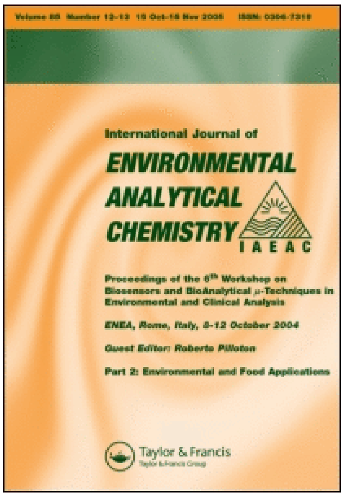

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Sequential extraction partitioning of metals, sulfur, and phosphorus in bottom ash from a coal-fired power plant

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Sequential extraction partitioning of metals, sulfur, and phosphorus in bottom ash from a coal-fired power plant

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A five-stage sequential extraction procedure was used to determine the partitioning of 16 metals (Cd, Cr, Cu, Mo, Pb, Zn, As, Co, V, Ni, Ba, Al, Be, Fe, Mn, and Ti), sulfur (S), and phosphorus (P) in bottom ash from a coal-fired power plant of Fortum Power and Heat Oy Inkoo Power Plant in southern Finland, into the following fractions: (1) water-soluble fraction (H_2O), (2) exchangeable fraction (CH_3COOH), (3) easily reduced fraction ($NH_2OH–HCl$), (4) oxidizable fraction ($H_2O_2 + CH_3COONH_4$), and (5) residual fraction ($HF + HNO_3 + HCl$). Although the metals were extractable in all fractions, the highest concentrations of most of the metals occurred in the residual fraction. Although, from the utilization point of view, the total element concentrations in the bottom ash were lower than the current Finnish limit values for fertilizers used in agriculture and in forestry, the partitioning study helps to evaluate the extractability efficiency of different elements. The knowledge of extractability of elements is important if inorganic materials and by-products, e.g. waste, are utilized.

Keywords: Ash; Bioavailability; Coal; Extraction; Leaching

1. Introduction

Coal is the most abundant and widely spread fossil fuel energy resource in the world. In Finland, the use of coal has significance especially in southern Finland and on the coast, where there are no peat resources. However, the incineration of coal produces a considerable amount of ash, which is usually disposed of in landfills. It is estimated that, in Finland alone, the incineration of coal for energy (i.e. heat and electricity) produces about 900,000 tonnes of bottom and fly ash per year. However, the rise in the costs of landfill waste disposal and introduction of regulations designed to conserve the environment have added to the problems of acquiring new sites for disposal. Therefore, alternatives to disposal are being investigated, and there is a growing trend

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towards the utilization of waste and industrial by-products in the Finnish industry and energy production.

In Finland, the properties of solid waste, especially when they are utilized or taken to a landfill, have to be known. Coal contains significant quantities of various inorganic nutrients, as well as heavy metals, and during combustion, its mineral matter undergoes a series of physical and chemical changes. As a result, most of the inorganic nutrients and heavy metals in coal are retained in the ash [1]. The total elemental concentrations represent a source term only for the unrealistic environmental scenario in which the entire mineral structure of the solid material is dissolved. Thus, measurement of the total concentration of metals provides relatively misleading information for assessing the bioavailability and mobility of metals. In order to estimate the real bioavailability of metals and their potential toxicity, it is necessary to determine not only the total concentrations but also the different chemical forms or processes binding the heavy metals to the solid phase of the sample [2].

Extraction is a procedure that brings solids and liquids into contact with each other under defined conditions. Extraction tests are widely used as tools to estimate the release potential of constituents from waste materials over a range of possible waste-management activities, including recycling or reuse, for assessing the efficacy of waste-treatment processes, and after disposal [3]. Sequential extraction tests are designed to treat the material with different solutions, resulting in the allocation of constituents into separate fractions. Such an approach provides information on which chemical conditions are needed to obtain different extraction efficiencies. Extraction is a procedure that is widely applied for the partitioning of elements from various environmental samples such as soil, sediment, airborne particulate matter, sludge, waste, etc., and has become a common term in the environmental analytical field [4]. Extraction does not necessarily mean total decomposition, and the extractable recoveries of analytes are generally lower than the total concentrations. Recoveries can reach the total values only if an element is completely soluble in the extraction solvent. Extraction studies are carried out in the assessment of worst-case environmental scenarios, in which the components of the sample become soluble and mobile [5].

Although the separation of different chemical forms of heavy metals is a very time-consuming and demanding task, the use of a sequential extraction partitioning does provide important information. Therefore, several sequential extraction schemes have been developed to predict the partitioning of metals between different fractions. Most of them mimic the basic method initially developed by Tessier *et al.* [6]. They used the procedure to partition metals into the following fractions: (1) exchangeable fraction, representing the most easily available metals, (2) acid-soluble (carbonate bound) fraction, (3) reducible (Fe–Mn oxide bound) fraction, (4) oxidizable (organically + sulfide bound) fraction, and (5) residual fraction, which is tightly bound to the silicate matrix of the sample. If heavy metals exist as loosely bound fractions, such as the soluble or exchangeable fraction, then they tend to be readily mobile and dispersed, whereas metals associated with the silicate matrix are not easily separated or mobilized [7].

Bioavailability is a measure of the environmental mobility of elements. The loosely bound fractions, e.g. the water-soluble fraction and the fraction extractable with ammonium acetate or acetic acid, are much more environmentally mobile than those associated with the silicate structure, i.e. extractable with a mixture of strong mineral acids. Thus, the loosely bound fractions are most likely to be released into aqueous solutions and are thus potentially bioavailable [4].

2. Background

2.1 *Review of the sequential leaching for element partitioning in solid samples*

When the sequential leaching procedure is applied for the partitioning of heavy metals in environmental samples (e.g. ash, sludge, sediment, soil, etc.), the ability of different leaching agents to release metal ions depends on their association with specific fractions in the sample. Extractants like electrolytes, weak acids, and chelating agents release metals from coordination sites, while strong acids and redox agents are capable of releasing additional quantities of metals as a result of the decomposition of the solid matrix [4, 8].

The metals extracted in the water-soluble fraction (H_2O) are relatively mobile and thus may be readily leachable (extractable) and potentially bioavailable. In water extraction, the driving forces influencing the partial dissolution of matrix components are solubility, the diffusion rate of the element forming part of the matrix, and the wash-off of compounds on the surface of the matrix. This fraction consists of the metals that are easily soluble, e.g. in the form of chlorides and sulfates [9]. It is also the most readily available metal fraction from the point of view of the environment, and thus the leaching of metals in this fraction is a major environmental concern [4].

The exchangeable fraction, that is extractable with CH_3COOH, gives an indication of the amount of metals bound on the surface of the particles, as well as metals that are released as acid-soluble salts such as carbonates. Some of the Fe and Mn oxides and hydroxides are also dissolved in this stage [4, 9]. This fraction is bioavailable and corresponds to the form of metals that are most available for plant uptake, and can be released by merely changing the ionic strength of the medium. This fraction includes metals that are absorbed on the solid surface by relatively weak electrostatic interaction, metals that can be released by ion-exchange processes, and metals which are precipitated or co-precipitated with carbonates [4]. The elevated concentrations of elements in this fraction may be due to the complexing ability of the mono-dentated organic ligands, such as those formed with acetate (i.e. acetic acid) used as an extractant in this stage [10]. The use of acetic acid as extractant emulates the organic acids produced from decomposing waste in anaerobic environments such as landfill, since, in the acetogenesis phase during the anaerobic degradation of organic matter, carboxylic acids (e.g. acetic acid), volatile fatty acids and ethanol are produced and transformed into acetate, carbon dioxide, and hydrogen by acidogeneous bacteria [10]. According to Svensson *et al.* [11], acetic acid is a realistic choice to emulate a plausible worst-case scenario for the co-disposal of waste materials with municipal solid waste.

The easily reduced fraction, that is extractable with $NH_2OH–HCl$, usually consists of oxides of manganese and iron that are extracted together. The use of hydroxylamine hydrochloride as extractant in this fraction influences the complexation of metals with chloride. Hydroxylamine hydrochloride is a strong reducing agent, and its use simulates anoxic conditions that are likely to occur in a natural medium [12]. The Fe and Mn oxides act as a cement or are present as nodules between the particles or coating them. The elements are strongly bound to these oxides but are thermodynamically unstable in anoxic conditions [13]. The metals in this fraction can be mobilized with increasing reducing or oxidizing conditions in the environment. This means that the metals in this fraction are potentially bioavailable.

The oxidizable fraction, in which the combination of H_2O_2/NH_4OAc is used, corresponds to metals that are organically bound or occur as oxidizable minerals, e.g. sulfides. This fraction usually also corresponds to organically bound metals. As metals bound to this fraction can be released under oxidizing conditions, an oxidation process is usually applied to leach out metals associated with the above-mentioned phases [4]. The hydrogen peroxide (H_2O_2), which is used as an oxidizing reagent in this fraction, is a strong oxidant ($E^\circ = 1.77\,V$). In general, hydrogen peroxide applied to a heated medium (e.g. 85°C) is the reagent preferred for dissolving organic matter as a compromise between the complete degradation of organic matter and the minimum alteration of silicates; heating promotes the oxidation process. Besides the extraction of cations by ammonium ions, partial removal of some elements may occur due to complexation with acetate anions [14].

The residual fraction, in which the combination of $HF + HNO_3 + HCl$ is used, is the non-mobile fraction and is potentially the least harmful. The metals associated with this fraction are retained within the crystal lattice of minerals and inside crystallized odixes, can only be mobilized as a result of weathering, and therefore have only very long-term effects [4]. From the environmental point of view, the mineral acid mixture of $HF + HNO_3 + HCl$ used in extraction stage 5 can never be found in nature. Although fraction 5 can be dissolved in laboratory conditions, this fraction is not likely to be dissolved under the conditions normally found in nature, and it is therefore called the inert phase. Thus, this fraction is an assessment of the worst-case environmental scenario in which all the components of the waste material become soluble and mobile [4, 5].

2.2 *Aims of the study*

The main purpose of this study was to obtain information about the physical and chemical properties (i.e. plant nutrient concentrations, loss on ignition, dry matter content, neutralizing and reactivity values, pH, and electrical conductivity), as well as the partitioning and extractability of 16 metals (Cd, Cr, Cu, Mo, Pb, Zn, As, Co, V, Ni, Ba, Al, Be, Fe, Mn, and Ti), sulfur (S), and phosphorus (P) in bottom ash originating from the 660 MW coal-fired power plant of Fortum Power and Heat Oy Inkoo Power Plant located in southern Finland. In Finland, the properties of solid wastes and industrial by-products, especially when they are utilized or taken to a landfill, have to be investigated. The general principle applied in utilization and in landfill approval is that the composition and extractability of the waste have to be known.

This study is a part of a major project in which the sequential extraction procedure is used for assessing the metal partitioning in different types of waste, such as fly ash originating from a fluidized bed co-combustion boiler (i.e. peat and wood) of a pulp and article mill complex [15], and wood ash originating from a grate-fired boiler at a small municipal district heating plant [16].

3. Experimental

3.1 *Sampling*

The bottom ash investigated in this study was obtained from the coal-fired power plant (660 MW) of the Fortum Power and Heat Oy Inkoo Power Plant which uses the pulverization technique for the incineration of coal. The incineration temperature in the combustion chamber is ca. 1000–1400°C. The bottom ash was sampled from the heap of the bottom ash, in which the bottom ash is collected. The sampling period represented normal process conditions for the plant. A coning and quartering method was applied repeatedly to reduce the wet ash sample to a size suitable for the laboratory analysis. After sampling, the sample was stored in a polyethylene bottle in a refrigerator (+4°C) until analysis.

3.2 *Determination of the physical and chemical properties*

The pH and electrical conductivity (EC) of the bottom ash was determined by a combination pH/EC analyser equipped with a Thermo Orion Sure Flow pH electrode (Turnhout, Belgium), and a Phoenix conductivity electrode with a cell constant of 1.0. pH and EC was determined at a solid : liquid (S/L) ratio of 1 : 2.5 (v/v).

Determination of the dry-matter content of the bottom ash was carried out according to the European standard [17], in which a sample is dried overnight to a constant mass in an oven at 105°C. The organic-matter content, expressed as the loss-on-ignition (LOI), was determined according to the European standard [18], in which an oven-dried (105°C) sample is dry-digested overnight in a muffle furnace (Box Furnace, Lindberg, Blue M, Asheville, NC) at 550°C. Determination of the total organic carbon (TOC) content in the ash was carried out according to the European standard [19] using a Leco CHN-600 analyser (Leco, St. Joseph, MI), in which a sample is combusted, and the evaluated carbon dioxide is measured by infrared spectrometry.

The neutralizing (liming effect) and reactivity values were determined according to the SFS-EN 12945 standard [20] and SFS-EN 13971 standard [21], respectively. In the determination of the neutralizing value, the dried sample was dissolved in a specific quantity of a standard hydrochloric acid solution. Determination of the excess acid was carried out by titration with a standard sodium hydroxide solution. Determination of the reactivity value is based on the decomposition of carbonates with acid.

3.3 *Determination of the nutrient (P, Ca, Na, K, S, Mg, Cu, and Zn) concentrations in ash*

The determination of easily soluble nutrients such as P, Ca, Na, K, S, Mg, Cu, and Zn in bottom ash was carried out according to the procedure of MTT Agrifood Research Finland [22]. Before the nutrient determination on the bottom ash, the sample was dried overnight to a constant mass at 105°C in a drying oven (Termaks) according to the European standard [17].

Easily soluble P, Ca, Na, K, S, and Mg were extracted with 0.5 M acidic ammonium acetate (pH 4.65). In the extraction of Cu and Zn, the acidic (pH 4.65) ammonium acetate extract contained 0.02 M ethylenediaminetetra-acetic acid disodium salt (Na_2EDTA).

Ammonium acetate extraction is widely used as an indicator of nutrient availability, but it does not give the total concentrations of elements in environmental samples such as waste, sludge or soil [23]. In both extraction procedures, one volume part of dry sample (i.e. ash) was shaken with 10 parts of extraction solution for 1 h. Before analysis, the extract was separated from the solid residue by filtration through a Schleicher & Schuell 589 blue ribbon filter article (12.5-mm diameter).

The concentration of P in the extract was determined spectrophotometrically by the Molybdenum Blue method [24] using an automatic Foss–Tecator FIAStar 5000 flow-injection analyser (Högnes, Sweden). The concentrations of Ca, Na, K, S, and Mg were determined by inductively coupled plasma optical emission spectrometer (ICP/OES, Thermo Elemental Iris Intrepid II XDL, Franklin, MA), and the concentrations of Cu and Zn by flame atomic absorption spectrometer (FAAS, Perkin-Elmer Aanalyst 700, Norwalk, CT).

3.4 *Determination of the total element concentrations in ash*

For the determination of total element concentrations (Cd, Cu, Pb, Cr, Mo, Zn, As, Co, V, Ni, Ba, Al, Be, Fe, Mn, Ti, S, Ca, Mg, K, P, Hg) in the bottom ash, the dried sample was decomposed (digested) with a mixture of HF (3 mL) and HNO_3 (9 mL) in a CEM Mars 5 microprocessor controlled microwave oven with CEM HP 500 Teflon vessels (CEM, Matthews, NC) using US EPA method 3052 [25]. After cooling the digestion vessels, 5 mL of H_3BO_3 (27.5 g/500 mL) was added and the mixture heated for 7 min in the microwave oven. The cooled solutions were transferred to 100-mL volumetric flasks, and the solutions diluted to volume with ultrapure water. The ultrapure water was generated by an Elgastat Prima reserve osmosis and Elgastat Maxima ion-exchange water-purification system. All reagents and acids were suprapure or pro-analysis quality.

Except for Hg, the total element concentrations in the ash samples were determined with a Thermo Elemental IRIS Intrepid II XDL Duo inductively coupled plasma optical emission spectrometer. The concentration of Hg in the ash was determined with a Perkin-Elmer Aanalyst 700 cold-vapour atomic absorption spectrometry equipped with a Perkin-Elmer FIAS 400 and AS 90plus autosampler.

3.5 *Sequential extraction procedure and element determinations in the extracts*

For the partitioning of metals, sulfur and phosphorus between the water-soluble (H_2O), exchangeable (CH_3COOH), easily reduced ($HONH_3Cl$), oxidizable ($H_2O_2 + CH_3COONH_4$) and residual fractions ($HF + HNO_3 + HCl$), we used the five-stage sequential leaching procedure given in table 1. In this context, it is worth noting that leaching stages 2–4 of the procedure follow the protocol proposed by the Standard, Measurements and Testing Program (formerly BCR Program) of the European Commission [4, 26, 27]. The BCR procedure has been widely applied for heavy-metal fractionation in various matrices, e.g. ash, soil, sediment, and sludge [4, 13].

However, in the first stage (i.e. extraction stage 1), we estimated the extraction of elements in ultrapure distilled water acidified with HNO_3 (pH 4.0). Water extraction is recommended as the first step before the BCR procedure because the extraction of water-soluble species yields very important information required in evaluating the risk

Table 1. Sequential extraction procedure for element partitioning in bottom ash from a coal-fired power plant.

Stage	Fraction	Reagents/1 g of sample	Shaking time and temperature
1	Water-soluble	40 mL H_2O (pH = 4.0)	16 h at 25°C
2	Exchangeable	40 mL 0.1 M CH_3COOH (pH = 2.9)	16 h at 25°C
3	Easily reduced	40 mL 0.1 M $NH_2OH{\cdot}HCl$ (pH = 2.0)	16 h at 25°C
4	Oxidizable	10 mL 30% H_2O_2 (evaporation)	1 h at 85°C
		+10 mL 30% H_2O_2 (evaporation)	1 h at 85°C
		+50 mL 1 M CH_3COONH_4 (pH = 2.0)	16 h at 25°C
5	Residual	20 mL HF (evaporation)	8 h at 90°C
		+20 mL HF + 20 mL 65% HNO_3	6 h at 25°C
		+20 mL 30% HCl	6 h at 25°C

of environmental pollution by dumping waste since, in nature, water is an important vector of harmful compounds into the environment [4, 8, 28]. However, distilled water, acidified with HNO_3, has a higher ionic strength than demineralized water. This type of water is, in fact, what the waste material comes into contact with under normal conditions in a landfill, and it simulates acidic rainwater [12].

We have used this extraction procedure in our previous studies for assessing the extractability of heavy metals in fly ash [15] originating from a fluidized bed co-combustion boiler (i.e. peat and wood) at the pulp and article mill complex of Stora Enso Oyj Veitsiluoto Mill and in a grate-fired boiler wood ash originating from a small (6 MW) municipal-district heating plant [16]. By keeping the sequential extraction procedure and chemical analysis uniform for different waste fractions, we can compare the total heavy-metal concentrations and extractability of the metals in the individual waste fractions between the separate industrial plants.

Partitioning was carried out by shaking 4 g of ash with the extractant. The sequential extraction procedure given in table 1 is for a solid sample of 1 g. Thus, because our sample was 4 g, the reagents volumes used for extraction were 4-fold those given in table 1. The extraction was carried out in polypropylene bottles. In order to minimize possible chemical and/or microbiological changes in the ash during the extraction procedure, the extraction was carried out using ash samples as such, instead of dried samples. After each extraction step, the extracts were separated from the solid residue by filtration through a 0.45 µm membrane filter (47-mm diameter). In order to avoid losses between the leaching stages, the filters and adhering ash particles from the previous extraction stage were also included in the next stage. After addition of 200 µL of 65% HNO_3 in the supernatant phase (not in stage 5 because it was already strongly acidic), it was stored in a refrigerator (+4°C) until the element determinations. The element concentrations in the extracts (i.e. extraction stages 1–5) were determined with a Thermo Elemental IRIS Intrepid II XDL Duo inductively coupled plasma optical emission spectrometer.

4. Results and discussion

4.1 *Physical and chemical properties of the ash*

According to table 2, the pH of the bottom ash was alkaline (pH 9.6). In this context, it is also worth noting that, after extracting the bottom ash with acidified water (pH 4.0)

Table 2. Concentrations (mean ± SD) of easily soluble nutrients in the bottom ash, as well as the physical and chemical properties of ash originating from the coal-fired power plant of Fortum Power and Heat Oy Inkoo Power Plant.

Nutrient/parameter	Unit[a]	Bottom ash[b]
Ca	$g\,kg^{-1}$ (dw)	3.20 ± 0.1
Mg	$g\,kg^{-1}$ (dw)	1.20 ± 0.05
Na	$g\,kg^{-1}$ (dw)	1.40 ± 0.02
K	$g\,kg^{-1}$ (dw)	0.09 ± 0.003
S	$g\,kg^{-1}$ (dw)	0.19 ± 0.009
P	$g\,kg^{-1}$ (dw)	0.06 ± 0.003
Cu	$mg\,kg^{-1}$ (dw)	0.77 ± 0.08
Zn	$mg\,kg^{-1}$ (dw)	0.92 ± 0.05
TOC	$g\,kg^{-1}$ (dw)	128
Loss on ignition (550°C)	% (dw)	27.7 ± 1.5
Dry matter content (105°C)	%	57.7 ± 0.8
Neutralizing value (NV)	% (Ca; dw)	2.7 ± 0.1
Reactivity value (r_{ac})	% (Ca; dw)	1.0 ± 0.2
pH	–	9.6 ± 0.05
Electrical conductivity (EC)	$mS\,cm^{-1}$	1.7 ± 0.08

[a] Concentrations are expressed on a dry-weight (dw) basis.
[b] Results are means of triplicate samples.

in stage 1, the pH of the extract solution was 9.8. According to Van Herck and Vandecasteele [9], an alkaline pH indicates that some of the dissolved metals occur as basic metal salts, oxides, hydroxides, and/or carbonates. Thus, the proportions of soluble basic metal salts, oxides, hydroxides, and carbonates in the bottom ash therefore outweigh the proportion of soluble acid components, and the bottom ash subsequently generates an alkaline pH. The relatively high TOC value of 12.8% ($128\,g\,kg^{-1}$; d.w.) indicates that the bottom ash contains unburnable organic material. However, although the organic carbon content (i.e. TOC) we obtained is relatively high, it is in good agreement with the value of 12.7% reported by Ugurly [29] and with the values of 11–15% reported by Lasagni *et al.* [30]. Although the LOI is widely attributed to the amount of combustible matter of the sample [18, 31–32], according to the findings of Payá *et al.* [33], it does not represent well the amount of unburned carbon in coal ash, but rather the volatile fraction. The LOI/TOC ratio (2.1) we obtained agrees with the findings of Payá *et al.* [33], who reported that the LOI of pulverized coal ash is usually twice as high as the carbon content. According to Payá *et al.* [33], this phenomenon is due to the fact that coal ash contains several other compounds which also decompose on heating. According to Heiri *et al.* [32], other reactions than burning of organic matter can take place at 550°C, e.g. dehydration of metal oxides and loss of volatile salts.

The acid neutralizing value (NV) of 2.7% for bottom ash expressed as Ca equivalents (d.w.) indicates that 14.1 tonnes of bottom ash would be required to replace 1 tonne of a commercial ground limestone produced by SMA Saxo Mineral Ltd, the neutralizing value of which is 38% (Ca equivalents; d.w.). The reactivity value (r_{ac}) was derived in order to assess the speed and effectiveness of the neutralizing potential of the liming material in the ash. The r_{ac}/NV ratio indicates that the so-called 'fast acting' capacity is ca. 37% for bottom ash. This means that bottom ash has a liming effect and is therefore a potential soil conditioner and a pH buffer. The Ca concentration of $3.2\,g\,kg^{-1}$ (d.w.)

in bottom ash is twice as high as the typical value of $1.6\,\mathrm{g\,kg^{-1}}$ (d.w.) in arable land in Central Finland [15]. The elevated Ca concentration indicates that the bottom ash is also a potential agent for soil remediation and improving soil fertility if it is used as a fertilizer. The relatively low dry-matter content (57.7%) of the bottom ash is due to fact that the ash is transferred from the boiler to water tank, which acts as a water seal for pressure.

4.2 *Total concentrations of elements in the ash*

Table 3 shows the total concentrations of elements in the bottom ash. From the environmental point of view, it is worth noting that the total concentration of P in the ash was as high as $1070\,\mathrm{mg\,kg^{-1}}$ (d.w). According to table 2, however, the concentration of easily soluble P in the ash was only $60\,\mathrm{mg\,kg^{-1}}$ (d.w). Ammonium acetate extraction, which extracts the metals in easily soluble forms, is widely used as an indicator of plant-nutrient availability [23]. The low extractability of P in the ash is due to the fact that easily soluble P was determined by ammonium acetate extraction following the Molybdenum Blue colorimetric method, which involves only the formation of molybdenum blue colour by the reaction between orthophosphate and molybdate ions [24]. Therefore, due to the low solubility of phosphate, it is not likely that the use of ash as a soil remediation agent will lead to the eutrophication of watercourses.

In order to assess whether the ash is acceptable as agricultural and forestry fertilizer, we compared the total heavy-metal concentrations in the ash to the maximal allowable heavy-metal concentrations for fertilizers used in agriculture and in forestry, set on the basis of the Finnish legislation [34–36]. According to table 3, the total element concentrations in the bottom ash were significantly lower than the current Finnish limit values for fertilizers used in agriculture and in forestry. The Finnish limit values for maximal allowable heavy-metal concentrations for fertilizers used in agriculture and in forestry came into force in March 2007, and they follow regulation (EC) No. 2003/2003 of the European Parliament and the Council, dated 13 October 2003, relating to fertilizers [37]. However, in this context, we would like to point out that the utilization of industrial residues always requires approval by the competent authority. Due to the differences in the physical and chemical properties of industrial wastes, caution must be exercised if the waste is to be applied in the natural environment.

If the results of total element concentrations using USEPA method 3052 (i.e. concentrations after microwave oven digestion with a mixture of HF and HNO_3) are compared with the sequential extraction analysis (i.e. sum of extraction stages 1–5), it is clear that the sum of the five stages (fractions) was in relatively good agreement with the total digestion results (see table 3). The recoveries for all elements except for V, Fe, and Ti were between 89 and 107%. Therefore, we can conclude that the most of the elements in bottom ash could be extracted quantitatively by the sequential extraction procedure used in this work.

4.3 *Partitioning of heavy metals, sulfur, and phosphorus in the ash*

The partitioning of heavy metals, sulfur, and phosphorus in the bottom ash after a five-stage sequential extraction procedure between the water-soluble fraction (H_2O), exchangeable fraction (CH_3COOH), easily reduced fraction (NH_2OH–HCl), oxidizable

Table 3. Total element concentrations (mean ± SD) in the bottom ash using the USEPA method 3052, the sum of element concentration in extraction stages 1–5, recoveries (%), as well as the current Finnish limit values for fertilizers in agriculture and forestry.

	Bottom ash[a,b]				
	Total concentration	Bottom ash			
Element	USAEPA 3052	Sum of extraction stages 1–5	R[c] (%)	Limit value[a] (agricultural use)	Limit value[a] (forest fertilizer)
Cd	<0.3	0.27	(90)	1.5	15
Cu	34.7 ± 0.9	34.6	99.7	600	700
Pb	11.5 ± 0.3	10.7	93.0	100	150
Cr	35.4 ± 1.9	32.6	92.1	300	300
Mo	3.00 ± 0.15	2.97	99.0		
Zn	36.7 ± 1.2	37.9	103	1500	4500
As	7.5 ± 0.1	7.1	94.6	25	30
Co	16.6 ± 0.4	16.1	96.9		
V	71.5 ± 2.1	61.2	85.6		
Ni	33.9 ± 0.9	33.5	98.8	100	150
Ba	1140 ± 44	1126	98.8		
Al	22,700 ± 681	20,205	89.0		
Be	2.20 ± 0.06	2.35	107		
Fe	31,600 ± 643	27,219	86.1		
Mn	540 ± 12	561	104		
Ti	2930 ± 115	1910	65.1		
S	620 ± 25	617	99.5		
Ca	20,100 ± 473				
Mg	1960 ± 34.6				
K	8290 ± 251				
P	1070 ± 36	1022	95.5		
Hg	<0.1			1.0	1.0

[a] All concentrations ($mg\,kg^{-1}$) are expressed on a dry-weight (dw) basis.
[b] Results are means of triplicate sample.
[c] The recovery (R) = [sum of metal concentrations in extraction stages 1–5/total element concentration] × 100.

fraction ($H_2O_2 + CH_3COONH_4$), and residual fraction ($HF + HNO_3 + HCl$) are shown in figure 1. Except for As, Cd, and S, the residual fraction was the predominant matrix for most of the elements. This means that the major part of the elements retained in the bottom ash is difficult to extract (leach) out under conditions normally found in nature. Although the total element concentrations in the bottom ash were low, partitioning helps to evaluate the extractability efficiency of different element. The knowledge of the extractability of metals is important, since, according to Wahlström and Laine-Ylijoki [38], if inorganic materials and by-products, e.g. waste, are utilized in earth works, the content of harmful compounds must be low, and the harmful components must be tightly bound to the matrix.

From the environmental point of view, it is worth noting the relatively low proportion (15.0%) of Cd in the residual fraction. Cadmium is one of the heavy metals considered to be the major priority concern due to its toxicity. However, its toxicity is mainly related to its bioavailable and not to its total concentration [39]. In the bottom ash, Cd was mainly partitioned in the oxidizable fraction (28.3%) and equal (i.e. 18.9%) in the water-soluble, exchangeable, and easily reduced fractions. The low organic matter in ash is a favourable phenomenon, since, if present, the organic matter may form soluble or insoluble complexes with toxic heavy metals, preventing them from migrating in the soil [4].

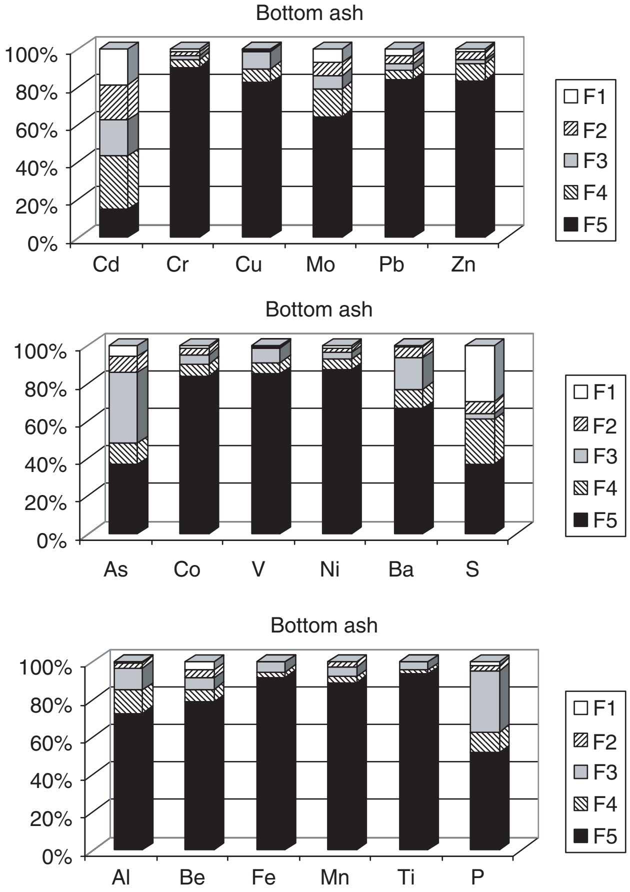

Figure 1. Partitioning of metals, sulfur, and phosphorus in coal-fired bottom ash between the water-soluble fraction (F1), exchangeable fraction (F2), easily reduced fraction (F3), oxidizable fraction (F4), and residual fraction (F5).

Sulfur showed a considerable partitioning in the water-soluble fraction (29.3%). However, according to Alloway and Ayres [40], sulfur is not a chemical substance considered to be a major priority concern. The partitioning of P in extraction stages 1–5 also supports the low extractability of phosphorus in the ash. According to figure 1, most of the phosphorus (51.8%) was partitioned in fraction 5, which requires the use of a mineral acid mixture of $HF + HNO_3 + HCl$. The partitioning of P in the water-soluble fraction (i.e. stage 1) was only 1.8%, which is negligible compared with the total P concentration. Therefore, due to the low solubility of phosphorus, it is not likely that the use of ash as a soil remediation agent will easily lead to the eutrophication of watercourses.

5. Conclusions

The policy of recycling and the eco-efficient utilization of ash require control over the undesired release of contaminants into the environment. The total metal contents in ash give no indication of the quantities of metals that are in fact mobile and bioavailable or transferable into the environment. Therefore, it is important to estimate the extraction potential of toxic metals when assessing the possible environmental impacts associated with ash reuse and disposal. Although heavy metals were extractable in all fractions, the highest concentrations of most of the heavy metals occurred in the residual fraction ($HF + HNO_3 + HCl$). This kind of strong mineral acid mixture can never be found in nature, and so the residual fraction is not likely to be dissolved easily under the conditions normally found in nature. From the utilization point of view, it is notable that the total element concentrations in the bottom ash were significantly lower than the current Finnish limit values for ash used as a fertilizer in agriculture and in forestry. However, the partitioning helps to evaluate the extractability efficiency of different elements. The knowledge of extractability of elements is important if inorganic materials and by-products, e.g. waste, are utilized.

The Ca ($3.2\,\mathrm{g\,kg^{-1}}$; d.w.) and Mg ($1.2\,\mathrm{g\,kg^{-1}}$; d.w.) concentrations in the ash were ca. 2 and 6 times higher than the typical values of 1.6 and $0.2\,\mathrm{g\,kg^{-1}}$ (d.w.), respectively, in arable land in central Finland. The ash was alkaline ($\mathrm{pH} \sim 9.6$) and had a liming effect (i.e. neutralizing value) of 2.7% expressed as Ca equivalents (d.w.). The slightly elevated Ca and Mg concentrations indicate that the bottom ash from the coal-fired power plant is a potential agent for soil remediation and improving soil fertility. The pH and liming effect value indicate that ash has a pH-buffering capacity.

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