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Recirculation of biomass ashes onto forest soils: ash composition, mineralogy and leaching properties

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Abstract

In Denmark, increasing amounts of wood ashes are generated from biomass combustion for energy production. The utilisation of ashes on top of forest soil for liming purposes has been proposed as an alternative to landfilling. Danish wood ash samples were collected and characterised with respect to chemical composition, mineralogy and leaching properties (batch leaching at L/S 2 and 10 L/kg, and pH-dependent leaching at 10 L/kg). Large variations in the ash liming properties were observed ($ANC_{7.5}$: 1.8-6.4 meq H^+/g), indicating that similar soil application dosages may result in different liming effects. High contents of Ca, Si, P, K and Mg were observed in all samples, while the highest contents of S and N were found in fly ashes and mixed ashes (combination of fly and bottom ashes). Similarly, the highest contents of some trace metals, e.g. Cd, Mo and Se, were observed for fly ash. Releases of major, minor and trace elements were affected significantly by pH: high releases of PO_4^{3-}, Mg, Zn, Cu and Cd were found for acidic conditions relevant to forest soils, while the highest releases of Mo and Cr were observed in alkaline conditions. Mineral phases were selected based on XRD analyses and the existing literature, and they were applied as inputs for the geochemical modelling of pH-dependent leaching. Mineral dissolution was found adequate for a wide range of major elements and nutrients, while the description of trace elements could be done only for parts of the pH-range. Content and leaching of PAHs were observed below detection limits. The source-term release of Ca, K, Mg, Mn, and P in acidic conditions relevant to forest soils was higher than ten years of atmospheric deposition, in contrast to the relatively low release of Al, Fe and Na. The potential release of Cd was found to be the most critical element compared with soil quality criteria, whereas the maximum theoretical loads of Ba, Cd, Cr, Sr, Mo, Ni, Pb, Sb, Se, Sn and V were relatively low.

Abbreviations

ANC: acid neutralisation capacity; BA: bottom ash; CSH: calcium-silicate hydrates; DOC: dissolved organic carbon; dw: dry weight; FA: fly ash; ICP: inductively coupled plasma; LOD: limit of detection; MA: mixed ash; MSWI: municipal solid waste incineration; OCP: octacalcium phosphate; PAH: polycyclic aromatic hydrocarbon; SI: saturation index; SQC: soil quality criteria; TOC: total organic carbon; XRD: X-ray diffraction

1. INTRODUCTION

Many European countries are introducing increasing amounts of renewable energy sources at the expense of fossil fuels (European Commission, 2015). In addition to wind and photovoltaic options, biomass often plays an important role in this transition. The Danish district heating system is based on many distributed combined heat-and-power plants supplying both electricity and district heating for the surrounding local region. Many of these plants utilise wood chips as fuel for combustion, and many of the larger coal power plants are currently being converted into wood pellet combustors, at the expense of coal. This follows the current Danish energy strategy of being fossil fuel independent by 2050 (The Danish Council on Climate Change, 2015). The production of electricity from wood has shown a significant increase within the last decade, i.e. from 0.8 PJ to 8 PJ in the period 2000 – 2015 (Danish Energy Agency, 2016). The increased use of woody biomass fuels, however, results in the increased production of wood ashes; in Denmark, about 22,300 tonnes dry weight (dw) of wood ash was produced in 2012 (Skov and Ingerslev, 2013).

The use of wood ashes on forest and agricultural soil is regulated in some European countries, such as Denmark, Finland, Sweden, Austria and Germany (van Eijk et al., 2012). In Denmark, for example, the dosage of ash applied to forest soil (DEPA, 2008) is regulated depending on (i) the content of specific contaminants in the ash, (ii) the need for plant fertiliser and (iii) the ash's electrical conductivity: a maximum of three tonnes/ha can be applied over a period of 10 years, but not more than three times within the last 75 years. There are approximately 615,000 hectares of forest land in Denmark, which in principle could receive wood ashes. Nevertheless, most of the wood ashes currently produced in Denmark are collected in containers at individual plants and landfilled (Ingerslev et al., 2014), most likely because of the small capacity of the Danish power plants (and therefore relatively small quantities of ashes), stringent legislation limits, concerns about their composition and leachability and the costs associated with the chemical analysis and documentation of ash quality. However, with increasing amounts of wood ashes being generated, landfilling is not a viable solution from a long-term perspective, in that the sustainability of wood combustion requires the continuous renewal of forest biomass and the input of nutrients. The application of wood ashes in forestry may contribute to the recirculation of nutrients (e.g. K, Mg, Ca and P) as well as offer liming effects on the soil (Pitman, 2006) – using three tonnes of wood ashes on top of soil was reported to have a liming effect comparable to one tonne of CaO (Karltun et al., 2008). On the other hand, recirculating wood ashes onto forest soil may also result in undesired releases of contaminants. Specific focus, for example, has been placed on Cd, which has been investigated for its potential bioavailability and toxicity in relation to specific soil ecosystems (e.g. Cruz-Paredes et al., 2017; Fritze et al., 2001; Perkiömäki and Fritze, 2005). Hence, although the potential for increasing the recirculation of wood ashes to forestry may exist in Denmark, further clarification on the consequences of this process is needed.

According to the available literature, the composition of wood ash has been addressed as a function of biomass fuel (Drift et al., 2001; Reimann et al., 2008; Werkelin et al., 2011), furnace operating parameters (Etiégni and Campbell, 1991; Misra et al., 1993; Sarenbo, 2009), combustion technology (Freire et al., 2015; Lanzerstorfer, 2015; Pöykiö et al., 2007) and different ash types (Dahl et al., 2009; Ingerslev et al., 2011; Sano et al., 2013). Several authors have investigated the leaching of wood ash, by applying different methods such as sequential extractions, batch leaching tests and percolation tests (Liodakis et al., 2009; Mellbo et al., 2008; Pöykiö et al., 2012; Sano et al., 2013; Steenari et al., 1998, 1999; Supancic et al., 2014). However, due to the different leaching test conditions applied in these studies, a direct comparison of results taken from individual studies is not possible. Despite a recent study by Freire et al. (2015), who characterised the leaching of a few wood ash samples under different leaching conditions, existing literature is relatively fragmented, Moreover, a systematic evaluation of the variability of leaching from a wider range of ashes, and an evaluation of the leaching mechanisms controlling the release of nutrients and contaminants from these ashes, is largely missing. A consistent evaluation of the leaching properties of these ashes is needed as the basis for future changes in the regulatory framework targeting the minimisation of the landfilling of wood ashes.

The overall aim of this study is to provide a consistent evaluation of the leaching properties of wood ashes, in order to improve the knowledge necessary for recirculating these combustion residues onto forest soils. This includes the following specific objectives: (i) to document variability in ash composition and leaching behaviour over a range of wood ash samples, (ii) to evaluate the effects of pH in relation to leaching for selected ashes, (iii) to identify and interpret key mechanisms controlling leaching by means of geochemical modelling and (iv) to evaluate potential source-term releases onto forest soils with respect to soil quality criteria and atmospheric deposition.

2. MATERIALS AND METHODS

2.1 Sampling and material handling

Ashes from ten different Danish biomass combustion facilities (see Table S1 in Supplementary Material for more details on the characteristics of these plants) receiving wood chips, mainly from *Picea Abies*, were sampled in the period January – March 2014. Depending on the specific technology, freshly generated bottom ash (BA) and fly ash (FA) may be collected at the plant through two separate flows or one single mixed flow (fresh mixed ash: MA). The latter was a specific case of closed ash conveyer systems, where it was not possible to sample BA and FA separately. Consequently, the ratio between BA and FA in the MA samples was not known. A total of sixteen wood ash samples were collected: three BA, four FA and nine MA samples. Sample names used in the following text refer to the ash type, i.e. *BA*, *FA* or *MA*, followed by a number representing the plant, i.e. *1-10*, and an optional letter, i.e. *a, b* or *c*, indicating the replicate number (where relevant). Upon receipt of the samples at the laboratory, the mass of each sample was reduced by quartering and splitting, using a riffle splitter in accordance with ASTM C702/C702M: 2011. All samples were stored in airtight plastic containers at 10ºC prior to testing and characterisation.

2.2 Ash characterisation

Moisture content was determined on 100 g subsamples according to EN 1097–5: 2008. Next, the dry material was crushed in a jaw crusher and then pulverised in a vibratory disc mill (agate discs). Approximately 0.2 g subsamples of the powder were obtained by consecutive riffle splitting and used for determining total organic carbon (TOC; EN 13137: 2001; LECO induction furnace CS-200 Analyser) and contents of C, S, N and H (Elemental Analyser - Vario MACRO cube); triplicate analyses were carried out. The elemental composition of the wood ash samples was determined in duplicates using 0.25 g of pulverised material for microwave-assisted acid digestion (Multiwave Anton Paar 3000) according to EN 13656: 2003, using 6 ml of HNO_3 (65 %), 2 ml of HCl (37 %), 2 ml of HF (40 %) and 12 H_3BO_3 (10 %). In addition, 2 ml of H_2O_2 (30 %) was added to enhance the oxidation of residual organic matter. The digestates were analysed by inductively coupled plasma (ICP) mass spectrometry (7700x, Agilent Technologies) for the content of Al, Ag, As, Au, Ba, Be, Ca, Cd, Ce, Co, Cr, Cs, Cu, Er, Eu, Fe, Ga, Gd, Ge, Hf, Ho, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, Sb, Sc, Se, Si, Sm, Sn, Sr, Ta, Tb, Ti, Tl, Tm, V, W, Yb, Zr and Zn, and by ICP optical emission spectrometry (Varian Vista-MPX) for the content of Ca, K, Mn and S. The same procedure was repeated to a reference material, i.e. *BCR-176R*, to validate the results.

To facilitate more detailed characterisation, based on the results of the elemental content analyses, two ash samples were selected with the following characteristics: a) one ash sample with the highest Cd content among the sixteen samples (FA-2b, consisting of fly ash) and b) one ash sample complying with the current Danish limit values (DEPA, 2008) for utilising wood ashes on top of forest soils (MA-9c, a mixed ash consisting of both fly ash and bottom ash). As such, the two selected samples represented a “worst case scenario” with regards to the content of Cd, and a “typical situation” with ashes that are today allowed for recirculation in forestry settings. Further characterisation of the two selected samples, i.e. MA-9c and FA-2b, included: (i) determining particle size distribution, (ii) XRD scanning, (iii) analysis of the content of polycyclic aromatic hydrocarbons (PAHs; US EPA, 2008), using GC-MS after Soxhlet extraction using dichloromethane (US EPA 8270D, 2014), (iv) and leaching characterisation based on a range of different leaching tests (Section 2.4 and 2.5). Particle size distribution was determined in triplicate according to EN 933-1:2012, using 250 g of previously dried (110°C) samples by means of 13 stainless steel sieves with mesh sizes ranging between 0.063 µm and 25 mm. XRD scanning was carried out on pulverised samples of MA-9c and FA-2b, using a Philips PW 1830 X-ray diffractometer equipped with a copper tube operated at 40 kV and 50 mA. Diffraction patterns were collected over a 2-theta range from 2° to 65°, employing an angular step of 0.05° and a count time of 2 s.

2.3 Batch leaching experiments

All sixteen samples, except FA-1 and FA-3 (insufficient sample amounts), were subjected to a batch leaching test (EN 12457-1:2002) at a liquid-to-solid (L/S) ratio of 2 L/kg. In addition, MA-9c and FA-2b underwent a batch leaching test at L/S 10 L/kg (EN 12457-2:2002). Electrical conductivity and pH were measured in unfiltered eluates immediately after the leaching test. Eluates were then filtered (0.45 µm, Polytetrafluoroethylene) and divided into a number of subsamples for subsequent analysis. Subsamples intended for ICP analysis were acidified by adding HNO_3 (p.a.) to pH <2, while subsamples for analysis of chlorides (potentiometric titration with $AgNO_3$,Tim 865 Titration Manager), dissolved organic carbon (DOC) and dissolved total carbon (Shimadzu TOC 5000A Analyser) were not acidified. All eluate samples were kept at 4°C prior to the analyses.

2.4 pH-dependent batch leaching experiments

The influence of pH on the leaching of MA-9c and FA-2b was tested according to CEN/TS 14997:2006(E), using a computer-controlled titration system. Eight pH values were investigated: 2, 4, 5.5, 7, 8.5, 10, 11.5 and natural pH (without the addition of acid). The acid neutralisation capacity (ANC) of both ash samples was tested prior to the actual leaching test (see Section S1 in Supplementary Material for more details on the ANC test). About 60 g dw of ash was added with distilled water and continuously mixed, and then HNO_3 was added to achieve and maintain the predefined pH values for 48 hours. At the end of the experiment, pH, electrical conductivity and redox potential were measured in the eluate samples, which were then filtered (0.45 µm, Polytetrafluoroethylene), acidified for the fraction undergoing ICP measurements, stored and finally analysed similarly to eluates from the batch leaching test.

2.5 Equilibrium column experiments for organic compounds

The release of organic compounds from MA-9c and FA-2b was evaluated using an equilibrium column test according to Nordtest TR576 (2004). In this test, the leachant (0.005 M $CaCl_2$ and 0.5 g NaN_3) was recirculated (flow rate: 20 ml/h) by the sample being packed in a stainless steel column for 6 days (L/S ratio 6 L/kg). At the end of the test, pH and conductivity were measured in the eluates, and these were then analysed for sixteen PAH compounds, as defined by US EPA (2008), using a GC-MS after extraction with acetone/pentane (1:1), according to the Danish method Reflab 4:2008.

2.6 Geochemical modelling of pH-dependent leaching

The results of the pH-dependent leaching experiments were used to describe the leaching behaviour of major components (K, Ca, Si, Mg, Mn, Al, Fe, PO_4^{3-} and SO_4^{2-}) in both samples, using the so-called “geochemical multi-surface modelling approach” (Dijkstra et al., 2008). All model calculations were carried out using the ORCHESTRA modelling framework (Meeussen, 2003) embedded in a LeachXS database/expert system (http://www.leachxs.com/lxsdll.html). Thermodynamic data from the MINTEQA2 thermodynamic database, as modified by Butera et al. (2015), were used.

In the first modelling step, chemical speciation of the solutions obtained from the pH-dependent batch leaching experiments was used to identify “plausible” (explained later) mineral solubility controlling phases assuming equilibrium conditions. In a subsequent modelling step, the total concentrations of available trace metal(-loid)s were included in the calculations. These metal(-loid)s were allowed to react with different reactive surfaces through sorption (explained later), while ion competition was enabled. Similarly to the approach taken by Dijkstra et al. (2006b), total available trace metal(-loid) concentrations were estimated from the maximum values obtained in the pH-dependent leaching experiments. Except for Mo, which showed maximum solution concentrations at pH~10, all other trace metal(-loid)s (i.e. including oxyanion-forming metalloids such as As, Cr, Sb, Se and V) showed maximum solution concentrations at pH 2.

Ion adsorption onto DOC was included by means of the NICA-Donnan model (Kinniburgh et al., 1996), using generic adsorption reactions (Milne et al., 2003). Adsorption onto Fe-/Al-(hydr)oxides was calculated using the generalised two-layer model provided by Dzombak and Morel (Dzombak and Morel, 1990). The availability of sorption surfaces was represented by amounts of reactive Fe- and Al-(hydr)oxides, and the amounts of Fe- and Al-(hydr)oxides were estimated based on Fe and Al solution concentrations measured in the eluates from the pH-dependent leaching tests at pH 2, since the majority of Fe- and Al- (hydr)oxides dissolve at this pH (Gayer et al., 1958; Gayer and Woontner, 1956). While the amounts of available (hydr)oxides may also be estimated via selective extractions (e.g. Apul et al., 2010; Dijkstra et al., 2006a), both approaches represent indirect estimations associated with some uncertainty. Here, estimations based on eluate concentrations at low pH were considered appropriate, while it is acknowledged that compared to dedicated selective extractions, the approach used herein may possibly cause an overestimation of reactive site concentrations, which may in turn overestimate the significance of adsorption in the geochemical model.

As mentioned earlier, “plausible” solubility-controlling minerals were selected based on initial speciation calculations. Selection was based on a step-wise procedure. First, minerals with saturation indices (SI) within the interval ±0.5 were listed – SI around “0” indicate that a particular mineral is approaching equilibrium with the solution and may thus control (provided it is physically present) solution concentrations of its components. This initial list is theoretical and can be rather extensive depending on the number of minerals present in the mineralogy database used by the speciation model. Therefore, additional confirmation is needed to evaluate whether a certain mineral is actually present (or likely to be present) in the modelled system. Despite the challenges caused by a relatively large fraction of the material being non-crystalline, results from XRD analyses are useful in confirming the presence of many major mineral phases.

The results of our own XRD analyses, carried out for both samples, were combined with information from the literature (e.g. Freire et al., 2015; Magdziarz et al., 2016; Vassilev et al., 2013). Nevertheless, since more than 200 different mineral phases have been found in different types of “bioashes” (Vassilev et al., 2013), only minerals found in more than five independent studies were considered “plausible” in our model. For the fly ash (FA-2b), the final list of “plausible” mineral phases put into the geochemical model of the pH-dependent leaching included phases determined by our XRD analysis (calcite, portlandite, quartz, periclase, maghemite and calcium silicate) and phases identified from the literature (gibbsite, microcline, leucite, magadiite, CSH, brucite, birnessite, hydroxyapatite, octacalcium phosphate (OCP) and $Ba_{0.5}Sr_{0.5}SO_4$). Analogically, for the mixed ash

(MA-9c), the list included calcite, lime, portlandite, quartz, ankerite, magnesite (based on the XRD results) and calcium silicate, CSH, OCP, microcline, maghemite, leucite, magadiite, brucite, birnessite, zincite and $Ba_{0.5}Sr_{0.5}SO_4$ (based on the literature). Table S2 in Supplementary Material provides the full list of minerals identified during this study, along with the respective chemical formula.

Two models were tested: Model I and Model II. Model I included (i) metal availabilities, (ii) "plausible" solubility controlling minerals, (iii) reactive Fe-(hydr)oxide sites approximated by "ferrihydrite" (surface area of 600 m^2/g and capacity of $1.37 \cdot 10^{-4}$ kg/kg and $9.73 \cdot 10^{-5}$ kg/kg for MA-9c and FA-2b, respectively) and (iv) a polynomial description of the DOC concentration as a function of pH. Model II was identical to Model I, albeit with the addition of adsorption to Al-(hydr)oxides. Similarly to Fe-(hydr)oxides, the maximum content of reactive Al-(hydr)oxides was estimated from the pH-dependent leaching data for Al (at pH 2) and treated as a surrogate sorbent to the Fe-(hydr)oxides (Dijkstra et al., 2006a, 2006b). The combined contribution of Fe- and Al-(hydr)oxides yielded $7.62 \cdot 10^{-3}$ kg/kg and $7.83 \cdot 10^{-3}$ kg/kg of "ferrihydrite" for MA-9c and FA-2b, respectively. Model II additionally included – based on literature screening and calculated SIs – a few additional mineral phases that might be relevant in the mineral assemblage: $Cu(OH)_{2(s)}$, $PbMoO_4$, willemite, $ZnO_{(s)}$ and Cl-pyromorphite. In order to ensure ion competition, all calculations were carried out simultaneously for Al, Ba, Ca, Cd, Cl^-, CO_3^{2-}, Cr, Cu, Fe, Si, As, K, Li, Mg, Mn, Mo, Na, Ni, Pb, PO_4^{3-}, Sb, Se, Sr, SO_4^{2-}, V, Zn and DOC. An oxidising environment was assumed during the calculations (pe + pH = 15).

2.7 Comparison with soil quality and atmospheric deposition

To evaluate the potential source-term releases from wood ashes when applied to top of soil, a hypothetical scenario was considered, based on the two samples MA-9c and FA-2b. In this scenario, the two ashes were assumed to be placed on top of 1 m^2 of an acidic Danish forest soil with a pH value in the range 3-5 (for typical pH values in Danish soil, refer to Balstrøm et al. (2013)), at the maximum allowed dosage of 300 g/m^2 (see Introduction). In forest applications, wood ashes are typically spread on top of the soil and not further worked with it. Due to the limited amount of ash added to the top of the soil, overall ash leaching could be expected to be dominated by the acidic properties of the soil, rather than the alkaline properties of the ashes. As such, the source-term release from the ashes was estimated based on pH-dependent leaching (pH 3-5, L/S 10 L/kg), itself based on the defined ash dosage (300 g/m^2) and soil area (1 m^2), and it was expressed in mg/m^2. In addition, the maximum theoretical load of nutrients and potential contaminants entering the soil was evaluated based on ash composition, assuming that all solid contents would be released into the soil at some point in time. Although this is unlikely to happen within a foreseeable time frame (see Astrup et al., 2006), the maximum theoretical loads can still be compared with soil quality criteria levels (described in the following paragraph) to indicate the level of relevance. Similarly to the ash source-term releases, maximum theoretical loads were expressed in mg/m^2. The potential soil-leachate interaction is beyond the scope of this investigation.

Ash contents and calculated releases were compared with data for Danish atmospheric deposition (Hovmand and Kystol, 2013) and soil quality criteria (SQC) for "very sensitive land use" (DEPA, 2015). In Denmark, wood ashes cannot be recirculated on top of forest soil sooner than ten years from the last application (DEPA, 2008); accordingly, ten years' worth of cumulative atmospheric depositions (based on average annual data) were chosen for comparison with wood ash levels. Atmospheric deposition data were expressed in mg/(m^2 ·10y). As there are no SQC for Co, Sr or V, the reported soil values for these elements referred to typical Danish farmland contents (DEPA, 1995), average mineral soil composition (Capo et al., 1998) and California Human Health Screening Levels in the case of a residential scenario (OEHHA, 2010), respectively.

SQC (expressed in mg/kg) were converted into threshold values (expressed per volume of soil, i.e. mg/(m^2 ·cm)), assuming a soil area of 1 m^2, a soil depth of 1 cm and a soil bulk density of 1.1-1.5 g/cm^3. The rationale for choosing a soil depth of 1 cm was to allow direct comparison between the "layer" of ash (300 g/m^2) and the uppermost part of the soil.

3. RESULTS AND DISCUSSION

3.1 Ash composition

Table 1 shows the chemical composition of the sixteen ash samples grouped by ash type, i.e. BA, FA and MA, compared to values found in relevant literature. A detailed composition of MA-9c and FA-2b is presented in Supplementary Material (Table S3), together with particle size distribution curves (Figure S1) showing 90 % and 70 % of FA-2b and MA-9c as being smaller than 1 mm (similar curves were reported by Lanzerstorfer (2015) and Supancic et al. (2014) for grate-fired wood ashes).

<Table 1>

The chemical composition of the sixteen samples was comparable to literature values for all major, minor and trace elements. The most abundant elements were Ca and Si with contents of about 10^5 mg/kg dw. With regards to typical plant nutrients, high contents of P, K and Mg were found (about 10^4 mg/kg dw), whereas the content of N was observed to be related strongly to the ash type (i.e. <400 mg/kg dw and up to 4900 mg/kg dw in the case of BA and FA, respectively), most likely because of the low volatising point of N in the combustion chamber. S content varied by up to two orders of magnitude (10^2 – 10^4 mg/kg), with the highest values found in FA samples. The same partitioning tendency was observed for Cu and Zn (10^1 – 10^2 mg/kg and 10^1 – 10^3 mg/kg, respectively). Several trace metal(-loid)s seemed occasionally to be enriched in FA samples compared with BA samples, i.e. Cd, Mo, Se, Sn, Sr and Tl; however, the content of trace metal(-loid)s in the samples showed to be generally independent of the actual ash type, e.g. As, Ba, Co, Cr, Ni, Pb, Sb and V. These findings were consistent with other wood ash studies (e.g. Freire et al., 2015; Ingerslev et al., 2011; Pöykiö et al., 2012).

The overall levels of “critical elements”, as defined by the European Commission (2014), and other trace elements were comparable to Vassilev et al. (2014), except for Ce, La, Nd and Nb, but typically lower than municipal solid waste incineration (MSWI) BA and considerably lower than typical ore concentrations (see Allegrini et al. (2014) and the literature cited herein). Detailed information about these elements is provided in Table S4 in Supplementary Material and will not be discussed further.

TOC levels in the sixteen samples were generally between 0.28 % and 33 % (except for a few high values for FA-1, FA-3 and MA-7), which was comparable with the 0.8 %-13 % reported by Bjurström et al. (2014).

3.2 X-Ray Diffraction (XRD)

The XRD analysis of MA-9c indicated calcite, lime, portlandite, quartz, ankerite and magnesite, while FA-2b contained calcite, portlandite, quartz, periclase, maghemite and calcium silicate (Figure 1). These results are in agreement with a recent review of “bioash” mineralogy data by Vassilev et al. (2013).

<Figure 1>

3.3 Batch leaching results

Results of the batch leaching tests are presented in Table 2 together with literature data for wood ashes. Overall, the release of major components, nutrients and typical elements of environmental concern reflected levels found in the literature. Detailed results for “critical elements” and other trace elements can be found in Supplementary Material (Table S5) and will not be discussed further.

<Table 2>

All leachates were strongly alkaline, with pH ranging between 11.9 and 13.8 (mean value of 13.2). Electrical conductivity was measured between 9.2 and 69 mS/cm, showing a positive correlation with K concentrations: high (/low) K leachate concentrations reflected in high (/low) electrical conductivity values, and vice versa. The release of DOC was between 10^{-3} and 10^{-1} mg/kg dw at L/S 2 L/kg, while dissolved total carbon levels were between 10^{-2} and 10^{0} mg/kg dw.

The release of Cl, K, Na, and S appeared to be dominated by the rapid dissolution of readily soluble phases. Significant amounts of these elements were released in the batch leaching test at L/S 2 L/kg by all ash samples: Cl, Na and S were released in the range of 10^{2}-10^{3} mg/kg dw, while the release of K was between 10^{3} and 10^{4} mg/kg dw. Furthermore, comparable releases at L/S 2 L/kg and at 10 L/kg were observed for each of the two samples subjected to both types of batch leaching test (i.e. MA-9c and FA-2b). This kind of leaching behaviour reflects a mechanism also known as “availability controlled leaching” (Kosson et al., 1996), which is typical for readily soluble phases. Overall, the release of Cl, K, Na and S reflected typical literature ranges, whereas the release of Na from BA samples (i.e. 280 – 1000 mg/kg at L/S 2 L/kg) was about five to six times higher than literature data (i.e. 42 – 200 mg/kg at L/S 10 L/kg).

The release of Ca (10^{1}-10^{2} mg/kg dw), Ba and Zn (10^{-2} – 10^{0} mg/kg dw), measured in leachates from the L/S 10 L/kg batch test, was higher than from the L/S 2 L/kg test, thereby suggesting that their release was controlled by mineral solubility, similar to that observed in in MSWI BA (Dijkstra et al., 2006a; Hyks et al., 2009). Cu, Fe, Mg, Mn, P and Zn were released at very low levels and generally below 1 mg/kg at L/S 2 L/kg. Solution concentrations of Cd, Co, Sb, Sn and Tl were typically found below their respective limit of detection (LOD), regardless of ash type. The release of Mo was in the order of 10^{-1}-10^{0} mg/kg dw, and similar releases were shown at both L/S 2 L/kg and 10 L/kg, thus suggesting the leaching of this element to be availability controlled. The release of Cr, Ni, and V varied significantly, i.e. 10^{-3}-10^{0} mg/kg dw (L/S 2 L/kg), across all sample types, while a narrower release range was observed for Pb, Se and Sr. Similar releases have been established in wood ash literature (see Table 2).

3.4 Content and leaching of PAHs

The solid content of PAHs was below LOD (<0.20 mg/kg dw) in both MA9c and FA-2b, while literature data showed relatively large variations in PAHs levels, namely 0.015 – 17 mg/kg (Bundt et al., 2001; Freire et al., 2015; Johansson and van Bavel, 2003; Masto et al., 2015; Pitman, 2006; Sarenbo, 2009; Straka and Havelcová, 2012), where high values have been explained by insufficient oxidation during the combustion process (Sarenbo, 2009; Straka and Havelcová, 2012; Vehlow and Dalager, 2011). The observed PAH levels in the ashes tested herein were about two orders of magnitude below Danish limit values for the utilisation of wood ash on the top of soil, i.e.12 mg/kg (DEPA, 2008), and about one order of magnitude below Danish SQC defined for soils intended for “very sensitive land use”, i.e. 4 mg/kg (DEPA, 2015).

The leaching of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]pyrene, dibenz[a,h]anthracene, benzo[ghi]perylene and indeno[1,2,3-cd]pyrene was below LOD (0.01 µg/l) in eluates from both FA-2b and MA-9c subjected to an equilibrium column test. Similarly, the leaching of benz[a]anthracene/chrysene and benzo[bjk]fluoranthene was below LOD (0.02 µg/l). The low PAH levels observed in the experiments did not provide a basis to investigate potential interactions between the leaching of organic and inorganic compounds. Likewise, Enell et al. (2008) reported low PAH leachability from wood fly ash pellets, despite their considerably higher PAHs content (1.8 g/kg dw), as only about 0.02 % of the initial PAHs content was released at L/S 1600 L/kg. As such, while biomass ashes have been shown to contain organic pollutants as a consequence of incomplete combustion, the two ashes selected here indicated low levels. While this may not exclude high contents in ashes from other plants, results from these two samples, in combination with the literature, may suggest that the release of PAHs is not a primary concern with respect to the recirculation of wood ashes onto forest soil.

3.5 Results of the pH-dependent leaching test

3.5.1 Acid neutralising capacity

In spite of similar natural pH values, i.e. ~12.7 at L/S 10 L/kg, the ANC of the two materials differed significantly (Figure S2 in Supplementary Material): ANC at the end-point of pH 2 (ANC_2) was 6.5 meq H^+/g dw and 15.5 meq H^+/g dw for MA-9c and FA-2b, respectively. Similarly, $ANC_{7.5}$, i.e. the point of consumption of carbonates, hydroxides and soluble basic silicate hydrates (Johnson et al., 1995), exhibited clear differences for the two samples: 1.8 meq H^+/g and 6.4 meq H^+/g for MA-9c and FA-2b, respectively. This indicated higher contents of carbonates, hydroxides and silicates in the fly ash sample, as confirmed also by the XRD results, which indicated high intensities especially for calcite and portlandite peaks for FA-2b. In line with our findings, Freire et al. (2015) reported ANC_4 values of 1.2-2.1 meq H^+/g dw and 3.6-9.6 meq H^+/g dw for wood BA and wood FA, respectively.

3.5.2 pH-dependent leaching of major components and nutrients

The pH-dependent leaching of Na, K, Cl, Ca, Mg, Fe, Si, Al and PO_4^{3-} is shown as a series of points in Figure 2, together with the results of geochemical model calculations (Model I, see Section 2.6), which are presented as lines. In general, the leaching trends of the major ions were described adequately by the selected mineral phases (see Section 2.6). Most importantly, no significant differences were observed between the leaching trends for FA-2b and MA-9c. Similarly to the leaching observed for other types of thermal residues, such as coal fly ash, MSWI BA and MSWI air pollution control residues (Dijkstra et al., 2006a; Hjelmar, 1990; Hyks et al., 2007), the leaching of Na, K and Cl from the wood ashes was rather independent of pH, while the leached amounts correlated well with those observed from the batch tests at both L/S 2 L/kg and L/S 10 L/kg. However, as also observed here but not captured by geochemical modelling, a slight dependence on pH for the leaching of Na and K was shown by Freire et al. (2015) in the case of wood BAs.

<Figure 2>

Overall, the leaching of other major elements was similar to the leaching observed for MSWI BA and wood ashes. These results are discussed only briefly: Ca and Mg showed decreasing releases toward an alkaline pH (Astrup et al., 2006; Dijkstra et al., 2006a; Freire et al., 2015), the release of SO_4^{2-} was relatively pH-independent and Fe and Si increased toward acidic pH values (Astrup et al., 2006; Dijkstra et al., 2006a). Despite the generally low concentration levels of Fe, mostly in the range 0.01-0.1 mg/L, the dissolution of maghemite was observed to describe adequately Fe leaching in the very acidic (pH $\leq$4) and very alkaline (pH >11) leachates. Leaching of Al could be approximated by leucite dissolution at pH <5. On the other hand, the leaching of Al was close to, or below, LOD (0.1 mg/l) at pH >5, which is in contrast with relatively high solution concentrations of Al observed in alkaline conditions for MSWI residues (Astrup et al., 2006; Dijkstra et al., 2006a) and other wood ashes (Freire et al., 2015).

Between pH 13 and pH 8, the leaching of PO_4^{3-} was pH-independent. Below pH 8, leaching increased by three orders of magnitude toward an acidic pH. Apatite precipitation is likely to occur at neutral to alkaline pH, as also indicated by the positive SI calculated for hydroxyapatite and chlorapatite. The leaching of Ba

(Figure S3 in Supplementary Material) was described adequately by using a $Ba_{0.5}Sr_{0.5}SO_4$ solid solution (Astrup et al., 2006), which also provided reasonable agreement with the observed Sr leaching (Figure 3).

Similarly to the results provided by Dijkstra et al. (2006a) and Hyks et al. (2007) for MSWI ashes, DOC leaching (Figure S3 in Supplementary Material) was found to be rather independent of pH; however, DOC levels observed for the selected ash samples were up to ten times lower than the values reported in the literature for MSWI ashes despite the high TOC contents observed in both types of wood ash (Table 1). This large discrepancy between “total” and “dissolved” organic carbon is likely caused by the fact that a considerable fraction of TOC consists of elemental carbon (i.e. soot, char formed during incomplete combustion of organic matter), which is abundant in bioash (Bjurström et al., 2014; Vassilev et al., 2013) and relatively insoluble.

3.5.3 pH-dependent leaching of trace metals and metalloids

The pH-dependent leaching of Cd, Cr, Cu, As, Mo, Ni, Pb, Sb, Se, Sr, V and Zn is shown as points in Figure 3, while the results of the geochemical modelling are shown as lines. Two types of line are shown for each material, reflecting the results for Model I and Model II (see Section 2.6).

<Figure 3>

Although Model II generally resulted in a better description of the analytical data, model predictions for Mo and Sb did not respond to the increased amounts of sorption reactive sites. In MSWI BA, the decrease in Mo leaching at pH <6 has been described by the solubility of $CaMoO_{4(s)}$ (Dijkstra et al., 2006b); however, including this mineral in our model had no influence on the results. Similarly, although the leaching of Sb decreased toward high pH values (with a minimum around pH 10.5 – 11), which may indicate the precipitation of several Sb-bearing mineral phase(s) e.g. $Ca[Sb(OH)_6]_2$, ettringite or roméite (Cornelis et al., 2012), including these minerals in the mineral assemblage had no influence on the modelling results.

Overall, Model II provided a reasonable description of the leaching of Cr, Cu, As, Ni, Pb, Se, V and Zn. Model predictions for Cd, Mo, Sb and Se were less accurate, because no suitable mineral phase with the potential to improve model predictions could be identified from speciation calculations or the literature. On the other hand, no thermodynamic data fitting was carried out in either model: the affinity of different ions for sorption sites was not fitted, and the included sorption and DOC complexation models were used in their default setup.

Given the available amounts of Ca and PO_4^{3-}, apatite is expected to precipitate in the neutral-alkaline pH range. Many studies have confirmed the capacity of (hydro-)apatite to sorb trace metals (e.g. Alther et al., 2005;

Chen et al., 1997a) even in different pH conditions (Chen et al., 1997b). Therefore, we suspect that future model predictions may be improved if a more exhaustive thermodynamic dataset for (hydro-)apatite becomes available.

3.6 Implications for forestry utilisation

In Section 2.7, the application of 300 g/m^2 of MA-9c or FA-2b ashes on top of acidic forest soil (pH 3-5) was assumed, and the source-term release from the ash was assumed to be governed by the acidic soil conditions; therefore, ash leaching was estimated based on pH-dependent results (pH 3-5). Ash composition and releases were compared with ten years' worth of atmospheric depositions, and it was assumed that the SQC for "very sensitive land use" had to comply within the very first centimetre of soil (see Figure 4).

<Figure 4>

While both ash samples were strongly alkaline (pH 12.7 at L/S 10 L/kg), the same application scenario (in terms of ash dosage) for these materials will likely result in different liming effects, because of the large differences in their ANCs as well as alkaline species content (see Section 3.5.1).

Based on the elemental composition of the ashes, the maximum theoretical loads of Ba, Cd, Cr, Sr, Mo, Ni, Pb, Sb, Se, Sn and V were always below the selected SQC levels, and above/close to their expected atmospheric deposition over a period of ten years. It is worth noting that because of the higher contents of Cd, Mo, Se, Sn, Sr and Tl in the FA-2b ash, higher loads of these elements should be expected in the case of FA-2b application, compared to MA-9c. Theoretical loads, despite not being necessarily representative of actual leachable amounts, can still be used for a preliminary screening to evaluate the amount of contaminants and/or nutrients added to the soil in comparison with SQC and background levels.

Soluble elements, i.e. K, Cl, Na and S as indicated in Section 3.3, would likely be released shortly after ash application, e.g. with the first rainfall, while the source-term release of other macro-/micro- nutrients (e.g. Cu, Mg, Mn, P and Zn) and trace metals may depend on pH. The estimated ash release of Ca, K, Mg, Mn, and P was of the same order of magnitude as, or higher than, ten years of atmospheric depositions, contrary to the relatively low release of Al, Fe and Na.

The source-term release of most elements of typical environmental concern, e.g. As, Ba, Cr, Cu, Mo, Ni, Pb, Sb, Se, Sn, Tl and Zn, was estimated at levels below, or close to, atmospheric deposition. Similarly, the potential ash release of Co, Sr and V was significantly lower than the selected reference soil levels (Capo et al., 1998; DEPA, 1995; OEHHA, 2010). On the other hand, the estimated release of Cd appeared close to the selected SQC in the case of FA-2b. Remember that FA-2b was selected specifically because of its relatively high Cd content (i.e. 16.3 mg/kg), though still within Danish legislation limits (i.e. 20 mg/kg; DEPA (2008)). This supports the notion that the attention paid to Cd as a potential critical element in wood ashes, because of its potential toxicity and bioavailability (see Introduction), may be justified.

Overall, the results from this study suggested that wood ash utilisation at a dosage of three tonnes per hectare (300 g/m^2) of acidic forest soil does not appear critical compared with atmospheric deposition and SQC. However, high application dosages of wood ash (i.e. largely above three tonnes per hectare) with high Cd contents should be avoided. In general, recirculation of MA and BA may be prioritised over FA, because of the relatively high content (and potential release) of contaminants in this fraction (e.g. Cd, Mo, Se, Sn, Sr and Tl). Potential soil contamination from PAHs appeared minor, as both contents and source-term releases were observed to be low (below detectable levels in our analyses and well below the SQC levels defined for “very sensitive land use”) in the selected ash samples.

While ash leaching is affected by a variety of aspects upon application to forest soils, e.g. redox conditions, interaction with the soil organic matter, sorption, transport, repartitioning, mineralisation and re-volatilisation of organic compounds (for more details on the mobility of inorganic compounds into the soil refer to Carter et al. (2009) and Fang et al. (2017), whereas for the organic compounds refer to Aichner et al. (2015), Komprdová et al. (2016) and Obrist et al. (2015)), the above estimations nevertheless offer general insights into the source-term release of nutrients and contaminants onto soil.

4. CONCLUSIONS

Ca, Si, P, K and Mg abounded in the investigated wood ashes, while relatively high contents of S and N were observed in fly ashes and mixed ashes compared with bottom ashes. For some fly ash samples, relatively high contents of Cd, Mo, Se, Sn, Sr and Tl were found. The leaching of most elements changed as a function of the solution pH, except for K, Cl, Na and SO_4^{2-}, which were found to be rather independent of pH. While relatively high leaching of PO_4^{3-}, Mg, Zn, Cu and Cd was observed for pH conditions relevant to acidic forest soils, Cr and Mo increased leaching more toward alkaline conditions. For most major, minor and trace elements, leaching was described adequately by a geochemical speciation model based on mineral dissolution involving a relatively limited set of mineral phases. The maximum theoretical loads of Ba, Cd, Cr, Sr, Mo, Ni, Pb, Sb, Se, Sn and V were below the selected soil quality criteria levels, whereas the source-term release of Cd was identified as of potential concern compared with these levels. The expected release of nutrients such as Ca, Mg, Mn, P and K appeared significant compared to atmospheric deposition. Similar wood ash application rates can result in different liming effects, depending on their alkaline species content. Similar scenario-based assessments of the source-term releases of nutrients and contaminants can be made prior to ash application in specific cases, based on site-specific soil characteristics and information about precipitation.

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Table 1. Composition of wood ash samples in comparison with typical literature values (primarily from grate-fired wood ashes), grouped by ash type (BA, FA and MA). Minimum and maximum contents within each ash group are reported. Results are expressed in mg/kg dw, unless differently specified. [n.m.: not measured; MC: moisture content; TOC: total organic carbon].

	BA – this study	**BA - literature a)**	**FA – this study**	**FA - literature a)**	**MA – this study**	**MA - literature a)**
samples	BA- 1, 2, 3		FA- 1, 2a, 2b, 3		MA- 4, 5, 6, 7, 8, 9a, 9b, 9c, 10	
MC [%]	8.07 - 29.5	19 - 31	28.1 - 60.2	0.2 - 52	0.0672 - 54.5	n.m.
TOC [%]	0.639 - 2.85	<0.05	7.39 - 32.8	1.6	0.472 - 19.1	0.52 - 13
NUTRIENTS AND MAJOR COMPONENTS						
Al	14300 - 16800	16000 - 40000	5920 - 11800	3600 - 26000	9020 - 16500	1700 - 40000
Ca	79400 - 162000	130000 - 300000	104000 - 263000	120000 - 280000	75600 - 214000	24000 - 340000
Cl	n.m.	<20 - 4700	n.m.	1600 - 11000	n.m.	210 - 14000
Cu	64.6 - 111	69 - 200	106 - 161	140 - 1100	71.4 - 195	78 - 440
Fe	4610 - 6570	6000 - 26000	2880 - 8300	1500 - 59000	5000 - 15000	1600 - 25000
K	35800 - 73200	40000 - 47000	40000 - 60300	50000 - 160000	35800 - 80000	25000 - 250000
Mg	16500 - 20600	12000 - 44000	19300 - 32900	20000 - 50000	12800 - 39900	16000 - 80000
Mn	3470 - 19400	4300 - 27000	4030 - 30300	1300 - 23000	3060 - 19000	3500 - 19000
N	<400	150	1670 - 4930	2500 - 2500	<400 - 2600	600 - 5000
Na	8260 - 11100	4800 - 12000	6650 - 12000	3100 - 8300	6590 - 11300	500 - 37000
P	8310 - 17400	7200 - 22000	10200 - 22900	4300 - 20000	10000 - 26500	3200 - 21000
S	153 - 967	270 - 2400	4210 - 15300	5800 - 25000	1540 - 5950	1300 - 52000
Si	208000 - 273000	120000 - 250000	45600 - 124000	11000 - 82000	124000 - 271000	17000 - 260000
Zn	73.9 - 234	65 - 950	446 - 1120	370 - 40000	18.4 - 737	26 - 2800
TYPICAL ELEMENTS OF ENVIRONMENTAL CONCERN						
As	2.17 - 3.19	1.4	2.68 - 6.98	1.5 - 24	2.24 - 7.67	0.09 - 74
Ba	802 - 1400	1600 - 2200	797 - 2320	1200 - 4300	684 - 1880	420 - 2700
Cd	0.158 - 0.467	<0.2 - 5.7	7.32 - 16.3	5.1 - 34	0.109 - 8.82	<2 - 31
Co	4.23 - 7.3	6.7 - 11	5.79 - 9.69	11 - 13	3.76 - 7.72	<3 - 77
Cr	24.9 - 69.5	64 - 320	26.5 - 62.7	32 - 290	22 - 217	14 - 260
Hg	n.m.	0.02 - 0.1	n.m.	1.7	n.m.	0.06 - 1.2
Mo	1.06 - 1.84	1 - 5.8	1.46 - 4.29	8.6 - 16	1.14 - 4.36	1.2 - 120
Ni	27.4 - 38.6	22 - 200	22.4 - 52.5	19 - 74	31.2 - 44.7	12 - 500
Pb	4.74 - 79.8	4 - 40	10.7 - 73.8	25 - 470	0.682 - 36.4	13 - 130
Sb	0.496 - 3.48	0.86 - 2.3	0.721 - 5.83	1.7 - 3	0.69 - 3.11	0.71 - 94
Se	<16.7	<0,1	<16.7	0.24 - 2.1	<16.7	16
Sn	<0.305 - 1	11 - 16	1.21 - 6.37	15 - 22	1.07 - 3.14	2.1 - 4.4
Sr	466 - 783	610 - 710	578 - 1240	750 - 2100	449 - 959	320 - 1200
Tl	0.172 - 0.473	n.m.	0.975 - 1.98	n.m.	0.0624 - 1.49	n.m.
V	10.4 - 18.4	26 - 64	6.75 - 18.2	5.1 - 43	11.3 - 18.6	3.4 - 56

a): Etiégni and Campbell (1991); Etiegni et al. (1991); Holmberg et al. (2000); Huang et al. (1992); Ingerslev et al. (2014); Narodoslawsky and Obernberger (1996); Poykio et al. (2007); Pöykiö et al. (2009); SLU (2008); Steenari et al. (1999); Supancic et al. (2014); Vassilev et al. (2014b).

Table 2. Compliance leaching test results in comparison with literature values, grouped by ash type (BA, FA and MA). Results are expressed in mg/kg dw, unless differently specified. Minimum and maximum contents within each ash group are reported. Leaching tests were carried out at the L/S ratio 2 L/kg (EN 12457-1:2002) and 10 L/kg (EN 12457-3:2002). [n.m.: not-measured; * : indicates that the value only refers to FA-2b or MA-9c].

	BA (L/S 2)	**FA (L/S 2)**	**FA (L/S 10)**	**MA (L/S 2)**	**MA (L/S 10)**	**BA- Literature [a] (L/S 10)**	**FA- Literature [a] (L/S 10)**
samples	BA- 1, 2, 3	FA- 2a, 2b	FA-2b	MA- 4, 5, 6, 7, 8, 9a, 9b, 9c, 10	MA-9c	-	-
pH [-]	12.9 - 13.3	13.1 - 13.9	12.7	11.9 - 13.8	12.7	10.7 - 13.5	11.9 - 13
EC [mS/cm]	12 - 43	64 - 69	19.9	9.2 - 67	14.3	1.466 - 15.88	3.7
DOC	68 - 120	78 - 160	86	6.6 - 630	12	-	0.192 - 29
NUTRIENTS AND MAJOR COMPONENTS							
Al	0.72 - 8.6	<0.25	<1.2	<0.25 - 24	<1.2	<1 - 35	5.3
Ca	22 - 220	16 - 320	4700	<8 - 1500	7000	100 - 8980	2700 - 10790
Cl	77 - 320	2500 - 3400	3200	84 - 3600	750	1.21 - 800	7000 - 34000
Cu	0.013 - 0.23	0.025 - 0.15	0.066	<0.0043 - 0.55	<0.021	0.03 - <0.5	0.08 - <0.5
Fe	<0.012	<0.013	<0.062	<0.017	<0.062	0.03 - <0.5	0.034 - <0.5
K	2700 - 14000	25000 - 29000	28000	4400 - 39000	9500	384 - 14200	3413 - 30000
Mg	<0.032	<0.034	0.26	<0.032 - 1.5	0.43	<0.2 - 3	<0.2 - 2.35
Mn	0.011 - 0.065	<0.011 - 0.018	<0.053	<0.011 - 0.46	<0.053	0.02 - 0.14	0.009 - <0.2
Na	280 - 1000	2200 - 3500	2400	340 - 4100	1000	42 - 204	700 - 6000
P	<0.59 - 1.2	<0.61	<2.9	<0.59 - 1.6	<2.9	<5	0.13
S		1700*	1600*	420*	410*	7 - 1040	500 - 16700
Si	<0.35 - 230	<0.36 - 3.3	<1.8	<0.35 - 570	<1.8	<10 - 122	5.6 - 38
Zn	<0.063	0.24 - 0.38	0.31	<0.067 - 1.9	2.8	<0.2	<0.2 - 51
TYPICAL ELEMENTS OF ENVIRONMENTAL CONCERN							
As	<0.0044 - 0.048	<0.0046 - 0.005	<0.022	<0.0044 - 0.61	<0.022	<5	0.044
Ba	0.059 - 1.4	0.22 - 0.59	2.9	0.015 - 0.75	5.9	1.27 - 131	2.7 - 145
Cd	<0.0014	<0.0014	<0.007	<0.0015	<0.0069	<0.03	0.0004 - <0.02
Co	<0.001 - 0.0024	<0.001 - 0.0032	<0.005	<0.001 - 0.023	<0.005	<0.2	0.001 - 0.001
Cr	0.13 - 5.7	1.2 - 6.2	6.2	<0.0046 - 4.5	0.29	0.08 - 0.91	0.01 - 38
Hg	n.m.	n.m.	n.m.	n.m.	n.m.	-	-
Mo	0.25 - 0.38	0.46 - 1.1	1.1	0.25 - 1.7	0.26	<0.2	0.78 - 5.4
Ni	0.03 - 0.067	<0.0046 - 0.28	1.1	0.023 - 0.87	0.94	<0.5	0.009 - <0.5
Pb	<0.0013 - 0.014	0.011 - 0.054	0.09	<0.0014 - 0.021	0.036	0.11 - <0.5	<0.5 - 157
Sb	<0.0024 - 0.0035	<0.0025	<0.012	<0.0024 - 0.11	<0.012	-	<0.05 - 0.18
Se	<0.014 - 0.027	0.23 - 0.68	0.34	0.053 - 0.54	0.2	-	0.14 - 1.5
Sn	<0.0025	<0.0026	<0.012	<0.0025 - 0.006	<0.012	-	0.004 - 0.004
Sr	0.1 - 3.8	3.3 - 11	56	0.073 - 26	61	-	33
Tl	<0.00036 - 0.00078	<0.00037	<0.0018	<0.00036 - 0.0008	<0.0018	-	-
V	0.0019 - 0.51	0.0019 - 0.0019	<0.0073	<0.0015 - 3.2	<0.0073	<0.1	0.035

[a]: Freire et al. (2015); Pöykiö et al. (2009); Steenari and Karlfeldt Fedje (2010); Supancic et al. (2014); Van Der Sloot and Van Zomeren (2010).

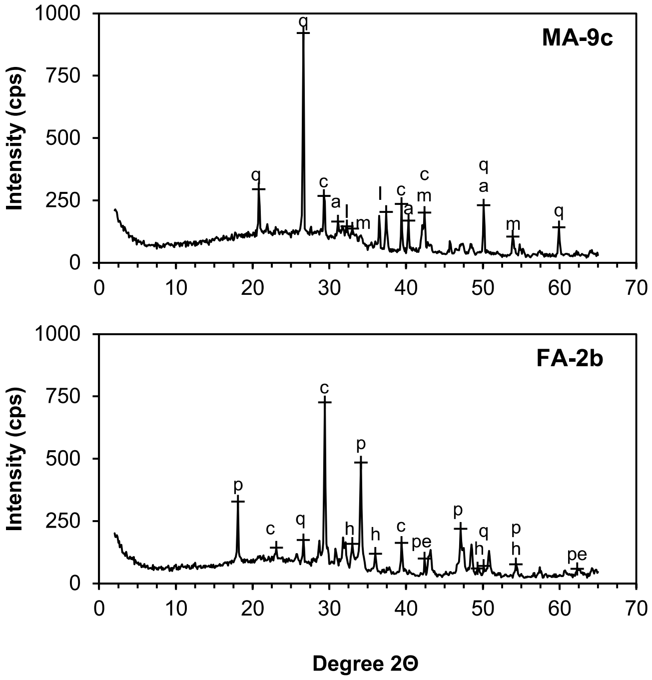

Figure 1. XRD patterns for samples MA-9c and FA-2b and mineral phase identification. [a: ankerite; c: calcite; h: hematite; m: magnesite; p: portlandite; pe: periclase; q: quartz; s: calcium silicate; l: lime].

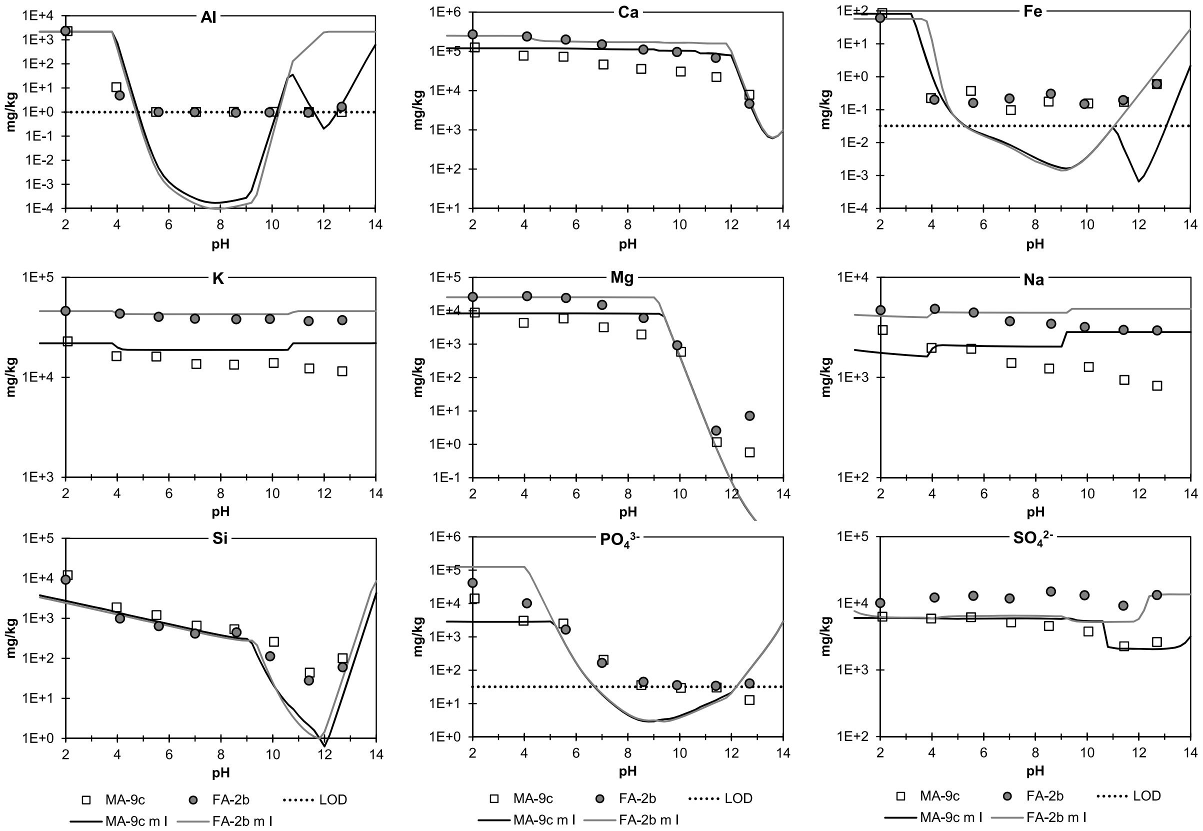

Figure 2. pH-dependent leaching test results in comparison with the geochemical model predictions: major components and nutrients. The results are expressed as leached amount (in mg/kg dw). Dots and squares series represent measured values for FA-2b and MA-9c, respectively. Full lines represent Model I (m I) predictions. [LOD: limit of detection]

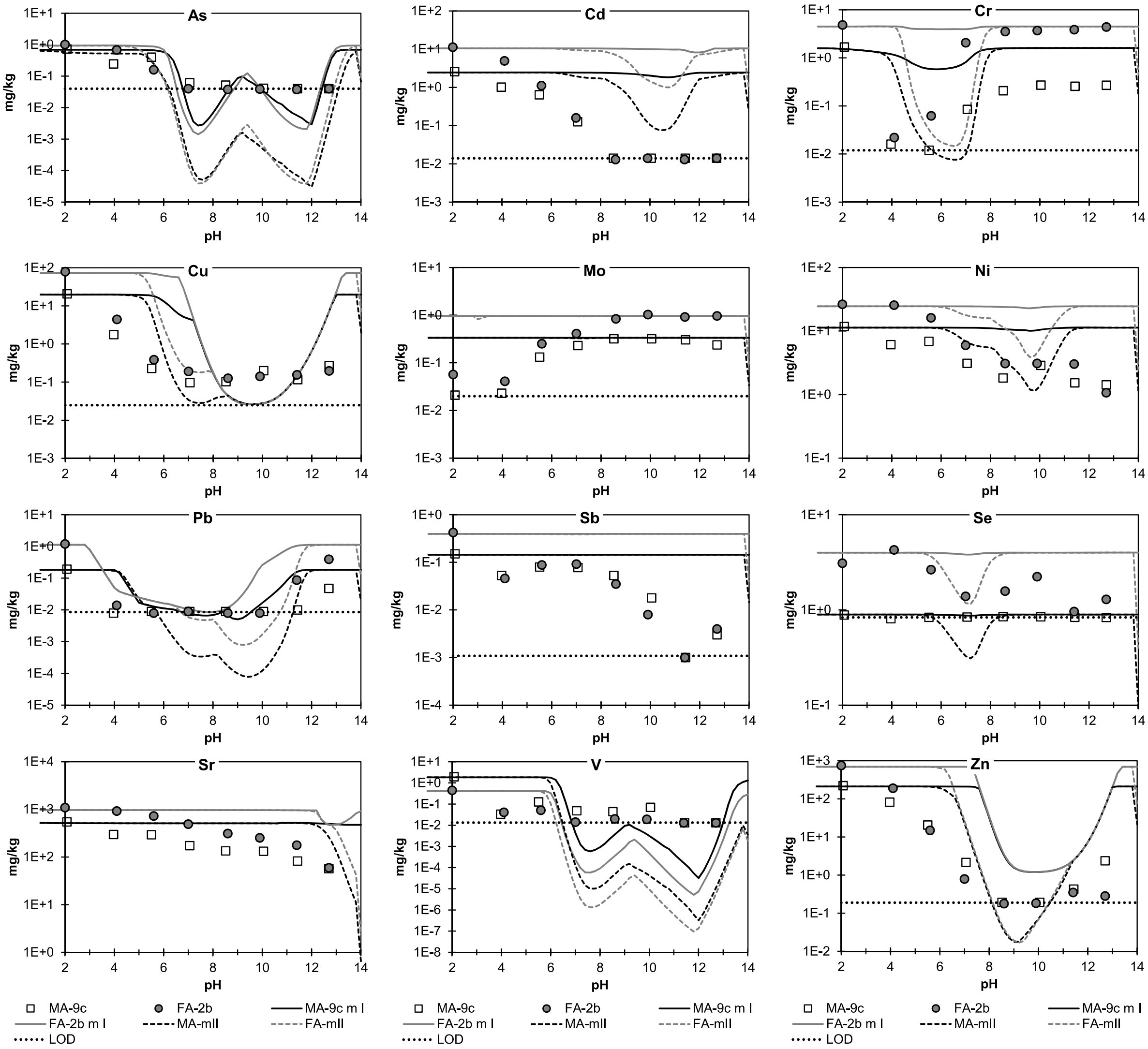

Figure 3. pH-dependent leaching test results in comparison with the geochemical model predictions: trace metals and metalloids. The results are expressed as leached amount (in mg/kg dw). Dots and squares series represent measured values for FA-2b and MA-9c, respectively. Full lines represent Model I (m I) predictions, whereas dashed lines represent Model II (m II) predictions. [LOD: limit of detection]

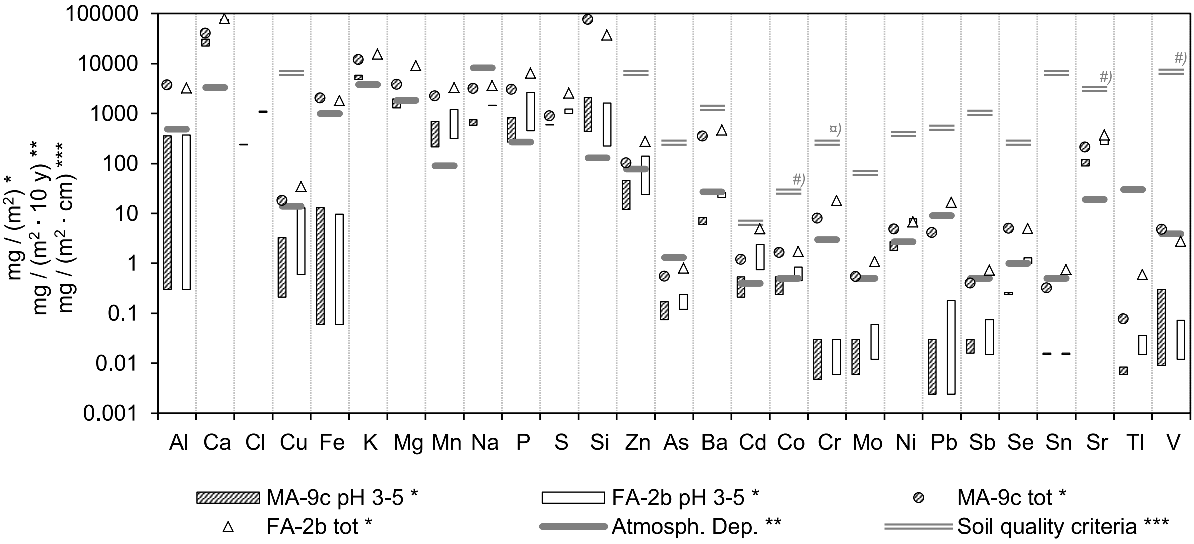

Figure 4. Composition and source-term release of the two selected ash samples, i.e. MA-9c and FA-2b, in comparison with ten years' worth of Danish atmospheric deposition (Hovmand and Kystol, 2013) and Danish SQC for "very sensitive land use" (DEPA, 2015), assuming an ash dosage of 300 g/m^2 and that the SQC had to comply within the first centimetre of soil (soil density of 1.1-1.5 g/cm^3). Ash release data reflect the observed leaching from pH-dependent tests at the pH 3-5. [¤): soil quality criteria for Cr refers to Cr (VI) only; **#)**: soil values for Co, Sr and V refer to typical Danish farmland contents (DEPA, 1995), average mineral soil composition (Capo et al., 1998), and California Human Health Screening Levels in the case of a residential scenario (OEHHA, 2010), respectively].

SUPPLEMENTARY MATERIAL

Recirculation of biomass ashes onto forest soils: ash composition, mineralogy and leaching properties

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Table S1. Wood ash samples and combustion facilities: main characteristics.

Sample	Ash type	Combustion plant	Combustion technology	Use of wood chips period: 2014 – 2015 (tonnes wood chips /year)
BA-1	Bottom	Ebeltoft (I)	Grate fired	11000
BA-2	Bottom	Ebeltoft (II)	Grate fired	9000
BA-3	Bottom	Herning	Grate fired	252000
FA-1	Fly	Ebeltoft (I)	Grate fired	18000
FA-2a	Fly	Ebeltoft (II)	Grate fired	11000
FA-2b	Fly	Ebeltoft (II)	Grate fired	9000
FA-3	Fly	Herning	Grate fired	252000
MA-4	Mixed	Trustrup	Grate fired	4500
MA-5	Mixed	Allingåbro	Grate fired	5000
MA-6	Mixed	Kjellerup	Grate fired	17000
MA-7	Mixed	Assens J	Grate fired	5500
MA-8	Mixed	Galten	Grate fired	14900
MA-9a	Mixed	Brande	Grate fired	8500
MA-9b	Mixed	Brande	Grate fired	8500
MA-9c	Mixed	Brande	Grate fired	8500
MA-10	Mixed	Harboør	Gasification	9000

Table S2. List of mineral phases identified in this study, both from XRD analyses and geochemical modelling.

Mineral Name	Chemical formula
Ankerite	$Ca(Fe,Mg,Mn)(CO_3)_2$
$Ba_{0.5}Sr_{0.5}So_4$	$Ba_{0.5}Sr_{0.5}SO_4$
Birnessite	$(Na_{0.3}Ca_{0.1}K_{0.1})(Mn^{4+},Mn^{3+})_2O_4\cdot 1.5\ H_2O$
Brucite	$Mg(OH)_2$
Calcite	$CaCO_3$
Calcium silicate	Ca_2O_4Si
Calcium silicate hydrates	examples: Tobermorite: $Ca_5Si_6O_{16}(OH)_2\cdot 4H_2O$; Jennite: $Ca_9Si_6O_{18}(OH)_6\cdot 8H_2O$
Cl-pyromorphite	$Pb_5(PO_4)_3Cl$
$Cu(OH)_{2(s)}$	$Cu(OH)_2$
Gibbsite	$Al(OH)_3$
Hydroxyapatite	$Ca_5(PO_4)_3(OH)$
Leucite	$K[AlSi_2O_6]$
Magadiite	$NaSi_7O_{13}(OH)_3\cdot 4(H_2O)$
Lime	CaO
Maghemite	$\gamma\text{-}Fe_2O_3$
Magnesite	$MgCO_3$
Microcline	$KAlSi_3O_8$
Octacalcium phosphate	$Ca_8H_2(PO_4)_6\cdot 5H_2O$
$PbMoO_4$	$PbMoO_4$
Portlandite	$Ca(OH)_2$
Quartz	SiO_2
Willemite	Zn_2SiO_4
Zincite	$(Zn,Mn)O$
$ZnO_{(s)}$	ZnO

Table S3. Chemical composition of MA-9c and FA-2b. Results are expressed in mg/kg dw, unless differently specified. The pH of the ashes refers to the value measured after batch leaching tests at L/S 10 L/kg. [MC: moisture content; TOC: total organic carbon]

	MA-9c	**FA-2b**		**MA-9c**	**FA-2b**
pH (-)	12.7	12.7	**Mo**	1.81 (4.5 %)	3.61 (14 %)
MC (%)	0.15 (35 %)	47.3 (4.4 %)	**N**	700 (2.9 %)	1670 (3.5 %)
TOC (%)	5.84 (2.5 %)	7.39 (29 %)	**Na**	10500 (8.0 %)	12000 (25 %)
C (%)	6.64 (0.77 %)	8.28 (0.80 %)	**Nb**	4.99 (4.9 %)	2.7 (9.2 %)
Ag	0.268 (2.5 %)	0.728 (2.0 %)	**Nd**	6.22 (1.6 %)	5.62 (1.8 %)
Al	12400 (4.7 %)	10800 (14 %)	**Ni**	16.1 (2.0 %)	22.4 (0.76 %)
As	1.82 (3.8 %)	2.68 (8.8 %)	**P**	10000 (2.6 %)	21400 (1.8 %)
Au	0.145 (43 %)	0.145 (9.3 %)	**Pb**	13.8 (4.6 %)	55.3 (2.0 %)
Ba	1170 (9.9 %)	1550 (0.056 %)	**Pd**	0.366 (46 %)	<0.512
Be	1.91 (58 %)	0.798 (1.6 %)	**Pr**	1.68 (1.0 %)	1.5 (2.3 %)
Ca	135000 (2.8 %)	263000 (3.1 %)	**Pt**	0.0115 (36 %)	0.0124 (73 %)
Cd	3.99 (3.4 %)	16.3 (0.74 %)	**Rb**	73 (0.65 %)	75.4 (0.79 %)
Ce	17.5 (6.2 %)	15.1 (26 %)	**Re**	0.0738 (35 %)	0.0999 (21 %)
Co	5.49 (0.21 %)	5.79 (2.0 %)	**Rh**	<0.01	<0.01
Cr	26.6 (3.1 %)	60.6 (3.4 %)	**Ru**	0.201 (110 %)	0.0122 (120 %)
Cs	1.28 (23 %)	<1.05	**S**	2450 (5.3 %)	8490 (2.8 %)
Cu	60.4 (2.9 %)	115 (1.0 %)	**Sb**	1.33 (3.0 %)	2.44 (1.6 %)
Dy	1.09 (2.2 %)	0.934 (2.0 %)	**Sc**	2.43 (3.8 %)	1.73 (5.1 %)
Er	0.69 (4.4 %)	0.549 (2.3 %)	**Se**	<16.7	<16.7
Eu	0.373 (0.84 %)	0.315 (3.6 %)	**Si**	254000 (6.3 %)	124000 (33 %)
Fe	6720 (1.9 %)	6090 (2.4 %)	**Sm**	1.19 (1.3 %)	1.09 (2.5 %)
Ga	3.33 (1.1 %)	2.76 (8.4 %)	**Sn**	1.07 (3.6 %)	2.51 (3.3 %)
Gd	1.25 (2.5 %)	1.08 (2.9 %)	**Sr**	708 (3.1 %)	1240 (3.6 %)
Ge	1.54 (3.9 %)	1.21 (5.6 %)	**Ta**	0.877 (13 %)	0.438 (17 %)
Hf	3.27 (8.9 %)	1.68 (25.3 %)	**Tb**	0.195 (1.6 %)	0.169 (2.5 %)
Ho	0.245 (3.9 %)	0.204 (1.6 %)	**Th**	2.25 (5.0 %)	1.54 (11 %)
In	0.104 (110 %)	0.0154 (7.4 %)	**Ti**	1120 (1.9 %)	616 (9.8 %)
Ir	0.134 (100 %)	<0.011	**Tl**	0.217 (0.93 %)	1.98 (2.8 %)
K	39400 (3.8 %)	51200 (4.7 %)	**Tm**	0.114 (7.0 %)	0.0854 (3.6 %)
La	7.98 (1.6 %)	7.02 (2.1 %)	**V**	15.9 (3.4 %)	9.18 (1.3 %)
Li	5.7 (27 %)	6.73 (0.17 %)	**W**	12 (44 %)	12 (30 %)
Lu	0.123 (11 %)	0.0836 (3.5 %)	**Yb**	0.719 (6.8 %)	0.512 (4.9 %)
Mg	12700 (2.3 %)	30000 (3.1 %)	**Zn**	340 (3.2 %)	924 (0.78 %)
Mn	7430 (2.7 %)	11000 (1.6 %)	**Zr**	94.2 (1.2 %)	55.2 (30 %)

Table S4. Content of critical elements, as defined in European Commission (2014), and additional trace elements in wood ash samples, grouped by ash type: bottom ash (BA), fly ash (FA) and mixed ash (MA). Minimum and maximum contents are reported. Results are expressed in mg/kg dw.

	BA	**FA**	**MA**
samples	BA- 1, 2, 3	FA- 1, 2a, 2b, 3	MA- 4, 5, 6, 7, 8, 9a, 9b, 9c, 10
OTHER TRACE AND CRITICAL ELEMENTS			
Ag	<0.26 - 0.40	<0.26 - 1.05	<0.26 – 2.0
Au	0.0408 - 0.225	0.053 - 0.145	0.0207 - 0.136
Be	1.61 - 3.89	0.798 - 7.19	0.985 - 6.29
Ce	9.96 - 21.5	6.37 - 16.1	10.2 - 14.5
Cs	<1.05 - 2.05	<1.05 - 4.94	<0.71 - 15.8
Er	0.326 - 0.744	0.185 - 0.549	0.402 - 0.558
Eu	0.188 - 0.313	0.083 - 0.315	0.179 - 0.271
Ga	4.03 - 4.57	<2.76 - 4.58	<2.62 - 5.27
Gd	0.697 - 1.6	0.462 - 1.34	0.711 - 1.22
Ge	0.871 - 0.947	0.528 - 1.21	0.641 - 1.32
Hf	0.851 - 2.04	0.359 - 1.68	0.904 - 2.1
Ho	0.0783 - 0.238	0.0278 - 0.204	0.111 - 0.192
In	<0.005 - 0.2	<0.0101 - 0.2	<0.005 - 0.2
Ir	0.0169 - 0.291	<0.011 - 0.517	0.0115 - 0.976
La	5.67 - 11.2	3.67 - 8.49	5.86 - 8.21
Li	5.0 - 9.87	5.12 - 16.5	3.67 - 8.35
Lu	0.0209 - 0.114	<0.009 - 0.0836	0.0298 - 0.0882
Nb	2.36 - 5.83	1.2 - 5.58	3.03 - 5.21
Nd	3.64 - 8.84	2.33 - 6.62	3.9 - 5.94
Pd	<0.22 - 0.512	<0.512 - 1.45	<0.22 - 0.512
Pr	1.13 - 2.54	0.698 - 1.86	1.21 - 1.7
Pt	0.0091 - 0.0143	0.0124 - 0.0327	<0.0115 - 0.0323
Rb	83.9 - 148	75.4 - 143	64.7 - 396
Re	0.058 - 0.135	0.0615 - 0.13	<0.04 - 0.117
Rh	<0.01	<0.01	<0.01
Ru	<0.002 - 0.4	<0.002 - 0.4	<0.002 - 0.4
Sc	1.95 - 2.32	<1.11 - 1.77	1.59 - 2.47
Sm	0.737 - 1.49	0.437 - 1.24	0.761 - 1.15
Ta	0.175 - 0.307	0.0423 - 0.438	0.126 - 0.381
Tb	0.0975 - 0.195	0.0522 - 0.169	0.112 - 0.149
Ti	696 - 1750	371 - 4530	747 - 1580
Tm	0.0224 - 0.117	<0.022 - 0.102	<0.022 - 0.101
W	0.537 - 1.49	0.905 - 12	0.504 - 1.53
Yb	0.329 - 0.653	0.14 - 0.512	0.359 - 0.594
Zr	32.9 - 78.6	13.6 - 55.2	35.3 - 86

Table S5. Compliance leaching test results, grouped by ash type (BA, FA and MA): “other trace and critical elements”. Results are expressed in mg/kg dw. Minimum and maximum contents are reported. Leaching tests were carried out at the L/S ratio 2 L/kg (EN 12457-1:2002) and 10 L/kg (EN 12457-3:2002).

	BA (L/S 2)	**FA (L/S 2)**	**MA (L/S 2)**	**MA (L/S 10)**	**FA (L/S 10)**
samples	BA- 1, 2, 3	FA- 2a, 2b	MA- 4, 5, 6, 7, 8, 9a, 9b, 9c, 10	MA-9c	FA-2b
OTHER TRACE AND CRITICAL ELEMENTS					
Ag	<0.0026 - 0	<0.0026 - 0.0036	<0.0026	<0.013	<0.013
Au	<0.00018 - 0.0016	<0.00019	<0.00018 - 0.0028	<0.0009	<0.0009
Be	0.0055 - 0.0063	<0.0022 - 0.012	<0.0023 - 0.017	0.039	0.043
Ce	<0.00051	<0.00053	<0.00069	<0.0025	<0.0025
Cs	0.043 - 0.14	0.38 - 0.45	0.055 - 1.3	0.13	0.36
Er	<0.00036	<0.00037	<0.00049	0.0019	<0.0018
Eu	0.00015 - 0.0002	<0.00014	<0.00013 - 0.00045	<0.00066	<0.00066
Ga	<0.0088 - 0.031	<0.0092	<0.0088 - 0.21	<0.044	<0.044
Gd	0.00022 - 0.00033	<0.00012 - 0.00027	0.00016 - 0.021	0.0019	0.00098
Ge	<0.00085 - 0.0026	<0.00088 - 0.012	<0.00091 - 0.0065	0.011	0.014
Hf	<0.00025 - 0	<0.00026	<0.00025	<0.0013	<0.0013
Ho	<0.00018 - 0.00023	<0.00019	<0.0002 - 0.00038	0.0012	<0.00092
In	<0.000046	0.000049 - 0.00095	<0.000046 - 0.00068	<0.00023	<0.00023
Ir	<0.00011 - 0.00051	<0.00011 - 0.0064	<0.00011 - 0.059	<0.00056	<0.00056
La	<0.0011	<0.0012	<0.0015	<0.0055	<0.0055
Li	0.03 - 0.26	0.053 - 0.23	0.013 - 0.14	0.17	0.63
Lu	<0.00026 - 0.00026	<0.00027	<0.00035 - 0.00039	<0.0013	<0.0013
Nb	<0.00022	<0.00023	<0.00022	<0.0011	<0.0011
Nd	<0.00049 - 0.00053	<0.00051 - 0.00053	<0.00067	<0.0025	<0.0025
Pd	<0.0051	<0.0053	<0.007	<0.026	<0.026
Pr	<0.00035 - 0.00039	<0.00036 - 0.00045	<0.00048 - 0.006	0.002	0.0019
Pt	<0.000065 - 0.00018	<0.000067 - 0.000065	<0.000065 - 0.00021	<0.00032	0.0004
Rb	6.4 - 38	53 - 88	11 - 140	22	57
Re	0.00011 - 0.00057	0.00015 - 0.00073	0.00018 - 0.0017	<0.00041	0.00097
Rh	<0.000099 - 0	<0.0001	<0.000099	<0.0005	<0.0005
Ru	0.00013 - 0.00023	0.00086 - 0.0009	<0.000024 - 0.003	0.0012	0.0017
Sc	<0.0044	<0.0045	<0.006 - 0.04	<0.022	<0.022
Sm	<0.00019 - 0.00037	<0.00019 - 0.00054	<0.0002 - 0.00085	0.0017	0.0019
Ta	<0.00057	<0.00059	<0.00077	<0.0028	<0.0028
Tb	<0.000048	<0.00005	<0.000048	<0.00024	<0.00024
Ti	<0.012 - 0.053	<0.013	<0.012 - 0.046	<0.06	<0.06
Tm	<0.00024 - 0.00028	<0.00025	<0.00024 - 0.00031	0.0013	<0.0012
W	0.045 - 0.21	0.0081 - 0.2	0.006 - 0.52	0.036	0.16
Yb	<0.00035 - 0.00038	<0.00036 - 0.00037	<0.00035 - 0.00038	0.0019	<0.0017
Zr	<0.0000094	<0.0000098	<0.0000094 - 0.000051	<0.000047	<0.000047

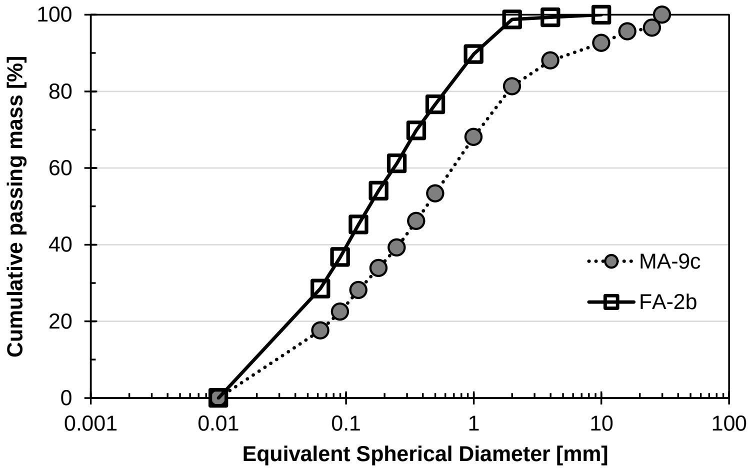

Figure S1. Particle size distribution curves for MA-9c and FA-2b.

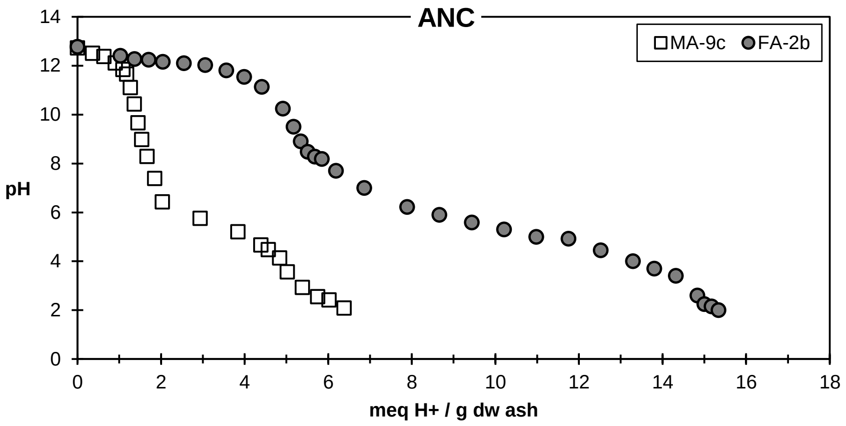

Figure S2. Acid neutralisation capacity (ANC) curves for FA-2b and MA-9c.

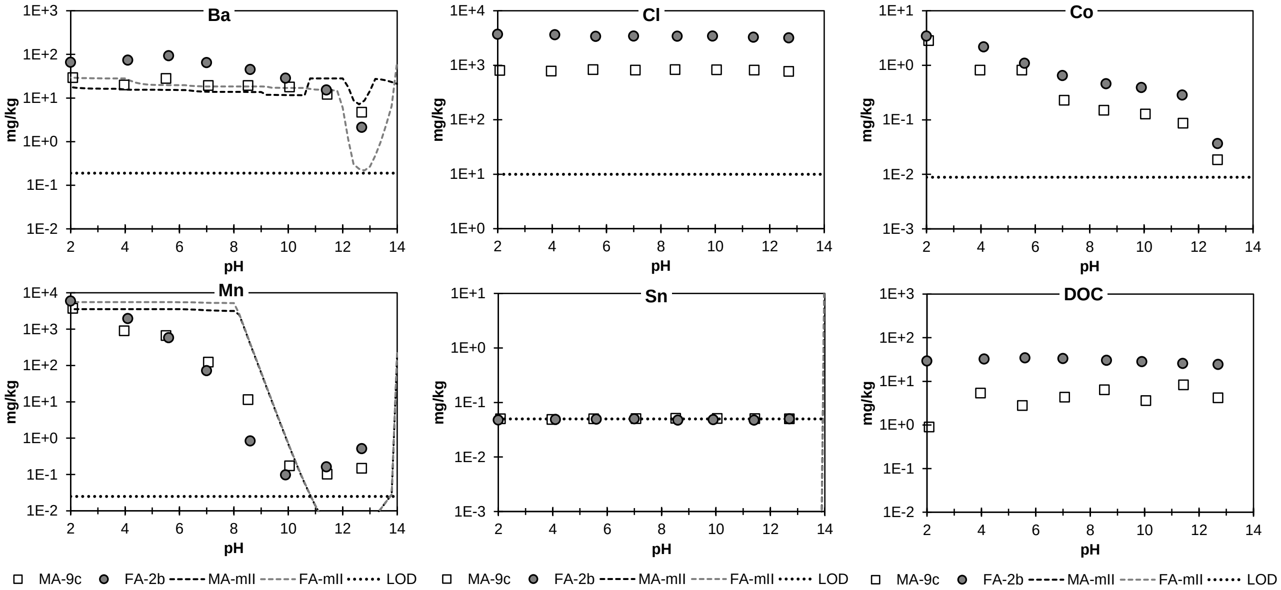

Figure S3. pH-dependent leaching test results in comparison with geochemical model predictions: Ba, Cl, Co, Mn, Sn, Tl and DOC. The results are expressed as leached amount (in mg/kg dw). Dots and squares series represent measured values for FA-2b and MA-9c, respectively. Dashed lines represent Model II (m II) predictions. [LOD: limit of detection]

Section S1. Acid neutralisation capacity (ANC):

ANC was determined according to CEN/TS 14997:2006 (E) using 60 g of ash wet weight and adding distilled water until the L/S ratio 9 L/kg. The mixture was mixed for about an hour, and let it settled for 10 minutes before measuring the solution pH. Next, small amounts of HNO_3 were added, the mixture was mixed for 20 minutes, let it settled for 5 minutes and the solution pH was measured; new acid was added and the procedure was repeated until a pH of 2 was measured.