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

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23 **Abstract**

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

43

44 **Abbreviations**

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

49

50 **1. INTRODUCTION**

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

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

80 et al., 2001; Perkiömäki and Fritze, 2005). Hence, although the potential for increasing the recirculation of wood  
81 ashes to forestry may exist in Denmark, further clarification on the consequences of this process is needed.

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

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

103

## 104 **2. MATERIALS AND METHODS**

### 105 **2.1 Sampling and material handling**

106 Ashes from ten different Danish biomass combustion facilities (see Table S1 in Supplementary Material for more  
107 details on the characteristics of these plants) receiving wood chips, mainly from *Picea Abies*, were sampled in  
108 the period January – March 2014. Depending on the specific technology, freshly generated bottom ash (BA) and

109 fly ash (FA) may be collected at the plant through two separate flows or one single mixed flow (fresh mixed ash:  
110 MA). The latter was a specific case of closed ash conveyer systems, where it was not possible to sample BA and  
111 FA separately. Consequently, the ratio between BA and FA in the MA samples was not known. A total of sixteen  
112 wood ash samples were collected: three BA, four FA and nine MA samples. Sample names used in the following  
113 text refer to the ash type, i.e. *BA*, *FA* or *MA*, followed by a number representing the plant, i.e. *I-10*, and an  
114 optional letter, i.e. *a*, *b* or *c*, indicating the replicate number (where relevant). Upon receipt of the samples at the  
115 laboratory, the mass of each sample was reduced by quartering and splitting, using a riffle splitter in accordance  
116 with ASTM C702/C702M: 2011. All samples were stored in airtight plastic containers at 10°C prior to testing  
117 and characterisation.

118

## 119 **2.2 Ash characterisation**

120 Moisture content was determined on 100 g subsamples according to EN 1097-5: 2008. Next, the dry material  
121 was crushed in a jaw crusher and then pulverised in a vibratory disc mill (agate discs). Approximately 0.2 g  
122 subsamples of the powder were obtained by consecutive riffle splitting and used for determining total organic  
123 carbon (TOC; EN 13137: 2001; LECO induction furnace CS-200 Analyser) and contents of C, S, N and H  
124 (Elemental Analyser - Vario MACRO cube); triplicate analyses were carried out. The elemental composition of  
125 the wood ash samples was determined in duplicates using 0.25 g of pulverised material for microwave-assisted  
126 acid digestion (Multiwave Anton Paar 3000) according to EN 13656: 2003, using 6 ml of HNO<sub>3</sub> (65 %), 2 ml of  
127 HCl (37 %), 2 ml of HF (40 %) and 12 H<sub>3</sub>BO<sub>3</sub> (10 %). In addition, 2 ml of H<sub>2</sub>O<sub>2</sub> (30 %) was added to enhance  
128 the oxidation of residual organic matter. The digestates were analysed by inductively coupled plasma (ICP) mass  
129 spectrometry (7700x, Agilent Technologies) for the content of Al, Ag, As, Au, Ba, Be, Ca, Cd, Ce, Co, Cr, Cs,  
130 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,  
131 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  
132 spectrometry (Varian Vista-MPX) for the content of Ca, K, Mn and S. The same procedure was repeated to a  
133 reference material, i.e. *BCR-176R*, to validate the results.

134 To facilitate more detailed characterisation, based on the results of the elemental content analyses, two  
135 ash samples were selected with the following characteristics: a) one ash sample with the highest Cd content  
136 among the sixteen samples (FA-2b, consisting of fly ash) and b) one ash sample complying with the current  
137 Danish limit values (DEPA, 2008) for utilising wood ashes on top of forest soils (MA-9c, a mixed ash consisting

138 of both fly ash and bottom ash). As such, the two selected samples represented a “worst case scenario” with  
139 regards to the content of Cd, and a “typical situation” with ashes that are today allowed for recirculation in  
140 forestry settings. Further characterisation of the two selected samples, i.e. MA-9c and FA-2b, included: (i)  
141 determining particle size distribution, (ii) XRD scanning, (iii) analysis of the content of polycyclic aromatic  
142 hydrocarbons (PAHs; US EPA, 2008), using GC-MS after Soxhlet extraction using dichloromethane (US EPA  
143 8270D, 2014), (iv) and leaching characterisation based on a range of different leaching tests (Section 2.4 and  
144 2.5). Particle size distribution was determined in triplicate according to EN 933-1:2012, using 250 g of  
145 previously dried (110°C) samples by means of 13 stainless steel sieves with mesh sizes ranging between 0.063  
146 µm and 25 mm. XRD scanning was carried out on pulverised samples of MA-9c and FA-2b, using a Philips PW  
147 1830 X-ray diffractometer equipped with a copper tube operated at 40 kV and 50 mA. Diffraction patterns were  
148 collected over a 2-theta range from 2° to 65°, employing an angular step of 0.05° and a count time of 2 s.

149

### 150 **2.3 Batch leaching experiments**

151 All sixteen samples, except FA-1 and FA-3 (insufficient sample amounts), were subjected to a batch leaching  
152 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  
153 batch leaching test at L/S 10 L/kg (EN 12457-2:2002). Electrical conductivity and pH were measured in  
154 unfiltered eluates immediately after the leaching test. Eluates were then filtered (0.45 µm,  
155 Polytetrafluoroethylene) and divided into a number of subsamples for subsequent analysis. Subsamples intended  
156 for ICP analysis were acidified by adding HNO<sub>3</sub> (p.a.) to pH <2, while subsamples for analysis of chlorides  
157 (potentiometric titration with AgNO<sub>3</sub>, Tim 865 Titration Manager), dissolved organic carbon (DOC) and  
158 dissolved total carbon (Shimadzu TOC 5000A Analyser) were not acidified. All eluate samples were kept at 4°C  
159 prior to the analyses.

160

### 161 **2.4 pH-dependent batch leaching experiments**

162 The influence of pH on the leaching of MA-9c and FA-2b was tested according to CEN/TS 14997:2006(E),  
163 using a computer-controlled titration system. Eight pH values were investigated: 2, 4, 5.5, 7, 8.5, 10, 11.5 and  
164 natural pH (without the addition of acid). The acid neutralisation capacity (ANC) of both ash samples was tested  
165 prior to the actual leaching test (see Section S1 in Supplementary Material for more details on the ANC test).  
166 About 60 g dw of ash was added with distilled water and continuously mixed, and then HNO<sub>3</sub> was added to

167 achieve and maintain the predefined pH values for 48 hours. At the end of the experiment, pH, electrical  
168 conductivity and redox potential were measured in the eluate samples, which were then filtered (0.45 µm,  
169 Polytetrafluoroethylene), acidified for the fraction undergoing ICP measurements, stored and finally analysed  
170 similarly to eluates from the batch leaching test.

171

## 172 **2.5 Equilibrium column experiments for organic compounds**

173 The release of organic compounds from MA-9c and FA-2b was evaluated using an equilibrium column test  
174 according to Nordtest TR576 (2004). In this test, the leachant (0.005 M CaCl<sub>2</sub> and 0.5 g NaN<sub>3</sub>) was recirculated  
175 (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  
176 end of the test, pH and conductivity were measured in the eluates, and these were then analysed for sixteen PAH  
177 compounds, as defined by US EPA (2008), using a GC-MS after extraction with acetone/pentane (1:1),  
178 according to the Danish method Reflab 4:2008.

179

## 180 **2.6 Geochemical modelling of pH-dependent leaching**

181 The results of the pH-dependent leaching experiments were used to describe the leaching behaviour of major  
182 components (K, Ca, Si, Mg, Mn, Al, Fe, PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup>) in both samples, using the so-called “geochemical  
183 multi-surface modelling approach” (Dijkstra et al., 2008). All model calculations were carried out using the  
184 ORCHESTRA modelling framework (Meeussen, 2003) embedded in a LeachXS database/expert system  
185 (<http://www.leachxs.com/lxsdll.html>). Thermodynamic data from the MINTQA2 thermodynamic database, as  
186 modified by Butera et al. (2015), were used.

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

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

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

217 The results of our own XRD analyses, carried out for both samples, were combined with information  
218 from the literature (e.g. Freire et al., 2015; Magdziarz et al., 2016; Vassilev et al., 2013). Nevertheless, since  
219 more than 200 different mineral phases have been found in different types of “bioashes” (Vassilev et al., 2013),  
220 only minerals found in more than five independent studies were considered “plausible” in our model. For the fly  
221 ash (FA-2b), the final list of “plausible” mineral phases put into the geochemical model of the pH-dependent  
222 leaching included phases determined by our XRD analysis (calcite, portlandite, quartz, periclase, maghemite and  
223 calcium silicate) and phases identified from the literature (gibbsite, microcline, leucite, magadiite, CSH, brucite,  
224 birnessite, hydroxyapatite, octacalcium phosphate (OCP) and  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{SO}_4$ ). Analogically, for the mixed ash

225 (MA-9c), the list included calcite, lime, portlandite, quartz, ankerite, magnesite (based on the XRD results) and  
226 calcium silicate, CSH, OCP, microcline, maghemite, leucite, magadiite, brucite, birnessite, zincite and  
227  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{SO}_4$  (based on the literature). Table S2 in Supplementary Material provides the full list of minerals  
228 identified during this study, along with the respective chemical formula.

229 Two models were tested: Model I and Model II. Model I included (i) metal availabilities, (ii)  
230 “plausible” solubility controlling minerals, (iii) reactive Fe-(hydr)oxide sites approximated by “ferrihydrite”  
231 (surface area of  $600 \text{ m}^2/\text{g}$  and capacity of  $1.37 \cdot 10^{-4} \text{ kg/kg}$  and  $9.73 \cdot 10^{-5} \text{ kg/kg}$  for MA-9c and FA-2b,  
232 respectively) and (iv) a polynomial description of the DOC concentration as a function of pH. Model II was  
233 identical to Model I, albeit with the addition of adsorption to Al-(hydr)oxides. Similarly to Fe-(hydr)oxides, the  
234 maximum content of reactive Al-(hydr)oxides was estimated from the pH-dependent leaching data for Al (at pH  
235 2) and treated as a surrogate sorbent to the Fe-(hydr)oxides (Dijkstra et al., 2006a, 2006b). The combined  
236 contribution of Fe- and Al-(hydr)oxides yielded  $7.62 \cdot 10^{-3} \text{ kg/kg}$  and  $7.83 \cdot 10^{-3} \text{ kg/kg}$  of “ferrihydrite” for MA-9c  
237 and FA-2b, respectively. Model II additionally included – based on literature screening and calculated SIs – a  
238 few additional mineral phases that might be relevant in the mineral assemblage:  $\text{Cu}(\text{OH})_{2(s)}$ ,  $\text{PbMoO}_4$ , willemite,  
239  $\text{ZnO}_{(s)}$  and Cl-pyromorphite. In order to ensure ion competition, all calculations were carried out simultaneously  
240 for Al, Ba, Ca, Cd,  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ , Cr, Cu, Fe, Si, As, K, Li, Mg, Mn, Mo, Na, Ni, Pb,  $\text{PO}_4^{3-}$ , Sb, Se, Sr,  $\text{SO}_4^{2-}$ , V, Zn  
241 and DOC. An oxidising environment was assumed during the calculations ( $\text{pe} + \text{pH} = 15$ ).

242

## 243 **2.7 Comparison with soil quality and atmospheric deposition**

244 To evaluate the potential source-term releases from wood ashes when applied to top of soil, a hypothetical  
245 scenario was considered, based on the two samples MA-9c and FA-2b. In this scenario, the two ashes were  
246 assumed to be placed on top of  $1 \text{ m}^2$  of an acidic Danish forest soil with a pH value in the range 3-5 (for typical  
247 pH values in Danish soil, refer to Balstrøm et al. (2013)), at the maximum allowed dosage of  $300 \text{ g/m}^2$  (see  
248 Introduction). In forest applications, wood ashes are typically spread on top of the soil and not further worked  
249 with it. Due to the limited amount of ash added to the top of the soil, overall ash leaching could be expected to be  
250 dominated by the acidic properties of the soil, rather than the alkaline properties of the ashes. As such, the  
251 source-term release from the ashes was estimated based on pH-dependent leaching (pH 3-5, L/S 10 L/kg), itself  
252 based on the defined ash dosage ( $300 \text{ g/m}^2$ ) and soil area ( $1 \text{ m}^2$ ), and it was expressed in  $\text{mg/m}^2$ . In addition, the  
253 maximum theoretical load of nutrients and potential contaminants entering the soil was evaluated based on ash

254 composition, assuming that all solid contents would be released into the soil at some point in time. Although this  
255 is unlikely to happen within a foreseeable time frame (see Astrup et al., 2006), the maximum theoretical loads  
256 can still be compared with soil quality criteria levels (described in the following paragraph) to indicate the level  
257 of relevance. Similarly to the ash source-term releases, maximum theoretical loads were expressed in  $\text{mg}/\text{m}^2$ .  
258 The potential soil-leachate interaction is beyond the scope of this investigation.

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

267 SQC (expressed in  $\text{mg}/\text{kg}$ ) were converted into threshold values (expressed per volume of soil, i.e.  
268  $\text{mg}/(\text{m}^2 \cdot \text{cm})$ ), assuming a soil area of  $1 \text{ m}^2$ , a soil depth of 1 cm and a soil bulk density of  $1.1\text{-}1.5 \text{ g}/\text{cm}^3$ . The  
269 rationale for choosing a soil depth of 1 cm was to allow direct comparison between the “layer” of ash ( $300 \text{ g}/\text{m}^2$ )  
270 and the uppermost part of the soil.

271

## 272 **3. RESULTS AND DISCUSSION**

### 273 **3.1 Ash composition**

274 Table 1 shows the chemical composition of the sixteen ash samples grouped by ash type, i.e. BA, FA and MA,  
275 compared to values found in relevant literature. A detailed composition of MA-9c and FA-2b is presented in  
276 Supplementary Material (Table S3), together with particle size distribution curves (Figure S1) showing 90 % and  
277 70 % of FA-2b and MA-9c as being smaller than 1 mm (similar curves were reported by Lanzerstorfer (2015)  
278 and Supancic et al. (2014) for grate-fired wood ashes).

279

#### <Table 1>

280 The chemical composition of the sixteen samples was comparable to literature values for all major,  
281 minor and trace elements. The most abundant elements were Ca and Si with contents of about  $10^5 \text{ mg}/\text{kg dw}$ .  
282 With regards to typical plant nutrients, high contents of P, K and Mg were found (about  $10^4 \text{ mg}/\text{kg dw}$ ), whereas

283 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  
284 dw in the case of BA and FA, respectively), most likely because of the low volatizing point of N in the  
285 combustion chamber. S content varied by up to two orders of magnitude ( $10^2 - 10^4$  mg/kg), with the highest  
286 values found in FA samples. The same partitioning tendency was observed for Cu and Zn ( $10^1 - 10^2$  mg/kg and  
287  $10^1 - 10^3$  mg/kg, respectively). Several trace metal(-loid)s seemed occasionally to be enriched in FA samples  
288 compared with BA samples, i.e. Cd, Mo, Se, Sn, Sr and Tl; however, the content of trace metal(-loid)s in the  
289 samples showed to be generally independent of the actual ash type, e.g. As, Ba, Co, Cr, Ni, Pb, Sb and V. These  
290 findings were consistent with other wood ash studies (e.g. Freire et al., 2015; Ingerslev et al., 2011; Pöykiö et al.,  
291 2012).

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

297 TOC levels in the sixteen samples were generally between 0.28 % and 33 % (except for a few high  
298 values for FA-1, FA-3 and MA-7), which was comparable with the 0.8 %-13 % reported by Bjurström et al.  
299 (2014).

300

### 301 **3.2 X-Ray Diffraction (XRD)**

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

305 <Figure 1>

306

### 307 **3.3 Batch leaching results**

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

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<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.,

341 2015; Johansson and van Bavel, 2003; Masto et al., 2015; Pitman, 2006; Sarenbo, 2009; Straka and Havelcová,  
342 2012), where high values have been explained by insufficient oxidation during the combustion process (Sarenbo,  
343 2009; Straka and Havelcová, 2012; Vehlow and Dalager, 2011). The observed PAH levels in the ashes tested  
344 herein were about two orders of magnitude below Danish limit values for the utilisation of wood ash on the top  
345 of soil, i.e. 12 mg/kg (DEPA, 2008), and about one order of magnitude below Danish SQC defined for soils  
346 intended for “very sensitive land use”, i.e. 4 mg/kg (DEPA, 2015).

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

359

### 360 **3.5 Results of the pH-dependent leaching test**

#### 361 **3.5.1 Acid neutralising capacity**

362 In spite of similar natural pH values, i.e. ~12.7 at L/S 10 L/kg, the ANC of the two materials differed  
363 significantly (Figure S2 in Supplementary Material): ANC at the end-point of pH 2 (ANC<sub>2</sub>) was 6.5 meq H<sup>+</sup>/g  
364 dw and 15.5 meq H<sup>+</sup>/g dw for MA-9c and FA-2b, respectively. Similarly, ANC<sub>7.5</sub>, i.e. the point of consumption  
365 of carbonates, hydroxides and soluble basic silicate hydrates (Johnson et al., 1995), exhibited clear differences  
366 for the two samples: 1.8 meq H<sup>+</sup>/g and 6.4 meq H<sup>+</sup>/g for MA-9c and FA-2b, respectively. This indicated higher  
367 contents of carbonates, hydroxides and silicates in the fly ash sample, as confirmed also by the XRD results,  
368 which indicated high intensities especially for calcite and portlandite peaks for FA-2b. In line with our findings,

369 Freire et al. (2015) reported ANC<sub>4</sub> values of 1.2-2.1 meq H<sup>+</sup>/g dw and 3.6-9.6 meq H<sup>+</sup>/g dw for wood BA and  
370 wood FA, respectively.

371

### 372 **3.5.2 pH-dependent leaching of major components and nutrients**

373 The pH-dependent leaching of Na, K, Cl, Ca, Mg, Fe, Si, Al and PO<sub>4</sub><sup>3-</sup> is shown as a series of points in Figure 2,  
374 together with the results of geochemical model calculations (Model I, see Section 2.6), which are presented as  
375 lines. In general, the leaching trends of the major ions were described adequately by the selected mineral phases  
376 (see Section 2.6). Most importantly, no significant differences were observed between the leaching trends for  
377 FA-2b and MA-9c. Similarly to the leaching observed for other types of thermal residues, such as coal fly ash,  
378 MSWI BA and MSWI air pollution control residues (Dijkstra et al., 2006a; Hjelm, 1990; Hyks et al., 2007),  
379 the leaching of Na, K and Cl from the wood ashes was rather independent of pH, while the leached amounts  
380 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  
381 observed here but not captured by geochemical modelling, a slight dependence on pH for the leaching of Na and  
382 K was shown by Freire et al. (2015) in the case of wood BAs.

383

#### **<Figure 2>**

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

394 Between pH 13 and pH 8, the leaching of PO<sub>4</sub><sup>3-</sup> was pH-independent. Below pH 8, leaching increased  
395 by three orders of magnitude toward an acidic pH. Apatite precipitation is likely to occur at neutral to alkaline  
396 pH, as also indicated by the positive SI calculated for hydroxyapatite and chlorapatite. The leaching of Ba

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

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

406

### 407 **3.5.3 pH-dependent leaching of trace metals and metalloids**

408 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,  
409 while the results of the geochemical modelling are shown as lines. Two types of line are shown for each material,  
410 reflecting the results for Model I and Model II (see Section 2.6).

411

#### **<Figure 3>**

412 Although Model II generally resulted in a better description of the analytical data, model predictions for  
413 Mo and Sb did not respond to the increased amounts of sorption reactive sites. In MSWI BA, the decrease in Mo  
414 leaching at pH <6 has been described by the solubility of  $CaMoO_4(s)$  (Dijkstra et al., 2006b); however, including  
415 this mineral in our model had no influence on the results. Similarly, although the leaching of Sb decreased  
416 toward high pH values (with a minimum around pH 10.5 – 11), which may indicate the precipitation of several  
417 Sb-bearing mineral phase(s) e.g.  $Ca[Sb(OH)_6]_2$ , ettringite or roméite (Cornelis et al., 2012), including these  
418 minerals in the mineral assemblage had no influence on the modelling results.

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

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

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

428

### 429 **3.6 Implications for forestry utilisation**

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

435

#### <Figure 4>

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

439 Based on the elemental composition of the ashes, the maximum theoretical loads of Ba, Cd, Cr, Sr, Mo,  
440 Ni, Pb, Sb, Se, Sn and V were always below the selected SQC levels, and above/close to their expected  
441 atmospheric deposition over a period of ten years. It is worth noting that because of the higher contents of Cd,  
442 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  
443 application, compared to MA-9c. Theoretical loads, despite not being necessarily representative of actual  
444 leachable amounts, can still be used for a preliminary screening to evaluate the amount of contaminants and/or  
445 nutrients added to the soil in comparison with SQC and background levels.

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

451 The source-term release of most elements of typical environmental concern, e.g. As, Ba, Cr, Cu, Mo,  
452 Ni, Pb, Sb, Se, Sn, Tl and Zn, was estimated at levels below, or close to, atmospheric deposition. Similarly, the  
453 potential ash release of Co, Sr and V was significantly lower than the selected reference soil levels (Capo et al.,  
454 1998; DEPA, 1995; OEHHA, 2010). On the other hand, the estimated release of Cd appeared close to the

455 selected SQC in the case of FA-2b. Remember that FA-2b was selected specifically because of its relatively high  
456 Cd content (i.e. 16.3 mg/kg), though still within Danish legislation limits (i.e. 20 mg/kg; DEPA (2008)). This  
457 supports the notion that the attention paid to Cd as a potential critical element in wood ashes, because of its  
458 potential toxicity and bioavailability (see Introduction), may be justified.

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

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

473

#### 474 **4. CONCLUSIONS**

475 Ca, Si, P, K and Mg abounded in the investigated wood ashes, while relatively high contents of S and N were  
476 observed in fly ashes and mixed ashes compared with bottom ashes. For some fly ash samples, relatively high  
477 contents of Cd, Mo, Se, Sn, Sr and Tl were found. The leaching of most elements changed as a function of the  
478 solution pH, except for K, Cl, Na and SO<sub>4</sub><sup>2-</sup>, which were found to be rather independent of pH. While relatively  
479 high leaching of PO<sub>4</sub><sup>3-</sup>, Mg, Zn, Cu and Cd was observed for pH conditions relevant to acidic forest soils, Cr and  
480 Mo increased leaching more toward alkaline conditions. For most major, minor and trace elements, leaching was  
481 described adequately by a geochemical speciation model based on mineral dissolution involving a relatively  
482 limited set of mineral phases. The maximum theoretical loads of Ba, Cd, Cr, Sr, Mo, Ni, Pb, Sb, Se, Sn and V  
483 were below the selected soil quality criteria levels, whereas the source-term release of Cd was identified as of

484 potential concern compared with these levels. The expected release of nutrients such as Ca, Mg, Mn, P and K  
485 appeared significant compared to atmospheric deposition. Similar wood ash application rates can result in  
486 different liming effects, depending on their alkaline species content. Similar scenario-based assessments of the  
487 source-term releases of nutrients and contaminants can be made prior to ash application in specific cases, based  
488 on site-specific soil characteristics and information about precipitation.

489

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495

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

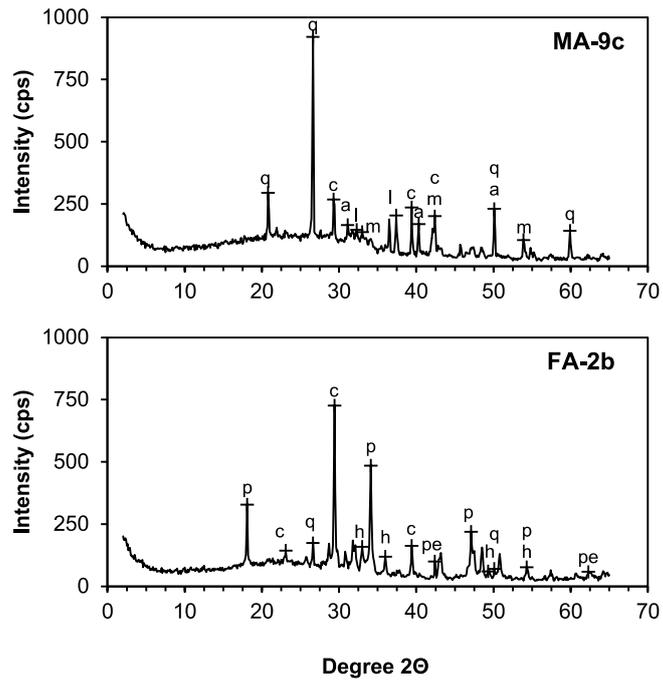
	<b>BA – this study</b>	<b>BA - literature <sup>a)</sup></b>	<b>FA – this study</b>	<b>FA - literature <sup>a)</sup></b>	<b>MA – this study</b>	<b>MA - literature <sup>a)</sup></b>
<b>samples</b>	BA- 1, 2, 3		FA- 1, 2a, 2b, 3		MA- 4, 5, 6, 7, 8, 9a, 9b, 9c, 10	
<b>MC [%]</b>	8.07 - 29.5	19 - 31	28.1 -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

720  
721 <sup>a)</sup>: Etiégni and Campbell (1991); Etiégni et al. (1991); Holmberg et al. (2000); Huang et al. (1992); Ingerslev et  
722 al. (2014); Narodoslowsky and Obernberger (1996); Poykio et al. (2007); Pöykiö et al. (2009); SLU (2008);  
723 Steenari et al. (1999); Supancic et al. (2014); Vassilev et al. (2014b).

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

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

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729 <sup>a)</sup>: Freire et al. (2015); Pöykö et al. (2009); Steenari and Karlfeldt Fedje (2010); Supancic et al. (2014); Van Der  
730 Sloot and Van Zomeren (2010).  
731

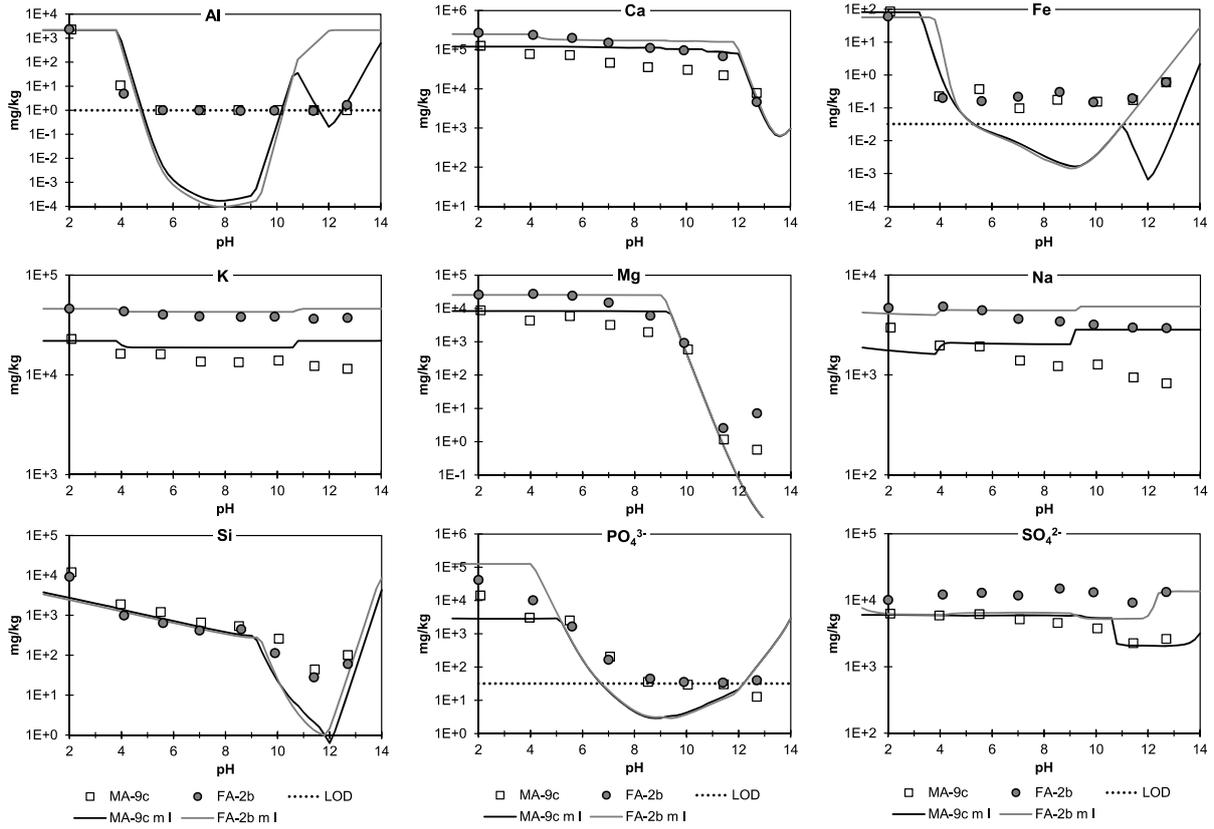


732

733 **Figure 1.** XRD patterns for samples MA-9c and FA-2b and mineral phase identification. [a: ankerite; c: calcite;

734 h: hematite; m: magnesite; p: portlandite; pe: periclase; q: quartz; s: calcium silicate; l: lime].

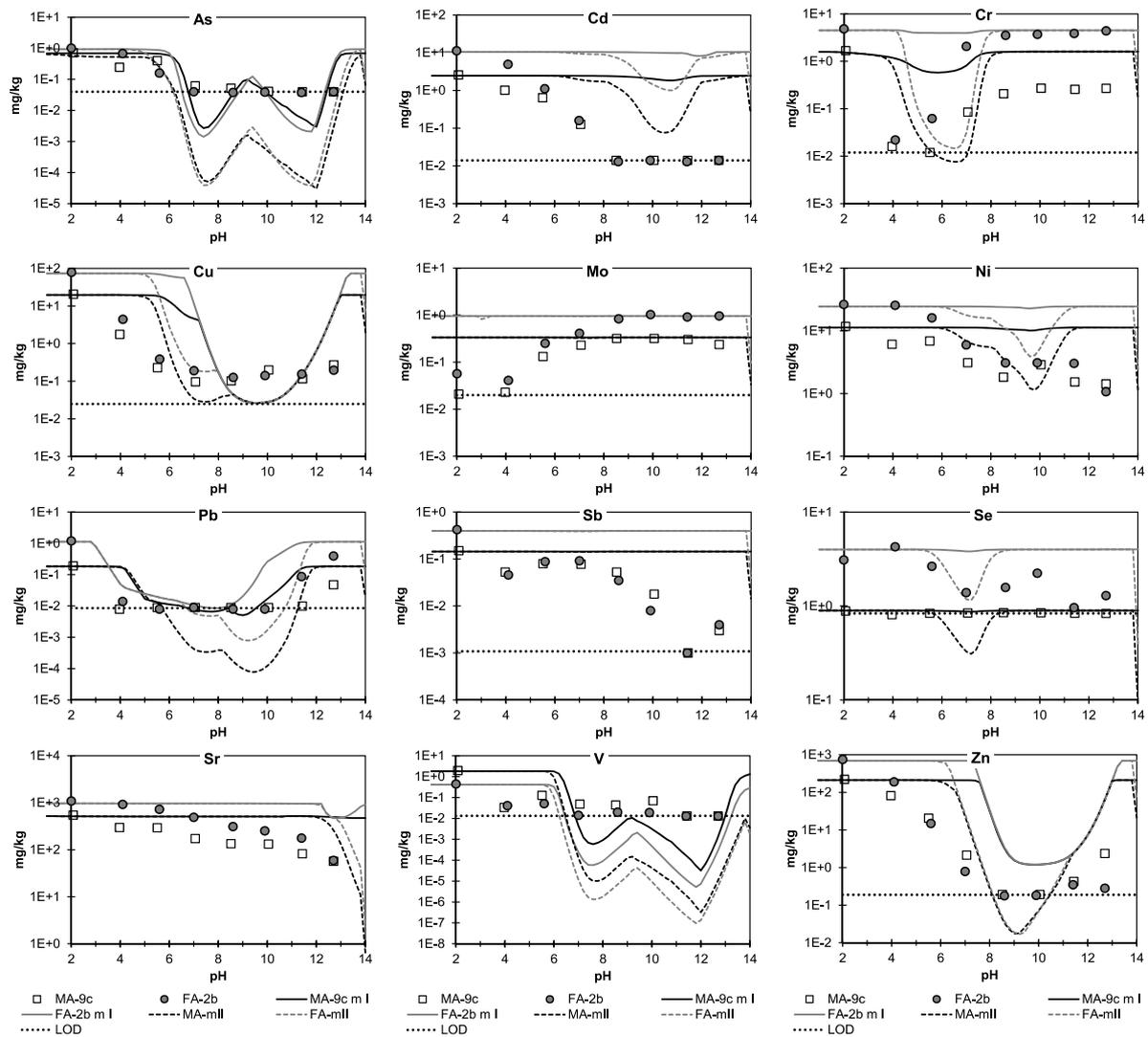
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736

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

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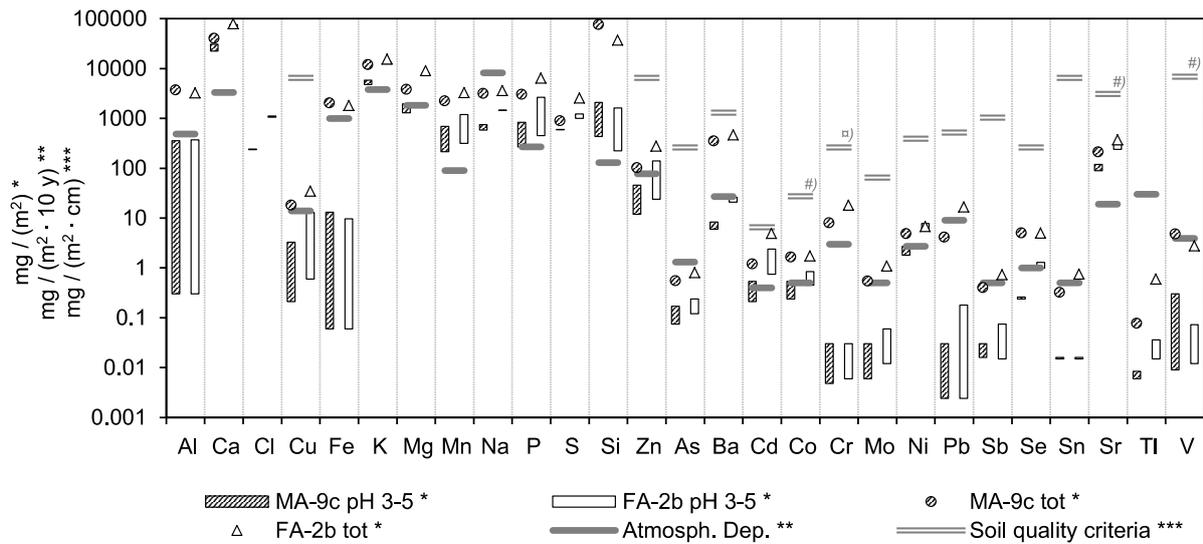
743 **Figure 3.** pH-dependent leaching test results in comparison with the geochemical model predictions: trace metals

744 and metalloids. The results are expressed as leached amount (in mg/kg dw). Dots and squares series represent

745 measured values for FA-2b and MA-9c, respectively. Full lines represent Model I (m I) predictions, whereas

746 dashed lines represent Model II (m II) predictions. [LOD: limit of detection]

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

757

758 **SUPPLEMENTARY MATERIAL**

759  
760 **Recirculation of biomass ashes onto forest soils: ash**  
761 **composition, mineralogy and leaching properties**

762  
763 *Maresca, A. <sup>\*a</sup>, Hyks, J. <sup>b</sup> & Astrup, T. F. <sup>a</sup>*

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776 <sup>\*)</sup> Corresponding author: almar@env.dtu.dk

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780 **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

781

782

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

Mineral Name	Chemical formula
Ankerite	$\text{Ca}(\text{Fe}, \text{Mg}, \text{Mn})(\text{CO}_3)_2$
$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{SO}_4$	$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{SO}_4$
Birnessite	$(\text{Na}_{0.3}\text{Ca}_{0.1}\text{K}_{0.1})(\text{Mn}^{4+}, \text{Mn}^{3+})_2\text{O}_4 \cdot 1.5 \text{H}_2\text{O}$
Brucite	$\text{Mg}(\text{OH})_2$
Calcite	$\text{CaCO}_3$
Calcium silicate	$\text{Ca}_2\text{O}_4\text{Si}$
Calcium silicate hydrates	examples: Tobermorite: $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ; Jennite: $\text{Ca}_9\text{Si}_6\text{O}_{18}(\text{OH})_6 \cdot 8\text{H}_2\text{O}$
Cl-pyromorphite	$\text{Pb}_5(\text{PO}_4)_3\text{Cl}$
$\text{Cu}(\text{OH})_{2(s)}$	$\text{Cu}(\text{OH})_2$
Gibbsite	$\text{Al}(\text{OH})_3$
Hydroxyapatite	$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$
Leucite	$\text{K}[\text{AlSi}_2\text{O}_6]$
Magadiite	$\text{NaSi}_7\text{O}_{13}(\text{OH})_3 \cdot 4(\text{H}_2\text{O})$
Lime	$\text{CaO}$
Maghemite	$\gamma\text{-Fe}_2\text{O}_3$
Magnesite	$\text{MgCO}_3$
Microcline	$\text{KAlSi}_3\text{O}_8$
Octacalcium phosphate	$\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$
$\text{PbMoO}_4$	$\text{PbMoO}_4$
Portlandite	$\text{Ca}(\text{OH})_2$
Quartz	$\text{SiO}_2$
Willemite	$\text{Zn}_2\text{SiO}_4$
Zincite	$(\text{Zn}, \text{Mn})\text{O}$
$\text{ZnO}_{(s)}$	$\text{ZnO}$

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785

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

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

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

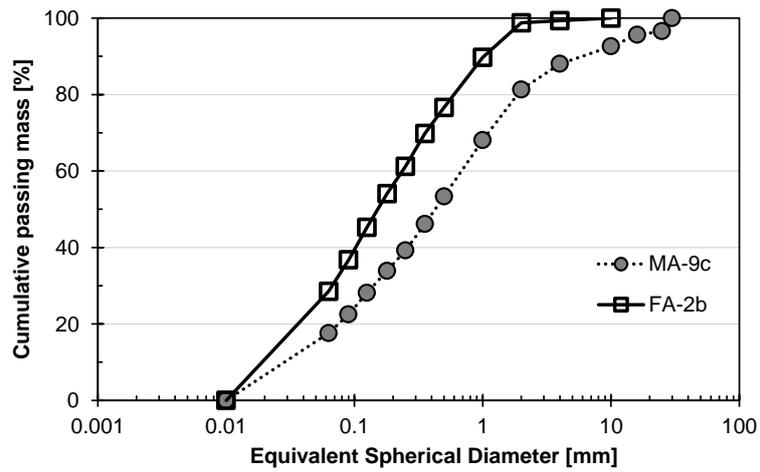
	<b>BA</b>	<b>FA</b>	<b>MA</b>
<b>samples</b>	BA- 1, 2, 3	FA- 1, 2a, 2b, 3	MA- 4, 5, 6, 7, 8, 9a, 9b, 9c, 10
<b>OTHER TRACE AND CRITICAL ELEMENTS</b>			
<b>Ag</b>	<0.26 - 0.40	<0.26 - 1.05	<0.26 - 2.0
<b>Au</b>	0.0408 - 0.225	0.053 - 0.145	0.0207 - 0.136
<b>Be</b>	1.61 - 3.89	0.798 - 7.19	0.985 - 6.29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

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796 **Table S5.** Compliance leaching test results, grouped by ash type (BA, FA and MA): “other trace and critical  
797 elements”. Results are expressed in mg/kg dw. Minimum and maximum contents are reported. Leaching tests  
798 were carried out at the L/S ratio 2 L/kg (EN 12457-1:2002) and 10 L/kg (EN 12457-3:2002).  
799

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



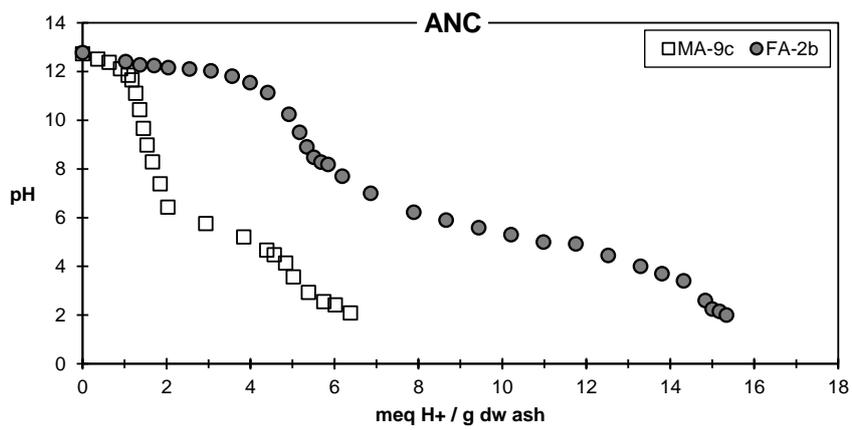
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802 **Figure S1.** Particle size distribution curves for MA-9c and FA-2b.

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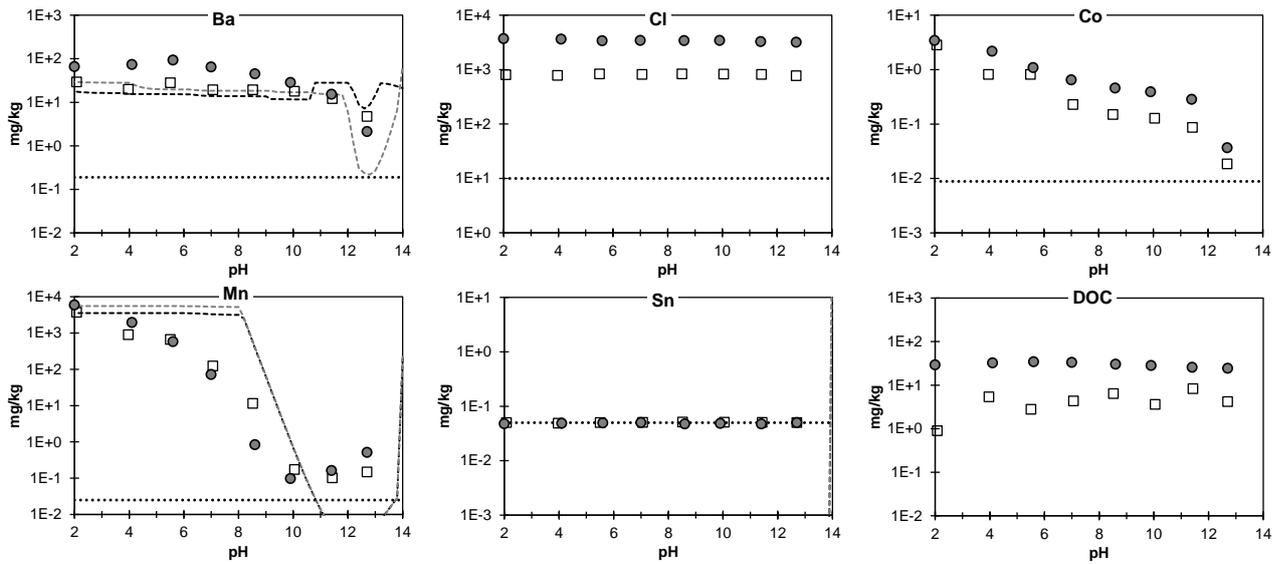
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807 **Figure S2.** Acid neutralisation capacity (ANC) curves for FA-2b and MA-9c.

808



809 □ MA-9c ● FA-2b -----MA-mII -----FA-mII ..... LOD □ MA-9c ● FA-2b -----MA-mII -----FA-mII ..... LOD □ MA-9c ● FA-2b -----MA-mII -----FA-mII ..... LOD

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

814

815 **Section S1. Acid neutralisation capacity (ANC):**

816 ANC was determined according to CEN/TS 14997:2006 (E) using 60 g of ash wet weight and adding distilled  
 817 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  
 818 measuring the solution pH. Next, small amounts of HNO<sub>3</sub> were added, the mixture was mixed for 20 minutes, let  
 819 it settled for 5 minutes and the solution pH was measured; new acid was added and the procedure was repeated  
 820 until a pH of 2 was measured.

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