Application of a Modified BCR Approach to Investigate the Mobility and Availability of Trace Elements (As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Zn, and Hg) from a Solid Residue Matrix Designed for Soil Amendment

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Abstract—Trace element speciation of an integrated soil amendment matrix was studied with a modified BCR sequential extraction procedure. The analysis included pseudo-total concentration determinations according to USEPA 3051A and relevant physicochemical properties by standardized methods. Based on the results, the soil amendment matrix possessed neutralization capacity comparable to commercial fertilizers. Additionally, the pseudo-total concentrations of all trace elements included in the Finnish regulation for agricultural fertilizers were lower than the respective statutory limit values. According to chemical speciation, the lability of trace elements increased in the following order: Hg < Cr < Co < Cu < As < Zn < Ni < Pb < Cd < V < Mo < Ba. The validity of the BCR approach as a tool for chemical speciation was confirmed by the additional acid digestion phase. Recovery of trace elements during the procedure assured the validity of the approach and indicated good quality of the analytical work.

Keywords—BCR, bioavailability, trace element, industrial residue, sequential extraction

I. INTRODUCTION

SEQUENTIAL extraction procedures are increasingly applied to attain information on the mobility and bioavailability of trace elements. The use of sequential extraction relies on the ability to provide detailed information of the origin, mode of occurrence, biological and physicochemical availability, mobilization and transport of trace elements [1]. As opposed to sequential extraction, total concentration determinations are

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widely used by e.g. legislative authorities. However, total concentration as a single basis for environmental impact assessment is clearly insufficient and has been widely questioned [1]-[4].

Chemical speciation refers to the concept of identifying and quantifying different species, forms or phases present in a certain material. In operationally defined fractionation, the species are generally classified on the basis of used reagents [4]. As a method for chemical speciation, sequential extraction procedures apply each successive reagent in order of increasing reactivity which thus correspond to association forms of decreased mobility [1].

The use of sequential extraction procedures began as early as in the 1970's, with the five-stage sequential test proposed by Tessier *et al.* [2]. However, as a large number of different procedures can be found from the literature, most of which are variants of the original Tessier *et al.* procedure, no specific approach has been fully accepted by the scientific community [4]-[5]. Consequently the Community Bureau of Reference (BCR), now the Standards, Measurements and Testing Programme of the European Commission, proposed a three-stage BCR extraction scheme in 1993 as an attempt to harmonize and standardize extraction methodology.The BCR procedure consist of the exchangeable i.e. acid-soluble (CH3COOH), easily reduced (NH_2 OH•HCl) and oxidizable (H_2O_2 + $CH3COONH_4$) fraction determinations and has been widely applied for e.g. sludges, fly ashes and other industrial wastes [5]-[7]. In this paper, a modified BCR procedure was applied to investigate the mobility and bioavailability of As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Zn and Hg from an integrated industrial residue matrix designed for soil amendment. In addition to the three-stages of the original BCR procedure, a residual fraction determination by microwave digestion with a mixture of HCl and HNO_3 according to USEPA 3051A [8] was performed subsequent the third extraction stage as an attempt to validate the procedure.

Pseudo-total concentrations of the respective trace elements were also determined from the base samples according to USEPA method 3051A [8], in which the dried sample is

digested in a microwave oven with a mixture of HCl (3 mL) and HNO$_3$ (9 mL). Although more aggressive extractant mixtures for the complete dissolution of the respective mineral lattice do exist (e.g. USEPA method 3052 [9], where HF and HNO$_3$ are used with microwave digestion), USEPA 3051A was adopted to enable comparison with the Finnish statutory limit values set for the use of e.g. ash fertilizers in agriculture and forestry. Additionally, relevant physicochemical properties were determined with standardized procedures. The aim of this paper is to discuss the bioavailability of trace elements with respect to the statutory limit values set for the use of agricultural and forest fertilizers and the functionality of the modified BCR approach as a tool for chemical speciation.

II. MATERIALS AND METHODS

Manufacturing procedure for the amendment matrix was adopted from conventional cement testing practices and comprised of mixing of individual elements, subsequent water addition and molding to pellet dimensions of app. 25 mm × 35 mm (width × height). Relative mixture ratios of the amendment concept are illustrated in Table I. A more detailed description of the background, individual residue characteristics and the manufacturing method is described elsewhere. Prior to analysis the soil amendment matrix was ground with a jaw crusher to a particle size (< 2 mm) suitable for laboratory analysis.

A. Determination of Relevant Physicochemical Properties

The determination of pH was performed at a solid to liquid (i.e. ultrapure water) -ratio of 1:5 (v/v) according to European standard SFS-EN 13037 [10] and electrical conductivity (EC)

TABLE I
COMPOSITION OF THE SOIL AMENDMENT MATRIX

Component	Amendment matrix
Binder	SLS^a 0.15, fly ash 0.15
Alkali	paper mill sludge 0.25,
aggregate	lime waste 0.45

Individual component quantities expressed in mass fractions prior to water addition (water/binder -ratio 1.00).
^{a}SLS = steel ladle slag.

at a solid to liquid -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 amendment matrix were carried out according to European standards SFS-EN 12879 [11], SFS-EN 13137 [12] and International standard SFS-ISO 11465 [13] respectively. Additionally, neutralizing (NV) and reactivity (RV) values were analyzed according to European standards SFS-EN 12945 [14] and SFS-EN 13971 [15] respectively.

B. Determination of Pseudo-Total Element Concentrations

For the determination of the pseudo-total element concentrations of As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Zn and

Hg, the ground and dried amendment sample was 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) according to USEPA method 3051A [8]. The cooled solution was transferred to a 100 mL volumetric flask and subsequently diluted to volume with ultrapure H$_2$O.

Except for Hg, total element concentrations of individual trace elements from the solution were determined with a Thermo Fisher Scientific iCAP6500 Duo (Thermo Fisher Scientific Inc., United Kingdom) inductively coupled plasma optical emission spectrometer (ICP-OES) equipped with a Cetac ASX-520 (CETAC Technologies, USA) autosampler. 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.

C. Chemical Speciation by Sequential Extraction

For the determination of trace element availability, a modified four-stage sequential BCR procedure was used. The original BCR procedure (for relevant nomenclature see [16]) is basically a modified and stripped-down version of the five-stage sequential extraction procedure originally proposed by Tessier *et al.* [2]. Additional descriptions of the procedure can be found from relevant literature, e.g. [3].

In the applied modified four-stage BCR procedure, an additional residual fraction determination by microwave digestion with a mixture of HCl and HNO$_3$ according to USEPA 3051A [8] was added subsequent to the third extraction stage as an attempt to validate the procedure. The four fractions of the procedure can be described as follows [1]-[2]:

1) The exchangeable (i.e. acid-soluble) fraction. Represents weakly adsorbed elements retained on the solid surface by relatively weak electrostatic interaction, elements that can be released by ion-exchange processes and elements that can be coprecipitated with carbonates. Most readily available from the environmental point of view.
2) The easily reduced fraction. Simulates anoxic conditions likely to occur in a natural medium and elements that are thermodynamically unstable and potentially bioavailable. Usually consists of oxides of Mn and Fe, the well-known sinks for trace elements in a surface environment.
3) The oxidizable fraction. Represents elements that are organically bound or occur as oxidizable minerals, e.g. sulphides. Not considered to be very mobile or bioavailable.
4) The residual fraction. Consists of primary and secondary minerals, in which elements are associated with the mineral lattice. Often referred to as the inert phase representing elements not likely to dissolve in conditions found in nature and thus a worst case environmental scenario regarding element mobilization.

1) The exchangeable (i.e. acid soluble) fraction

40 mL of acetic acid (CH$_3$COOH), concentration 0.1 mol·L$^-$

2) The easily reduced fraction

During the second phase 40 mL of hydroxylammonium chloride (NH$_2$OH·HCl), concentration 0.1 mol·L^{-1} and adjusted to pH 2.0 with HNO$_3$, was admixed with the residue from the previous phase in a 100 mL polypropylene flask. The extraction procedure was then performed as described above.

3) The oxidizable fraction

During the third phase 10 mL of 30% hydrogen peroxide (H$_2$O$_2$) was admixed with the residue from the previous phase in a 100 mL glass container. The container was covered and evaporated by heating the mixture in 85 ^{0} C for 1h. Subsequently, the treatment with H2O2 was repeated with a new aliquot. After cooling, 50 mL of ammonium acetate (CH$_3$COONH$_4$), in concentration 1 mol·L^{-1} and adjusted to pH 2.0 with HNO$_3$, was admixed with the residue. The extraction procedure was then performed as described above.

4) The residual fraction

The residue was 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 [8]. The cooled solution was transferred to a 100 mL volumetric flask and subsequently diluted to volume with ultrapure H$_2$O. Element concentrations of each of the extracts from successive phases were determined with a Thermo Fisher Scientific iCAP6500 Duo (Thermo Fisher Scientific Inc., United Kingdom) inductively coupled plasma optical emission spectrometer (ICP-OES) equipped with a Cetac ASX-520 (CETAC Technologies, USA) autosampler.

It must be noted that e.g. Tessier *et al.* [2] applied a mixture of HF-HClO$_4$ in residual digestion to assure complete dissolution of the residual fraction. In this investigation, a mixture of HCl and HNO$_3$ was used to enable procedure validation with the determined pseudo-total concentrations and comparison with the Finnish statutory limit values for e.g. ash fertilizers used in agriculture or forestry [17].

III. RESULTS AND DISCUSSION

A. Physicochemical Properties

As illustrated in Table II, the amendment matrix attested to a high pH value (12.1) indicating liming and buffering capacity. According to the EC value (11.2 ms·cm^{-1}), the leaching solution of the amendment matrix had a very low ionic strength, suggesting that only a minor part of the dissolved elements occurred as dissolved basic element salts. In this case, the low basic element salt concentration of the leaching solution is likely due to the ability of the binder materials, i.e. steel ladle slag and fly ash, to form mineral structures entailing a majority of elements otherwise appearing as element salts.

The LOI (0.7%, d.w.) and TOC (5.0 g·kg^{-1}, d.w.) values of the amendment matrix were relatively low suggesting that the organic matter content was low. Paper mill sludge used as reactive aggregate (see Table I) is the only constituent with substantial organic content (LOI 35.5%, d.w. [18]), and thus has an increasing effect in the LOI and TOC values. In this case, the low organic content is favourable as certain constituents of the amendment matrix are expected to contain high concentrations of potentially detrimental trace elements. Respectively, organic matter could form complexes with these trace elements. Once applied to natural environment, the degradation of organic matter content under oxidizing conditions could lead to the release of complexed trace elements [19].

The NV and RV of the amendment matrix were attested as very high. NV and RV are routinely used to evaluate the capacity and effectiveness of an amendment concept to neutralize soil acidity, thus depending on the content of soluble and hydrolysable bases. These bases generally occur as oxides, hydroxides, carbonates and silicates as cations such as Ca, Mg and K are the interactive counter-ions [7].

TABLE II
RELEVANT PHYSICOCHEMICAL PROPERTIES OF THE AMENDMENT MATRIX

Parameter	Unit	Amendment matrix
pH	-	12.1
Electrical conductivity	mS·cm^{-1}	11.2
LOI (loss on ignition, 550°C)	% (d.w.)	0.7
TOC (total organic carbon)	g·kg^{-1} (d.w.)	5.0
Dry matter content (105°C)	%	97.8
Neutralizing value (NV)	% (Ca-eq., d.w.)	39.5
Reactivity value (RV)	% (Ca-eq., d.w.)	35.6

d.w. = dry weight.

Reference [7] shows that the NV of a commercial ground limestone soil ameliorant is 38% (Ca-equivalents, d.w.). Hence, based on the NV, application the amendment matrix would result in a comparatively more effective neutralization of soil acidity.

B. Pseudo-Total Element Concentrations and Chemical Speciation

1) Pseudo-Total Concentrations

The pseudo-total trace element concentrations (HCl + HNO$_3$ [8]) of the amendment matrix and trace element fractionation according to the modified BCR sequential extraction procedure are presented in Table III. Additionally, trace element recovery percentages according to the individual sequential extraction fractions with respect to the pseudo-total concentration have also been provided.

TABLE III
PSEUDO-TOTAL CONCENTRATIONS (MG·KG[-1], D.W., USEPA 3051A) OF THE AMENDMENT MATRIX

Element	CH$_3$COOH	NH$_2$OH·HCl	H$_2$O$_2$+ CH$_3$COONH$_4$	HCl+HNO$_3$, residual	HCl+HNO$_3$, pseudo-total	Recovery[a] (%)
As	<0.6	<0.6	1.8	1.9	3.7	100.0
Ba	76	20.4	130	34.1	280	93.0
Cd	<0.08	<0.08	0.61	0.19	0.8	100.0
Co	<0.2	<0.2	0.5	0.7	1.0	120.0
Cr	<0.4	<0.4	20.2	73.4	94	99.6
Cu	<0.4	<0.4	7.3	8.5	15.8	100.0
Mo	<0.2	0.33	<0.25	0.65	1.3	75.4
Ni	<0.2	<0.2	7.0	6.7	15	91.3
Pb	<0.6	<0.6	4.2	3.5	7.6	101.3
V	<0.4	24.8	47.5	151	240	93.0
Zn	<0.4	<0.4	25.4	26.2	53.5	96.4
Hg	<0.02	<0.02	<0.025	<0.05	0.042	-

[a]Recovery = (the sum of four fractions expressed as a percentage of the independent pseudo-total concentration) . Individual recoveries attested as below limit of detection were excluded.

As can be noted from the pseudo-total concentration data, trace element concentrations of the amendment matrix were all lower than the respective Finnish statutory limit values set for the use of e.g. ash fertilizers in agriculture. According the Statute on fertilizer products [17], the following threshold limit values have been set in Finland for the use of e.g. biomass derived ash as an agricultural fertilizer (mg·kg^{-1}, d.w.): As 25; Cd 1.5; Cr 300; Cu 600; Pb 100; Ni 100; Zn 1,500; and Hg 1.0. Consequently, no limit values for the total concentrations of Ba, Co, Mo and V exist in the Finnish regulation regarding the use of agricultural or forest fertilizers. On the basis of pseudo-total concentrations and the Finnish Statute on fertilizer products by the Ministry of Agriculture and Forestry, no constraints for the utilization of the amendment concept as an agricultural fertilizer thus exist.

2) The Modified BCR Procedure

Chemical speciation of the elements based on the modified BCR procedure is illustrated in Figs. 1 and 2[1]. Based on the data, Ba, Mo and V were the most labile elements of the amendment concept. In the case of Ba (Fig. 1), recovery was dominated by the oxidisable fraction (46%) followed the exchangeable fraction (27%). The oxidisable fraction is generally considered to consist of stable high molecular weight compounds possible releasing small amounts of trace elements during extended time frames [20]. It is thus not considered to be very mobile or bioavailable, but could be released through the decomposition of e.g. organic matter. The acid-soluble fraction, however, is approximately equivalent to the sum of water-soluble, exchangeable and carbonate-bound fractions and is the most active, mobile and available phase of an element [21]. Ba recovery in this fraction was 76 mg·kg^{-1} (d.w.) amounting to a considerable 27% of the pseudo-total concentration of the element.

Reference [22] states that Ba is an ubiquitous element with a background concentration of 100-3000 mg·kg^{-1} (d.w.) in natural soils. However, ingestion of Ba in soluble forms is considered highly toxic for animals and human beings [22]. Although the pseudo-total concentration of Ba was attested as rather low (280 mg·kg^{-1}, d.w.), a high recovered proportion in the acid-soluble fraction suggests Ba phytoavailability and the need for further investigation regarding plant contamination in the case of agricultural fertilization.
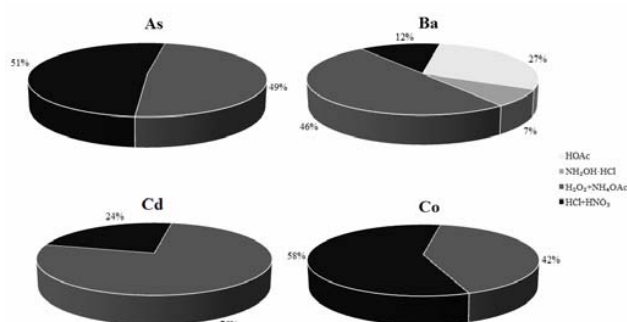

Fig. 1 Chemical speciation of As, Ba, Cd and Co of the amendment matrix according to the modified BCR procedure.

Mo showed considerable availability in the easily reduced fraction by a recovery of 0.33 mg·kg^{-1} (d.w.) amounting to 25% of the respective pseudo-total concentration. The easily reduced fraction can be considered as a poorly labile fraction [21] consisting of elements available by e.g. thermodynamic changes in a natural medium. Although a recovery of 0.33 mg·kg^{-1} (d.w.) in the poorly labile fraction indicates potential bioavailability, the low pseudo-total concentration (1.3 mg·kg^{-1}, d.w.) and the fact that 50% of the pseudo-total concentration was recovered in the residual fraction (Fig. 2), indicate that Mo availability is not major concern regarding the use of the amendment concept in fertilization.

In addition to Mo, V attested availability in the easily reduced fraction with a recovery of 24.8 mg·kg^{-1} (d.w.) amounting to approximately 10% (Fig. 2) of the respective pseudo-total concentration. However, considering the rather low pseudo-total concentration of V (240 mg·kg^{-1}, d.w.) and that a majority of V (63%) occurred in the residual fraction, V

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[1] Percentage calculation is based on pseudo-total concentrations, except in the case of Co and Pb where recovery amounted to > 100%. With Co and Pb, calculation is based on the sum of fraction recoveries.

availability does not seem to restrict utilization as an agricultural fertilizer. Co was attested available only in the oxidisable fraction (0.5 mg·kg^{-1}, d.w.) with a respective recovery of 42% regarding the pseudo-total concentration. The remaining 58% of Co was associated with the residual fraction.
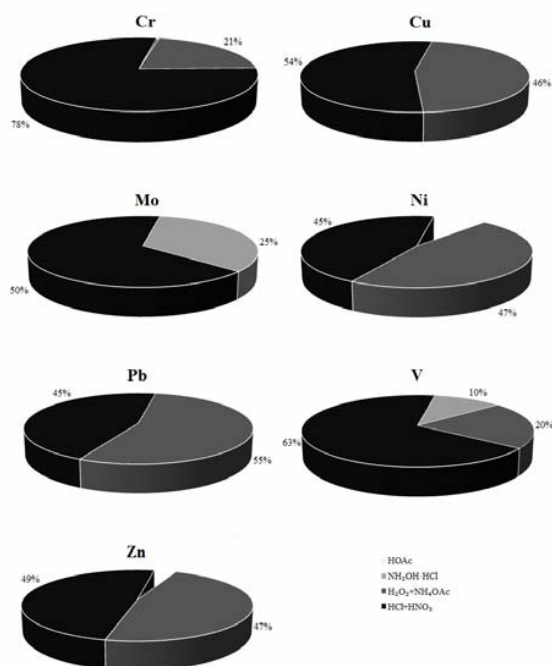

Fig. 2 Chemical speciation of Cr, Cu, Mo and Ni of the amendment matrix according to the modified BCR procedure

In the case of trace elements included in the Finnish fertilizer regulation, association was mainly dominated by recoveries in the residual fraction (expressed in d.w.): As 1.9 mg·kg^{-1} (51%); Cr 73.4 mg·kg^{-1} (78%); Cu 8.5 mg·kg^{-1} (54%); and Zn 26.2 mg·kg^{-1} (49%). With Cd, Ni and Pb, occurrence was mostly associated with the oxidizable fraction with respective recoveries of (expressed in d.w.): 0.61 mg·kg^{-1} (76%); 7.0 mg·kg^{-1} (47%); and 4.2 mg·kg^{-1} (55%). The physical interpretation of the oxidizable fraction as truly an indication of organic matter has been questioned [23]. In our case, high recoveries in the oxidisable fraction are most likely related to oxidizable minerals such as sulphides (LOI value 0.7%, d.w., as shown in Table II).

During the oxidizable fraction determination of sequential extraction procedures, CH$_3$COONH$_4$ is generally used subsequent to H$_2$O$_2$ to prevent element readsorption to the residual fraction [1]-[2]. Especially with materials generated in the aggressive conditions of high temperature processes, such as fly ashes and metallurgical slags, target elements could be more strongly bound to specific phases (e.g. sulphides) and could require stronger extractants than H$_2$O$_2$

compared to various other samples investigated by sequential extraction procedures (e.g. sediments and sludges). This could lead to underestimations regarding the occurrence of sulphide phases. The use of stronger reagents with enhanced selectivity in dissolving sulphides, such as HNO$_3$, however could endanger the dissolution of additional silicate phases generally regarded as occurring in the residual fraction [1]. However, based on the data provided by the modified BCR approach, the quantities and distribution of As, Cd, Cr, Cu, Ni, Pb, Zn and Hg does not suggest bioavailability in conditions normally found in nature.

3) Validity of The Modified BCR Procedure

As illustrated in Table III, the recovery of elements included in the BCR procedure generally ranged from 91.3% to 101.3% indicating good quality of the analytical work and validity of the procedure. Only in the case of Co and Mo, could the procedure be questioned with recoveries of 120.0% and 75.4%, respectively. The aforementioned divergences are most likely associated with the low pseudo-total concentrations of the elements leading to individual recoveries below the limit of detection during the procedure. For this same reason Hg was excluded from Figs. 1 and 2 and from the recovery percentage calculation presented Table III.

IV. CONCLUSIONS

Based on the presented data, application of the soil amendment matrix would result in soil acidity neutralization comparable to commercial fertilizers. Additionally, all elements included in the Finnish regulation for agricultural fertilizers attested to pseudo-total concentrations lower than the respective statutory limit values. Based on the modified BCR procedure, the mobility of trace elements increased in the following order: Hg < Cr < Co < Cu < As < Zn < Ni < Pb < Cd < V < Mo < Ba. Only Ba was considerably labile in the acid-soluble fraction (76 mg·kg^{-1}, d.w., by CH$_3$COOH), amounting to a recovery of 27% of the respective pseudo-total concentration, thus indicating potential bioavailability. The validity of the BCR procedure as a tool for chemical speciation was confirmed by an additional acid digestion subsequent to the procedure. Recovery of the studied trace elements during the procedure indicated good quality of the analytical work and assured the validity of the BCR procedure.

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