



Column leaching from a Danish forest soil amended with wood ashes: fate of major and trace elements

Maresca, Alberto; Hansen, M.; Ingerslev, M.; Fruergaard Astrup, Thomas

Published in:
Biomass and Bioenergy

Link to article, DOI:
[10.1016/j.biombioe.2017.12.014](https://doi.org/10.1016/j.biombioe.2017.12.014)

Publication date:
2018

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Maresca, A., Hansen, M., Ingerslev, M., & Fruergaard Astrup, T. (2018). Column leaching from a Danish forest soil amended with wood ashes: fate of major and trace elements. *Biomass and Bioenergy*, 109, 91-99. <https://doi.org/10.1016/j.biombioe.2017.12.014>

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7 *Maresca, A.^{*a)}, Hansen M.^{b)}, Ingerslev M.^{b)} and Astrup, T.F^{a)}.*
8
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10
11 ^{a)} Technical University of Denmark, Department of Environmental Engineering, Building 115,
12 Bygningstorvet, 2800 Kgs. Lyngby, Denmark

13 ^{b)} University of Copenhagen, Department of Geosciences and Natural Resource Management,
14 Rolighedsvej 23, 1958 Frederiksberg C, Denmark
15

16
17
18
19
20
21 ^{*)} Corresponding author: almar@env.dtu.dk
22

23 **Abstract**

24 Application of wood ashes onto two Danish forest soil horizons (A- and O-horizons) was investigated through a series
25 of column experiments for ash dosages of 3, 9 and 30 Mg ha⁻¹. Developments in the composition of the percolating soil
26 solutions were investigated both in a short- (below 0.5 m³ m⁻² of infiltrating water) and long-term perspective (until 2.0
27 m³ m⁻² of infiltrating water). The higher the ash dosage, the higher the percolation of readily soluble elements (K, Cl,
28 Mg and S) occurred within a short-term perspective. This initial washout of soluble elements resulted in the exchange of
29 ions in the soil, thereby causing other soil bound elements to be released and the pH to decrease temporarily. Wood ash
30 application also promoted an increase in the long-term leaching of As, Cu, K, P and Si beyond the O-horizon layer
31 (until ~2.0 m³ m⁻²), while the migration of trace elements through this soil horizon appeared to be of limited concern
32 compared with Danish groundwater quality criteria. Relatively similar effects were observed for both the use of 3 and 9
33 Mg ha⁻¹ dosages on the composition of the percolating soil solutions. Low mobility of Cd, Co, Cr, Cu, Mo, Ni, Pb, Se,
34 V and Zn was observed. The released amounts were generally limited to a few percentage points of their total contents
35 in the columns. The potential accumulation of trace elements within the forest soil should be evaluated with respect to
36 the specific case, if high ash dosages are intended for spreading.

37

38 **Keywords:** biomass; liming; release; soil solution; exchangeable cations

39

40 **Abbreviations:** ANC: acid neutralisation capacity; DOC: dissolved organic carbon; dw: dry weight; GQC: groundwater
41 quality criteria; ICP: inductively-coupled plasma; MS: mass spectrometry

42

43 **1. INTRODUCTION**

44 Increasing amounts of energy from biomass combustion are being generated in Europe [1]. In Denmark, a considerable
45 increase in the production of renewable energy from wood chips and wood pellets was observed in the period 2000-
46 2015, i.e. from 5.7 PJ to 16 PJ [2]. Wood ashes are produced during the combustion of wood, and because of the
47 increasing amounts of wood being used for energy purposes, more ashes are being generated. About 22,300 t dry weight
48 (dw) of wood ashes are estimated to have been generated in 2012 [3]. In Denmark, wood ashes are typically landfilled
49 [4], even though Danish legislation allows for their use on top of agricultural and forest lands for fertilising and liming
50 purposes [5].

51 Current Danish legislation allows for a maximum wood ash dosage of 3 Mg ha⁻¹ onto forest soil, to be
52 recirculated over a 10-year period, but not more than three times within a 75-year period [5]. More restricted dosages
53 may however be required depending on whether the ash complies with the defined ash quality criteria [5]. As far as the
54 ash quality criteria are complied with, there is no need for any ash pre-treatment (e.g. hardening) [5]. In line with
55 Danish legislation, the Swedish Forest Agency [6] recommends the use of approximately 2-3 t of wood ash per ha of
56 soil to compensate for the removal of base cations and the loss of alkalinity due to harvesting. However, in the case of
57 Sweden, it is recommended to use sufficiently hardened wood ashes [6]. While a wood ash dosage of 3 Mg ha⁻¹ has
58 been reported to have an approximate liming effect comparable to a quicklime dosage of 1 Mg ha⁻¹ [7], its actual
59 neutralisation value has been shown to vary widely across different samples, indicating that similar application dosages
60 may result in different liming effects: neutralising values in the range of 13-92 % of pure calcium carbonate were
61 reported by Vance [8] during the analysis of 18 wood ash samples. Likewise, ash composition has also been shown to
62 vary, depending on the type of fuel, the combustion technology and the boiler operating parameters (e.g. [9-11]).

63 Whether wood ashes are applied for fertilising or liming purposes, they will be expected to dissolve and their
64 leaching to interact with the soil. In order to address these processes, many studies have focused on the development
65 over time of the ash composition (to account for dissolved compounds; e.g. [12-15]), of the dissolved species in the
66 percolating soil solutions (to evaluate releases beyond specific soil depths; e.g. [14,16,17]) and of the extractable soil
67 components (to assess the extent of soil retention processes; e.g. [18-20]). Overall, short-term increases in the levels of
68 Al, sulphate, K and Na have been reported in percolating soil solutions shortly after wood ash application [21,22], while
69 elements of typical environmental concern (often identified as “heavy metals”) have shown low mobility in the soil and
70 no significant increase in the soil percolating water [21,22]. Depending on the dosage, the application of wood ash has
71 generally been shown to increase soil pH, cation exchange capacity and base saturation in the forest floor [18-20,23],
72 and to decrease soil exchangeable acidity [19,21,23] – effects that were documented to persist even 30 years after wood
73 ash application (i.e. long-term effects) [24]. While forest soil and wood ashes may be rather heterogeneous, the results
74 of previous studies focusing on the effects of wood ash applications have generally reported high reproducibility of the
75 experimental results across different replicates (e.g. [4,12,17]), i.e. limited variations in the analytical values.

76 In general, a relatively large number of studies have investigated the effects of wood ash application on the soil
77 chemistry (e.g. changes in the cation exchange capacity, composition and pH). On the other hand, the effects on the
78 percolating soil solutions have been often limited to a few key parameters (e.g. pH, electrical conductivity and a few
79 key elements), and to relatively short-term effects (see [14,16,17,25]). Furthermore, experimental setups differ across

80 different studies, making the results difficult to compare. More studies are needed in order to comprehensively evaluate
81 the effects of different wood ash dosages on the mobility of nutrients and trace elements for diverse soil types and over
82 longer times. The slow release of nutrients from the ash is considered a desired effect, as these may be taken up by local
83 soil organisms and surface plants [6]. Similarly, the release of elements of environmental concern should also be slow,
84 in order to limit potential toxic effects. Monitoring the composition of percolating soil solutions can provide insights
85 into the migration of nutrients and contaminants through the soil, and into the releasing rates.

86 This study aims to investigate, by means of laboratory column tests, the short- and long-term release of
87 selected inorganic elements from a Danish forest soil amended with wood ash. The topmost soil horizons (O- and A-
88 horizons) were tested against three wood ash dosages, namely 3, 9 and 30 Mg ha⁻¹. The focus was to evaluate whether
89 increasing dosages could potentially result in increasing element mobility overall. Specific objectives of this work were
90 to investigate (i) the development of pH and concentration levels in percolating soil solutions, (ii) the cumulative
91 release of nutrients and typical elements of environmental concern beyond the individual soil horizons and (iii) the
92 residual contents in the columns after 2.0 m³ of water infiltrating per m² of soil.

93

94 **2. MATERIAL AND METHODS**

95 **2.1 Ash and CaCO₃**

96 Wood ash from a Danish heat-only boiler facility (55° 56' 40" N; 9° 7' 19" E Lat/Lon, WGS84), operating with a grate-
97 fired system, was sampled. The combustion plant used wood chips, mainly from Norway spruce (*Picea abies*), as input
98 fuel. The woody biomass came from the thinning of local Norway spruce forests (in the radius of about 50 km from the
99 combustion facility). The trees were felled and dried on-site for about one year. These were then cut into chips and
100 delivered to the combustion facility without any further treatment. The combustion plant burns about 8,500 Mg of wood
101 chips every year. Bottom ash and fly ashes are mixed together in a single output flow, which transports the freshly
102 produced ashes into a container. A few hundred kilograms of these mixed ashes were sampled from the container itself.
103 The chemical composition and the basic leaching behaviour of this ash sample was determined in Maresca et al. [26,27]
104 with the reference "MA-9c" in Maresca et al. [26] and "MA" in Maresca et al. [27].

105 Wood ash particles >4mm were crushed by means of a jaw crusher and mixed with the rest of the ash. The acid
106 neutralisation capacity (ANC) of the ash was determined in accordance with CEN/TS 14997:2006 [28], whereby 30 g
107 of ash was mixed gently with deionised water in a closed batch test (liquid:solid ratio of 10:1) and small amounts of
108 HNO₃ were added following a step-wise procedure. Upon adding acid, the bottles were closed, the material was mixed

109 gently for 25 minutes, allowed to settle for 5 minutes and the solution pH was then measured. This procedure was
110 repeated until a final pH of 4.5 (ANC_{4.5}) was measured. The cumulative amounts of acid added and the observed pH of
111 the solution were plotted in the so-called “ANC curve”, which is presented in Figure S1 in Supplementary Material. The
112 final ANC_{4.5} of the ash was determined at 4.3 meq g⁻¹.

113 A subsample of laboratory reagent calcium carbonate (min. 95% of CaCO₃) was used during the percolation
114 tests (see Section 2.3). While this calcium carbonate is unlikely to be used for field application, laboratory-grade
115 calcium carbonate was used here as a well-defined source of alkalinity (or ANC). The ANC of calcium carbonate was
116 determined similarly to the ash, resulting in 19 meq g⁻¹ – see Figure S1.

117

118 **2.2 Soil sampling and characterisation**

119 Soil was sampled from a test site in the Gedhus plantation, northwest of Denmark (56° 16' 39" N; 9° 5' 7" E Lat/Lon,
120 WGS84), in a 57-year-old Norway spruce plantation in spring 2014. Note that, in Denmark, Norway spruce represents
121 the most common tree species of local wooded areas [29]. The plantation is a second-generation forest nestling on
122 heathland with a Podzol soil type. Mean annual temperature and precipitation are 8.4°C and 0.850 m³ m⁻², respectively,
123 in overall agreement with other forest lands in Western Denmark [30]. The site-specific net infiltration below the root
124 nutrient zone was measured earlier at 0.270 ± 0.090 m³ m⁻² year⁻¹ [31]. The Gedhus plantation's test site was
125 specifically established with the scope of testing the effects of wood ash application as part of the ASHBACK project
126 (which this study is also part of) – for more details about the ASHBACK project, please refer to the Acknowledgments
127 section.

128 The soil was sampled horizon-specifically from the O- and A-horizons (hereafter indicated as O-hor and A-
129 hor). The soil was dried at 50°C and sieved to <2 mm and <4 mm for the mineral and organic soil, respectively. The
130 bulk density of the individual soil horizons was determined in triplicate, based on the soil mass of volume-specific
131 samples. Particle size distribution of A-hor was determined using a Malvern Mastersizer 2000 according to DS/ISO
132 13320: 2009 [32]. Exchangeable cations were determined according to Stuanes et al. [33] after extracting the soil with a
133 80.04 kg m⁻³ NH₄NO₃ solution; amorphous and crystalline iron (hydr-)oxides were extracted with ascorbic acid (DS/EN
134 ISO 12782-1; [34]) and dithionite (DS/EN ISO 12782-2; [35]), respectively, whereas aluminium (hydr-)oxides were
135 extracted with ammonium oxalate/oxalic acid (DS/EN ISO 12782-3; [36]). All extracts were analysed by means of
136 inductively coupled plasma (ICP) mass spectrometry (-MS) analysis (iCAP Q ICP, Thermo Fisher Scientific).

137 Soil samples were ground finely to <1 mm, and multi-elemental analysis was performed using ICP-MS
138 (Agilent 7900, Agilent Technologies), after digesting the samples in PTFE vessels in a microwave oven with a nitric
139 acid/hydrogen peroxide solution at 250°C. Nineteen elements were analysed: Al, As, Ca, Cd, Co, Cr, Fe, K, Mg, Mn,
140 Mo, Na, Ni, P, Pb, S, Se, V and Zn. A ground subsample was analysed for C and N concentrations by dry combustion,
141 using a FLASH 20000 EA NC Analyser (Thermo Fisher Scientific).

142

143 **2.3 Percolation of soil columns**

144 Column percolation experiments were carried out using dry soil samples (50°C), wood ashes and calcium carbonate. A
145 total of 11 columns (ϕ : 5 cm; height: 35 cm) were run simultaneously. Each column employed a single soil horizon
146 only, which was packed to reflect the observed field conditions in terms of depth (6 cm for O-horizon and 10 cm for A-
147 horizon), bulk density (180 kg m^{-3} for O-hor and 650 kg m^{-3} for A-hor) and moisture content (69 % for O-hor and 32 %
148 for A-hor). To minimise the occurrence of channelling and preferential flows in the columns, up-flow percolating
149 conditions were used and a layer of acid-washed quartz sand was included underneath the soil. Nylon filters
150 (polyamide, mesh opening of $20 \mu\text{m}$) were used to avoid transporting particles out of the columns. Deionised water was
151 pumped into the columns at a flow rate of $\sim 50 \text{ cm}^3 \text{ day}^{-1}$ (equivalent to $\sim 0.025 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$) for about three months (i.e.
152 84 days). Similar column set-ups have been used in other soil investigations (e.g. [37]).

153 In the case of field applications, wood ashes will be spread on the soil surface, i.e. on top of the O-hor. Forest
154 soil is, however, heterogeneous and so it is the depth of O-hor. Furthermore, in concomitance with a rainfall event,
155 water may firstly get in contact with the ash and then percolate through the porous O-hor in one of the preferential
156 flows, entering the following horizon without having had the time to equilibrate with the previous one. In other words,
157 the case of having wood ashes and/or their leaching “by-passing” the uppermost O-hor may not be so remote. For
158 completeness, it was decided to extend the investigation of different wood ash dosages on both soil horizons, i.e. O- and
159 A-hor. Each soil horizon was tested against three ash dosages, i.e. 3, 9 and 30 Mg ha^{-1} (which given the column cross-
160 section area, corresponded to 0.59, 1.8 and 5.9 g of wood ash, respectively): columns O-3, O-9, O-30, A-3, A-9, and A-
161 30, where the initial letter refers to the soil horizon (O- and A-horizons) and the number refers to the ash dosage.
162 Subsamples of the original fresh (untreated) wood ash sample (Section 2.1) were used.

163 The wood ash sample was homogenised and the subsamples were separated after repetitive riffle-splitting and
164 quartering. In the columns, water infiltrated from the bottom to the top (up-flow percolating conditions); accordingly,
165 the ashes were mixed with the bottom-most 0.5 cm of soil. Two soil control columns, where no ash was applied, were

166 also included: O-0 and A-0. Two additional columns, one per soil horizon, were built as described earlier, albeit using
167 calcium carbonate instead of ashes: columns O-L and A-L. The dosage of CaCO_3 applied in these columns was 7 Mg
168 ha^{-1} (corresponding to 1.4 g of CaCO_3 in each of the column), which was calculated as being equivalent in terms of
169 ANC to the ash dosage of 30 Mg ha^{-1} . To test the potential release of trace elements from the acid-washed quartz sand,
170 a “blank column” (i.e. only filled with sand) was additionally included in the experimental setup.

171 Leachate samples of 50-100 cm^3 were collected continuously, and pH and electrical conductivity were
172 measured immediately. A selected number of samples were then centrifuged at 2290 relative centrifugal force (RCF) for
173 10 minutes (i.e. equivalent cut-off particle size of 0.45 μm) and the supernatant was split into two fractions. Samples
174 undergoing ICP-MS (7700x, Agilent Technologies) and optical emission spectrometry (Varian Vista-MPX) analyses
175 were acidified by adding HNO_3 (p.a.) to $\text{pH} < 2$ and then analysed for the concentrations of the same list of elements
176 measured for the soil (see Section 2.2), plus Sb and Si (and a few more elements, i.e. Ba, Be, Li, Rb, Sn, Sr and Tl,
177 which have not been described further here but are reported in the Supplementary Material figures). Samples intended
178 for anions (Thermo Scientific DIONEX ICS 5000 DC), i.e. chlorides, bromides and nitrates, dissolved organic carbon
179 (DOC) and total dissolved carbon (Shimadzu TOC 5000A Analyser) were not acidified.

180

181 **2.3.1 Concentration levels and cumulative releases**

182 The analytical concentrations were plotted in a logarithmic scale and the differences in concentration levels across the
183 individual treatments were evaluated. To facilitate the comparison across the individual columns, these differences in
184 the concentration levels were expressed as the ratio between the values observed in the leachates from the soil columns
185 treated with ash/ CaCO_3 and the values observed in the leachates from the control columns (see Section 3.3). Only
186 distinct differences were discussed, whereas smaller fluctuations and comparable concentration levels were not
187 specifically addressed as these were more likely to be connected to natural soil and/or wood ash heterogeneities. The
188 observed compositions of percolating soil solutions were compared with Danish groundwater quality criteria (GQC)
189 [38], to investigate if and which elements could appear to be of primary concern with regards to their concentration
190 levels.

191 The observed concentrations were interpolated and integrated over the cumulative volume of percolating water
192 (shape-preserving piecewise cubic interpolation and trapezoidal numerical integration in MATLAB®) to calculate the
193 cumulative release of nutrients and typical elements of environmental concern. In the case of concentrations below the
194 limit of quantitation, these were assumed to be equal to the limit of quantitation itself (potential overestimation). At the

195 end of the leaching tests, based on cumulative releases and on the initial total contents, residual contents in the
196 individual columns were calculated (at the cumulative infiltration volume of $0.5 \text{ m}^3 \text{ m}^{-2}$ and $2.0 \text{ m}^3 \text{ m}^{-2}$) and expressed
197 as a percentage of the initial levels.

198

199 **3. RESULTS AND DISCUSSION**

200 **3.1 Composition of soil and ash samples**

201 Table 1 reports the chemical composition of the ashes and the two soil horizons, i.e. O- and A-hor. The composition of
202 the soil fell within typical levels observed for Danish nutrient-poor forest soils [39,40], also with regards to the levels of
203 cation exchange capacity, pH and iron and aluminium (hydr-)oxides. The A-hor soil could be classified as a sandy soil
204 ($200\text{-}1400 \mu\text{m}$: 80.3 % dw; $20\text{-}200 \mu\text{m}$: 13.5 % dw; $0.2\text{-}20 \mu\text{m}$: 5.8 % dw; $<2 \mu\text{m}$: 0.3 % dw). As such, the investigated
205 forest soil may be considered to be a rather common soil in Denmark, where wood ashes may be applied onto. Indeed,
206 the soil composition, texture, pH, type of vegetation and rainfall, were all found to be in line with other Danish forest
207 soils [29,30,39–41].

208 Wood ash composition and leaching were within typical values found in the literature for similar kinds of
209 ashes (see [26,27] and therein literature), and complied with Danish quality criteria that allow wood ash to be spread
210 onto forest soils [5].

211

< "Table 1 here" >

212

213 **3.2 pH levels and electrical conductivity**

214 All soil columns, including the controls, exhibited an overall similar pH increase in the percolating soil solutions until
215 the cumulative infiltrating volume of $1.0 \text{ m}^3 \text{ m}^{-2}$, after which more stable pH levels were observed (pH ~ 5.9 in the case
216 of O-hor, and up to pH ~ 4.5 in A-hor) – see Figure 1. The comparable trends across all columns indicated that the initial
217 increase in pH was most likely connected to the washout of soil acidity, whereas the expected release of alkalinity from
218 both wood ashes and CaCO_3 did not provide any evidence of changes in the pH of the percolating solutions. Electrical
219 conductivity decreased rapidly in all columns (see Figure S2), even though with a little delay for the columns containing
220 the highest ash amounts (O-30 and A-30).

221 A slight variation from the overall pH trends described earlier was found for both the O-30 and the A-30
222 columns. These columns presented a small decrease in pH at the very beginning of the leaching test, followed by an
223 overall delay in approaching the pH levels of all the other columns (until $0.5 \text{ m}^3 \text{ m}^{-2}$). It is worth noting that while the

224 pH decreased, high electrical conductivity levels were observed. Similar observations have been reported in the past, for
225 example by Eriksson et al. [42], and this effect has often been ascribed to a “salt effect”: the relatively high amounts of
226 dissolved salts from the ash (responsible for the high electrical conductivity values) can displace exchangeable H^+ , Al^{3+}
227 and Mn^{2+} from the soil, therefore affecting the pH of the percolating soil solutions. While inconclusive, the slightly
228 higher concentration levels of Al (and to some extents also Mn) observed for O-30 and A-30 within the first $0.5\text{ m}^3\text{ m}^{-2}$
229 of cumulative infiltrated water may support the overall displacement of exchangeable Al^{3+} (and Mn^{2+}) from the soil (see
230 Figure S2).

231 < "Figure 1 here" >

232 < "Figure 2 on the following page" >

233

234 3.3 Composition of the percolating soil solutions

235 Figures 1 and 2 report the observed concentrations of selected major and trace elements in the collected soil solutions:
236 DOC, Ca, K, P, S and pH in Figure 1; and As, Cd, Cu, Cr, Pb and Zn in Figure 2. Additional elements are presented in
237 Figure S2 and S3. While the observed concentration values are shown in the figures, the following text only highlights
238 differences in terms of concentration levels between soil treatments and controls. Overall, for both the O-hor and the A-
239 hor columns, concentration levels decreased rapidly within the first three weeks of sampling (equivalent to $\sim 0.5\text{ m}^3\text{ m}^{-2}$
240 of infiltrated water passing through the individual columns). Similar observations were also reported during the column
241 leaching experiments of Eriksson [14]. The only element that visibly deviated from these overall trends was Fe – its
242 concentration first decreased, then increased by about one order of magnitude at $0.5\text{ m}^3\text{ m}^{-2}$ (up to $\sim 1000\text{ }\mu\text{g L}^{-1}$) and
243 finally slowly decreased toward the end of the test (see Section 3.6).

244 The largest overall variations in terms of concentration levels between O-hor columns treated with ash and the
245 O-hor control column were shown for K (about 2, 4 and 8 times higher for O-3, O-9 and O-30, respectively), P
246 (between 2 and 5 times higher), Si (up to 5, 8 and 13 times higher for O-3, O-9 and O-30, respectively), As (between 1
247 and 5 times higher) and Cu (up to 6 times higher for O-3 and O-9, and up to 9 times higher for O-30). Other elements
248 were also affected, but only at the beginning of the experiment: i.e. Cd, Cl, Mg and S. Danish GQCs [38] were
249 generally complied with by all O-hor columns leachates in the case of As, Cd, Cu, Cr, Mo, Ni, Sb and Zn. On the
250 contrary, the observed Pb levels were above GQCs until the infiltrating volume of $\sim 0.5\text{ m}^3\text{ m}^{-2}$, albeit this was shown by
251 all columns (even by the O-hor control column). In addition to these overall trends, slightly higher levels of Cd and Cu,
252 though still below Danish GQCs (limits of $0.5\text{ }\mu\text{g L}^{-1}$ for Cd and $100\text{ }\mu\text{g L}^{-1}$ for Cu), were observed in all leachates from

253 O-hor columns treated with ash before the cumulative infiltrating volume of $0.5 \text{ m}^3 \text{ m}^{-2}$ for Cd and $1.0 \text{ m}^3 \text{ m}^{-2}$ for Cu (an
254 effect that may have been promoted by DOC complexation processes [43,44] – see Section 3.6). Nitrates were always
255 measured below the limit of quantitation, i.e. $< 1 \text{ mg L}^{-1}$.

256 In the case of A-hor treated with ash, the largest overall variations in concentration levels relative to the A-hor
257 control column were observed for K (up to 3, 6 and 14 times higher for A-3, A-9 and A-30, respectively), P (in the
258 range of 3-6 times higher) and Si (about 3, 5 and 9 times higher for A-3, A-9 and A-30, respectively). Relatively large
259 variations in Cl, Mg and S levels were also observed, but only at the beginning of the experiment. Danish GQCs for Pb
260 were always exceeded, even by the control column: at the beginning of the test, Pb concentrations were about one order
261 of magnitude higher than the limits, whereas toward the end, they were very close to these levels. The observed levels
262 of As, Cd (, Cr) and Zn were also found to exceed the GQCs, but only at the very beginning of the experiment and
263 generally by all columns (even by the A-hor control column). Some slightly higher concentrations of Cd and Zn were
264 also observed in the case of A-30 leachates. Nitrates, irrespective of the soil treatment, were below 1 mg L^{-1} .

265 The concentration of DOC decreased from about $200\text{-}300 \text{ mg L}^{-1}$ for O-hor, and $400\text{-}500 \text{ mg L}^{-1}$ for A-hor, to
266 about 40 mg L^{-1} at $0.5 \text{ m}^3 \text{ m}^{-2}$. While the observed levels were similar across the individual soil treatments, slightly
267 higher values were reported in the case of wood ash application. Levels of about $15\text{-}25 \text{ mg L}^{-1}$ were observed toward
268 the end of the test.

269 The background levels of the leachates from the “blank column” were generally low compared to the columns
270 containing soil, except for Ca. More specifically, the concentration of Ca was typically slightly higher than the other
271 columns, especially during the first part of the experiment. This indicated that some residual contents of Ca were still
272 associated with the pretreated sand.

273

274 **3.4 Cumulative releases**

275 All columns showed relatively high cumulative releases of both major and trace elements within the first $0.5 \text{ m}^3 \text{ m}^{-2}$ of
276 infiltrating water (see Table S1 in Supplementary Material), after which lower releases were observed: cumulative
277 releases at $2.0 \text{ m}^3 \text{ m}^{-2}$ (shown in Table 2) were commonly, except for Fe, between 1 to 3 times higher than at $0.5 \text{ m}^3 \text{ m}^{-2}$.
278 In the following text, however, only cumulative releases at $2.0 \text{ m}^3 \text{ m}^{-2}$ are addressed, unless otherwise explicitly stated.

279

< "Table 2 here" >

280 Overall similar releases were observed from the comparison between the control columns and the calcium
281 carbonate treatments: cumulative releases were mostly limited to a ± 1.3 times difference (in a few cases ± 1.5 times

282 difference, but mainly for O-hor columns). Similar cumulative releases were also observed when comparing the
283 individual O-hor treatments with the respective A-hor treatments, for example O-9 against A-9: variations were
284 generally limited to ± 2 times difference. Slightly larger variations were observed in the cases of Al, Sb, Pb (between 3
285 and 5 times higher from the A-hor columns), K, Cu and Cl (up to 4 times lower from the A-hor columns). Within the
286 same soil horizon type, increasing ash dosages commonly resulted in higher cumulative releases of both nutrients and
287 typical elements of environmental concern; however, even though the ash dosage increased ten times, from 3 to 30 Mg
288 ha^{-1} , the observed increase in the calculated releases was never proportional – see Table 2.

289 Application of wood ash increased the amounts of common plant nutrients leaching beyond the individual soil
290 horizons. In particular, in accordance with the leaching trends reported in Figure 1 and S2, relatively large amounts of
291 K, Na and S were observed to be leached before the cumulative infiltrating volume of $0.5 \text{ m}^3 \text{ m}^{-2}$ (similar to other field
292 studies, where short-term releases of these elements were reported – see for example [14,16,17]), but also until the end
293 of the experiment. In the case of Mg and P, less pronounced differences between soil controls and soil treated with
294 wood ash were observed. However, a clear tendency for higher leached amounts of Mg and P in the case of wood ash
295 application was identified. In the literature, field applications of wood ash have been reported to increase the soil
296 exchangeable Mg (e.g. [17,19,20]) and extractable P [17,23,24,45] in the forest floor, whereas the concentration of Mg
297 and P in percolating soil solutions may not be necessarily affected [17,46]. In the case of Ca, the blank column released
298 about 2.2 g m^{-2} against the $0.53\text{-}1.2 \text{ g m}^{-2}$ observed in the other O-hor and A-hor columns. Field studies have generally
299 reported increases in the soil exchangeable Ca (e.g. [17,19,20]). This strong affinity between soil sorption sites and Ca
300 was likely to be the cause of the relatively low releases of Ca from the columns containing soil.

301 With regards to typical elements of environmental concern, the only elements for which releases between the
302 control columns and the highest ash treatments were larger than a twofold difference were As and Cu, and only in the
303 case of the O-hor columns: from 2.2 to 5.8 mg m^{-2} for As (from O-0 to O-30 columns, respectively), and from 2.0 to 7.6
304 mg m^{-2} for Cu (from O-0 to O-30 columns, respectively). These results indicate that the migration of Cd, Co, Cr, Mo,
305 Ni, Pb, Se and Zn beyond the individual soil horizons was not visibly enhanced by increasing ash dosages, not even at
306 the dosage of 30 Mg ha^{-1} .

307

308 **3.5 Residual contents in the columns**

309 Table 3 presents the calculated residual amounts in the columns at the cumulative infiltrating volume of $2.0 \text{ m}^3 \text{ m}^{-2}$,
310 expressed as a percentage of the initial amounts in the columns. Based on the relatively high releases calculated for K,

311 Na, P and S, these results support the notion that wood ash application may be used as a means of recycling these
312 nutrients back to forest soil. On the other hand, relatively high releases of As may also be expected (see Section 3.6).
313 All other elements were released only up to a few percentage points, and generally their levels were considerably below
314 10% (remember that limit of quantitation levels were assumed when the analytical values too low to be quantifiable).
315 Overall, the residual contents calculated herein were in agreement with the field experiment observations from
316 Ingerslev et al. [4] 2.5 years after wood ash application.

317 < "Table 3 here" >

318

319 **3.6 Discussion**

320 Current Danish legislation allows a maximum wood ash dosage of 3 Mg ha⁻¹, which may be applied three times within a
321 75-year period, irrespective of whether the ashes have been pre-treated earlier [5]. Accordingly, the dosages
322 investigated during this study represented a “typical” wood ash application (3 Mg ha⁻¹), an “extreme” dosage (30 Mg
323 ha⁻¹) and an “intermediate” situation where the 3x3 Mg ha⁻¹ (9 Mg ha⁻¹) are spread all at once. Fresh wood ashes were
324 tested in a series of up-flow soil column experiments up to the infiltration volume of ~2.2 m³ m⁻², which, given the local
325 infiltration rate of 270 ± 90 mm year⁻¹, corresponded to about 8.1 years in the field. While field application of fresh
326 wood ashes is allowed in Denmark, field conditions will likely put the ashes in favourable conditions (e.g. presence of
327 moisture and atmospheric CO₂) for the occurrence of hardening reactions (see Steenari & Lindqvist [47]), which would
328 gradually affect the ash mineralogy and possibly its leaching, too. It is likely, however, that the use of up-flow
329 percolating conditions during this study has limited the occurrence of these reactions.

330 Column results suggested that high dosages of untreated wood ashes or the use of wood ashes with high salt
331 content can temporarily decrease the pH of percolating soil solutions because of the potential interaction between the
332 ashes’ dissolved cations and the exchangeable acidity of the soil, i.e. the aforementioned “salt effect”. The ANC of the
333 wood ash sample was about 4.3 times lower than CaCO₃ but still within the range reported by Vance [8], thus
334 suggesting that potential soil liming effects should be expected. However, the pH levels in the percolating soil solutions
335 from the control columns exhibited no evidence of significant differences compared to the wood ash and CaCO₃
336 treatments, indicating that the dissolved alkalinity was neutralised by the individual soil horizons and did not migrate
337 beyond them. Similar observations were made by other studies, e.g. Eriksson [14], Gómez-Rey et al. [17] and
338 Fernández-Delgado Juarez [48].

339 Application of wood ash onto the O- and A-hor columns indicated a long-term enhancement in the leaching of
340 K, P and Si, whereas the leaching of Cl, Mg and S was only temporarily enhanced (short-term effect, corresponding to
341 less than two years on field). Overall, no breakthrough point in the individual concentration curves was identified,
342 suggesting that the retention capacity of the investigated soil horizons was not exceeded during the duration of our soil
343 column experiment. At the same time, as the concentration levels of typical elements of environmental concern were
344 generally observed below Danish GQCs [38], the migration of these elements through the soil may be of limited risk to
345 the environment.

346 Worth to be mentioned are the overall concentration trends of Cu, As and Pb. In particular, an increased
347 leaching of Cu beyond the O-hor was observed after wood ash application, likely supported by some DOC
348 complexation processes (e.g. [44]); these processes can possibly occur on field too. Similarly, higher amounts of As
349 were shown to percolate beyond O-hor columns. However, both the application of wood ash and calcium carbonate
350 enhanced the leaching of As from O-hor to a similar extent, suggesting that the observed amounts of As were mobilised
351 from the soil and not from the ash. The reason behind this increase in As levels remained uncertain (perhaps due to
352 some soil-exchangeable As being replaced by Ca^{2+} ions, or to a change in the As oxidation state from As(V) to As(III)),
353 which makes it difficult to extend these observations to field conditions. Nonetheless, the observed As levels were still
354 below Danish GQCs. With regards to Pb concentrations, these largely exceeded the GQC levels (especially in the case
355 of A-hor columns) albeit to a similar extent by all columns (even by the controls), suggesting a pH effect rather than an
356 ash application effect. Remember that soil acidity was washed out during our column experiment to a similar extent in
357 all columns (even by the control columns), an effect that is unlikely to occur on field. In any case, it is noteworthy that
358 the observed Pb levels were generally below or close to the Danish drinking water limit values of $10 \mu\text{g L}^{-1}$ [49],
359 thereby suggesting that Pb release may be of a limited environmental concern, too.

360 Based on the calculated residual amounts in the columns, relatively large amounts of nutrients such as K, Na, P
361 and S were calculated to percolate through the individual soil horizons, which in turn suggested that these elements may
362 be directly accessible to local soil organisms. The expected leaching of elements of typical environmental concern may
363 be very small, as the calculated residual amounts in the columns in all cases were larger than 90 % (except for As).

364 The application of 3 Mg ha^{-1} of wood ash resulted in relatively smooth variations compared to the control
365 columns, which in turn suggested relatively slow releases in the case of field-scale applications. The effects of using 9
366 Mg ha^{-1} were intermediate between the 3 and 30 Mg ha^{-1} , but overall closer to the 3 Mg ha^{-1} ; however, as the ash dosage
367 increases, higher amounts of readily soluble elements should be expected to percolate shortly after wood ash

368 application. At 30 Mg ha⁻¹, even though the migration of typical elements of environmental concern beyond the
369 individual soil horizons was not considerably higher than at 3 and 9 Mg ha⁻¹, risks of a potential accumulation of these
370 elements on the forest floor should be taken into account. Furthermore, “shock releases” of Cl, K, Mg and S may be
371 expected, and “salt effects” may occur.

372 Noteworthy that on field, rain events are discontinuous and the uppermost soil horizons will experience both
373 periods of aeration and saturation, in turn affecting the soil redox potential and the solubility of specific elements. On
374 the other hand, our soil columns were always saturated of water because of the continuous up-flow percolating
375 conditions. It is very likely that the rate of dissolution of redox-sensitive elements may have been affected by this
376 experimental choice. In the case of Fe, for example, it was suspected that the observed variation in Fe levels was caused
377 by a change in its oxidation state from Fe(III) to Fe(II) (making it more soluble), promoted by the saturated column
378 conditions and/or the ongoing degradation of the soil’s organic matter (see similar findings in Fang et al. [37]).
379 Accordingly, some limitations may exist when trying to extend the results of redox-sensitive elements to field
380 conditions.

381

382 **4. CONCLUSIONS**

383 The effect of different wood ash dosages on Danish forest soil was investigated through a series of column experiments.
384 Within the boundaries of our experimental framework, wood ash application promoted a short-term leaching of readily
385 soluble elements like K, Cl, Mg and S within the first 0.5 m³ m⁻² of infiltrating water (corresponding to less than two
386 years on field), and a more prolonged leaching of K, P and Si, which lasted until the end of the experiment (~2.0 m³ m⁻²).
387 An increase in the concentration levels of trace elements like As, Cd, Cu and Se in the percolating solutions from O-
388 horizon was also observed, albeit these were detected within the levels defined by Danish ground- and drinking- water
389 quality criteria. Low migration through the soil of Al, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Se, V and Zn was
390 observed, for which cumulative releases were generally observed at a few percentage points compared to the total
391 column contents. Inversely, considerably higher releases of K, Na, P and S were demonstrated, suggesting that soil
392 applications can be used as a means to recirculate these elements back to forestry. In general, relatively limited and
393 comparable effects were observed from the use of 3 and 9 Mg ha⁻¹ in the composition of the percolating soil solutions,
394 except for the levels of readily soluble elements. On the other hand, if ash dosages considerable larger than the currently
395 allowed 3 Mg ha⁻¹ are intended for spreading, the observed low mobility of trace elements should be investigated
396 further with respect to the potential for accumulation in the forest soils.

397

398 **ACKNOWLEDGEMENTS**

399 We wish to thank the Solid Waste Group at DTU Environment for help received during the collection of percolating
400 soil solutions, and Sinh Hy Nguyen for his support in the lab. Stefan Trapp and Thomas H. Christensen are kindly
401 acknowledged for their inputs during the interpretation of the results. This work was financed by The Danish Council
402 for Strategic Research (Grant no 0603-00587B) and the Technical University of Denmark and it is part of the
403 ASHBACK project (<http://www.ashback.dk/>).

404

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528 **Table 1.** Composition of wood ash and soil O- and A- horizons. Results are expressed per dry weight of material. [-: not
529 analysed; TOC: total organic carbon; HFO: sum of amorphous and crystalline iron (hydr-)oxides; Al-ox: aluminium
530 (hydr-)oxides; CEC: cation exchange capacity]

	unit	O-hor	A-hor	Wood ash
TOC	g kg ⁻¹	422	98.8	66.4
N	g kg ⁻¹	13.2	2.68	7.00
HFO	mmol kg ⁻¹	11.5	10.3	-
Al-ox	mmol kg ⁻¹	10.0	11.9	-
CEC	cmol kg ⁻¹	12.9	4.87	-
Al	mg kg ⁻¹	740	952	12400
As	mg kg ⁻¹	0.688	1.17	1.82
B	mg kg ⁻¹	<1.61	<1.60	n.a.
Ca	mg kg ⁻¹	1210	178	135000
Cd	mg kg ⁻¹	0.280	0.258	3.99
Co	mg kg ⁻¹	0.230	0.165	5.49
Cr	mg kg ⁻¹	1.98	2.21	26.6
Cu	mg kg ⁻¹	3.83	1.12	60.4
Fe	mg kg ⁻¹	797	743	6720
K	mg kg ⁻¹	570	312	39400
Mg	mg kg ⁻¹	723	74.6	12700
Mn	mg kg ⁻¹	20.6	16.2	7430
Mo	mg kg ⁻¹	0.257	0.193	1.81
Na	mg kg ⁻¹	431	162	10500
Ni	mg kg ⁻¹	1.54	0.598	16.1
P	mg kg ⁻¹	338	47.9	10000
Pb	mg kg ⁻¹	16.5	19.4	13.8
S	mg kg ⁻¹	895	191	2450
Sb	mg kg ⁻¹	-	-	1.33
Se	mg kg ⁻¹	0.318	0.325	<16.7
Si	mg kg ⁻¹	-	-	254000
V	mg kg ⁻¹	2.87	2.24	15.9
Zn	mg kg ⁻¹	17.6	5.69	340

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536 **Table 2.** Calculated cumulative releases from the individual O- and A-horizon columns. Results are expressed in mg m⁻²
 537 ² and refer to the cumulative infiltration volume of 2.0 m³ m⁻².

	Cumulative releases (mg m ⁻²)									
	O-hor					A-hor				
	O-0	O-3	O-9	O-30	O-L	A-0	A-3	A-9	A-30	A-L
Al	140	160	160	170	130	590	620	710	860	510
As	2.2	5.1	5.0	5.8	5.9	6.9	7.5	8.9	9.4	7.3
Ca	770	730	740	1200	640	530	570	710	1100	530
Cd	0.20	0.22	0.23	0.27	0.20	0.29	0.30	0.32	0.52	0.23
Cl	2000	2200	3300	4700	2700	1000	1200	1500	3000	840
Co	0.18	0.28	0.33	0.21	0.15	0.26	0.34	0.36	0.46	0.29
Cr	0.58	0.61	0.68	0.55	0.48	1.2	1.1	1.2	1.1	0.88
Cu	2.0	4.9	5.3	7.6	3.0	2.8	2.7	3.1	2.9	2.5
Fe	980	1100	1100	890	750	1000	1100	1400	1400	1000
K	4600	8600	15000	29000	6300	2400	2800	5600	17000	1900
Mg	200	310	350	630	390	250	310	460	1300	190
Mn	6.2	12	15	15	8.6	5.0	37	9.4	13	3.6
Mo	0.26	0.26	0.25	0.34	0.26	0.34	0.38	0.46	0.52	0.39
Na	4200	5400	7300	9500	5200	6500	7200	9000	11000	6200
Ni	1.1	1.4	1.4	1.4	1.1	1.6	2.2	1.8	2.1	1.3
P	1700	3100	4300	3800	1500	1600	3100	4100	4400	990
Pb	2.3	2.8	2.5	3.4	2.8	10	9.9	12	14	8.9
S	1300	1700	2900	7100	1200	1400	2100	3500	9900	1100
Sb	0.14	0.14	0.16	0.19	0.13	0.51	0.47	0.56	0.49	0.42
Se	0.33	0.35	0.38	0.45	0.32	0.53	0.49	0.54	0.62	0.41
Si	4900	18000	29000	42000	24000	3200	10000	16000	30000	4100
V	2.5	3.4	3.5	2.9	2.3	4.5	5.2	5.4	5.7	4.1
Zn	17	28	20	22	17	21	25	51	33	23
DOC	56000	65000	73000	88000	74000	96000	100000	110000	130000	95000

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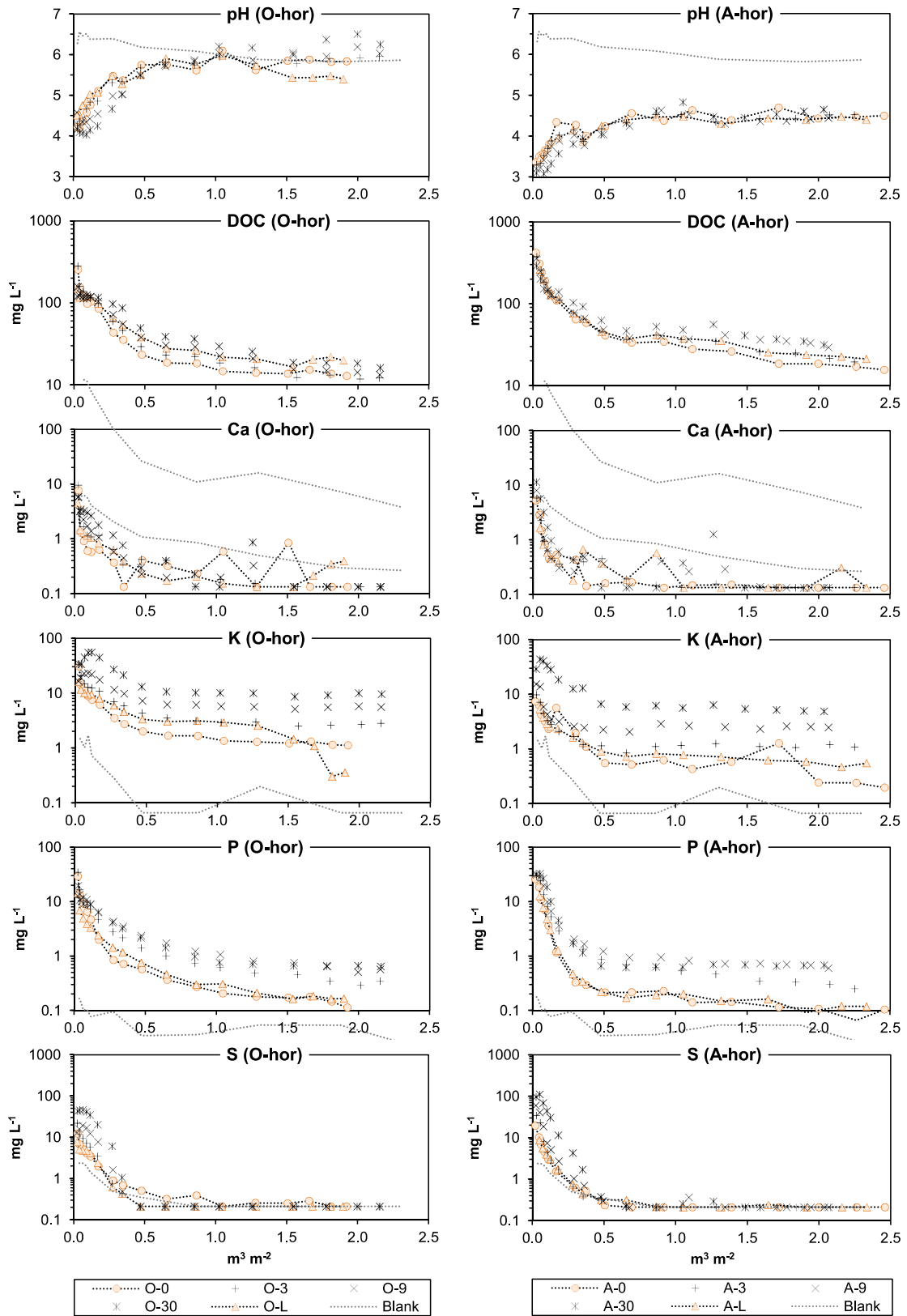
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540 **Table 3.** Calculated residual amounts of selected elements in the columns, at the cumulative infiltration volume of 2.0
 541 m³ m⁻². Results are expressed as a fraction (%) of the initial contents in the columns. [-0: indicates a full depletion of
 542 the element, as calculated from the released amounts]

	Residual amounts (%)									
	O-hor					A-hor				
	O-0	O-3	O-9	O-30	O-L	A-0	A-3	A-9	A-30	A-L
Al	98	99	99	100	98	99	99	99	99	99
As	70	36	45	55	21	91	90	89	89	90
Ca	94	99	99	100	100	95	99	99	100	100
Cd	93	95	97	98	93	98	98	98	98	99
Co	93	93	96	99	94	98	97	98	98	97
Cr	97	98	99	99	98	99	99	99	100	99
Cu	95	92	94	97	93	96	97	98	99	97
Fe	89	90	92	97	91	98	98	97	98	98
K	25	52	64	77	-0	88	91	90	88	91
Mg	97	97	98	99	95	95	96	97	97	96
Mn	97	100	100	100	96	100	99	100	100	100
Mo	91	92	94	96	91	97	97	97	97	97
Na	10	31	48	74	-0	38	47	55	74	41
Ni	93	93	96	98	93	96	95	97	98	97
P	53	53	66	89	59	49	49	66	87	68
Pb	99	98	99	98	98	99	99	99	99	99
S	87	84	76	58	88	89	84	76	50	91
Se	90	94	97	99	91	97	98	98	99	98
V	92	90	92	96	93	97	97	97	97	97
Zn	91	90	96	98	91	94	95	92	98	94

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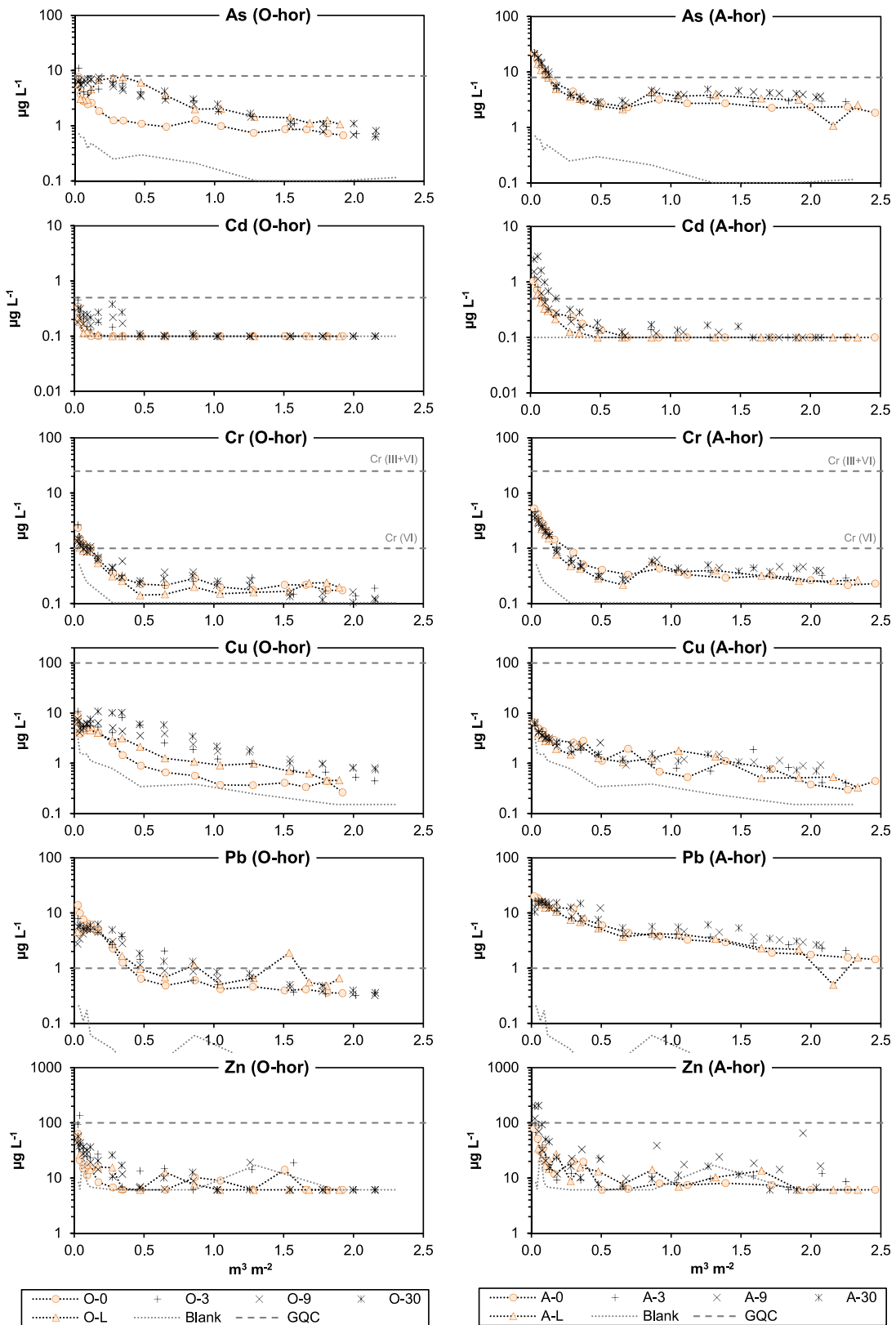
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Figure 1. Concentration levels of selected major elements (Ca, K, P, S, DOC and pH) in the collected soil percolating solutions. Results are expressed in mg L⁻¹ and are plotted against the cumulative infiltrating water (m³ m⁻²). [Blank: blank column].



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550 **Figure 2.** Concentration levels of selected trace elements (As, Cd, Cr, Cu, Pb and Zn) in the collected soil percolating
 551 solutions. Results are expressed in $\mu\text{g L}^{-1}$ and are plotted against the cumulative infiltrating water ($\text{m}^3 \text{m}^{-2}$). [Blank:
 552 blank column; GQC: Danish groundwater quality criteria].

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SUPPLEMENTARY MATERIAL

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Recirculation of wood combustion ashes onto Danish forest soil: release of nutrients and heavy metals

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*Maresca, A. ^{*a)}, Hansen M. ^{b)}, Ingerslev M. ^{b)} and Astrup, T.F ^{a)}.*

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^{a)} Technical University of Denmark, Department of Environmental Engineering, Building 115,
Bygningstorvet, 2800 Kgs. Lyngby, Denmark

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^{b)} University of Copenhagen, Department of Geosciences and Natural Resource Management,
Rolighedsvej 23, 1958 Frederiksberg C, Denmark

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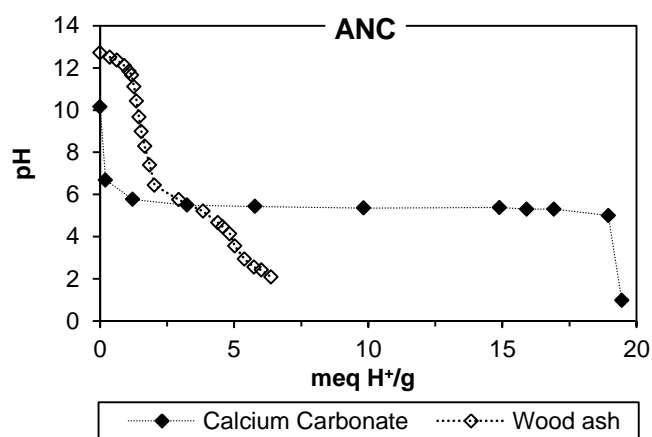
^{*)} Corresponding author: almar@env.dtu.dk

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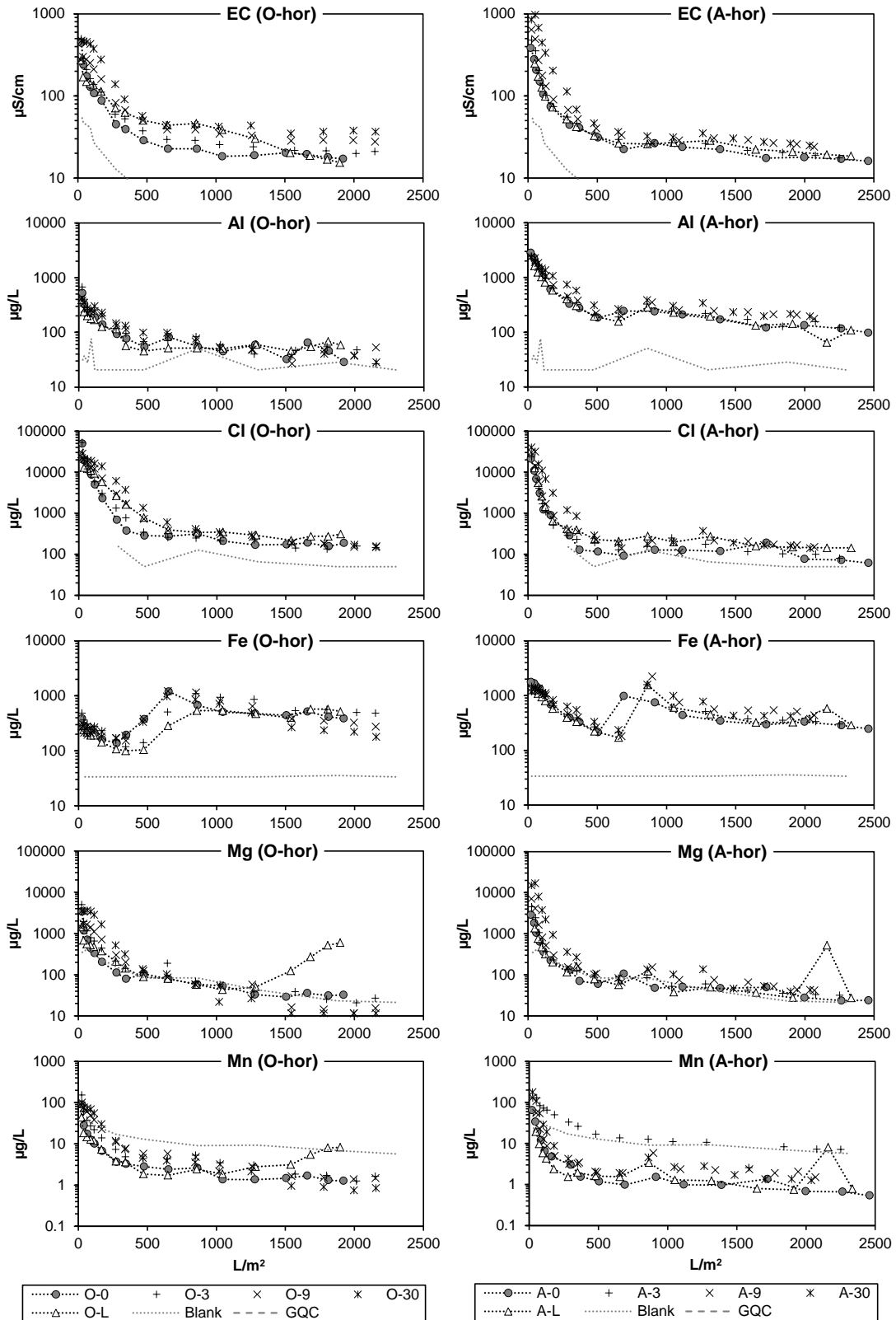
575 **Table S1.** Calculated cumulative releases from the individual O- and A-horizon columns. Results are expressed in
 576 mg/m² and refer to the cumulative infiltration volume of 500 L/m².

	Cumulative releases (mg/m ²)									
	O-hor					A-hor				
	O-0	O-3	O-9	O-30	O-L	A-0	A-3	A-9	A-30	A-L
Al	58	76	78	83	53	320	320	340	450	230
As	0.83	2.4	2.6	2.6	2.9	3.0	2.8	3.1	3.1	2.2
Ca	260	450	460	690	340	310	330	360	580	210
Cd	0.052	0.068	0.081	0.12	0.052	0.14	0.14	0.16	0.31	0.085
Cl	1600	1900	2800	4200	2300	850	930	1200	2700	520
Co	0.066	0.098	0.12	0.091	0.052	0.13	0.12	0.13	0.2	0.096
Cr	0.27	0.29	0.31	0.25	0.22	0.66	0.55	0.51	0.49	0.36
Cu	1.3	2.8	2.4	4.0	1.7	1.4	1.1	1.2	1.2	0.92
Fe	100	92	110	100	65	310	300	310	350	220
K	2500	4200	6600	15000	3100	1400	1100	1900	8800	850
Mg	130	220	280	580	140	170	230	350	1100	110
Mn	3.6	7.0	10	12	3.2	3.4	22	5.4	9.2	1.4
Mo	0.069	0.07	0.066	0.074	0.068	0.15	0.16	0.17	0.16	0.13
Na	2900	4000	4800	6000	3800	4600	5300	6700	9300	3700
Ni	0.49	0.66	0.66	0.71	0.46	0.75	1.2	0.65	0.89	0.45
P	1300	2200	2700	2500	1100	1400	2300	2900	3400	740
Pb	1.6	1.7	1.5	2.1	1.5	5.4	4.6	5.3	6.3	4.0
S	920	1400	2600	6800	850	1100	1800	3100	9500	710
Sb	0.047	0.054	0.059	0.071	0.055	0.19	0.16	0.17	0.16	0.14
Se	0.10	0.12	0.14	0.23	0.092	0.28	0.26	0.27	0.34	0.17
Si	2100	8300	12000	16000	8100	1700	5600	8900	16000	1800
V	0.64	0.80	0.94	0.83	0.61	2.1	1.7	1.7	1.8	1.2
Zn	4.4	11	7.1	10	6.2	9.9	10	13	18	7.5
DOC	33000	39000	41000	47000	40000	55000	53000	54000	58000	45000

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 581 **Figure S1.** Acid neutralization capacity (ANC) curve for calcium carbonate and wood ash, carried out according to
 582 CEN/TS 14997:2006 at the L/S 10 L/kg.
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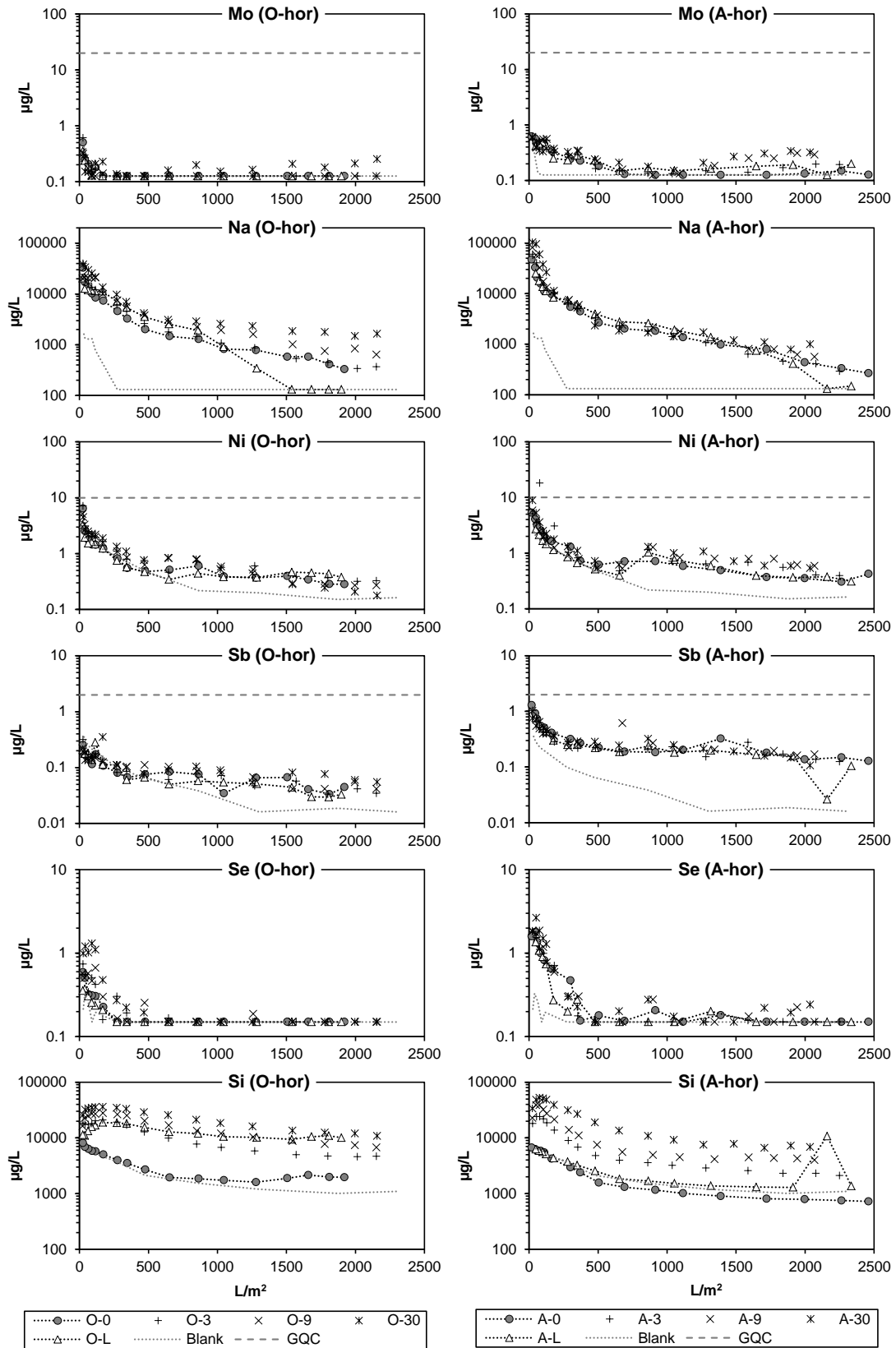
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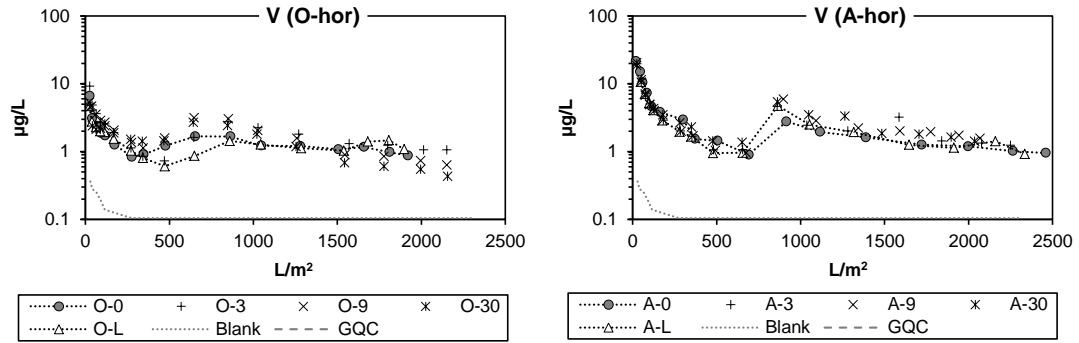
Figure S2a. Concentration levels of additional elements not included in Figure 1 and 2 in the collected soil percolating solutions. Results are expressed in µg/L and are plotted against the cumulative infiltrating water (L/m²). [Blank: blank column; GQC: Danish groundwater quality criteria].



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589 **Figure S2b.** (continued) Concentration levels of additional elements not included in Figure 1 and 2 in the collected soil
 590 percolating solutions. Results are expressed in µg/L and are plotted against the cumulative infiltrating water (L/m²).
 591 [Blank: blank column; GQC: Danish groundwater quality criteria].

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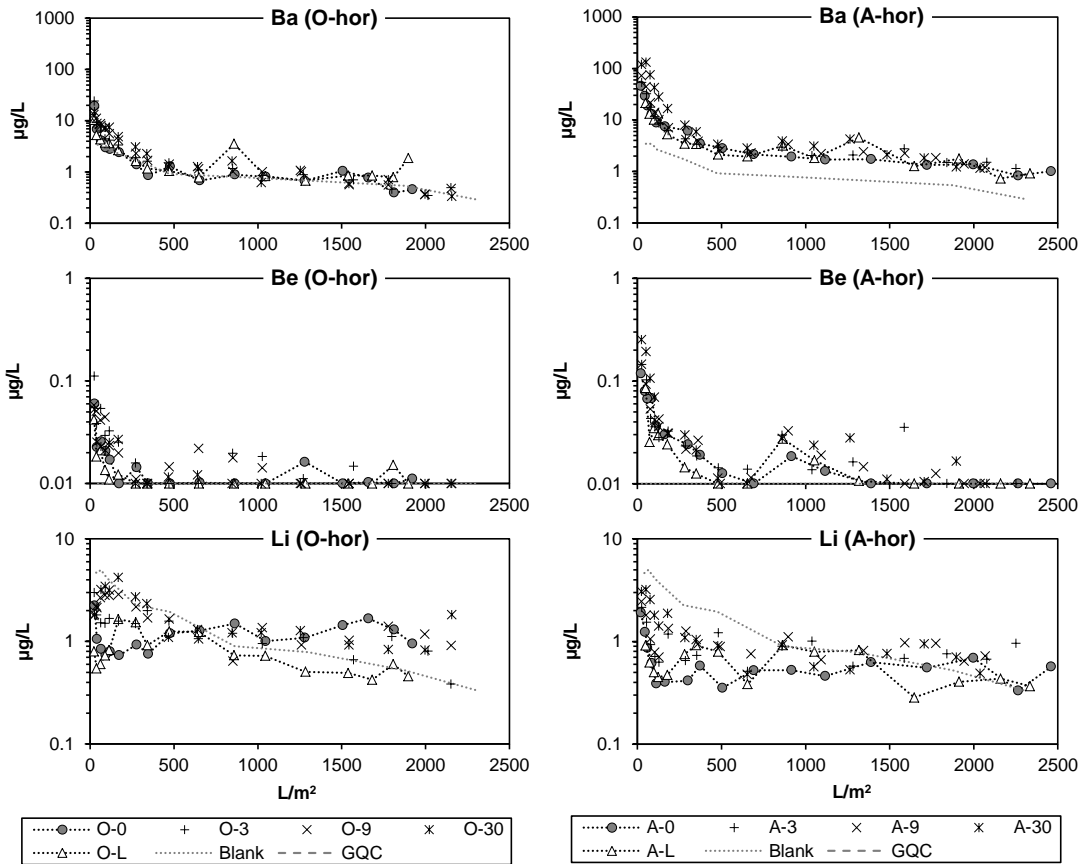
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Figure S2c. (continued) Concentration levels of additional elements not included in Figure 1 and 2 in the collected soil percolating solutions. Results are expressed in $\mu\text{g/L}$ and are plotted against the cumulative infiltrating water (L/m^2). [Blank: blank column; GQC: Danish groundwater quality criteria].



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Figure S3a. Concentration levels of additional elements (not described in the text) in the collected soil percolating solutions. Results are expressed in $\mu\text{g/L}$ and are plotted against the cumulative infiltrating water (L/m^2). [Blank: blank column; GQC: Danish groundwater quality criteria].

