was reverse for Ca; namely it was bound to non-soluble Fraction (VI) in the bulk soil and bound to reducible Fraction (IV) in the rhizosphere soil.

Potassium was predominantly bound to carbonates (Fraction II) in all bulk (33-78%) and rhizosphere (37-63%) samples, except in the rhizosphere of Soil+BioS, in which Fraction IV was by 4% (insignificantly) larger than the Fraction II.

Phosphorus was mainly found in the reducible Fraction III in all bulk and rhizosphere soil samples (Figure 3). Only in the bulk soil amended with CaKPO₄, was P mainly available (Fraction I) (Figure 3).

In the bulk samples, S was predominantly bound to crystalline Fe oxyhydroxides (38-45%), while in the rhizosphere, Fraction III was almost twice as large (ca 84%). Only in soil containing fly ashes, about the same amount of S was bound to Fraction IV in both bulk and

rhizosphere.

Both Cr and Fe were bound to crystalline Fe oxyhydroxides in the bulk samples, while in the rhizosphere they were predominantly non-soluble (Fraction VI) (Figure 4).

Figure 3. Chemical fractionation of macronutrients in bulk and rhizosphere soil amended with residues and their mixtures. I - exchangeable, II - bound to carbonates (acid-soluble),

III - bound to poorly crystalline Fe(III) oxyhydroxides (reducible), IV – bound to crystalline Fe-Mn oxides (reducible), V – bound to organic matter and secondary sulphides (oxidisable), VI - residual fraction (non-soluble).

Figure 4. Chemical fractionation of micronutrients in bulk and rhizosphere soil amended with residues and their mixtures. I - exchangeable, II - bound to carbonates (acid-soluble), III - bound to poorly crystalline Fe(III) oxyhydroxides (reducible), IV – bound to crystalline Fe-Mn oxides (reducible), V – bound to organic matter and secondary sulphides (oxidisable), VI - residual fraction (non-soluble).

In the bulk soil, Cu was bound to crystalline Fe-Mn oxides (Fraction IV). The largest amount of Cu in Soil+BFA was bound to organic matter (Fraction V) in the bulk sample. In the rhizosphere samples, Cu was predominantly bound to carbonates (Fraction II). In the bulk soil amended with biosolids, Cu was also mostly bound to carbonates (66%), while in the rhizosphere samples, it was mainly bound to poorly crystalline Fe oxyhydroxides (35%) followed by bound to carbonate Fraction II (31%).

Manganese was mostly found in residual Fraction VI in the bulk samples except in those that contained biofuel fly ash (Figure 4). Nickel in bulk samples, was predominantly bound to crystalline Fe-Mn oxides (Fraction IV) (39-59%), whilst a significant amount (93-97%) of Ni was found in non-soluble (Fraction VI) in the rhizosphere samples.

Zinc was distributed mainly between the two fractions II and III in the soils containing fly ashes (Figure 4). Only the extracts from soil amended with MSWI fly ashes contained a substantial amount of mostly soluble Zn (10.9-18.2%), while in the rest of bulk and rhizosphere samples, the most available Zn varied from 0.6 to 4.4%.

Potentially toxic elements

Aluminium was least soluble of all potentially toxic elements. It was predominantly found in the non-soluble Fraction (VI) in all bulk (39-63%) and rhizosphere (49-64%) samples (Figure 5).

Figure 5. Chemical fractionation of potentially toxic elements in bulk and rhizosphere soil amended with residues and their mixtures. I - exchangeable, II - bound to carbonates (acid-soluble), III - bound to poorly crystalline Fe(III) oxyhydroxides (reducible), IV – bound to crystalline Fe-Mn oxides (reducible), V – bound to organic matter and secondary sulphides (oxidisable), VI - residual fraction (non-soluble).

Arsenic was predominantly bound to Fraction IV (crystalline Fe-Mn oxides) in all bulk samples (44-52%), while in the rhizosphere it was mostly bound to poorly crystalline Fe hydroxides (76-79%) almost in all samples. About 90% of the Cd was bound to Fraction III (poorly crystalline Fe hydroxides) in the rhizosphere, while in bulk samples Cd was predominantly bound to Fraction IV (33-51%).

Lead was predominantly bound to crystalline Fe-Mn oxides (Fraction IV) in almost all of the

samples except bulk samples of soil amended with biosolids and soil containing MSWI fly ash (52-56%). In soil amended with bio fuel fly ash and soil amended with biosolids no significant difference in As, Cd and Pb concentrations between bulk soil and rhizosphere was observed.

4. Discussion

Phosphorus is one of the primary plant nutrients, but in most soils it is relatively unavailable for plant uptake. A strong P fixation in soil is an important reason why only a fraction of applied P fertilizers are taken up by plants. Combining the industrial residues had a positive effect on P phytoavailability as P concentration in the pore water notably increased. Though the most soluble P fraction was found in the soil mixed with the synthesized additives, plants grown in soil amended with biosolids developed the largest biomass and were able to accumulate a significant amount of P (3297 mg/kg dw), whereas the concentration of P in the pore water of the soil was relatively low (0.8 mg/l). Plants are capable of solubilising some of the strongly bound P, e.g. bound to Fe oxides, through exudation of organic acids (Jan et al., 2013), but the high P accumulation in plants might also be the reason for the low dissolved P in soil. Some noticeable differences found in P fractionation in bulk and rhizosphere soil, suggests that P supply in the form of amendments, especially in biosolids, can provide plants with phytoavailable P without increasing the risks for losing it through leaching.

Other nutrients, such as Fe, Mn, Zn and Cu, may also become available for plants through rhizosphere acidification by root exudates even at the low availability of these elements (Marschner et al., 1989). It was shown by the fractionation test that, the residual fraction of these elements was significantly larger in rhizosphere soil as compared to bulk soil, and this

indicates that there was an enhanced plant uptake from the more soluble fractions. It is therefore to be expected that potentially toxic elements that are associated with Fe and Mn oxides, such as As, may also be solubilised to some extent and also be taken up by plants (Kumpiene et al., 2012). However, concentration of As in plant biomass from all soil mixtures was non-detectable. Since P is considered to be a chemical analogue for As in soil (Adriano, 2001), it might be expected that substantially higher P concentrations in the mixtures suppressed As uptake. This may be the case if all P and As is inorganic and appear in the same minerals. However, the concentrations of P and As vary between the various materials used, and thus the P/As ratio is high in BioS (778) and low in MFA (5). Phosphorus in BioS is largely organic whilst As in MFA is inorganic. Thus, the P/As ratio in the pore water might be expected to change with time, depending on the availability of one and the other together with the selectivity of the uptake. Arsenic is typically occurring in MSWI ash at < 0.1% levels as a result of the difficulties to separate all copper, chromium and arsenic (CCA) impregnated wood.

The concentrations of Cd and Pb in plant biomass were negligible. It appears likely that the uptake of these elements was also diminished by P. The ability of P amendments to reduce Pb availability and phytoavailability is frequently observed in Pb contaminated soils (e.g. Hettiarachchi and Pierzynski, 2002). Similar observations are reported for Cd (Panwar et al. 1999; Brown et al., 2004). The suggested mechanism responsible for the low concentrations of Cd and Pb in the above-ground biomass is a P-induced decrease in metal translocation from roots to shoots (Chen et al., 2007; Qiu et al., 2011). Also precipitation of metal phosphates may contribute to the observed of metal translocation from roots to shoots (Padmavathiamma. and Li, 2007).

Cadmium also has its chemical analogue, which is Zn, and antagonistic behavior of these

two elements for plant uptake is often observed (Lee et al., 2004; Wang et al., 2011) despite a considerably larger atomic radius of Cd as compared to Zn. Applying Zn-rich residue mixtures to soil might further help to counteract Cd uptake by plants. High concentrations of chloride ions, on the other hand, have been shown to increase dissolved Cd and the plant uptake (Smolders et al., 1997), and this might explain the higher Cd concentration in soil containing MSWI-mixtures. In spite of this, Cd translocation to the above-ground plant parts remained low. Lead in plants was below detectable limits.

Cadmium and Pb along with Hg and As are of particular interest since the use of these elements as well as releases of them in the form of emissions, is restricted in many countries due to their toxicity to animals and humans (Månsson et al., 2012). Cadmium values in vegetable foodstuffs are set in EU to 0.05-0.2 mg/kg wet weight (EC 1881/2006) and in animal feedstuff (12% moisture content) with vegetable origin to 1 mg/kg (EC 87/2005). Plants contained <0.04-0.09 mg/kg Cd, and at 12% moisture content it would be 0.035-0.08 mg/kg. Both values are below the permissible limits. Although the plants were grown only for seven weeks and somewhat higher metal accumulation can be expected in fully grown vegetation, the risk for exceeding the limit values for animal foodstuff might still be low.

Among potentially toxic elements, only the uptake of Al was substantial compared to the leached concentrations from individual residues (BFA and BioS) and their mixtures. In general, solubility of Al is undesirable due to its toxic effects on plants. In all soil mixtures, the dissolved Al concentrations in soil pore water were within the tolerable limits for plants (<1.6 g/l depending on the plant species) (Poschenrieder et al., 2008). Aluminium is rarely a problem in neutral soils as it can easily react with phosphates, sulphates and other organic and inorganic ligands at pH>5 that would keep dissolved Al in not-toxic concentrations (Delhaize and Ryan, 1995; Ma et al., 2001). Therefore application of slightly alkaline mixtures

on acidic soil would be beneficial in reducing potential Al toxicity to plants.

Even though plant uptake of most elements was largest in plants that had grown in soil with BioS-BFA mixture, the biomass was the lowest compared to the plants from the other pots. It is quite common that high elemental concentrations are observed when the biomass production is low, and vice versa (e.g. Oudeh et al., 2002). The largest concentrations of K, Mg, P, S, Cu and Zn in pore water were found in the soil-BioS-MFA mixture, and this is the highest availability of these elements that was observed for any of the plants. However, plants did not grow in this mixture at all. The EC was particularly high in the pore water of soil containing amendments with MSWI fly ash, and this is an indication of high soil salinity. This appears to be the main reason for the undeveloped vegetation in these pots (Conesa et al., 2011). High salinity of soil could reduce germination by limiting water absorption by the seeds, also by both osmotic stress and specific ion toxicity (Almansouri et al., 2001). Most of the chlorine probably comes from the lime that may have been used in order to capture hydrochloric acid in the fumes during the incineration process. Ashes with lower concentrations of chlorides should therefore be selected when considering their use as soil fertilizers.

The unexpectedly low biomass development in soil containing mixtures of residues was most likely due to the form in which the residues were applied. In this study, fresh fly ashes were added as powders. Applying fresh residues to soil typically results in pH changes and consequently in the release of various elements to the pore water, i.e. immediate availability to plant roots. A slower release of nutrients was observed in a forest fertilized with pelletized biosolids compared to liquid sludge application (Kelty et al., 2004). Slow release of nutrients can be advantageous for perennial plants and especially trees since the nutrients would be available during a long time. Future work should thus include granulated /pelletized residue

mixtures.

5. Conclusions

The plant pot experiment, in which fresh residues were mixed with soil, showed that the plants did not grow as expected. The largest concentrations of nutrients K, Mg, P, S, Cu and Zn in the pore water were found in the soil mixture with biosolids and MSWI fly ash; however plants did not grow at all in mixtures containing the latter, most likely due to the high concentration of chlorides in this ash. Notably, not only nutrients played the main role in the biomass production, but also other compounds or chemical reactions that occurred in the mixtures which have to be investigated further. Also, the use of aged fly ash should be further investigated, as the fertilizer properties might change during its preparation.

As the conflicting information exists about element availability in soil amended with biosolids, so the results showed, that P availability in soil increased with biosolids addition and the availability of Cd and Pb in soil did not change compared to the unamended soil. But the plant uptake of P was 57% higher in soil amended with biosolids and that of Cd and Pb was similar as in the unamended soil.

The proportions of various residues (namely bio fuel fly ash and biosolids) can be adjusted in order to balance the amount and availability of macro elements, while the possible increase of potentially toxic elements is expected to have little impact on the plant uptake as it was shown in this study. This was also supported by the results from the pore water analysis, where the concentrations of potentially toxic elements dissolved in soil pore water were very low.

With regard to utilization of the residues studied as soil amendments (except MSWI fly ash), the assessment tools used here may help to evaluate if the residues can be beneficial for the

biomass production without any substantial risk for the environment. The focus in this study was on the availability of nutrients and potentially toxic elements for plants, however other substances and potentially hazardous compounds have not been investigated. Therefore precautions should be always taken while considering the use of residues as soil amendments and additional analysis should be performed.

Acknowledgements

The study is financed by the EU Regional Development Fund Objective 2 project North Waste Infrastructure.

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