Utilization of steel, pulp and paper industry solid residues in forest soil amendment: Relevant physicochemical properties and heavy metal availability

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ABSTRACT

Industrial residue application to soil was investigated by integrating granulated blast furnace or converter steel slag with residues from the pulp and paper industry in various formulations. Specimen analysis included relevant physicochemical properties, total element concentrations ($HCl + HNO_3$ digestion, USEPA 3051) and chemical speciation of chosen heavy metals (CH_3COOH, $NH_2OH \cdot HCl$ and $H_2O_2 + H_2O_2 + CH_3COONH_4$, the BCR method). Produced matrices showed liming effects comparable to commercial ground limestone and included significant quantities of soluble vital nutrients. The use of converter steel slag, however, led to significant increases in the total concentrations of Cr and V. Subsequently, total Cr was attested to occur as Cr(III) by $Na_2CO_3 + NaOH$ digestion followed by IC UV/VIS–PCR (USEPA 3060A). Additionally, 80.6% of the total concentration of Cr ($370\,mg\,kg^{-1}$, d.w.) occurred in the residual fraction. However, 46.0% of the total concentration of V ($2470\,mg\,kg^{-1}$, d.w.) occurred in the easily reduced fraction indicating potential bioavailability.

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1. Introduction

Industrial residue application to soil is being increasingly investigated to facilitate de-acidification of soils and could become a future alternative option to chemical fertilizers. Although the application of chemical fertilizers can have the ability to boost short-term crop production, attempts to increase soil pH often result in a lack numerous bio-essential nutrients and the organic material required for the long-term, healthy functioning of the soil [1]. Primary and secondary nutrients N, P, K, S, Ca and Mg are often deficient in acidic soils and trace elements, such as Mn, can be become soluble in toxic quantities [2].

As the manufacture of commercial chemical fertilizers often relies heavily on resource intensive and environmentally detrimental processes, such as mineral extraction and calcination, research regarding the possibilities for fertilizer substitution by available industrial residues should be emphasized. The pulp, paper and steel industries in particular generate a wide-ranging spectrum of solid residues with characteristics that could be beneficial in soil amendment.

In integrated pulp and papermaking, several inorganic (ashes, green liquor dregs, slaker grits and lime wastes) and organic (wastewater treatment sludges) residues are generated. Generally, these residues are incinerated in the solid fuel boilers of the respective facilities or disposed to landfill [3]. In the case of integrated iron and steel production, generated residues are mainly inorganic slags of various composition originating from the main unit processes. Prevalent disposal options include their use in the construction industry, in agricultural liming or disposal to landfill [4,5].

Solid residues from the pulp, paper and steel industries have been widely investigated for use in soil amendment [6–10], and have subsequently shown promise as replacements for their commercial alternatives. In the study conducted by Cabral et al. [6] fly ash from wood incineration and green liquor dregs and slaker grits from the chemical recovery cycle of a pulp mill were investigated for use as alternative liming materials. Their results were promising regarding the replacement of commercial agricultural limestone.

Ali and Shahram [7] reported the utilization of converter slag from steel making in the amelioration of acidic soils and stated that there was substantial potential but that the use of converter slag needed further research regarding soluble V concentrations. Additionally, Jordan and Rodriguez [3] studied plant growth under the effect of ash, fly ash, primary pulp mill sludge, green liquor dregs and slaker grits. The authors concluded that despite of high concentrations of essential Ca, Mg, K and P, more research was needed

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to attest the usability of these residues in the amendment of poor or acidic soils.

Despite of the promising results regarding the use of individual residue fractions in soil amendment, integration of residues from different industry sectors into a distinctive concept could provide additional benefits. Problems related to physical handling and distribution could be eased through the manufacture of pellets with proper dimensions, pH shock effects from easily soluble salts could be attenuated by avoiding rapid dissolution [11] and control of alkaline metal release could be attained by use of suitable binders. Additionally, increasing the broader sustainability of manufacturing processes with respect to soil nutrient recycling back to forest ecosystems [12] and avoiding the impacts of primary fertilizer production should not be forgotten.

However, as the aforementioned residues can also be regarded as industrial wastes, certain parameters with potential environmental impacts upon utilization should be assessed. This article reports the physicochemical properties and heavy metal availability of pellets made by integrating granulated blast furnace (GBFS) or converter steel slag from integrated iron and steel production with fly ash, paper mill sludge, lime waste and green liquor dregs from pulp and paper making. Physicochemical properties and total heavy metal concentrations of the respective matrices were determined with standardized methods. The BCR[1] sequential extraction procedure, which has been applied for a wide range of sludges, fly ashes and other industrial residues [13–15], was applied to attain information on the mobility and bioavailability of chosen heavy metals.

2. Experimental

2.1. Sampling

Steel, pulp and paper industry residuals were sampled from two industrial facilities located in Northern Finland. GBFS and converter steel slag samples were collected at a slag pit of an integrated iron and steel mill at a particle size of less than 4 mm. Sampling was performed during a one-day period and represented slag generated during normal plant operating conditions. Slag samples were stored in steel containers in room temperature and humidity until matrix manufacture.

In case of the pulp and paper mill, fly ash was sampled from an ash outlet subsequent to an electrostatic precipitator used for purging the flue gases generated during the incineration of approximately 50% of clean forest residues (i.e., bark, wood chips and saw dust) and 50% of commercial peat fuel. Green liquor dregs samples were collected at a dreg percolator used to separate the insoluble solids from green liquor during chemical recovery. Lime waste sampling was carried out at a lime kiln outlet used for purging the contents of the kiln in abnormal situations. Paper mill sludge sampling was performed at a recovery process used at the mill for recycling paper pigments as fillers in fine paper production. The samples were stored in 10 dm³ polyethylene containers in room temperature and humidity, except for the paper mill sludge which was stored in a refrigerator (+4 °C) to prevent degradation of organic fiber content. Sampling was performed during a three-day period in normal plant operating conditions.

2.2. Sample preparation and matrix manufacture

Two different soil amendment matrices were produced using mixing and casting procedures from conventional cement testing.

Dried and ground green liquor dregs were mixed with lime waste, paper mill sludge, fly ash and ground GBFS or converter steel slag according to Table 1 before admixing water to enable fly ash and slag hydration (water/binder ratio 1.125). Water addition was followed by a mixing period before respective quantities of the slurry were cast in cubic moulds of 1 dm³ and in cylindrical moulds of app. 25 mm in width and 35 mm in height. Cubic 1 dm³ moulds were used to guarantee a homogeneous mixture of matrix components for chemical analysis. Subsequent to casting, the moulds were subjected to vibration and cured in room temperature and humidity to produce a solidified matrix.

Fly ash and lime waste samples were not subjected to any pretreatment prior to mixing as the apparent fineness of both materials was clearly suitable for a dry mixing procedure prior to water addition. The only ingredient with an apparent moisture content was paper mill sludge [16], which however did not seem to affect the uniform dispersion of individual elements in the matrices produced.

2.3. Determination of relevant physicochemical properties

The determination of pH and electrical conductivity were performed at a solid to liquid (S/L) ratio of 1:2.5 (v/v). The determination of loss on ignition (LOI) and total organic carbon (TOC) values and the dry matter content of the matrices were carried out according to SFS-EN 12879, SFS-EN 13137 and SFS-ISO 11465 respectively. Additionally, neutralizing (NV) and reactivity (r_{ac}) values were analyzed according to SFS-EN 12945 and SFS-EN 13971 respectively. Prior to analysis procedures the solid specimens were ground with a jaw crusher to a particle size (<2 mm) suitable for laboratory analysis.

2.4. Determination of total element and plant nutrient concentrations

For the determination of total element concentrations, the ground and dried samples were digested with a mixture of HCl (3 mL) and HNO$_3$ (9 mL) in a CEM Mars 5 microprocessor controlled microwave oven with CEM HP 500 Teflon vessels (CEM Corp., Matthew, USA) using USEPA method 3051A[2]. The cooled solution was transferred to a 100 mL volumetric flask and subsequently diluted to volume with H$_2$O.

Except for Hg, total element concentrations of individual heavy metals from the solution were determined with a Thermo Electron IRIS Intrepid II XDL Duo (Franklin, USA) inductively coupled plasma optical emission spectrometer (ICP-OES). In the case of Hg, total element concentration was determined with a Perklin Elmer Analyst 700 cold vapour atomic absorption spectrometer (Norwalk, USA) equipped with a Perkin Elmer FIAS 400 and AS 90 plus autosampler.

Easily available plant nutrient (Ca, Mg, Na, K, P, S, Cu, Zn and Mn) concentrations were determined according to the procedure of MTT Agrifood Research Finland [18], where 1 volume part of dry sample is shaken with 10 parts of extraction solution for 1 h. Ca, Mg, Na, K, P and S were extracted with 0.5 mol L^{-1} acidic ammonium acetate (pH = 4.65). In the case of Cu, Zn and Mn, the acidic ammonium acetate solution contained 0.02 mol L^{-1} ethylenediaminetetra-acetic acid disodium salt (Na$_2$EDTA). After extract and solid residue separation through filtration Ca, Mg, Na, K and S concentrations were determined by ICP-OES and Cu, Zn and Mn concentrations by FAAS.

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[1] Community Bureau of Reference (Bureau Communautaire de Référence, BCR) now the EC Standards, Measurements and Testing Programme.

[2] Although more aggressive extractant mixtures for the complete dissolution of the respective mineral lattice do exist (e.g., USEPA method 3052, where HF and HNO$_3$ are used with microwave digestion), USEPA 3051 was adopted to ensure comparability with fertilizer regulation [17].

Table 1
Composition of produced matrices.

Component	Matrix I	Matrix II
Binder[a]	GGBFS 0.15, fly ash 0.15	GSS 0.15, fly ash 0.15
Alkali aggregate[a]	Paper mill sludge 0.30, GLD 0.10, lime waste 0.30	Paper mill sludge 0.30, GLD 0.10, lime waste 0.30

GGBFS: ground granulated blast furnace slag.
GSS: ground converter steel slag.
GLD: green liquor dregs.
[a] Individual component quantities expressed in mass fractions prior to water addition.

The concentration of P was determined spectrophotometrically.

2.5. Sequential extraction

For the determination of As, Cd, Cr, Cu, Ni, Pb, V and Zn availability, the three-stage sequential BCR procedure was used, see Table 2. The BCR procedure is basically a modified and stripped-down version of the five-stage sequential extraction procedure originally proposed by Tessier et al. [19] and has been widely applied for the evaluation of metal availability from various matrices, e.g., sediment, soil, sludge, ash and other industrial residues [13–15]. More detailed descriptions of the procedure can be found elsewhere, see e.g., [20].

In addition to the three-stage BCR procedure, the residual fraction was determined by calculation. As digestion of the residue is not specified in the BCR procedure, as it is in e.g., the five-stage procedure by Tessier et al. [19], the residual fraction was calculated as the difference between the total element concentration and the sum of all previous fractions [14].

3. Results and discussion

3.1. Relevant physicochemical properties

As shown in Table 3, both Matrices I and II attested to high pH values indicating liming and buffering capacities and thus clear potential for soil conditioning. Additionally, as stated by the low EC values, the extraction solutions of the matrices had very low ionic strengths. Hence, only a minor part of the dissolved metals would be expected to occur as dissolved basic metal salts. In this case, the utilization of ground GBFS or converter steel slag in tandem with fly ash most likely resulted in the entailment of otherwise available metals to the mineral structures of the slag-fly ash binders during hydration.

The LOI and TOC values of the matrices were low, suggesting that the organic material content was low. As shown in Table 1, paper mill sludge was included in the formulations, and was the only constituent with significant organic contents (LOI 35.5%, d.w. as attested by Kuokkanen et al. [16]). In this case, the low organics content is favorable due the expected high concentrations of heavy metals. These heavy metals could form complexes with organic material in certain conditions. Once applied to natural environments, the degradation of organic matter in e.g., oxidizing conditions could lead to the release of complexed heavy metals [21].

As illustrated in Table 3, the neutralizing (NV) and reactivity (r_{ac}) values of the matrices were attested as high. NV is one the most important indices in evaluating the liming effect of a material regarding its application as a fertilizer [15]. The capacity of a material to neutralize soil acidity depends on the amount of hydrolysable bases, which generally occur as oxides, hydroxides, carbonates and silicates. Cations such as Ca, Mg and K are the interactive counterions. According to the liming effect value of commercial ground limestone, which is 38% (Ca-equivalents, d.w.) [15], 1.03 and 1.06 tonnes of Matrices I and II respectively would be needed to replace 1 tonne of commercial ground limestone produced by SMA Mineral Ltd.

In the case of easily available plant nutrient concentrations (Table 3), Matrices I and II would increase available Ca, Mg, Na, K (only in the case of Matrix I) and S in organic and mineral soils normally found in the Ostrobothnia region of Northern Finland. Additionally, micronutrient concentrations Cu, Zn and Mn were also higher than in respective soils. These results indicate that the potential amendment effect provided by Matrices I and II would not only be limited to neutralizing soil acidity, as the matrices would also contribute to soil fertility by increasing available concentrations of vital nutrients.

3.2. Total element concentrations and chemical speciation

3.2.1. Total element concentrations

Results regarding the USEPA 3051A total element concentration determinations are shown in Table 4. Based on the results, the total concentrations of As, Cu, Ni, Pb, Zn and Hg were lower than the respective limit values for the use of e.g., ash fertilizers in agriculture and forestry, but Cd in both matrices exceeded respective limit value regarding use as agricultural fertilizer [17]. However, attested concentrations of Cd were lower than the limit value of Cd for fertilizers used in forestry.

Only the total concentration of Cr in Matrix II exceeded respective limit value for fertilizers used in forestry. Additionally, an elevated total concentration V was detected in the case of Matrix II. Currently, no limit value for the total concentration of V has been

Table 2
Chemical reagents and analytical conditions of the three-stage sequential BCR extraction procedure.

Step	Fraction	Extraction procedure	Nominal target phases
1	Exchangeable	40 mL of 0.1 mol L^{-1} CH$_3$COOH per 1 g of dry sample was shaken for 16 h at 25 °C.	Water and acid-soluble
2	Easily reduced	40 mL of 0.1 mol L^{-1} NH$_2$OH·HCl (adjusted to pH 2.0 with HNO$_3$) was admixed with the residue and shaken for 16 h at 25 °C.	Iron/manganese oxyhydroxides
3	Oxidisable	10 mL of 30% H$_2$O$_2$ was admixed with the residue and digested at 85 °C for 1 h. Subsequently, the treatment with H$_2$O$_2$ was repeated with a new aliquot. After 50 mL of 1 mol L^{-1} CH$_3$COONH$_4$ (adjusted to pH 2.0 with HNO$_3$) was admixed with the residue and shaken for 16 h at 25 °C.	Organic matter and sulfides

Table 3
Physicochemical properties and easily available plant nutrient concentrations. As reference, easily available plant nutrient concentrations of organic and mineral soils normally found in the Ostrobothnia region of Northern Finland are given [15].

Parameter/element	Unit	Matrix I	Matrix II	Soil (organic; mineral)
pH		12.9	13.0	
Electrical conductivity (EC)	mS cm^{-1}	8.8	9.8	
LOI (loss on ignition, 550 °C)	% (d.w.)	6.3	5.1	
TOC (total organic carbon)	g kg^{-1} (d.w.)	18	20	
Dry matter content (105 °C)	%	97.1	97.0	
Neutralising value (NV)	% (Ca, d.w.)	36.6	35.8	
Reactivity value (r_{ac})	% (Ca, d.w.)	34.1	33.3	
Ca	mg kg^{-1} (d.w.)	180,000	201,000	3340; 960
Mg	mg kg^{-1} (d.w.)	10,200	5000	520; 135
Na	mg kg^{-1} (d.w.)	4900	4100	35; 14
K	mg kg^{-1} (d.w.)	950	750	130; 770
P	mg kg^{-1} (d.w.)	8	2	180; 120
S	mg kg^{-1} (d.w.)	3000	2700	130; 23
Cu	mg kg^{-1} (d.w.)	20	22	8.5; 3.3
Zn	mg kg^{-1} (d.w.)	110	96	11; 3.8
Mn	mg kg^{-1} (d.w.)	1390	700	94; 28

set in the Finnish fertilizer regulation and the availability of *V* from Matrix II is discussed in detail in Section 3.2.2.

The elevated total concentration of Cr in Matrix II is most likely due to the replacement of GBFS with converter steel slag as illustrated in Table 1. In converter steel slag Cr occurs only in the non-toxic trivalent form Cr(III) and mostly depends on the quality of iron ore and recycled steel scrap [5]. In general, Cr occurs in the environment in two distinct valence states, which mainly stipulate its toxicity. The trivalent Cr(III) is naturally present in the environment and the hexavalent Cr(VI), which is a known carcinogen, mutagen and teratogen, occurs mainly due to anthropogenic activities [22].

In the Finnish fertilizer regulation, the differences between the trivalent and hexavalent valence states of Cr were acknowledged in 2009 [23]. As a result, the statutory limit value for the total concentration of Cr regarding the use of converter steel slag (as such) for liming was revised. The total concentration limit value of Cr (i.e., 300 mg kg^{-1}) was converted to a limit value for soluble Cr(VI), which was set at 2 mg kg^{-1} (d.w.). Although no directly comparable

limit values for concepts as presented in this paper currently exist in the Finnish fertilizer regulation, reference is made to the limit value for Cr(VI) in converter steel slag used as a liming agent.

3.2.2. Cr(VI) analysis

To ascertain the valence state(s) of Cr in the converter steel slag matrix (Matrix II), two methods were applied to determine (i) soluble Cr(VI) and (ii) total Cr(VI) as follows:

(i) Soluble Cr(VI) was determined from solution attained by applying the two-stage batch leaching test according to SFS-EN 12457-3. As a result, the cumulative L/S 10 fraction was used. The soluble Cr(VI) concentration, and respective total concentration of soluble Cr, were determined by ion chromatography (IC) using post-column reaction (PCR) followed by ultraviolet/visible (UV/VIS) spectroscopy.
(ii) Total Cr(VI) was determined according to USEPA 3060A, where the sample is digested with a mixture of Na_2CO_3 and NaOH. The total concentration of Cr(VI) was determined by IC UV/VIS–PCR as described above.

Based on the results, soluble Cr occurs only in the toxic hexavalent Cr(VI) form. However, although the two-stage batch test SFS-EN 12457-3 followed by IC UV/VIS–PCR gave equivalent values (i.e., 0.4 mg kg^{-1}, d.w.) for soluble Cr(VI) and the total concentration of soluble Cr, the total concentration of Cr(VI) according to USEPA 3060A remained below the limit of detection (<3 mg kg^{-1}, d.w.). Thus, the data supports the conclusion that the total concentration of Cr consist entirely of Cr(III).

According to the respective Finnish limit value for soluble Cr(VI) in converter steel slag used (as such) in liming (i.e., 2 mg kg^{-1}, d.w. [22]) and the low total concentration of Cr(VI), Cr(VI) availability from the converter steel slag matrix (Matrix II) does not seem to restrict use in liming. Although concerns regarding the possible release of Cr(VI) after oxidation of Cr(III) by e.g., Mn-oxides have been reported [22], alkaline conditions induced by Matrix II extraction should tend to stabilize Cr(VI). However, reduction of Cr(VI) to Cr(III) has also been reported to occur in alkaline reducing soils [24] and could possibly understate the existence of Cr(VI).

3.3. Chemical speciation – the BCR procedure

Heavy metal recovery in the exchangeable fraction of the BCR procedure was negligible regarding all elements from both Matrices I and II, as shown in Figs. 1 and 2. Only Cr and Cu recoveries
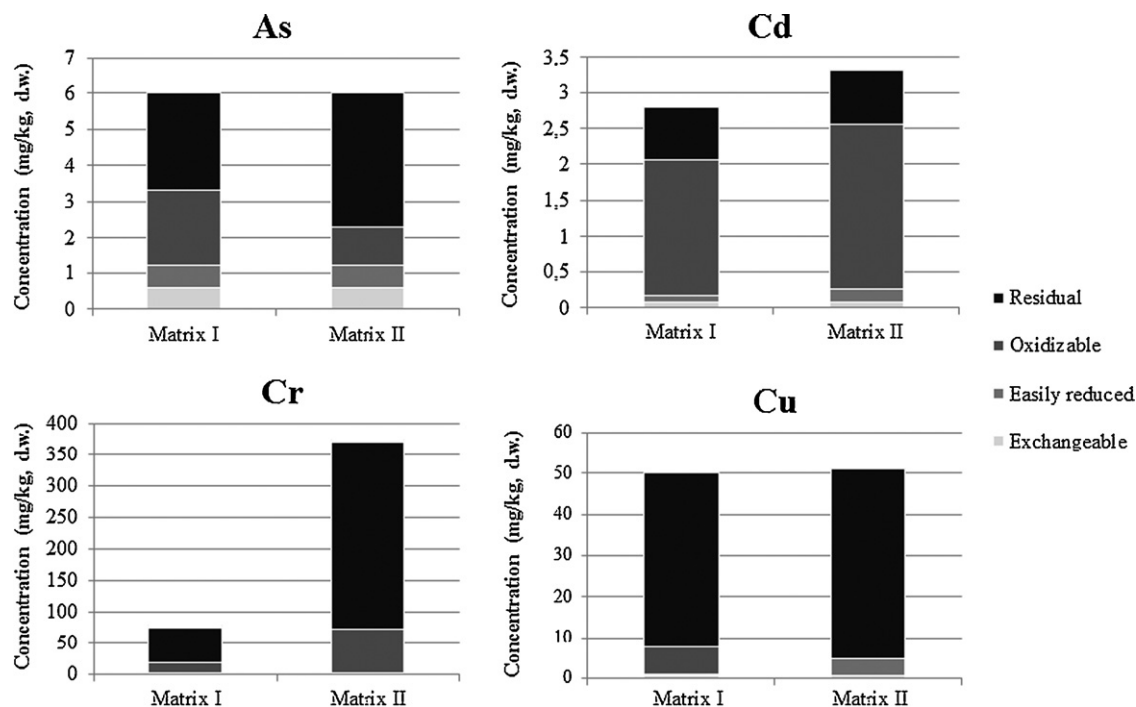
Table 4
Total element concentrations according to USEPA 3051A (mg kg^{-1}, d.w.) with respective Finnish statutory limit values (mg kg^{-1}, d.w.) set for the use of e.g., ash fertilizers in agriculture and forestry [17].

Element	Matrix I	Matrix II	Fertilizer limit value	
			Agriculture	Forestry
As	6	6	25	30
B	20	21		
Ba	400	340		
Be	<1	2		
Cd	2.8	3.3	1.5	15
Co	3	3		
Cr	75	370	300	300
Cu	50	51	600	700
Mo	<1	<1		
Ni	16	16	100	150
Pb	20	20	100	150
Sb	<4	<4		
Se	<4	<4		
Sn	<2	<2		
Ti	1420	1040		
V	140	2740		
Zn	300	320	1500	4500
Hg	<0.04	<0.04	1.0	1.0

Tables 1, 3 and 4 are partly reproduced from "M. Mäkelä, G. Watkins, O. Dahl, H. Nurmesniemi, R. Pöykiö, Integration of solid residues from the steel and pulp and paper industries for forest soil amendment, J. Residuals Sci. Technol. 7 (2010), 191–198. Lancaster, PA: DEStech Publications Inc.".

Fig. 1. As, Cd, Cr and Cu availability (mg kg^{-1}, d.w.) according to the three-stage sequential BCR extraction procedure.
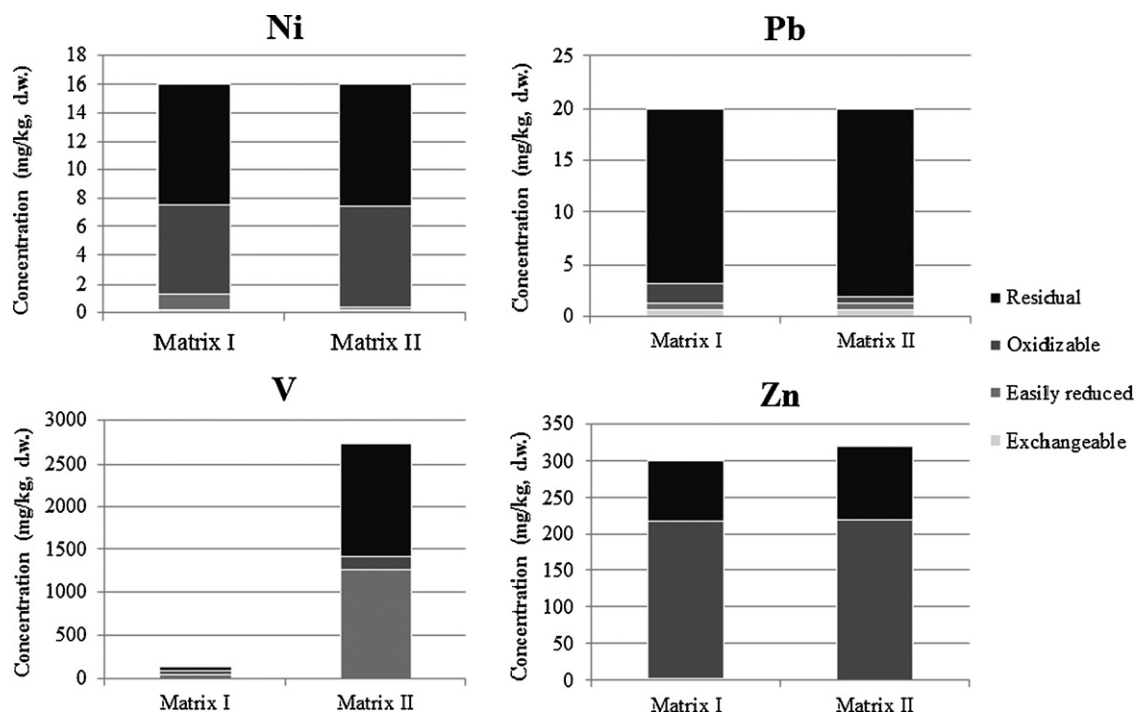

Fig. 2. Ni, Pb, V and Zn availability (mg kg^{-1}, d.w.) according to the three-stage sequential BCR extraction procedure.

exceeded the limit of detection[3], resulting in recoveries of 0.7% and 0.1% for Cr and 1.3% and 1.3% for Cu regarding the total concentrations of Matrices I and II, respectively. Generally, the exchangeable

fraction consists of weakly adsorbed metals retained on particle solid surfaces by weak electrostatic interaction, metals releasable by ion-exchange processes and metals able to coprecipitate with carbonates [25]. Thus the exchangeable fraction represents metals which are most readily bioavailable, e.g., reduction of pH could cause remobilization of metals [25].

In the easily reduced fraction, heavy metal recovery was dominated by V from Matrix II (illustrated in Figs. 1 and 2). 46.0% of the respective total concentration was attained. Considering the

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[3] In the case of As availability in the exchangeable and easily reduced fractions of both Matrices I and II (shown in Fig. 1), the numerical values "<0.6 mg kg^{-1}, d.w." were taken as "0.6 mg kg^{-1}, d.w." leading to exaggerated recoveries in the graphical illustration.

low total concentration of V in Matrix I (Table 4 in Section 3.2.1) and respective low recoveries during the BCR procedure (Fig. 2), elevated concentrations of V in Matrix II are most likely due to the replacement of GBFS with converter steel slag in the formulation. As explained by Fuentes et al. [13], the easily reduced fraction usually consists of oxides of Fe and Mn which are thermodynamically unstable in e.g., anoxic conditions. Hence, notable recoveries in the easily reduced fraction can be considered as an indication of potential bioavailability.

As mentioned in Section 3.2.1, no limit value for the total concentration of V currently exists in the Finnish fertilizer regulation. However, significant recovery in the easily reduced fraction confirms the concern stated by Ali and Shahram [7] regarding the need for further studies in respect of impacts of V on soil. In addition to V, an elevated recovery of Cu was detected from Matrix II compared to Matrix I. However, Cu recovery amounted to only 8.4% of the respective total concentration.

In the oxidizable fraction, the major part of the total concentrations of Cd and Zn were recovered from both Matrices I and II. In the case of Cd, recovery amounted to 67.9% and 69.7% of the total concentrations of Matrices I and II, respectively. The oxidizable fraction is generally considered to represent metals which are incorporated in stable, high molecular weight humic substances or occur as oxidizable minerals, e.g., sulfides, and is not considered to be very mobile or bioavailable [25,26]. However, degradation of organic matter could lead to the release of metals associated with e.g., organic components [25]. The LOI and TOC values illustrated in Table 3 (Section 3.1) indicate the low organic content of both Matrices I and II.

In the case of Zn, recovery in the oxidizable fraction was 72.0% and 68.4% of the respective total concentrations of Matrices I and II. Despite the high recoveries of Zn in this fraction, the low organic content in both Matrices I and II, in addition to the low total concentrations of Zn in respect of the statutory limit values, indicate that Zn availability is not a major concern regarding Matrices I and II.

In addition to Cd and Zn, Cu showed the highest availability from Matrix II in the oxidizable fraction resulting in 71.6% of the respective total concentration. With Matrix I, Cu recovery in the oxidizable fraction resulted in only 13.2% of the respective total concentration. Significant variation among the single fraction recoveries between Matrices I and II are likely to be associated with the hydraulic binding properties of GBFS and converter steel slag. In general, GBFS exhibits cementitious properties comparable to Portland cement whereas converter steel slag possesses only weak cementitious properties [27].

As, Cr, Ni, Pb and Cu (only in the case of Matrix I) were attested to occur mostly in the residual fraction. In this study the residual fraction was determined by calculation based on the work of Smeda and Zyrnicki [14]. As a result, the following portions were attained: As 45.0% and 61.7%; Cr 84.6% and 80.6%; Ni 53.1% and 53.8%; Pb 84.5% and 90.3%, for Matrices I and II respectively. In the case of Cu in Matrix I, the residual fraction amounted to 84.6% of the respective total concentration.

Generally, the residual fraction consists of primary and secondary silicates and minerals, which are able to retain elements within the crystalline structure [20]. Thus, elements occurring in the residual fraction are not considered to be available to the environment in natural conditions. It must be noted that even though more aggressive extractant mixtures than HCl and HNO_3 for the complete dissolution of the respective mineral lattice do exist (e.g., HF and HNO_3 according to USEPA 3052), HCl and HNO_3 were used for the total concentration determination to ensure comparability with the Finnish fertilizer regulation [17]. The use

of HCl and HNO_3 has been supported by e.g., Bruder-Hubscher et al. [20].

4. Conclusions

Based on the presented results, the integration of steel, pulp and paper industry solid residues shows promise in acidic soil amendment. In particular, the results for the use of GBFS with pulp and paper industry residues seem encouraging regarding the replacement of commercial fertilizers. However, with the utilization of converter steel slag, elevated total concentrations of Cr and V were detected. The data supports the conclusion that soluble Cr (0.4 mg kg^{-1}, d.w.) occurred as Cr(VI) even though the total concentration of Cr(VI) remained below the limit of detection (<3.0 mg kg^{-1}, d.w.). Additionally, 80.6% of the total concentration of Cr was associated with the residual fraction. In the case of V, 46.0% of the respective total concentration was identified as occurring in the easily reduced fraction, indicating potential bioavailability through e.g., thermodynamic changes in a natural medium.

References

[1] D. Chaudhuri, S. Tripathy, H. Veeresh, M.A. Powell, B.R. Hart, Mobility and bioavailability of selected heavy metals in coal ash- and sewage sludge-amended acid soil, Environ. Geol. 44 (2003) 419–432.
[2] N.S. Bolan, D.C. Adriano, D. Curtin, Soil acidification and liming interactions with nutrient and heavy metal transformation and bioavailability, Adv. Agron. 78 (2003) 215–272.
[3] M. Jordan, E. Rodriguez, Effect of solid residues from the cellulose industry on plant growth, J. Plant Nutr. Soil Sci. 167 (2004) 351–356.
[4] C. Shi, J. Qian, High performance cementing materials from industrial slags – a review, Resour. Conserv. Recycl. 29 (2000) 195–207.
[5] M. Rex, Environmental aspects of the use of iron and steel slags as agricultural lime, in: J. Geiseler, M. Dean (Eds.), Proceedings of the 3rd European Slag Conference, EUROSLAG publication no. 2, Duisburg, 2003, pp. 137–150.
[6] F. Cabral, H.M. Ribeiro, L. Hilário, L. Machado, E. Vasconselos, Use of pulp mill inorganic wastes as alternative liming materials, Bioresour. Technol. 99 (2008) 8294–8298.
[7] M.T. Ali, S.H. Shahram, Converter slag as a liming agent in the amelioration of acidic soils, Int. J. Agric. Biol. 9 (2007) 715–720.
[8] R. Pöykiö, H. Nurmesniemi, Calcium carbonate waste from an integrated pulp and paper mill as a potential liming agent, Environ. Chem. Lett. 6 (2008) 47–51.
[9] C. Ribbing, Environmentally friendly use of non-coal ashes in Sweden, Waste Manage. 27 (2007) 1428–1435.
[10] H. Nurmesniemi, T. Pöykiö, Sequential leaching of heavy metals in fibre clay from a chemical wastewater treatment plant at a paper mill, J. Residuals Sci. Technol. 3 (2006) 25–33.
[11] M. Mahmoudkhani, T. Richards, H. Theliander, Recycling of solid residues to the forest – experimental and theoretical study of the release of sodium from lime mud and green liquor dregs aggregates, Process Saf. Environ. Prot. 82 (2004) 230–237.
[12] L. Augusto, M.R. Bakker, C. Meredieu, Wood ash applications to temperate forest ecosystems–potential benefits and drawbacks, Plant Soil 306 (2008) 181–198.
[13] A. Fuentes, M. Lloréns, J. Sáez, A. Soler, M.I. Aguilar, J.F. Ortuño, V.F. Meseguer, Simple and sequential extractions of heavy metals from different sewage sludges, Chemosphere 54 (2004) 1039–1047.
[14] A. Smeda, W. Zyrcniki, Application of sequential extraction and the ICP-AES method for study of the partitioning of metals in fly ashes, Microchem. J. 72 (2002) 9–16.
[15] H. Nurmesniemi, R. Pöykiö, G. Watkins, O. Dahl, Total and extractable heavy metal, phosphorous and sulfur concentrations in slaker grits from the causticizing process of a pulp mill for use as a soil amendment, Chem. Speciation Bioavail. 22 (2010) 87–97.
[16] T. Kuokkanen, H. Nurmesniemi, R. Pöykiö, K. Kujala, J. Kaakinen, M. Kuokkanen, Chemical and leaching properties of paper mill sludge, Chem. Speciation Bioavail. 20 (2008) 123–134.
[17] Ministry of Agriculture and Forestry, Finland, Statute (12/07) on fertiliser products (in Finnish). Dn:o 656/01/2007. Available at: http://www.finlex.fi/fi/viranomaiset/normi/400001/28518, 2010 (accessed in December 2010).

[18] M. Yli-Halla, J. Palko, Mineral element content of oats (Avena satina L.) in an acid sulphate soil area of Tupos village, Nothern Finland, J. Agric. Sci. Finland 59 (1987) 73–78.

[19] A. Tessier, P.G.C. Campbell, M. Bisson, Sequential extraction procedure for the speciation of particulate trace metals, Anal. Chem. 51 (1979) 844–851.

[20] V. Bruder-Hubscher, F. Lagarde, M.J.F. Leroy, C. Coughanowr, F. Enguehard, Application of a sequential extraction procedure to study the release of elements from municipal solid waste incineration bottom ash, Anal. Chim. Acta 451 (2002) 285–295.

[21] T.G. Kazi, M.K. Jamali, G.H. Kazi, M.B. Arain, H.I. Afridi, A. Siddiqui, Evaluating the mobility of toxic metals in untreated industrial wastewater sludge using a BCR sequential extraction procedure and a leaching test, Anal. Bioanal. Chem. 383 (2005) 297–304.

[22] D. Fandeur, F. Juillot, G. Morin, L. Olivi, A. Cognini, S.M. Webb, J.P. Ambrosi, E. Fritsch, F. Guyot, G.E. Brown Jr., XANES evidence for oxidation of Cr(III) to Cr(VI) by Mn-oxides in a lateritic regolith developed on serpen-tinized ultramafic rocks of New Caledonia, Environ. Sci. Technol. 43 (2009) 7384–7390.

[23] Ministry of Agriculture and Forestry, Finland, Statute on changing the 12/2007 Statute on Fertiliser Products (in Finnish). Dn:o 682/14/2009. Available at: http://www.finlex.fi/fi/viranomaiset/normi/400001/34441, 2010 (accessed in December 2010).

[24] R.J. Vitale, G.R. Mussoline, K.A. Rinehimer, J.C. Petura, B.R. James, Extraction of sparingly soluble chromate from soils: evaluation of methods and E_h-pH effects, Environ. Sci. Technol. 31 (1997) 390–394.

[25] A.V. Filgueiras, I. Lavilla, C. Bendicho, Chemical sequential extraction for metal partitioning in environmental solid samples, J. Environ. Monit. 4 (2002) 823–857.

[26] P. Van Herck, C. Vandecasteele, Evaluation of the use of a sequential extraction procedure for the characterization and treatment of metal containing solid waste, Waste Manage. 21 (2001) 685–694.

[27] C. Shi, Steel slag – its production, processing, characteristics, and cementitious properties, J. Mater. Civil Eng. 16 (2004) 230–236.