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Long-term leaching of nutrients and contaminants from wood combustion ashes

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21 **Abstract**

22 With increasing amounts of woody biomass being combusted for energy purposes worldwide, more wood ash is being
23 generated and needs management. As an alternative to landfilling, residues may be utilised for liming and fertilising
24 purposes on forest soils. Comprehensive evaluations of long-term leaching from these residues are needed in order to
25 assess potential environmental impacts associated with their utilisation. Two Danish wood ash samples, one fly ash and
26 one mixed ash (a combination of fly ash and bottom ash), were evaluated in long-term percolation column tests (up to
27 L/S ~2000 L/kg), in order to quantify the release of major, minor and trace metal(loid)s. While columns of three
28 different lengths were used, the leaching of individual elements could be described as a function of the L/S ratio –
29 irrespective of the column length. At L/S 1000 L/kg, the cumulative releases of K, S, Na, Ca and Rb were at 40-100 %
30 of their respective solid contents, followed by Ba, Cr, Sb, Sr and V at 15-40 % and Al, Mg, Zn, Cd, Co, Fe, Pb, Tl, Mn
31 and P at <5 %. Speciation calculations indicated that i) the observed concentrations of Ca, Mg, Al, Ba, Si and sulphate
32 from both ash types could be described through the dissolution/precipitation of a limited set of minerals and that ii)
33 leaching of silicates should be included in long-term assessment of alkalinity release from wood ashes. Non-equilibrium
34 conditions were indicated by flow interruptions. However, the presence of non-equilibrium did not have significant
35 effect on the calculated cumulative releases at high L/S ratios. Based on the assessment of cumulative releases at L/S 10
36 L/kg and L/S 1000 L/kg it is concluded that low L/S-based data may not provide sufficient background for prediction of
37 long-term release from wood ash, in particular for Ba, Cr, Sb and V, and less critically also for As, Cd, Cu, Mo and Ni.

38

39 **Keywords:** biomass ash; liming; MSWI; flow interruption; geochemical modelling; column

40

41 **Abbreviations:**

42 ANC: acid neutralisation capacity; DOC: dissolved organic carbon; LOQ: limit of quantification; MSWI: municipal
43 solid waste incineration; WAC: waste acceptance criteria

44

45 **1. INTRODUCTION**

46 The combustion of biomass for energy purposes is expanding worldwide, especially in countries like Denmark (The
47 Danish Council on Climate Change, 2015) with concrete targets for the phase-out of fossil resources. This phase-out
48 often involves the expansion of biomass combustion, with wood as a common energy source. Accordingly, increasing
49 amounts of wood chips or wood pellets are currently being combusted in Denmark for energy purposes, i.e. from 5.7 PJ

50 in 2005 to 16 PJ in 2015 (Danish Energy Agency, 2017), leading to the generation of about 22,300 metric tons dry
51 weight of wood ash in 2012 (Skov and Ingerslev, 2013).

52 Instead of landfilling, wood ash utilisation on top of forest and agricultural soils has been seen as a more
53 sustainable solution – which would utilise the ash liming potential (e.g. Huang et al., 1992; Meiwes, 1995; Pitman,
54 2006) and recirculate primary plant nutrients (N, P and K) present in these materials. Nevertheless, as wood ash
55 application may lead to soil/water contamination if high levels of toxic elements are released, wood ash application has
56 been regulated in many European countries (e.g. Denmark, Finland, Sweden, Austria and Germany) by setting limits for
57 maximum dosages and threshold values for “heavy metals”, as well as by providing guidelines for wood ash
58 application. To ensure meaningfulness of such guidelines and to evaluate potential benefits/risks associated with the
59 utilisation of wood ash on soils, a comprehensive characterisation of the long-term release of nutrients, liming
60 components and environmentally problematic elements is needed, also with regards to leaching mechanisms.

61 Depending on the combustion technology and the configuration of the ash discharge unit, three types of wood
62 ashes are typically generated: bottom ash, fly ash and mixed ash (combination of fly ash and bottom ash). The
63 composition of the different types of wood ash has been investigated in the past (e.g. Ingerslev et al., 2011; Maresca et
64 al., 2017) together with the impact of different fuel types (e.g. Reimann et al., 2008; Werkelin et al., 2011), combustion
65 technologies (e.g. Drift et al., 2001; Freire et al., 2015) and boiler operating parameters (e.g. Demeyer et al., 2001;
66 Misra et al., 1993). Overall, Ca, K and Si are the most abundant elements ($10^4 - 10^5$ mg/kg), followed by Mg, P, Na, Fe,
67 Mn and S (10^3-10^4 mg/kg) and different “trace elements” (i.e. $<10^3$ mg/kg). Similar to other ash types, for example
68 municipal solid waste incineration (MSWI) ashes, volatile elements (e.g. N, Cd, Pb, and Zn) are generally enriched in
69 wood fly ash compared to wood bottom ash (Maresca et al., 2017). The pH of freshly generated wood ash lies between
70 12 and 14 at L/S 2 L/kg (Maresca et al., 2017).

71 The short-term leaching behaviour of wood ash has been studied primarily for compliance purposes by means
72 of batch and/or column leaching tests, carried out at a liquid-to-solid (L/S) ratio smaller than 20 L/kg. Batch leaching
73 tests at L/S 2 L/kg, 10 L/kg and 16 L/kg were applied, and both distilled and acidified distilled water were used as
74 leachant media (e.g. Freire et al., 2015; Maresca et al., 2017; Sano et al., 2013; Supancic et al., 2014). Similarly, column
75 test studies have employed columns of different sizes, packed with different amounts of ash, operated at different flow
76 rates and under different leaching media (e.g. Chirenje et al., 2002; Mellbo et al., 2008).

77 Leaching at L/S > 20 L/kg has been primarily investigated to assess long-term releases in relation to potential
78 wood ash utilisation scenarios. Single step or multiple step batch tests were generally used (Holmberg et al., 2000;

79 Larsson and Westling, 1998; Ludwig et al., 2005; Steenari et al., 1999a, 1999b; Steenari and Karlfeldt Fedje, 2010),
80 rather than column leaching experiments (e.g. Eriksson, 1996; Liodakis et al., 2009). Similar to the characterization of
81 the short-term leaching, the impact of different ash types, treatments (e.g. granulated and pelletised ash, with or without
82 additives) and wood fuel types have been investigated. Both distilled water and acidified distilled water (with e.g. HCl,
83 HNO₃ or H₂SO₄) were used (Larsson and Westling, 1998; Ludwig et al., 2005; Steenari et al., 1999b). L/S ratio used in
84 the batch test studies varied between 16 L/kg and 60,000 L/kg – thirty steps at 2000 L/kg (e.g. Larsson and Westling,
85 1998; Steenari and Karlfeldt Fedje, 2010). In addition, many studies focused on the release of major elements (e.g. Ca,
86 K, Mg, Na and sulphate), whilst trace elements were often overlooked. Some studies have focused on fresh ashes,
87 others on aged (carbonated, hardened) ashes. Overall, the wide range of different test parameters (e.g. ash type,
88 leachant, L/S ratio, investigated elements and pre-treatments) makes direct comparison of the results difficult.

89 Although geochemical speciation modelling has been used to describe potential mechanisms controlling the
90 release from MSWI ash (e.g. Astrup et al., 2006; Dijkstra et al., 2002; Meima and Comans, 1999), to our knowledge,
91 only few studies applied geochemical modelling on a wide range of elements in wood ash leachates (Maresca et al.,
92 2017; Steenari et al., 1999a) and wood gasification ashes (Allegrini et al., 2011; van der Sloot and van Zomeren, 2010).
93 However, none of these studies addressed long-term leaching by means of a column leaching experiments. Evaluating
94 the leaching mechanisms from fresh ashes may provide a consistent and relevant baseline, which is needed for
95 identifying the effects of ageing of ashes in the field. So far such an evaluation has not been provided for a wide range
96 of elements and at the high L/S ratios.

97 The aim of this paper is: i) to systematically assess the release of nutrients and elements of possible
98 environmental concern from fresh wood ashes by means of long-term percolation tests; ii) to evaluate equilibrium
99 conditions during the columns leaching experiments and to identify mineral phases which may control the leaching of
100 nutrients and trace metal(loid)s; iii) to estimate the long-term cumulative release of nutrients, trace metal(loid)s and
101 alkalinity from wood ash; and iv) to compare the long-term releases with the releases obtained at low L/S ratios.

102

103 **2. MATERIALS AND METHODS**

104 **2.1 Sampling and material handling**

105 Fresh combustion ashes were sampled directly from the ash discharge unit at two grate-fired combustion plants in
106 Denmark, which use wood chips as fuel (mainly from *Picea abies*). One fly ash sample (FA) and one mixed ash sample

107 (MA) were collected. The ashes were split in the laboratory according to ASTM C702/C702M:2011 and stored in
108 hermetically closed buckets at 10⁰C prior to further use.

109 <Table 1>

110

111 2.2 Ash characterisation

112 The chemical composition of MA and FA was investigated in Maresca et al. (2017) with the references “MA-9c” and
113 “FA-2b”, respectively. Section S1, in Supplementary Material, provides a summary of the methodology used by
114 Maresca et al. (2017) for characterising MA and FA, while Table 1 shows the overall composition of these wood ash
115 samples. In general, the content of major, minor and trace elements in both MA and FA fell within typical ranges
116 reported in other wood ash studies – see Maresca et al. (2017) and therein literature.

117

118 2.3 Up-flow percolation experiments

119 Two types of column leaching experiments were carried out for MA and FA: a continuous column leaching experiment
120 and a flow-interrupted column leaching experiment. In both cases, MA and FA were sieved prior to packing the
121 columns and particles >4 mm were crushed in a jaw crusher. Table 2 provides an overview of the individual columns.

122 <Table 2>

123

124 2.3.1 Continuous columns

125 The continuous column leaching experiments were based on EN 14405: 2017. For both MA and FA three columns
126 (acrylic glass; ø: 5cm) of different lengths were used: “long” (referred to as MA-L and FA-L), “medium” (MA-M and
127 FA-M) and “short” (MA-S and FA-S). A thin layer (1.5 cm) of acid-washed sand was placed at the top and bottom of
128 all columns, together with nylon filters (PA 6.6; mesh opening: 20 µm) used to prevent transport of particles into the
129 adjacent tubing.

130 The columns were equilibrated with distilled water for three days via continuous recirculation of the leachate
131 (EN 14405: 2017). Thereafter, an average flow rate of 12 ± 1 mL/h was maintained for the entire duration of the
132 experiment (~5 months). The entire mass of leachate coming from each column was collected by means of PE bottles of
133 different volumes. At relatively low cumulative L/S ratios about 50-100 mL of leachate was collected per bottle,
134 whereas at higher cumulative L/S ratios about 250-1000 mL of leachate was collected per bottle. The weight of all
135 bottles was recorded to keep track of the cumulative volume of the leachate; pH and conductivity were measured in all

136 bottles. Chemical analysis of leachate was carried out for a selected number of samples. The samples were filtered
137 (PTFE filters; mesh opening: 0.45 μm) and divided into two fractions. The first fraction was acidified to $\text{pH} < 2$
138 (HNO_3), and analysed by means of ICP-MS and ICP-OES for the concentration of Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu,
139 Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, S, Sb, Si, Sr, V and Zn. The other fraction was analysed directly for the
140 concentration of dissolved organic carbon (DOC) and dissolved total carbon using a carbon analyser, whereas chloride,
141 sulphate, nitrate and bromide were determined by ion chromatography.

142 Cumulative releases were calculated based on the observed analytical concentrations and plotted against the
143 L/S ratio (see Section 3.1.1 and 3.1.2). Concentrations below the actual limit of quantification (LOQ) were assumed
144 equal to the LOQ (i.e. potential overestimation).

145

146 **2.3.2 Flow-interrupted columns**

147 The presence and impact of possible non-equilibrium conditions on the leaching from MA-L and FA-L were
148 investigated by means of flow interruptions. These were carried out in two additional columns identical to the -L
149 columns in terms of design, packing, operation and leachate sampling and treatment: MA-L_FI and FA-L_FI. Two sets
150 of flow interruptions were carried out, in either system, at L/S 2 L/kg and L/S 50 L/kg, to reflect conditions typical for
151 short- and long-term leaching, respectively. Following the approach of Hyks et al. (2009) – who observed leachate
152 concentrations to approach equilibrium during a one-month long period of flow interruptions in columns packed with
153 MSWI bottom ash – each flow interruption set was designed with the intention of collecting four leachate samples with
154 cumulative retention times ranging from one to four weeks. More specifically, during each flow interruption set, the
155 inlet column flow was stopped and the system was left undisturbed for seven days. The flow was then restarted and a
156 leachate volume corresponding to 1/4 of the estimated pore volume was collected from the outlet – pore volume of each
157 column was estimated independently based on the water-filled porosity (see Section S2 for details). Then, the inlet flow
158 was stopped again for another seven days. This procedure was repeated three times, thus yielding four samples collected
159 during one month of flow interruptions.

160

161 **2.4 Geochemical modelling**

162 Solution speciation of leachates from both continuous columns and flow-interrupted columns were used as inputs for
163 speciation modelling using the ORCHESTRA code (Meeussen, 2003). DOC complexation was included, using the
164 NICA-Donnan model (Kinniburgh et al., 1996) with the generic adsorption reactions defined by Milne et al. (2003).

165 Activity coefficients were calculated based on the Davies equation, and oxidising conditions ($\text{pH} + \text{pE} = 15$) were
166 assumed during speciation calculations. Thermodynamic data from the modified MINTEQA2 thermodynamic database
167 (see Butera et al., 2015) were used.

168 “Plausible” minerals, potentially controlling the solution concentrations of different elements, were selected
169 based on their calculated saturation indices (SIs). The full list of identified minerals is provided in Table S1. Theoretical
170 leachate concentrations in equilibrium with the selected minerals were modelled based on the approach suggested by
171 Astrup et al. (2006) and compared with the observed concentrations. The minerals most likely controlling leaching were
172 identified based on proximity between theoretical and observed concentration curves. Finally, the list of “plausible”
173 minerals was compared with findings in the existing literature and the results of previous XRD scanning carried out for
174 the ashes investigated here (see Maresca et al., 2017).

175 The cumulative release of alkalinity was calculated from the solution speciation. Two types of alkalinity were
176 considered: standard and total. Standard alkalinity was calculated as $\text{St. Alk.} = 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{OH}^-]$, where the
177 square brackets represent the molar concentration of the different species. Total alkalinity included other possibly
178 relevant solution species: $\text{Tot. Alk.} = \text{St. Alk.} + 2[\text{PO}_4^{3-}] + [\text{HPO}_4^{2-}] + [\text{SiO}(\text{OH})_3^-] - [\text{H}^+] - [\text{HSO}_4^-]$.

179

180 **3. RESULTS AND DISCUSSION**

181 **3.1 Continuous columns**

182 Since MA and FA had significantly different moisture content, different amounts of either material were packed in the
183 columns, which in turn reached rather different cumulative L/S ratios during the course of the leaching experiment (see
184 Table 2). In general, similar concentration levels were observed when comparing the analytical concentrations and the
185 modelled results of -S, -M and -L columns against each other (within the same ash sample) as a function of the L/S
186 ratio. Therefore, the observed leachate compositions and speciation results will be described as a function of the L/S
187 ratio, rather than being discussed separately for each individual column.

188 Figures 1 and S1 report the results from continuous columns in terms of cumulative releases, whereas Figure 2
189 compares the observed composition of the leachates with the results from speciation calculations for -S columns (Figure
190 S2 and S3 do it for -L columns). The rationale for selecting specific elements to be shown in the main text, rather than
191 in the Supplementary Material, is to report a representative number of major, minor and trace elements, characteristic of
192 different leaching behaviours (e.g. availability or solubility controlled) and adequate fit with the modelled
193 concentrations, and does not affect the way the individual elements are described in the following text.

194 <Figure 1>

195 <Figure 2>

196

197 3.1.1 pH and major elements

198 Both materials showed decreasing leachate pH, from the initial value of 12.5 to 10.9 at L/S 1000 L/kg (further
199 decreasing by about half of a unit in the FA column at L/S 2300 L/kg). The pH decrease in FA leachates was a little
200 slower compared to the MA leachates, which reflected the higher ANC of FA relative to MA (i.e. $ANC_{4.5} = 13$ meq
201 H^+/g for FA and 5.3 meq H^+/g for MA; see Maresca et al., 2017).

202 For K, Na, S and chloride (and Rb), a relatively fast initial washout was observed for both MA and FA. The
203 solution concentrations of these elements decreased by two to three orders of magnitude before L/S 2 L/kg and L/S 10
204 L/kg for MA and FA, respectively (see Figures 1 and S1). A rapid decrease in the electrical conductivity was observed
205 as well (Figure S1). Similar leaching behaviours and concentration levels were reported by Freire et al. (2015),
206 Holmberg et al. (2000) and Supancic et al. (2014), despite their use of different types of leaching tests. Based on the
207 observed trends, the initial leaching of K, Na and chloride appeared to be linked to dissolution of readily soluble salts
208 (e.g. NaCl, KCl), whereas the solution concentration of S (and Ba) could be explained by dissolution/precipitation of
209 barite before L/S 10 L/kg for MA and before L/S 100 L/kg for FA. At higher L/S ratios, no mineral was found in the
210 database which could be used to explain the observed low concentrations of S (and Ba).

211 Relatively large amounts of Ca were released before the L/S 50 L/kg for MA (~30 g/kg) and before L/S 50
212 L/kg for FA (~90 mg/kg); later releases were gentler as indicated by the cumulative release curve (Figure 1). At L/S
213 1000 L/kg the cumulative release of Ca corresponded to about 40-43 % of the ashes' total Ca content. Similar trends
214 were reported by Steenari et al. (1999b) during sequential batch leaching tests. The calculated SIs suggested that Ca
215 release from MA columns was controlled by calcite and calcium silicate hydrates (such as jennite) over most of the L/S
216 range investigated here. At the same time, hilgenstokite and merwinite also provided an adequate description of the
217 observed Ca concentrations at L/S < 50 L/kg, whereas Ca levels at L/S < 2 L/kg appeared to be controlled by
218 portlandite. For the FA columns, jennite, tobermorite, calcite and hilgenstokite could be used to explain the observed Ca
219 concentrations until L/S 100 L/kg, whereas portlandite and merwinite seemed important at L/S below 20 L/kg.

220 In comparison with the total contents in the ashes, the release of Al and Mg was observed to be low, but steady
221 (except for the increasing Mg releases at L/S above 1500 L/kg for FA) – see Figures 1 and S1. Similar results have been
222 reported by other wood ash studies, despite the different operating conditions and L/S ratios therein used (Freire et al.,

223 2015; Holmberg et al., 2000; Steenari and Karlfeldt Fedje, 2010; Supancic et al., 2014; van der Sloot and van Zomeren,
224 2010). SIs calculated for MA leachates suggested hydrotalcite as the main phase controlling the leaching of Mg while
225 also brucite, clinoenstatite and forsterite could be used to explain solution concentrations at L/S > 50 L/kg. Al
226 concentrations could also be controlled by hydrotalcite, albeit only until L/S 100-250 L/kg (visible only for -L and -M
227 column leachates), whereas diaspore appeared more likely to control Al at higher L/S ratios. With regard to FA
228 leachates, Mg concentrations could be described adequately by åkermanite at L/S ratios below 20 L/kg, while
229 åkermanite, brucite, forsterite and clinoenstatite were found relevant at higher L/S ratios. Tricalcium aluminate hydrate
230 provided an adequate description of the observed Al trends in the -L and -M column leachates until L/S 150 L/kg, but
231 modelled values overestimated the observed concentrations by one to two orders of magnitude; at the higher L/S ratios,
232 modelled concentrations for diaspore slowly approached the observed Al concentrations.

233 The release of Si increased rapidly after the L/S 200 L/kg and cumulative releases of about 12 g/kg were
234 observed by the L/S 1000 L/kg for both MA and FA ashes (corresponding to 4.7 % and 9.7 % of the total Si content in
235 MA and FA ashes, respectively) – further increasing up to ~21 g/kg in the case of FA ashes at L/S 2300 L/kg. Si
236 concentrations corresponded well with the solubility of the same silicates mentioned for Ca and Mg, i.e. jennite (L/S 0-
237 500 L/kg), clinoenstatite (L/S 50-1000 L/kg), merwinite (L/S 0-50 L/kg) and possibly also wollastonite (L/S 500-1000
238 L/kg) for the MA columns. In the FA columns, tobermorite appeared adequate to describe Si concentrations across the
239 entire L/S range, while clinoenstatite also provided a good description of the observed Si concentrations. Again,
240 åkermanite, jennite, merwinite and wollastonite were identified as plausible mineral phases, albeit constrained to limited
241 L/S intervals.

242 P concentrations were generally below LOQ (<20 µg/L) except for the very initial leachates (L/S < 2 L/kg),
243 where concentrations up to 80 µg/L and 37 µg/L were found for FA and MA, respectively. Likewise, Freire et al.
244 (2015), Maresca et al. (2017) and Supancic et al. (2014) reported concentration levels of P below LOQ in their L/S 10
245 L/kg batch tests. Hilgenstockite, a tetracalcium phosphate (structurally similar yet more soluble than apatite minerals)
246 found in P-rich slag, could explain the measured P concentrations before they decreased below LOQ.

247 Fe concentrations were mostly found below LOQ (<1.3 µg/L) except for the initial release (i.e. before the L/S
248 1 L/kg for MA columns and L/S 5 L/kg for FA columns) showing concentrations up to 20 µg/L. Low leaching of Fe is
249 likely caused by precipitation of FeO(OH), such as lepidocrocite or goethite.

250 Overall, the results of speciation calculations were found to be in general agreement with (i) results of X-ray
251 diffraction analyses of MA and FA ashes (Maresca et al., 2017), (ii) results of independent speciation modelling carried

252 out for leachates from pH-dependent tests of MA and FA ashes (Maresca et al., 2017), (iii) information found in the
253 literature by other wood ash studies (Dahl et al., 2010; Freire et al., 2015; Holmberg and Claesson, 2001; Magdziarz et
254 al., 2016; van der Sloot and van Zomeren, 2010; Vassilev et al., 2013a) and (iv) previous geochemical modelling
255 calculations carried out for MSWI ash (Astrup et al., 2006; Hyks et al., 2011, 2009a; Meima and Comans, 1997; Sabbas
256 et al., 2003). Furthermore, mineral solubility played an important role in the release of major elements from the wood
257 ash samples investigated here.

258

259 3.1.2 Trace elements and DOC

260 Concentrations of several trace metals were below LOQ already at the very beginning of the column test (LOQ: 0.26
261 µg/L for As; 3.8 µg/L for Be; 0.20 µg/L for Cd; 0.045 µg/L for Co; 7.0 µg/l for Cu; 1.3 µg/L for Fe; 28 µg/L for Li; 5.9
262 µg/L for Mo; 4.4 µg/L for Ni; and 0.017 µg/L for Tl), except for some releases during the initial washout below L/S 2
263 L/kg. These overall trends were observed for all columns except FA-S in the case of Co, Ni and Tl, where slightly
264 higher releases were found – see Figure S1.

265 The initial leaching of DOC decreased rapidly by one order of magnitude from 17 mg/L for MA and 65 mg/L
266 for FA at L/S 5 L/kg, and then stabilised at 0.2-0.5 mg/L. Very low levels of DOC resulted in a limited impact of DOC-
267 Cu complexation; in fact, only about 6-14 % of the dissolved Cu was calculated to be complexed with DOC. Although
268 Cu(OH)₂ has been suggested for controlling Cu leaching in MSWI ashes (Dijkstra et al., 2006; Komonweeraket et al.,
269 2015), Cu(OH)₂ was calculated to be undersaturated by two orders of magnitude.

270 The majority of Pb was released before reaching L/S 20 L/kg for MA (~0.06 mg/kg) and L/S 150 L/kg for FA
271 (~0.5 mg/kg), but these releases were insignificant compared with the Pb solid content: 13.8 mg/kg in MA and 55.3
272 mg/kg in FA. Similarly, low releases of Pb have generally been reported by other wood ash studies (Freire et al., 2015;
273 Pöykiö et al., 2009; Supancic et al., 2014). While no significant complexation between DOC and Pb was identified,
274 inorganic complexation with hydroxyl - and to a much lower extent chloride ions was suggested by the speciation
275 calculations during the initial washout of Pb (before the L/S 10 L/kg). After this, Pb concentrations in MA leachates (~2
276 µg/L) slowly approached LOQ levels by the L/S 30 L/kg. On the contrary, stable Pb levels (~5 µg/L) in FA leachates
277 would point either to sorption controlled leaching and/or mineral solubility control (e.g. apatite-like minerals) before
278 L/S 50 L/kg. Afterwards, the Pb solution concentration decreased to LOQ levels by the L/S 150-200 L/kg indicating
279 mineral depletion.

280 The release of Cr differed considerably between the two ashes, yielding to relatively large differences in the
281 calculated cumulative releases: MA ashes released Cr very slowly during the entire duration of the column experiment
282 (~1 mg/kg at L/S 1000 L/kg), whereas FA ashes showed a rapid release of Cr by the cumulative L/S 200 L/kg (~9
283 mg/kg) followed by a slower releasing rate (~13 mg/kg at the cumulative L/S 2300 L/kg). Other wood ash-leaching
284 studies have generally measured Cr levels in L/S 10 L/kg batch tests, reporting levels anywhere between <0.5 mg/kg
285 and ~10 mg/kg (Freire et al., 2015; Ludwig et al., 2005; Supancic et al., 2014). While the use of BaCrO₄ or Ba(S, Cr)O₄
286 solid solution has been widely proposed in literature to describe the leaching of Cr from alkaline solid wastes, namely
287 MSWI air-pollution control residues, steel slag and fossil fuel combustion ashes (Cornelis et al., 2008), in this study
288 both minerals were strongly undersaturated.

289 The leaching of Sb was low, but steady and corresponded to respectively 20 % and 18 % of the Sb content in
290 MA and FA ashes being released at the cumulative L/S 1000 L/kg. A similar leaching behaviour was observed for V,
291 which cumulative release at L/S 1000 L/kg corresponded to about 30 % and 23 % of the total V content for MA and
292 FA, respectively. The observed concentration levels of Sb and V were in overall agreement with the levels reported by
293 other wood ash studies, at comparable L/S ratios (see Pöykiö et al., 2009; Supancic et al., 2014; van der Sloot and van
294 Zomeren, 2010). No suitable mineral with the potential to describe Sb and V concentration levels were found, as all
295 minerals in the database containing Sb and V were calculated to be strongly undersaturated. It should be noted,
296 however, that at alkaline conditions, oxyanions can substitute other major anions in many different solid solutions for
297 which the thermodynamic data are scarce.

298 Zn was mostly released before the L/S 30 L/kg for MA ash (1.3-3.0 mg/kg) and L/S 100 L/kg for FA ash (1.3-
299 4.0 mg/kg), after which concentrations below LOQ (1.8 µg/L) were generally observed. In the literature, both low
300 releases as well as higher releases can be found, i.e. <0.2-51 mg/kg at L/S 10 L/kg (Freire et al., 2015; Pöykiö et al.,
301 2009; Supancic et al., 2014). While zincite dissolution has sometimes been proposed to describe Zn leaching from
302 MSWI ashes (e.g. Astrup et al., 2006; Hyks et al., 2009b), in this study modelled concentrations for zincite
303 overestimated the observed concentrations by about two to three orders of magnitude. Though inconclusive, the lack of
304 fit suggested the occurrence of other processes such as surface complexation or surface precipitation onto other wood
305 ash phases – similarly to what was supposed by Poletini and Pomi (2004) for MSWI bottom ashes.

306 Sr was released rapidly before the L/S 50 L/kg (~120 mg/kg for MA ash and ~180 mg/kg for FA ash), and then
307 more slowly by the end of the column experiment. While all the minerals containing Sr were somewhat undersaturated,
308 strontianite for MA ash and Ba_{0.5}Sr_{0.5}SO₄ solid solution for FA ash overestimated Sr concentrations the least, with

309 differences in the concentration levels in the range of one to two orders of magnitude. The potential formation of new
310 solid solutions, less soluble than the ones available in the database, may have contributed to the lower observed
311 leaching of Sr. It is noteworthy that the same, or structurally similar, minerals were indicated also by Astrup et al.
312 (2006) and Hyks et al. (2009b) to describe the leaching of Sr from MSWI ashes.

313 With regard to Mo, except for the initial washout at L/S 5 L/kg for MA (0.3 mg/kg) and L/S 20 for FA ash (1.4
314 mg/kg), all other leachate samples presented Mo concentrations below LOQ. Ni concentrations were observed always
315 below LOQ levels (4.4 µg/L) in MA leachates; FA columns showed a rapid washout of Ni before the L/S 1 L/kg in the -
316 L and -M columns, whereas the -S column showed a slight increase in concentration until the L/S 100 L/kg (20 µg/L),
317 followed by a slow decrease until the L/S 250 L/kg (LOQ levels).

318 Overall, relatively large differences were observed between cumulative releases at L/S 10 L/kg and L/S 1000
319 L/kg, especially for Ba, Sb, V and Cr (see Table 3); in the case of As, Cd, Cu, Mo and Ni differences could not be
320 quantified accurately because their concentrations were observed below LOQ in many leachate samples. These results
321 indicated that considerable underestimations can occur if L/S 10 L/kg releases are used to estimate long-term releases.

322 While our leaching results were observed to be similar to observations reported in the literature, e.g. generally
323 lower levels at higher L/S ratios, our column experiments however illustrated different behaviours for some elements, in
324 particular Cr, Sb, V and Sr, which demonstrates that (sequential) batch tests may not be sufficient to capture
325 developments in leaching from a long-term perspective. With regards to the leaching mechanisms, mineral dissolution
326 played an important role in the release of trace elements, but other processes with the potential to affect the solution
327 concentration of these elements, such as complexation with both organic and inorganic species, surface complexation
328 onto other wood ash phases and formation of solid solutions, were likely to occur, too.

329 <Table 3>

330

331 **3.1.3 Potential effects of ageing**

332 It is noteworthy that while the results of this study provide a consistent characterization of the leaching properties of
333 wood ashes, some limitations may exist when attempting to extend the cumulative release data to wood ash application
334 scenarios – where the ashes, over time, will be subjected to aging reactions alongside with leaching. Studies of other
335 combustion ashes may provide indications of whether the cumulative releases from this study over- or underestimate
336 the release from aged wood ashes: ageing of MSWI ashes has been documented to increase leaching of oxyanions such
337 as As, Cr, Mo, and V, while leaching of cationic elements such as Pb, Zn, and Cd is generally decreasing (e.g. Sabbas et

338 al., 2003). This effect is generally ascribed to changes in mineralogy as well as the associated change in pH of the
339 leaching system (e.g. Astrup et al., 2006; Meima and Comans, 1999; Polettini and Pomi, 2004; Steenari and Lindqvist,
340 1997).

341 The results from speciation calculations provide an evaluation of potential mineral phases in the fresh ashes,
342 which may then be used as basis for evaluating potential changes in mineralogy when the ashes are exposed to air and
343 moisture, i.e. ageing of the ashes. From other wood ash studies, minerals such as carbonates, ettringite, gypsum,
344 hydrated silicates and aluminium-silicate phases can be expected in aged ashes (Holmberg and Claesson, 2001; Steenari
345 and Lindqvist, 1997); however, most of the potential mineral phases identified for the fresh ashes have been suggested
346 also for aged ashes in literature (Gori et al., 2011; Holmberg and Claesson, 2001; Vassilev et al., 2013b).

347

348 **3.2 Flow-interrupted columns**

349 A large impact of flow interruptions was observed on the measured pH as well as solutions concentrations of Al, Ba,
350 Ca, K, Mg, Na, Rb and V (illustrated in Figure 3). Other elements, namely Li, Sb and Sr, were also affected but to a
351 generally lower extent (illustrated in Figure S4). In general, increasing concentrations during flow interruptions may
352 indicate non-equilibrium conditions (maybe both chemical and physical non-equilibrium) most likely caused by
353 presence of a dual-porosity system in which the mass transfer between the mobile and the stagnant zone is controlled by
354 diffusion (slow). As the flow is stopped, diffusion from the stagnant zones can result in increasing concentrations. On
355 the other hand, decreasing solution concentrations during flow interruption may indicate mineral precipitation and/or
356 sorption, i.e. processes which were not occurring during the standard operation of the columns because of non-
357 equilibrium conditions. As indicated earlier, flow interruptions resulted in a slight pH increase in both columns, though
358 most pronounced for MA during the first flow interruption: an increase of 0.6-0.7 pH units. The change in pH, albeit
359 larger than what was previously observed for MSWI bottom ashes (Hyks et al., 2009a), indicated changes in solution
360 chemistry with extended contact times. Again, this points out to physical non-equilibrium (dual-porosity) and diffusion
361 of OH⁻ from the stagnant zone.

362 Ca concentration decreased during the two flow interruptions for MA, while almost no effect was observed for
363 FA. The changes in Ca concentrations could be described adequately by changes in equilibrium concentrations of the
364 same minerals proposed for the leaching of continuous -L columns (at comparable L/S ratios), indicating that Ca
365 mineral equilibrium was maintained during flow interruptions. Likewise, while a marked increase in Ba concentrations
366 was observed in the MA column during the first flow interruption, the changes in the solution concentrations of Ba

367 could be described by equilibrium with barite. Mg concentrations decreased during flow interruptions, but the predicted
368 minerals in equilibrium with the observed concentrations remained unchanged, i.e. hydrotalcite at L/S 2 L/kg, while
369 hydrotalcite, brucite, clinoenstatite and forsterite were at L/S 50 L/kg.

370 The observed concentrations of K, Na and Rb increased during flow interruptions for both MA and FA ashes,
371 though to different extents – see Figure 3. Analogously to the case of continuous columns, no specific mineral phase
372 could be identified to describe the solution concentrations of these alkali metals, suggesting that K, Na and Rb were
373 dissolved in the form of halides or (hydr-)oxides. Al concentrations in MA leachates increased considerably during the
374 first flow interruptions, at the same time approaching modelled concentrations for equilibrium with hydrotalcite.

375 Slight variations in the concentration of Li, Sb, Sr and V were also observed, but only in the case of MA
376 leachates and generally only with respect to one set of flow interruptions (i.e. either at L/S 2 L/kg or at L/S 50 L/kg).
377 These changes could not be related to changes in mineral solubility.

378 Overall, the FA and MA columns responded rather differently to flow interruptions. In general, the FA column
379 showed modest effects from flow interruptions, whereas clear effects were observed for the MA column. While
380 inconclusive, based on these results as well as literature data this difference in behaviour may be caused by differences
381 in particle size distributions, particle shapes and porosity, which may then affect mineral dissolution and overall
382 equilibrium conditions between the two materials.

383

384 **3.5 Wood ash potential and management**

385 **3.5.1 Primary nutrients**

386 Upon applying wood combustion ash on soil, the potential release of nutrients may improve the fertility of the soil,
387 especially if primary plant macronutrients (P, K and N) are released or become accessible for plant uptake. Phosphorous
388 (P) is relatively abundant in wood ash ($\sim 10^4$ mg/kg in our samples), but only a very small and typically barely
389 detectable fraction has been reported to be water-soluble (see Section 3.1.1). On the other hand, based on ammonium
390 citrate and citric acid extractions (common solvents used to test phosphatic fertilisers), wood ash appears to release
391 about 57-78 % of the total P content (Brod et al., 2015; Erich, 1991; Yusiharni et al., 2007). As such, these extraction
392 tests are somewhat in contrast to batch leaching experiments reported in the literature, as well as to our column
393 experiments, in which significantly lower releases were found. This may indicate that during conditions where the
394 leaching system is controlled by the ashes, P release can be expected to be low. On the other hand, if the more acidic

395 conditions of forest soils control the leaching system, the acidic conditions of typical availability tests may be more
396 relevant.

397 Potassium (K) is abundant in wood ash ($\sim 10^4$ mg/kg in our samples), but in contrast to P it is rather soluble and
398 readily available (see Section 3.1.1). Based on our column results, relatively large amounts of K can be expected to be
399 released shortly after ash application. On the contrary, relatively low nitrogen (N) contents are observed in wood ashes
400 compared to the input biomass fuel because of the low volatilisation temperature of N (e.g. Ingerslev et al., 2011; Misra
401 et al., 1993). Based on the potential release of N, P and K, the fertilising value of wood ashes may be limited, but still
402 potentially valuable in the case of acidic/neutral soils with P and/or K deficiencies, as it appears to be the case for many
403 western Denmark forest soils – where a widespread nutrient deficiency of P has been indicated (Ingerslev et al., 2001).

404

405 **3.5.2 Typical elements of environmental concern**

406 Standard batch, column and pH-dependent leaching tests are useful for both basic leaching characterisation and testing
407 compliance with regulatory limits. Table 3 compares results from the column experiments (at cumulative L/S 10 L/kg)
408 with the waste acceptance criteria (WAC) for landfilling (Directive 2003/33/EC). Both MA and FA complied with
409 WAC for landfills receiving non-hazardous waste, but they exceeded WAC for landfills receiving inert waste for Ba,
410 chloride and sulphate in the case of MA, and chloride, Cr, Mo and sulphate in the case of FA. This should not be
411 ignored, since wood ashes are considered useful for application on land in many countries. Moreover, in Denmark,
412 wood ash utilisation is currently not subjected to any specific leaching requirements, as the only limits defined by
413 Danish authorities are set for the total composition and electrical conductivity (which in turn define the maximum
414 allowed dosages; DEPA (2008)).

415

416 **3.5.3 Liming**

417 Both ash samples generated strongly alkaline leachates across the investigated L/S range, e.g. above pH 10.9 at L/S
418 1000 L/kg. The release of “total alkalinity” at L/S 1000 L/kg was calculated to be 3.8 meq/g for MA (equivalent to the
419 ANC of 0.19 g of CaCO_3) and 7.6 meq/g for FA (equivalent to the ANC of 0.38 g of CaCO_3) – which further increased
420 up to 9.0 meq/g for FA at L/S 2300 L/kg (i.e. ~ 0.45 g of CaCO_3). Although a wide range of results for calcium
421 carbonate equivalents of wood ashes has been reported in the literature, these levels have been typically observed
422 between one-third and two-thirds of pure limestone (Cabral et al., 2008; Erich, 1991; Vance, 1996). This is in overall

423 accordance with our releases of “total alkalinity”. As such, the herein investigated wood ashes may represent a
424 considerable liming potential for acidic soils.

425 Two types of alkalinity were calculated, namely “standard alkalinity” and “total alkalinity”. Until L/S 300 L/kg
426 for MA and 600 L/kg for FA these two values were comparable, but at higher L/S ratios “total alkalinity” was typically
427 about 20 % higher. This indicates not only that different alkaline species are released at higher L/S ratios, but also the
428 potential long-term importance of silicates after washout of carbonates, bicarbonates and hydroxides. Accordingly, it
429 was observed that “standard alkalinity” released at L/S 1000 L/kg corresponded to about 85 % of the ANC_{4.5} of MA and
430 64 % of the ANC_{4.5} of FA. This indicates that a large part of the actual buffer capacity of the ashes was depleted during
431 the – very long – column experiments, thereby supporting a potential change in the dissolved alkaline species.

432

433 **4. CONCLUSIONS**

434 Column leaching experiments involving two types of wood combustion ashes (fly ash and mixed ash) were completed,
435 covering L/S ratios up to 2300 L/kg. Despite potential non-equilibrium conditions, long-term leaching could be
436 described adequately as a function of the L/S ratio, by combining results from several columns of various lengths
437 together. The observed concentrations of Ca, Mg, Al, Ba, sulphate and Si from both ash materials could be described by
438 the dissolution of a limited selection of minerals, several of these relevant for more than a single element at the same
439 time. Depletion of more soluble mineral phases was likely to occur during our long-term leaching experiment, in turn
440 promoting favourable conditions for the dissolution of new minerals, stable at well-defined L/S intervals – as indicated
441 by the speciation calculations. In the case of trace elements, mineral dissolution alone was not sufficient to describe the
442 observed concentrations, indicating that other processes, such as surface complexation and formation of solid solutions
443 were likely to occur, too. At L/S 1000 L/kg, the cumulative releases of K, S, Na, Ca and Rb were observed at 40-100 %,
444 followed by Ba, Sb, Sr and V at 15-40 %, and with Al, Mg, Zn, Cd, Co, Fe, Pb, Tl, Mn and P at levels below 5 %. As
445 shown by the relatively large differences in the calculated cumulative releases, leaching data corresponding to L/S 10
446 L/kg are generally not sufficient for estimating leaching at considerably higher L/S ratios, e.g. 1000 L/kg. The observed
447 released alkalinity at the cumulative L/S 1000 L/kg corresponded to about 20-40 % of calcium carbonate equivalents,
448 indicating the relatively high liming value of the investigated wood ash samples.

449

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455

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597 and iron smelting slag as liming agents and P fertilisers. *Aust. J. Soil Res.* 45, 374–389. doi:10.1071/SR06136
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599

600 **Table 1.** Chemical characterisation of the wood ash samples, i.e. MA and FA. The values are expressed in mg/kg dry
601 weight, unless otherwise specified. All analyses were carried out in at least duplicates. Values in brackets represent the
602 relative standard deviation. [TOC: total organic carbon; MC: moisture content]. Adapted from Maresca et al. (2017).

	MA	FA
MC (%)	0.151	47.3
TOC	58400 (2.5 %)	73900 (29 %)
Al	12400 (4.7 %)	10800 (14 %)
As	1.82 (3.8 %)	2.68 (8.8 %)
Ba	1170 (9.9 %)	1550 (0.056 %)
Be	1.91 (58 %)	0.798 (1.6 %)
Ca	135000 (2.8 %)	263000 (3.1 %)
Cd	3.99 (3.4 %)	16.3 (0.74 %)
Co	5.49 (0.21 %)	5.79 (2.0 %)
Cr	26.6 (3.1 %)	60.6 (3.4 %)
Cu	60.4 (2.9 %)	115 (1.0 %)
Fe	6720 (1.9 %)	6090 (2.4 %)
K	39400 (3.8 %)	51200 (4.7 %)
Li	5.70 (27 %)	6.73 (0.17 %)
Mg	12700 (2.3 %)	30000 (3.1 %)
Mn	7430 (2.7 %)	11000 (1.6 %)
Mo	1.81 (4.5 %)	3.61 (14 %)
Na	10500 (8.0 %)	12000 (25 %)
N	700 (2.9 %)	1670 (3.5 %)
Ni	16.1 (2.0 %)	22.4 (0.76 %)
P	10000 (2.6 %)	21400 (1.8 %)
Pb	13.8 (4.6 %)	55.3 (2.0 %)
S	2450 (5.3 %)	8490 (2.8 %)
Sb	1.33 (3.0 %)	2.44 (1.6 %)
Se	<16.7	<16.7
Si	254000 (6.3 %)	124000 (33 %)
Sn	1.07 (3.6 %)	2.51 (3.3 %)
Sr	708 (3.1 %)	1240 (3.6 %)
Tl	0.217 (0.93 %)	1.98 (2.8 %)
V	15.9 (4.0 %)	9.18 (1.3 %)
Zn	340 (3.2 %)	924 (0.78 %)

603

604

605 **Table 2.** Main characteristics of the MA and FA columns. [-L: long column; -M: medium column; -S: short column;
 606 _FI: flow interrupted column; *: not available; _{ww}: wet weight].

		MA-L	MA-L_FI	MA-M	MA-S	FA-L	FA-L_FI	FA-M	FA-S
Column diameter	cm	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Column height	cm	30	30	13	4.5	30	30	13	4.5
Ash filling volume	cm ³	540	540	220	56	540	540	220	49
Ash amount	g _{ww}	530	530	210	43	540	510	210	34
Test duration	days	150	157	150	150	150	150	150	150
Final L/S ratio	L/kg	75	54	206	1020	146	101	388	2330
Estimated pore volume	cm ³	*	330	*	*	*	160	*	*

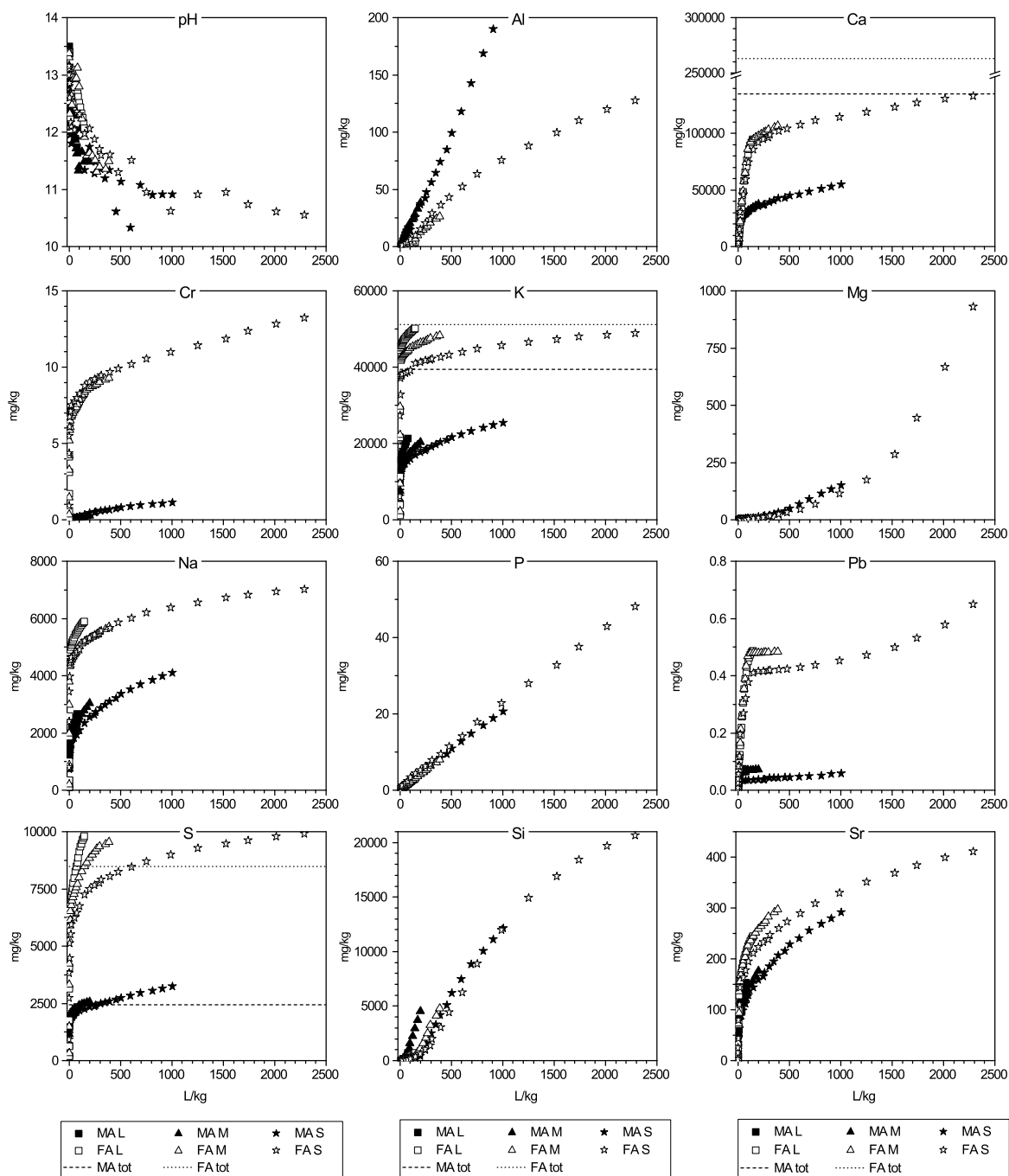
607

608 **Table 3.** Calculated cumulative releases from column tests, expressed per dry weight of material. Releases at L/S 10
609 L/kg are calculated based on -L columns data; releases at L/S 1000 L/kg are calculated based on -S columns data.
610 Waste acceptance criteria (WAC) for landfills receiving inert and non-hazardous waste are reported for comparison
611 (Directive 2003/33/EC). [**: the calculated release was >100%; <: the area underneath LOQ exceeded more than 30%
612 the overall area calculated for that specific element; ≈: the area underneath LOQ was in the range 10% - 30% of the
613 overall area calculated for that specific element]

	Released fraction	MA 10 L/kg	FA 10 L/kg	MA 1000 L/kg	FA 1000 L/kg
Al	%	0.0031	0.0032	1.6	0.64
As	%	0.24	<0.11	<14	<9.8
Ba	%	4.5	0.21	18	18
Ca	%	6.5	2.6	40	43
Cd	%	<0.049	<0.012	<4.9	<1.2
Cr	%	<0.025	11	4.1	18
Cu	%	<0.011	0.18	<12	<6.2
Fe	%	<0.0003	0.0006	<0.019	<0.030
K	%	39	89	64	88
Mg	%	0.0010	0.0004	1.1	0.30
Mn	%	<0.0001	<0.0001	<0.0099	<0.0067
Mo	%	≈16	34	<100**	<100**
N-NO ₃ ⁻	%	0.43	3.5	<2.6	8.9
Na	%	16	41	40	53
Ni	%	<0.27	≈0.23	<27	<26
P	%	<0.0020	≈0.0015	<0.20	<0.095
Pb	%	0.24	0.17	≈0.41	0.81
S	%	64	79	100**	100**
Sb	%	<0.064	<0.033	19	16
Si	%	0.0017	0.0050	4.8	11
Sr	%	12	10	41	27
V	%	<0.040	≈0.079	29	21
Zn	%	0.41	0.050	1.4	1.1
	Released fraction	MA 10 L/kg	FA 10 L/kg	WAC inert 10 L/kg	WAC non-haz. 10 L/kg
As	mg/kg	0.0043	<0.0029	0.5	2
Ba	mg/kg	52	3.2	20	100
Cd	mg/kg	<0.0020	<0.0019	0.04	1
Cl	mg/kg	960	4200	800	15000
Cr	mg/kg	<0.0066	6.9	0.5	10
Cu	mg/kg	<0.0066	0.21	2	50
Mo	mg/kg	≈0.29	1.2	0.5	10
Ni	mg/kg	<0.044	≈0.051	0.4	10
Pb	mg/kg	0.034	0.091	0.5	10
Sb	mg/kg	<0.0008	<0.0008	0.06	0.7
Zn	mg/kg	1.4	0.47	4	50
SO ₄ ²⁻	mg/kg	1500	5200	1000	20000
DOC	mg/kg	18	130	500	800

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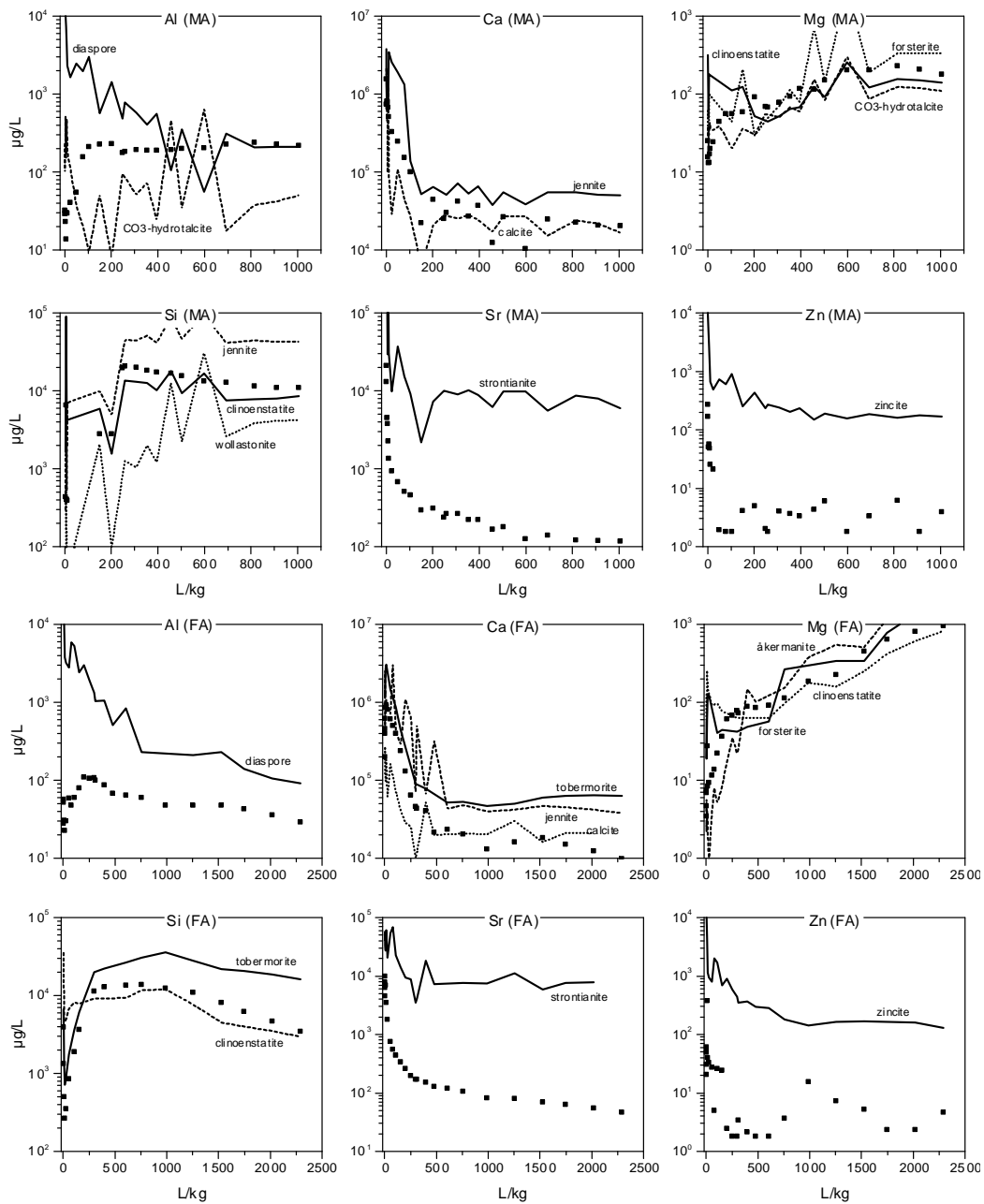
617 **Figure 1.** Cumulative releases of Al, Ca, Cr, K, Mg, Na, P, Pb, S, Si, Sr, and pH from continuous MA and FA columns.

618 Results are expressed in mg/kg, except for pH. Total contents in the ash samples are shown only for the elements which

619 cumulative release approached the total content levels. Note the break of the y-axis for Ca. [-L: long column; -M:

620 medium column; -S: short column].

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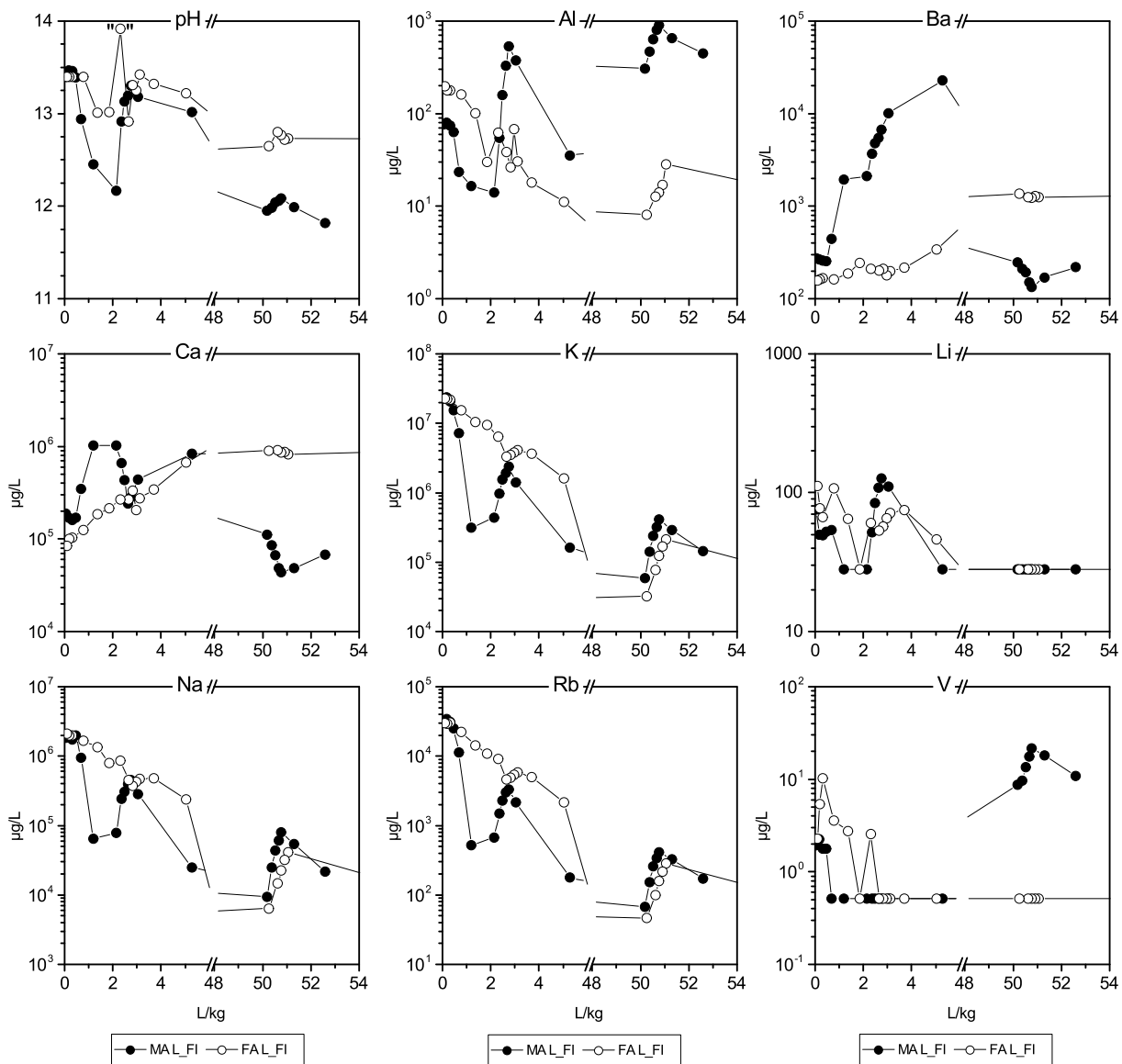
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Figure 2. Speciation model results in comparison with the observed concentrations for Al, Ca, Mg, Si, Sr and Zn in the leachates from -S columns, for MA (above) and FA (below) samples.



626

627 **Figure 3.** Concentration levels of Al, Ba, Ca, K and V leachates from interrupted columns (MA-L_FI and FA-L_FI)
 628 during the two flow-interruptions at L/S 2 L/kg and 50 L/kg. Results are expressed in µg/L. [-L: long column; _FI:
 629 flow-interrupted column; " ": indicates a possible outlier in the pH measurements]

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SUPPLEMENTARY MATERIAL

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Long-term leaching of nutrients and contaminants from wood combustion ashes

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Journal: Waste Management

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672 **1. Characterisation of wood ash samples**

673 Fresh subsamples of MA and FA were characterised for their moisture content (EN 1097–5:2008) at 110 °C; these dried
674 samples were crushed for the fraction above 4 mm (jaw crusher), and milled (vibratory disc mill, agate discs). The
675 pulverised samples were then split into subsamples of 0.5 g for the measurement of the total organic carbon (TOC; EN
676 13137: 2001; LECO induction furnace CS-200 Analyzer), and 0.2 g for the analysis of S and N (Elemental Analyzer -
677 Vario MACRO cube). Additional 0.25 g of pulverised ashes were acid digested (EN 13656: 2003) in a microwave oven
678 (Multiwave Anton Paar 3000) by using 6 ml of HNO₃ (65%), 2 ml of HCl (37%), 2 ml of HF (40%) and 12
679 H₃BO₃(10%); 2 ml of H₂O₂ (30%) were also added to support the oxidation of the residual organic matter. The digested
680 samples were analysed by means of ICP-MS (7700x, Agilent Technologies) for the content of Al, As, Ba, Be, Cd, Co,
681 Cr, Cu, Fe, Li, Mg, Mn, Mo, Ni, Pb, Rb, Sb, Se, Si, Sn, Sr, Tl, V and Zn, and by ICP-OES (Varian Vista-MPX)
682 for the content of Ca, K, Mn, Na and P.

683 Subsamples of the dried MA and FA (110 °C) ashes were additionally used for particles size distribution
684 analyses (EN 933-1: 2012) using 13 stainless steel sieves with mesh sizes in the range of 0.063 µm – 25 mm.

685

686 **2. Estimated pore volume**

687 Pore volume was estimated as follows:

- 688 - Step 1. Fill the column with sand, ash and filters according to EN 14405: 2017; close the column, and weigh it. To
689 be noted that this weight also includes the ash moisture content.
- 690 - Step 2. Take the column from Step 1 and fill it with water; weigh the column, and subtract the estimated water
691 contained in the sand pore volume.
- 692 - Step 3. Subtract the result from Step 2 by Step 1. This is the estimated pore volume.

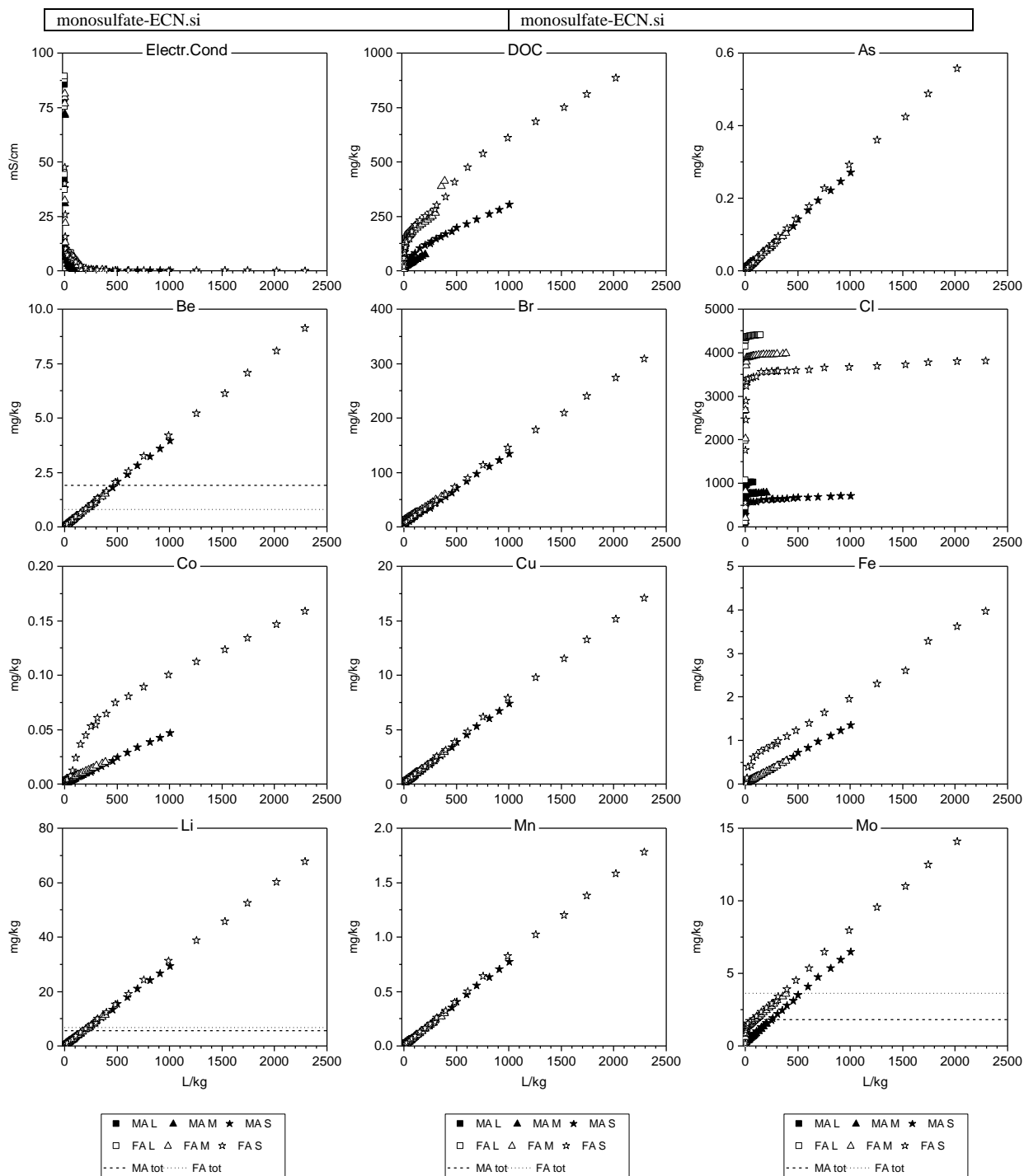
693 The average sand pore volume was determined based on previous tests.

694

695 **3. Additional Tables and Figures**

696 **Table S1.** List of minerals included in the geochemical model evaluation. The names of the minerals comply with the
 697 thermodynamic database used (ORCHESTRA code; Meeussen (2003)).

MA sample	FA sample
AA-3CaO-Al2O3[Ca[OH]2]0-5-[CaCO3]0-5-11-5H2O[s].si	AA-3CaO-Al2O3[Ca[OH]2]0-5-[CaCO3]0-5-11-5H2O[s].si
AA-3CaO-Al2O3-CaCO3-11H2O[s].si	AA-3CaO-Al2O3-6H2O[s].si
AA-3CaO-Fe2O3[Ca[OH]2]0-5[CaCO3]0-5-11-5H2O[s].si	AA-3CaO-Fe2O3[Ca[OH]2]0-5[CaCO3]0-5-11-5H2O[s].si
AA-3CaO-Fe2O3-6H2O[s].si	AA-3CaO-Fe2O3-6H2O[s].si
AA-Brucite.si	AA-3CaO-Fe2O3-CaCO3-11H2O[s].si
AA-CO3-hydrotalcite.si	AA-Brucite.si
AA-Calcite.si	AA-CO3-hydrotalcite.si
AA-Ettringite.si	AA-Calcite.si
AA-Fe-Ettringite.si	AA-Ettringite.si
AA-Fe[OH]3[microcr].si	AA-Fe-Ettringite.si
AA-Jennite.si	AA-Fe[OH]3[microcr].si
AA-Portlandite.si	AA-Jennite.si
AA-Tobermorite-I.si	AA-Portlandite.si
AA-Tobermorite-II.si	AA-Tobermorite-I.si
Aragonite.si	AA-Tobermorite-II.si
BaCaSO4[50%Ba].si	Akerminite.si
BaCaSO4[75%Ba].si	Aragonite.si
BaCrO4.si	BaCaSO4[50%Ba].si
BaSrSO4[50%Ba].si	BaCaSO4[75%Ba].si
Ba[SCr]O4[77%SO4].si	BaCrO4.si
Ba[SCr]O4[96%SO4].si	BaSrSO4[50%Ba].si
Barite.si	Ba[SCr]O4[77%SO4].si
Birmessite.si	Ba[SCr]O4[96%SO4].si
Brucite.si	Barite.si
CSH-ECN.si	Birmessite.si
Ca-Olivine.si	Bixbyite.si
Ca2V2O7.si	Brucite.si
Calcite.si	Bunsenite.si
Celestite.si	CSH-ECN.si
Clinoenstatite.si	Ca-Olivine.si
Cu[OH]2[s].si	Calcite.si
CuprousFerrite.si	Clinoenstatite.si
Diaspore.si	Cu[OH]2[s].si
Ettringite.si	CuprousFerrite.si
Ettringite-ECN.si	Diaspore.si
Fe[OH]2.7ClO.3.si	Ettringite.si
Forsterite.si	Ettringite-ECN.si
Franklinite.si	Fe[OH]2.7ClO.3.si
Goethite.si	Forsterite.si
Hilgenstockite.si	Franklinite.si
Lepidocrocite.si	Goethite.si
Maghemite.si	Hilgenstockite.si
Manganite.si	Larnite.si
Merwinite.si	Lepidocrocite.si
Microcline.si	Maghemite.si
Monticellite.si	Manganite.si
Montmorillonite.si	Merwinite.si
Muscovite.si	Monticellite.si
Na-Nontronite.si	Ni[OH]2[s].si
Ni2SiO4.si	Nsutite.si
Ni[OH]2[s].si	P-Wollstanite.si
Nsutite.si	Pb[OH]2[C].si
P-Wollstanite.si	Plattnerite.si
Portlandite.si	Portlandite.si
Quartz.si	Pyrolusite.si
Sepiolite[a].si	Quartz.si
Sepiolite[c].si	Schoepite.si
SrMoO4.si	Sepiolite[a].si
Strontianite.si	SrMoO4.si
Tenorite.si	Strontianite.si
Willemite.si	Tenorite.si
Wollastonite.si	Wollastonite.si
Zincite.si	Zincite.si
ZnSiO3.si	ZnSiO3.si

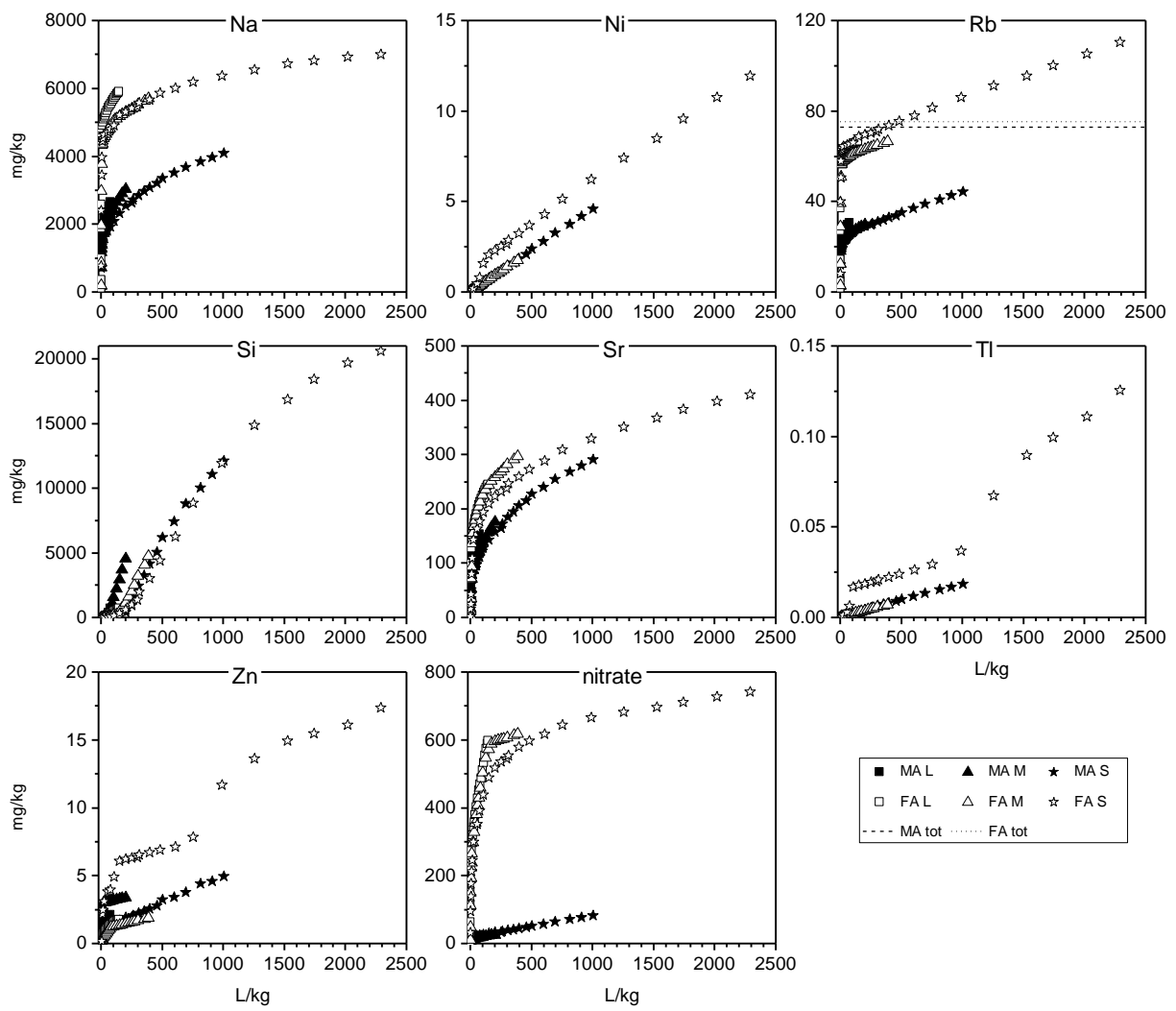


698

699 **Figure S1a.** Cumulative release of As, Be, Br, Cl, Co, Cu, Fe, Li, Mn, Mo, dissolved organic carbon (DOC) and
 700 electrical conductivity from continuous MA and FA columns. Results are expressed in mg/kg, except for the electrical
 701 conductivity (mS/cm). [-L: long column; -M: medium column; -S: short column].

702 (Figure S1 continues on the next page)

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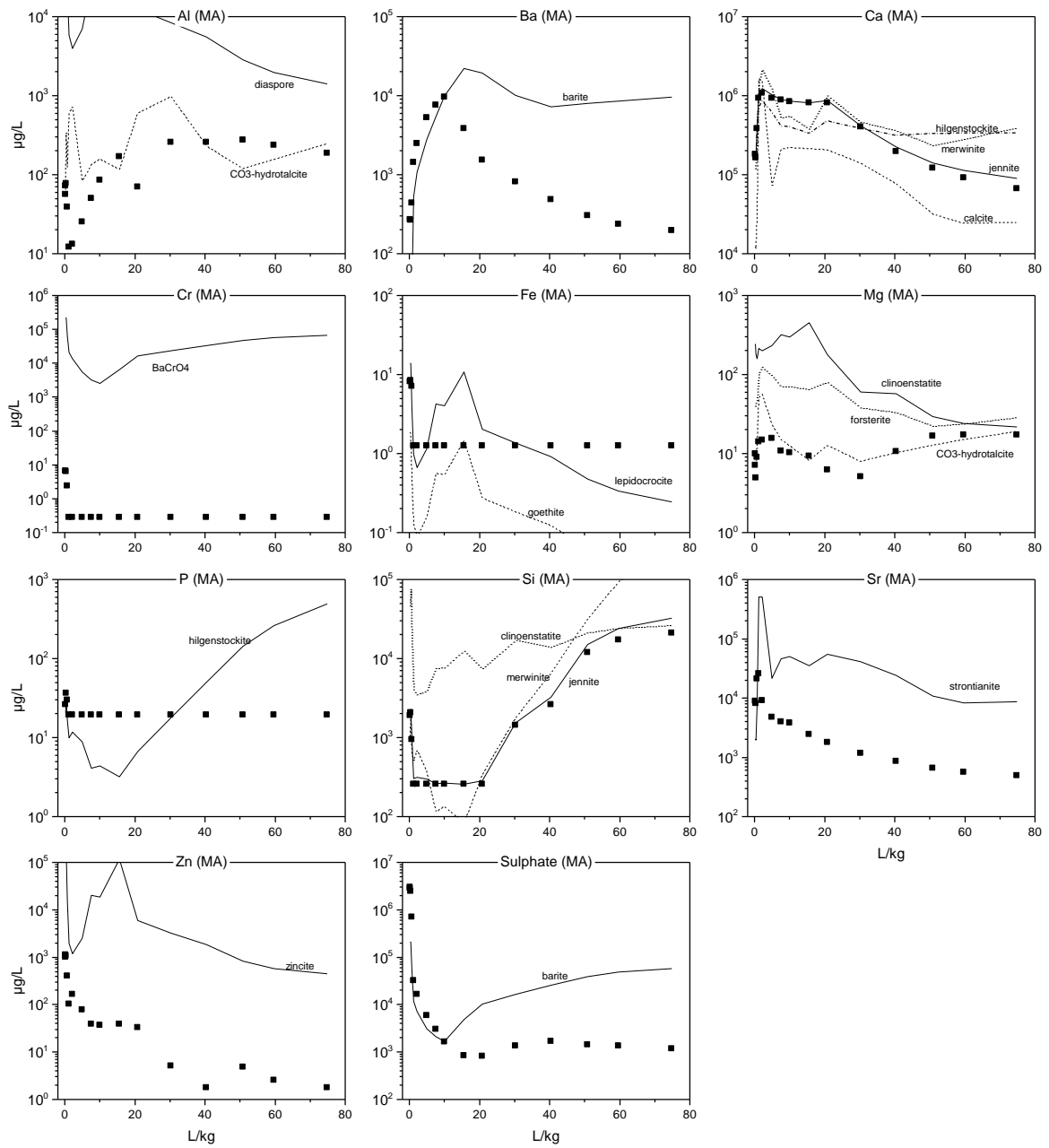


704

705 **Figure S1b. (continuation)** Cumulative release of Na, Ni, Rb, Si, Sr, Tl, Zn and nitrate from continuous MA and FA
 706 columns. Results are expressed in mg/kg. [-L: long column; -M: medium column; -S: short column].

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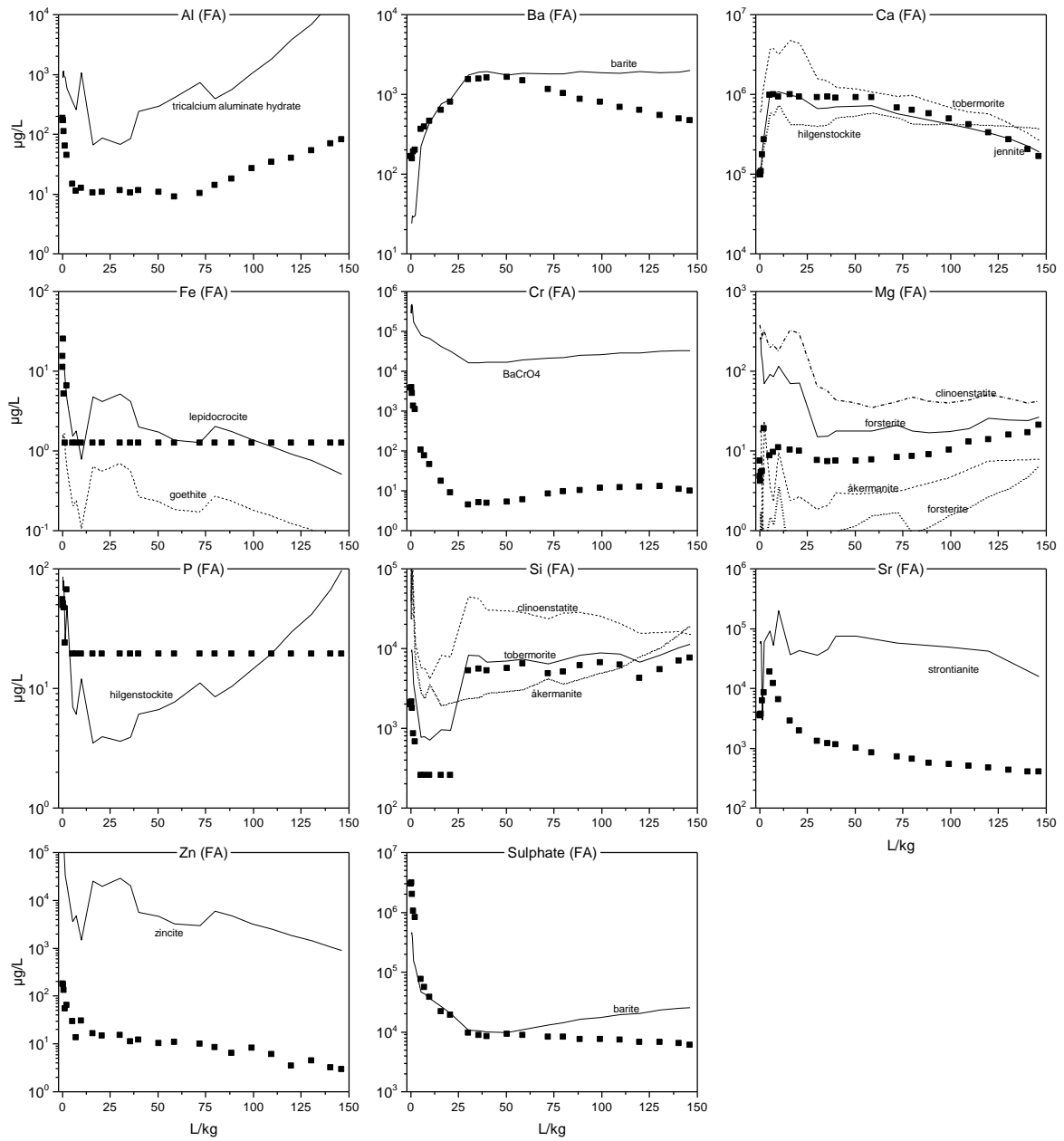


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710 **Figure S2.** Speciation model results in comparison with the observed concentrations for Al, Ba, Ca, Cr, Fe, Mg, P, Si,

711 Sr, Zn and sulphate in the leachates from MA-L columns.

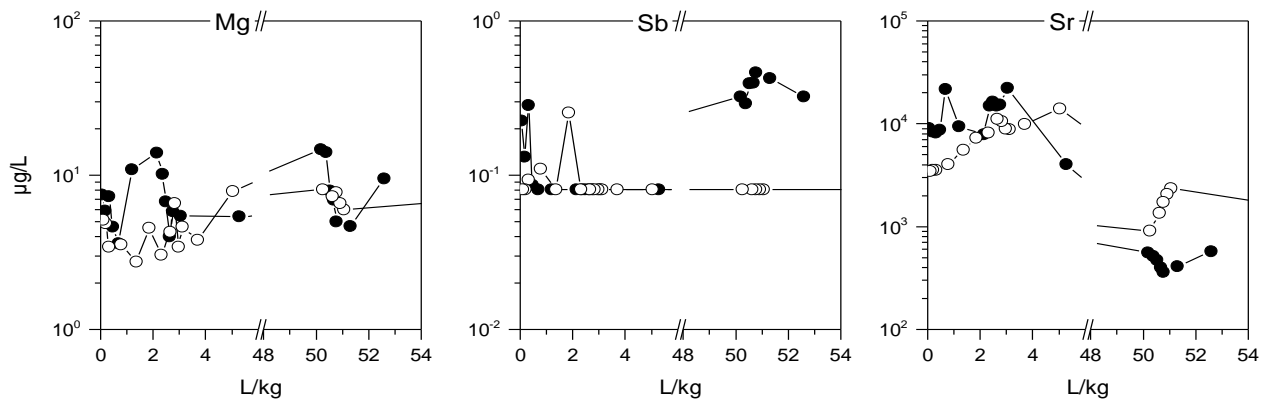
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714 **Figure S3.** Speciation model results in comparison with the observed concentrations for Al, Ba, Ca, Cr, Fe, Mg, P, Si,

715 Sr, Zn and sulphate in the leachates from FA-L columns.



716

717 **Figure S4.** Concentration levels of Mg, Sb and Sr in the leachates from interrupted columns (MA-L_FI and FA-L_FI)
 718 during the two flow-interruptions at L/S 2 L/kg and 50 L/kg. Results are expressed in µg/L.

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