

1 **Trace element and Pb isotope fingerprinting of atmospheric pollution sources:**  
2 **A case study from the east coast of Ireland**

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15 **Abstract**

16 Unravelling inputs of multiple air pollution sources and reconstructing their historic contribution  
17 can be a difficult task. Here, trace metal concentrations and Pb isotopes were measured in a  
18 radionuclide ( $^{210}\text{Pb}$ - $^{241}\text{Am}$ ) dated peat core from the Liffey Head bog (LHB) in eastern Ireland  
19 in order to reconstruct how different sources contributed to the atmospheric pollution over the  
20 past century. Highest enrichments in the heavy metals Pb, Cu, Ag, Sn, and Sb, together with  
21 a Pb isotope composition ( $^{206}\text{Pb}/^{204}\text{Pb}$ :  $18.351\pm 0.013$ ;  $^{206}\text{Pb}/^{207}\text{Pb}$ :  $1.174\pm 0.012$ ) close to that  
22 of the Wicklow mineralisation demonstrates significant aerial influx of heavy metals from local  
23 mining and smelting activities during the 19<sup>th</sup> century until ca. 1940's. A dramatic compositional  
24 shift defined by elevated Co, Cr, Ni, Mo, Zn, and V enrichments and a sharp transition towards  
25 unradiogenic  $^{206}\text{Pb}$  values ( $^{206}\text{Pb}/^{204}\text{Pb}$ :  $18.271\pm 0.013$  -  $17.678\pm 0.006$ ;  $^{206}\text{Pb}/^{207}\text{Pb}$ :  
26  $1.170\pm 0.012$  -  $1.135\pm 0.007$ ) is documented from the 1940's until ca. 2000. These are attributed  
27 to the atmospheric impact of fossil fuels and especially leaded petrol, modelled to have con-  
28 tributed between 6 and 78% to the total Pb pollution at this site. The subsequent turn to a more  
29 radiogenic Pb isotope signature since 2000 in Ireland is clearly documented in the investigated  
30 archive ( $^{206}\text{Pb}/^{204}\text{Pb}$ :  $17.930\pm 0.006$ ;  $^{206}\text{Pb}/^{207}\text{Pb}$ :  $1.148\pm 0.007$ ) and reflects the abolishment of  
31 leaded petrol. However, there remains a persisting and even increasing pollution in Ni, Mo,  
32 Cu, and especially Zn, collectively originating from countrywide use of fossil fuels (peat, coal,  
33 heating oil, and unleaded vehicle fuels) for domestic and industrial purposes. This illustrates  
34 the continued anthropogenic influence on important natural archives such as bogs in Ireland  
35 despite the phase-out of leaded petrol.

36

37 *Key words:* anthropogenic pollution, heavy metals, Pb isotopes, ombrotrophic peatland, Ire-  
38 land

39

## 40 1. Introduction

41 Anthropogenic activities are responsible for significant perturbations of the natural heavy metal  
42 cycles at the Earth's surface since at least 3000 years (Fábregas Valcarce et al., 2003). Om-  
43 brotrophic peatlands are considered excellent archives of historic atmospheric composition  
44 due to two key characteristics: i) the hydrological isolation from ground water and surface run-  
45 off ensures that the growing peat is exclusively fed by atmospheric inputs (i.e., dust, rain, snow,  
46 fog); and, ii) the inherently high abundance of complex-forming organic acids, together with a  
47 pH ranging between 4 and 5 enables the preservation of metal-bearing aerosols at the depth  
48 of their deposition (e.g., Shotyk and Le Roux, 2005; Zacccone et al., 2009). There is an increas-  
49 ing body of publications on historic atmospheric trace metal depositions, especially of Pb, Zn,  
50 Cu, Hg, As, Cd inferred from study of bogs from around the world, including Canada (e.g.,  
51 Boyle, 1977; Pratte et al., 2013; Shotyk, 1992), Europe (e.g., De Vleeschouwer et al., 2009;  
52 Martínez Cortizas et al., 2012; Shotyk et al., 2002), Australia (e.g., Marx et al., 2010; Stromsoe  
53 et al., 2015), China (e.g., Ferrat et al., 2012), and South America (e.g., De Vleeschouwer et  
54 al., 2014). These studies report temporal variations in natural dust depositions, while also doc-  
55 umenting significant changes in the atmospheric metal pollution load throughout the periods  
56 of modern industrialisation into recent times (i.e., post Pb-gasoline).

57 Radiogenic Pb isotope analyses are a robust tool to distinguish between natural and  
58 anthropogenic Pb inputs due to conservative behaviour in bogs, including very low mobility  
59 and insignificant post-depositional isotope fractionation (Shotyk et al., 2005 and references  
60 therein). The isotopic signature of Pb, which shows a broad compositional variability within the  
61 lithogenic units found at the Earth's surface is determined by the geological age and respective  
62 U-Th-Pb concentrations of the parent rock. For example, Precambrian Pb ores from the  
63 Brocken Hill deposit at Mt. Isa, Australia display an unradiogenic  $^{206}\text{Pb}/^{207}\text{Pb}$  of 1.04 (Town-  
64 send and Snape, 2002), whereas the Mississippi type Pb deposits in the USA carry a radiogenic  
65  $^{206}\text{Pb}/^{207}\text{Pb}$  signature ranging between 1.28 and 1.33 (Doe, 1970). Products manufactured us-  
66 ing these ores will inherit their respective isotope signature. The pre-polluted  $^{206}\text{Pb}/^{207}\text{Pb}$  values  
67 of Greenlandic ice (Rosman et al., 1997), bogs from Spain (Kylander et al., 2005), Switzerland

68 (Shotyk et al., 2001) as well as Sweden (Klaminder et al., 2003) range between 1.19 and 1.25.  
69 The temporal and geographic evolution of the Pb pollution fingerprint has helped to discrimi-  
70 nate between the impact of mining-smelting and leaded gasoline around the northern hemi-  
71 sphere (e.g., Bindler et al., 2004, Bränvall et al., 1997; Cloy et al., 2008; Kylander et al., 2005,  
72 2009; Le Roux et al., 2004, 2005; Martinez-Cortizas et al., 2012; Shotyk et al., 2002). While  
73 often deployed separately, the information obtained from combining trace elements and (Pb)  
74 isotopic compositions is more powerful in differentiating between complex multiple sources.  
75 To date, there is not a single study reporting Pb isotope chronologies in Irish peatlands, and  
76 only two studies which investigated atmospheric depositions of Pb, Cd, and Hg: Kippure bog,  
77 Clara bog, Bellacorick bog (Schell et al., 1997), Knockroe bog, and Letterfrack bog (Coggins  
78 et al., 2006), which, compared to other European areas is rather scarce. There is thus a strong  
79 necessity to geochemically explore the Irish archives in more detail, especially in view of the  
80 rich metallurgical history of the island and Ireland's potential subjection to trans-Atlantic metal  
81 transport.

82 In this study, we investigate the elemental pollution history in a bog from the Wicklow  
83 Mountains in eastern Ireland with a particular focus on the last century. The Wicklow uplands  
84 were Ireland's most important lead mining centre from 1824 AD until the first half of the 20<sup>th</sup>  
85 century (Schwartz and Critchley, 1996). The area documents extensive lead-silver-zinc and  
86 copper (Avoca) extractions, with ore dressing taking place on site and smelting conducted at  
87 Glenmalure (parallel valley), as well as in a coal operated smelter ~35 km NE from the mining  
88 locality at Ballycorus (Rynne, 2015). Subeconomic conditions coupled with poor infrastructure  
89 and a drop in Pb prices triggered by the South American market surplus resulted in closure of  
90 all mining activities in the Wicklow uplands in the 1940's-1950's. The Liffey Head peat (LHB)  
91 archive was selected for investigations due to its proximity to the metallurgical sites and its  
92 location at the east coast of Ireland, allowing also an investigation of trans-regional metal  
93 transport on easterly air streams. Further to the metals of interest (Pb-Zn-Ag-Cu), this study  
94 also investigates the enrichment histories of other heavy metals such as Sn, Sb, Co, Cr, Ni,  
95 Mo, and V deposited onto LHB. This is particularly important because most of these metals  
96 occur as impurities within Irish Cu and Pb-Ag-Zn mineralisation, while also associated with

97 emissions from combustion of fossil fuels, steel and iron manufacture, and refuse incineration  
98 (Nriagu and Pacyna, 1988). By combining the information gained from trace element and Pb  
99 isotope compositions, our aim is to deconvolute multiple input sources that have influenced  
100 the atmospheric metal composition over the last century at this site.

101

## 102 **2. Background and methods**

### 103 **2.1. Study area and sample collection**

104 In the Republic of Ireland, where ca. 1/6<sup>th</sup> (~1,200,000 hectares) of landmass is covered by  
105 peat, three basic peat formations are recognised: 1) raised bogs of the Central Plain, 2) blanket  
106 bogs dominating the western seaboard and the upland areas, and 3) fen peats (Hammond,  
107 1978). Most of the Irish blanket and montane bogs are around 6000-8000 years old with aver-  
108 age accumulation rates of 0.1-1.2 cm year<sup>-1</sup> (Hammond, 1978). The site investigated here,  
109 LHB in Co. Wicklow (N 53°09'32", W 6°17'33") is an ombrotrophic, montane-type blanket peat-  
110 land situated 25 km southwest of Dublin city and approximately 15 km from the east coast of  
111 Ireland (Fig. 1). Liffey Head occurs as a relatively flat bog with a series of pool complexes and  
112 lies between 490 and 520 m above sea level. The annual precipitation in this part of the Wick-  
113 low Mountains is high, with means between 1600 and 2400 mm a<sup>-1</sup> (*source: Meteorological*  
114 *Survey*). These conditions sustain a near-continuous deposition of atmospheric particulates  
115 onto the bog's surface. The upland area experiences aerosol transport from both westerly At-  
116 lantic winds, potentially carrying pollutants from mines in the midlands, and injections of east-  
117 erly air masses which direct pollutants from the UK and beyond (e.g., Bowman and McGet-  
118 tigan, 1994; Feeley et al., 2013). The bog is underlain by the Leinster batholith, a Caledonian  
119 age granitic intrusion with a strong I-type, calc-alkaline affinity (e.g., Oliver et al., 2002).

120 A vertical monolith of 115 m in length (10x10x115 cm) was extracted from the LHB in  
121 March 2015 from an area with living *Sphagnum* moss growth on top using a stainless steel  
122 Wardenaar corer. The core was sampled close to the centre of the bog at its highest elevation.  
123 On site, the core was wrapped in cling film and aluminium foil, placed in a wooden box, brought  
124 directly to the laboratory and stored in a dark room at ca. +2°C. Using a thin ceramic knife, the

125 core was cut into 115 one cm slices, each apportioned for individual analyses as described in  
126 detail below.

127

## 128 **2.2. Radiometric data and analysis**

129 The radioisotopes  $^{210}\text{Pb}$ ,  $^{137}\text{Cs}$ , and  $^{241}\text{Am}$  were analysed via gamma-spectrometry on a sub-  
130 set of samples to derive a chronology for the top section of the core. All analyses were per-  
131 formed on a planar HPGe gamma detector (Canberra) at the Alfred Wegener Institute for Polar  
132 and Marine Research in Bremerhaven, Germany. Peat samples were weighed and sealed with  
133 hot glue in gas-tight petri dishes to prevent loss of ingrowing  $^{222}\text{Rn}$ . Subsequently, samples  
134 were stored for >3 weeks to allow the relevant daughters of  $^{226}\text{Ra}$  to grow into secular equilib-  
135 rium. Lead-210 was measured at 46 keV,  $^{241}\text{Am}$  at 59 keV, and  $^{137}\text{Cs}$  at 661 keV. The presence  
136 of  $^{226}\text{Ra}$  was monitored at lines 186 keV, 295 keV, 351 keV, and 609 keV. Detectable  $^{226}\text{Ra}$   
137 was found in fewer than 50% of the samples, but its activity was less than 1% of the total  $^{210}\text{Pb}$ .  
138 Consequently, no correction for supported  $^{210}\text{Pb}$  was performed to avoid introducing unneces-  
139 sary inconsistencies through the profile. Lead-210 is not reported as excess  $^{210}\text{Pb}$  ( $^{210}\text{Pb}_{\text{ex}}$ ),  
140 while noting that nearly all  $^{210}\text{Pb}$  will be unsupported. Samples were counted until 1000 net  
141 counts of  $^{210}\text{Pb}$  were reached, or for maximum of  $6 \cdot 10^5$  seconds if 1000 counts were not  
142 reached within this time period. Variable sample masses were expected to affect the detector  
143 efficiencies via self-absorption, especially at the low energy range. This was addressed by  
144 determining mass-dependent efficiencies using IAEA-385 Irish Sea reference material for  
145  $^{210}\text{Pb}$  and  $^{241}\text{Am}$ . The uncertainty on these efficiencies was assumed to be 10% (1sd). For  
146  $^{137}\text{Cs}$ , an uncertainty of 5% (1sd) was expected, taking into account the inevitably variable  
147 geometry of the unprocessed peat samples. Counting errors were typically small compared to  
148 the uncertainty in the efficiencies. Therefore, we applied an error calculation based on the error  
149 propagation from detector efficiencies and counting statistics, without including the nominal  
150 uncertainty in the background determination.

151

## 152 **2.3. Bulk peat properties**

153 Moisture contents were determined by drying a 2 cm<sup>3</sup> subsample (2x1x1 each cm piece of  
154 peat) at 105°C for 24 hours. The organic matter contents were defined via the loss on ignition  
155 (LOI) by combusting the dried aliquot at 550°C for 6 hours in inert quartz glass crucibles. Bulk  
156 density (g cm<sup>-3</sup>) was analysed at 5 cm resolution for the deepest part (40-100 cm) and at 3 cm  
157 resolution for the section between 0 and 40 cm following the method of Dean (1974).

158

#### 159 **2.4. Trace element and Pb isotope analyses**

160 Trace element concentrations in peat samples were acquired at Trinity College Dublin, Ireland  
161 via solution quadrupole ICP-MS (SQ-ICP-MS) using a Thermo Scientific iCAP-Qc, and follow-  
162 ing the method described in Marx et al. (2010). A dedicated ash fraction was prepared for this  
163 purpose by combusting a peat aliquot for 6 hours at 450°C. Between 10 and 50 mg of resulting  
164 ash was transferred into 15 ml Teflon beakers into which 0.8 ml of a triple sub-boiling distilled  
165 conc. HF and 0.2 ml conc. HNO<sub>3</sub> (4:1) was added. The capped beakers were placed into a  
166 digestion block at 120°C for 72 hrs and agitated at least once every 24 hrs in a HEPA-filtered  
167 fume cupboard. After cool-down, drops were carefully collected before beakers were opened,  
168 and the solution was evaporated at 110°C. The residues were then dissolved with 1 ml of 6 M  
169 HCl to reduce any remaining organic components, and fluorides were converted by attacking  
170 with 2x0.5 ml conc. HNO<sub>3</sub> with evaporation to dryness between each step. Finally, the con-  
171 verted residue was dissolved in 3 ml of 2.5 M HNO<sub>3</sub> and subsequently topped up with additional  
172 Milli-Q water to produce 30 ml of 0.3 M HNO<sub>3</sub> solutions. Two blanks were prepared along with  
173 the samples throughout all ashing and digestion steps to account for potential contamination.

174

175 The ICP-MS analyses followed the procedure of Eggins et al. (1997) with modifications de-  
176 scribed by Babechuk et al. (2010) and Marx et al. (2010). For analyses, 2 ml solutions contain-  
177 ing a small aliquot of each stock solution was diluted with 2% HNO<sub>3</sub> and spiked with an internal  
178 standard containing a mixture of <sup>6</sup>Li, Rh, Re, Bi and <sup>235</sup>U, which is used for instrumental drift  
179 correction, covering the full mass range of ionisation potentials and analysed elements. In  
180 some cases, the sample contained so much Bi that this affected the signal from the internal  
181 standard, which was then excluded for drift correction (interpolating instead between Re and

182 U). Following Eggins et al. (1997), an additional external drift monitor was employed. Oxide/hy-  
183 droxide and dimer interferences were corrected according to Ulrich et al. (2010). Multiple di-  
184 gestions of the USGS W-2a reference material were used for calibration, and additional USGS  
185 reference materials BCR-2 and BHVO-2 were measured throughout the duration of the study  
186 as the quality control standards. One relative standard deviations (rsd) of the mean of multiple  
187 measurements of the respective standards were typically <2% for BHVO-2 and BCR-2 and the  
188 concentrations were comparable to the GeoReM preferred values (Jochum et al. 2016)  
189 demonstrating very good accuracy (low bias) of this dataset (*Appendix A.2*). The elements with  
190 poorer reproducibility (>2% rsd) and/or higher bias relative to preferred values are those at  
191 very low ng g<sup>-1</sup> concentrations or those known to be heterogeneous in the USGS materials  
192 (e.g. Kamber and Gladu, 2009; Weis et al., 2006). The concentrations determined for this study  
193 also agree well with longer term determinations on the reference materials from similar tech-  
194 niques that applied the same calibration values (e.g., Babechuk et al., 2015; Kamber, 2009).

195         Once element concentrations were acquired, the previously determined ash content  
196 obtained at 450°C for was used to back-calculate the element concentration in dry (pre-ashed)  
197 peat. These concentration values (in ng g<sup>-1</sup>) are reported in *Appendix A.1*. Dry peat concentra-  
198 tions were used for the calculation of enrichment factors (EF) and excess pollution.

199  
200 Lead isotope ratios of all peat samples analysed for trace element composition (n=41) were  
201 measured on the same quadrupole ICP-MS at Trinity College Dublin. Because trace element  
202 analyses consumed only a small fraction of the digest (<1%), the remaining stock solution was  
203 used for Pb purification on anion exchange resin (AGX-1x, 200-400 mesh) applying the HBr-  
204 HCl method described in Kamber and Gladu (2009). Total Pb yield was between 85-90% for  
205 all samples and the purity of the Pb solution was verified with a fast mass scan prior to isotope  
206 ratio analysis. Procedural blanks were negligible with amounts less than 0.1% of the total Pb.  
207 The quadrupole ICP-MS Pb analysis technique used followed Ulrich et al. (2010). Accuracy  
208 and precision of the Pb isotope ratios were determined from multiple analyses of SRM-NBS  
209 982 standard solution as shown in *Appendix A.3*. Bias was 95 ppm for <sup>206</sup>Pb/<sup>204</sup>Pb, 44 ppm  
210 <sup>208</sup>Pb/<sup>206</sup>Pb, and 25 ppm for <sup>207</sup>Pb/<sup>206</sup>Pb, relative to the values of Baker et al. (2004). Lead

211 isotope ratios of the rock-reference materials BHVO-2 (n=2) and BCR-2 (n=2), presented in  
212 Table 2 are close to or within the values reported by Woodhead and Hergt (2000) and Baker  
213 et al. (2004), demonstrating the good accuracy of this dataset, considering some heterogeneity  
214 in Pb isotope composition in these reference materials as a result of their contamination during  
215 powder preparation, as discussed elsewhere (e.g., Weis et al., 2006).

216 We note that in environmental studies, the most commonly used Pb isotope data presen-  
217 tation is the use of the following ratios:  $^{206}\text{Pb}/^{207}\text{Pb}$  or  $^{206}\text{Pb}/^{204}\text{Pb}$ . While the former is justified  
218 by a better analytical precision, a normalisation to  $^{204}\text{Pb}$  will result in the largest possible vari-  
219 ability between reservoirs. Furthermore, as previously pointed by Ellam (2004), an omission to  
220 include  $^{204}\text{Pb}$  in the data interpretation might result in a limitation of source characterisation.  
221 In this study, we performed the source apportionment with the conventional Pb diagram  
222 ( $^{207}\text{Pb}/^{204}\text{Pb}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$ ) which offers the best dispersion. For ease of reference and com-  
223 parison to previous studies, the calculated  $^{206}\text{Pb}/^{207}\text{Pb}$  values are also included.

224

### 225 **3. Results**

#### 226 ***3.1. Radionuclide chronology reconstruction***

227 The detection limit of  $^{210}\text{Pb}$  is located at 23-24 cm from the surface, indicating that almost the  
228 entire  $^{210}\text{Pb}$  inventory is captured within this peat segment. We find a  $^{210}\text{Pb}$  inventory of 4830  
229 Bq/m<sup>2</sup>. The  $^{210}\text{Pb}$  profile (Fig. 2a.) is relatively complex and does not show a monotonous de-  
230 crease with depth thus impeding the use of a constant initial concentration (CIC) approach.  
231 The more suitable  $^{210}\text{Pb}_{\text{xs}}$ -chronology is therefore a constant-rate-of-supply (CRS)-model (Ap-  
232 pleby and Oldfield 1978). The CRS-model can take variations in mass accumulation rates into  
233 account, while still relying on a constant supply rate of  $^{210}\text{Pb}$ , the absence of initial penetration  
234 (IP) of  $^{210}\text{Pb}$ , and a complete assessment of the  $^{210}\text{Pb}_{\text{xs}}$  inventory. Such a model for our core  
235 is shown in Figure 2e. The possible initial penetration of  $^{210}\text{Pb}$  in peat has been described  
236 elsewhere and may in principle be modelled, assuming a constant initial penetration and a  
237 constant rate of supply of  $^{210}\text{Pb}$  (IP-CRS model, Olid et al. 2016). However, this model may  
238 still show discrepancies to the record of artificial radionuclides (Olid et al. 2016), in particular  
239  $^{241}\text{Am}$ , which is a robust age marker, while not providing a continuous age record. We therefore

240 used constraints based on  $^{241}\text{Am}$  together with the distribution of the  $^{210}\text{Pb}$  inventory in order  
241 to derive the best possible age information.

242 Assuming that  $^{210}\text{Pb}$  is not mobile, the complete inventory reflecting 4-5 half-lives is found  
243 in the top 24 cm. This implies a limit of 88-110 years at 24 cm, close to the CRS dates, trans-  
244 lating into an average sedimentation rate of  $0.22\text{-}0.27\text{ cm yr}^{-1}$ . Slower accumulation would be  
245 expected if  $^{210}\text{Pb}$  was somewhat mobile, but still within the calculated upper limit. The sudden  
246 increase in  $^{210}\text{Pb}$  activity at 8.5 cm cannot be assigned to a change in supply rate, but likely  
247 represents a sudden collapse in the growth rate.

248 Americium-241 (Fig. 2b.) was found to be the least mobile among the investigated radi-  
249 onuclides, in agreement with findings of other studies (Gallagher et al., 2016). It was present  
250 at much lower activities and it was detectable only in few samples. The broad  $^{241}\text{Am}$  peak at  
251 10-11 cm likely reflects the atmospheric release from nuclear tests in 1963-1964 (e.g., Gal-  
252 lagher et al., 2005). This would translate to a record of 50 years with an average accumulation  
253 rate of  $0.21\text{ cm yr}^{-1}$  for the uppermost 11 cm. However, this is a minimum value as  $^{241}\text{Am}$  is  
254 also found at about half this activity in the sample below (at 12-13 cm), leaving the possibility  
255 that the actual  $^{241}\text{Am}$  peak can be extended down to 12 cm depth. A secondary, smaller  $^{241}\text{Am}$   
256 signal is found at 16.5 cm. This is in slight disagreement with  $^{210}\text{Pb}_{\text{xs}}$  CRS-model as 1963 would  
257 be expected below 17 cm.

258 Two additional samples investigated at depths of 70-71 cm and 94-95 cm from the sur-  
259 face yielded no  $^{210}\text{Pb}$  and  $^{241}\text{Am}$  activity, but a small signal of  $^{137}\text{Cs}$  ( $4.4\text{ Bq kg}^{-1}$ , Fig. 2c.). This  
260 observation suggests significant down core Cs mobility at our site, as also suggested from the  
261 plots in *Appendix B.1*, meaning that  $^{137}\text{Cs}$  is of little value in providing precise chronological  
262 information here. Caesium mobility has been demonstrated in several studies of organic, clay-  
263 rich, low pH atmospheric and terrestrial archives, limiting its application as a chronologic tool  
264 (e.g., Appleby et al., 1991; Kudelsky et al., 1996). Consequently,  $^{137}\text{Cs}$  activity was excluded  
265 from the chronology reconstruction of the LHB peat profile.

266 Combined, the activity profiles obtained from  $^{210}\text{Pb}$  ( $S < 0.27\text{ cm yr}^{-1}$ ) and  $^{241}\text{Am}$  ( $S > 0.21$   
267  $\text{cm yr}^{-1}$ , with a depth trend) yield an average accumulation of  $0.24 \pm 0.03\text{ cm yr}^{-1}$  for the upper-

268 most 24 cm of the LHB peat core. This result is in agreement with the average values calcu-  
269 lated for Irish bogs (Hammond, 1978). The  $^{210}\text{Pb}$ - $^{241}\text{Am}$  age-depth relationship for the upper-  
270 most 24 cm was derived based on the above information, and the results expressed as AD  
271 ages are presented along with element enrichment profiles in Figure 3 and 4.

272

### 273 **3.2. Bulk peat properties**

274 The organic matter (Fig. 2d.) and moisture contents are relatively constant throughout the core  
275 with values ranging between 96-99% and 88-96% (by wt.), respectively. Density (Fig. 2c.)  
276 ranges between 0.023-0.034 g cm<sup>-3</sup>, with the highest values detected in the segment between  
277 10 and 40 cm from the surface. Subtle fluctuations in the moisture and density contents (es-  
278 pecially in the uppermost 25 cm) indicate minor down-core compaction and decomposition,  
279 favouring element retention at deposition depth. High organic matter contents (or low ash con-  
280 tents) evidence low input of atmospheric dust, validating the ombrotrophic nature on the peat-  
281 land. The fluctuations are strongly anti-correlated with lithophile elements Ti ( $r^2=0.69$ ), Sr ( $r^2=$   
282  $0.74$ ), Sc ( $r^2=0.75$ ), Ta ( $r^2=0.95$ ), and Zr ( $r^2=0.8$ ), supporting that mineral dust is the dominant  
283 component of the residual incombustible ash (e.g., Shotyk et al., 2002).

284

### 285 **3.3. Trace element patterns along the extracted LHB peat monolith**

#### 286 **3.3.1. Geochemical data treatment**

287 A principal component analysis (PCA) has been suggested as a strategy to minimize the  
288 amount of factors governing enrichment in multi-element datasets such as the one presented  
289 here (e.g., Küttner et al., 2014; Martínez Cortizas et al., 2013; Muller et al., 2008). The main  
290 advantage of a factor analysis is that it allows the elements to be source-grouped according to  
291 their distribution patterns and loadings. We applied such PCA model for our dataset using the  
292 statistical software package PAST3 (Hammer et al., 2001). The results and interpretations are  
293 shown in *Appendix C*. In brief, three main components are able to explain 99.75% of the total  
294 variance. Factor 1 (PC1) accounts for the largest proportion of the variation (92.7%) with the  
295 other two factors, PC 2 and PC 3, accounting to 4.4% and 2.7% respectively. PC1 includes  
296 the elements Pb, In, Sn, Sb, Ga, Cd, Cu, Zn, Ag, Ti, with Pb showing the highest association

297 of 97%. PC2 groups the elements Ti, Zr, Ta, Ba, Li, As, Tl, Sr, and Rare Earth elements (REE)  
298 together, and PC3: Zn, W, Mo, Ni, Ti, Sr, Cr, and Fe. While 77% of Zn is shared with PC3,  
299 almost 15% of it is also shared with PC1, pointing to multiple sources controlling Zn enrichment  
300 in the LHB peat. Based on their element assemblages, the three element groups can be care-  
301 fully attributed to dust contributions from the historical Pb-Zn mining and smelting, natural ge-  
302 ogenic dust input, and emissions from fossil fuel combustion, respectively (*Appendix C*). The  
303 latter is yet to be characterised in more detail. We find that for the LHB dataset, the PCA  
304 approach offers a first insight into the major pollutant groups contributing to the element en-  
305 richment during the past century. However, in light of complex element apportioning to the  
306 respective components from co-occurring pollutants, the information obtained by the PCA is  
307 combined with other geochemical tools to better fingerprint sources contributing to metal en-  
308 richment in LHB.

309

### 310 **3.3.2. Enrichment factors (EF)**

311 When investigating anthropogenic pollution, upper crustal values (UCC) are sometimes used  
312 as a reference to extract the natural dust contributions. In doing so, metal enrichments are  
313 discussed relative to geogenic element backgrounds with a poorly soluble lithophile element,  
314 such as Ti, Sc, Sr, Zr, Al, Si, Y, Ta, or REE as a normalizer (e.g., Espi et al., 1997; Kempter et  
315 al., 1997; Marx et al., 2010; Shotyk, 1996). The use of the estimated UCC values as a measure  
316 for geogenic input has been, however, intensively debated in several studies (e.g., Martínez  
317 Cortizas et al., 2002; Reimann and De Caritat, 2000). The main criticism is that the calculated  
318 UCC values represent an average composition that is not necessarily representative of the  
319 local lithological background. This can ultimately result in an under- or overestimation of the  
320 natural geogenic budget transported into an archive. To overcome this issue, the interpretation  
321 of the element EF's relative to a local "baseline", representative for the area of interest has  
322 been proposed (e.g., Martínez Cortizas et al., 2002). This strategy is preferred for this study  
323 due to the versatile Irish geology, and trace element patterns are presented as enrichment  
324 factors (EF, Table 1) with respect to the average of the least polluted and compositionally most

325 consistent part of the core (62 and 100 cm from the surface). This “baseline” is used to calcu-  
326 late element EF’s at shallower depths, as described in [1].

327 [1]  $EF = [(metal/Ta)_{sample} / (metal/Ta)_{baseline}]$

328  
329 The EF were calculated using the element concentrations in dried peat (at 105°C). Although Ti  
330 shows the highest loading (80%) within PC2 (geogenic dust), its partial association with PC1  
331 (16% mining-smelting of local ores) and PC3 (*Appendix C*) restricts its application as natural  
332 dust indicator. We observe that, within this core, the best correlation with the residual ash (i.e.,  
333 geogenic dust content) is built with Ta ( $r^2 = 0.95$ , *Appendix B.2*). This is a strong argument that  
334 Ta is the best candidate to extract dust depositions in our core. Tantalum has been shown to  
335 be an excellent proxy for geogenic input (e.g., Babechuk et al., 2015; Marx et al., 2010), but  
336 its successful analysis requires an acid-digest with HF of high purity, as employed here.

337 The REE patterns show a typical UCC-like signature consistent with the nearby granitic  
338 bedrock with enrichments in the light REE over heavier REE (*Appendix B.3*). The REE patterns  
339 remain subparallel throughout the entire core, indicative of a homogeneous geogenic origin of  
340 the atmospheric dust.

341

### 342 **3.4. Excursions of element enrichment**

343 All trace element patterns show well-defined excursions of enrichments along the extracted  
344 LHB peat profile (Table 1 and *Appendix A.1* for raw concentrations). In Figure 3 we show a  
345 representative selection of the results. Lead, Cu, and Zn depositions increase jointly from 62  
346 cm depth (Fig. 3 and 4) and peak at different stages during the 20<sup>th</sup> century (Pb and Cu) until  
347 recently (Zn). Enhanced deposition is observed in a number of other metals which asynchro-  
348 nously reach their maxima between 1940 and 1960 (Ag and Sb), 1960 and 1970 (Ni), 1950’s  
349 and recently (Mo). Rare earth elements (REE) are highest between 10 and 20 cm, i.e., first  
350 half of the 20<sup>th</sup> century, to then decrease again significantly in recently growing *Sphagnum*  
351 moss (*Appendix B.3*). A rapid decline in their enrichments is also observed for a number of  
352 other elements (e.g., Ag, Pb, Sn, Sb, In, Cd, U; not shown) between 1970 - present, whereas

353 enrichments of Ni and Cu do not quite return to pre-anthropogenic levels and show diminished  
354 present-day atmospheric fallout (Fig. 3 and 5). Enrichment factors of Mo and Zn increase more  
355 rapidly from ca 1940 and reach highest values of 5 and 39, respectively in the sub-surface  
356 level of LHB.

357

### 358 **3.5. Lead isotope compositions**

359 Lead isotope ratios are presented together with EF of Cu, Zn, and Pb in Figure 4. Lead isotope  
360 composition of the peat is homogenous from the base of the core until ca. 18 cm ( $^{206}\text{Pb}/^{204}\text{Pb}$ :  
361 18.271-18.429,  $^{206}\text{Pb}/^{207}\text{Pb}$ : 1.171-1.179). A dramatic change towards unradiogenic Pb signa-  
362 ture, coincident with major EF peaks for Cu and Pb is seen between 18 cm and 9 cm, where  
363 a small plateau is reached ( $^{206}\text{Pb}/^{204}\text{Pb}$ : 17.712-18.123,  $^{206}\text{Pb}/^{207}\text{Pb}$ : 1.138-1.161). Most un-  
364 radiogenic values ( $^{206}\text{Pb}/^{204}\text{Pb}$ : 17.657-17.678,  $^{206}\text{Pb}/^{207}\text{Pb}$ : 1.135-1.136) are recorded at the  
365 depth interval between 8 and 4 cm from the surface. This period is followed by a reversal  
366 towards more radiogenic Pb isotope signature that extends up to the top of the bog. In detail,  
367 however, the modern isotope signature ( $^{206}\text{Pb}/^{204}\text{Pb}$ : 17.746-17.929,  $^{206}\text{Pb}/^{207}\text{Pb}$ : 1.137-1.148)  
368 does not quite return to the values below 18 cm.

369

## 370 **4. Discussion**

### 371 **4.1. Temporal patterns in metal enrichments and implications for element mobility**

372 Conservative behaviour of at least some elements within bogs is a prerequisite for their inter-  
373 pretation of atmospheric pollution histories. Experimental studies have demonstrated that  
374 strong complexation and fixation of metals onto the organic matter occurs in acidic environ-  
375 ments such as bogs (e.g., Pokrovsky et al., 2005a). The retention of the elements at the depth  
376 of deposition is aided by carbon oversaturation within biomass and pore water (Smith et al.,  
377 2004). Krosshavn et al. (1993) have shown that metals such as Cu, Zn, Cd, and Pb can some-  
378 times display variable binding capacities, depending on the vegetational background. Yet, the  
379 most favourable condition for the successful retention of metals onto the organic matter has  
380 been found to be at a pH of 4. The surface of LHB displays pH conditions ranging between 4  
381 and 4.5.

382 Little is known about the behaviour of transition metals and especially V, Cr, Ni, Co, Mo  
383 in peat archives. Therefore, interpreting their behaviour is often aided by the comparison to a  
384 relatively immobile metal, such as Pb. For example, by investigating their patterns in an om-  
385 brotrophic peatland from the Swiss Alps, Krachler et al. (2003) and Krachler and Shotyk (2004)  
386 have found that V, Cr, Ni, Co, Mo are effectively immobile within the peat column. The spatio-  
387 temporal enrichments of these elements were interpreted to render emissions from various  
388 anthropogenic sources such as steel production and combustion of fossil fuels.

389 In LHB, Cd, Ag, Sn, Sb, In, Co, Mo, Cr, and V are well-correlated with Pb ( $R^2=0.71$  to  
390  $0.88$ ) which is commonly accepted to be highly immobile in peat (Martínez Cortizas et al., 2012;  
391 Shotyk, 1996). Stronger shared variations are observed between Pb-Ag-Sn-Sb-In (e.g., Ag vs.  
392 Sb:  $R^2=0.93$ ), and Co-Mo-Cr-V-Zn (e.g., Co vs. V:  $R^2=0.91$ ) dividing this wider group of ele-  
393 ments into two suites. As suggested from the PCA, these elements correspond to the PC1 and  
394 PC3 groups. Further, the temporal deposition patterns of the Zn-Co-Mo-Cr-V (PC3) group dif-  
395 fer from those of Pb-Ag-Sn-Sb-In (PC1) by displaying a continuing upward trajectory of their  
396 enrichment when PC1 shows a decrease in its pollution load (Fig. 3 and *Appendix C*). The  
397 onset of Zn enrichment is coincident with that of Pb pointing towards a simultaneous pollution  
398 initiation rather than a down-core mobilisation of Zn. The diverging Pb and Zn enrichment pat-  
399 terns towards the top of the core, i.e., over the last 50 years ( $R^2=0.4$ , Fig. 4) reflect either i) the  
400 decreasing industrial use of the former (PC1) and increased utility of the latter (PC3), or ii) a  
401 different source/process responsible for the enrichment of metals in subsurface-layers of the  
402 bog. Minor Zn bioaccumulation in the living part of the bog cannot fully be excluded. However,  
403 its relevance to the total Zn budget and source apportioning is rather insignificant as shown  
404 from its >95% assignment to PC 1, 2, and 3. In the following chapter, we discuss in detail the  
405 complex behaviour of element enrichments in LHB in light of the known records of Irish indus-  
406 trial development. We combine the information obtained by PCA, EF's, and Pb isotopic com-  
407 position, and discuss the pollution patterns from the base of the core towards the surface, as  
408 chronologically subdivided in Figure 4.

409

#### 410 **4.2. The baseline (100-62 cm)**

411 Lithophile element ratios in this peat segment (e.g., Y/Sc=1.5; Ba/Sc=39 to 43; Nb/Th=0.83 to  
 412 1.35) are comparable to typical upper continental crust (UCC) compositions (Y/Sc=1.6;  
 413 Ba/Sc=41; Nb/Th=1.12, McLennan, 2001), which are close or within the values reported for  
 414 individual Wicklow granite units in the area (e.g., northern units Leinster batholith, Y/Sc=2.5 to  
 415 5; Ba/Sc=96 to 160; Nb/Th=0.9 to 7; Fritschele, 2016; Sweetman, 1987). This implies that the  
 416 local bedrock and soils are the dominant source of elements at this depth, justifying our base-  
 417 line selection. Lead isotope composition of the baseline,  $^{206}\text{Pb}/^{204}\text{Pb} = 18.387 \pm 0.012$  and  
 418  $^{207}\text{Pb}/^{204}\text{Pb} = 15.626 \pm 0.010$  ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.177 \pm 0.011$ ) together with excess Pb concentrations  
 419 [2] are used to calculate the natural, dust-free Pb isotopy of peat at shallower levels [3]. We  
 420 note, that similar patterns are obtained by deploying the previously proposed Ti, Zr, or Sc (e.g.,  
 421 Shotyk, 2002) instead of Ta.

422

423 [2] 
$$\text{Pb}_{\text{excess}} = \text{Pb}_{\text{con}} - [(\text{Pb}/\text{Ta})_{\text{sample}} / (\text{Pb}/\text{Ta})_{\text{baseline}}]$$

424 [3] 
$$^{20x}\text{Pb}/^{204}\text{Pb}_{\text{excess}} = [(^{20x}\text{Pb}/^{204}\text{Pb}_{\text{measured}} * \text{Pb}_{\text{con}}) - (^{20x}\text{Pb}/^{204}\text{Pb}_{\text{baseline}} * \text{Pb}_{\text{baseline}})] / \text{Pb}_{\text{excess}}$$

425

426 where the  $\text{Pb}_{\text{excess}}$  and  $^{20x}\text{Pb}/^{204}\text{Pb}_{\text{excess}}$  are the baseline corrected concentration and isotopic  
 427 composition of Pb in the polluted samples,  $\text{Pb}_{\text{con}}$  and  $^{20x}\text{Pb}/^{204}\text{Pb}_{\text{measured}}$  are the analysed Pb  
 428 concentration and isotopic compositions,  $\text{Pb}/\text{Ta}_{\text{sample}}$  is the ratio in the polluted part of the bog,  
 429  $\text{Pb}/\text{Ta}_{\text{baseline}}$  and  $^{20x}\text{Pb}/^{204}\text{Pb}_{\text{baseline}}$  represent the compositions of the baseline (100-62 cm), and  
 430  $\text{Pb}_{\text{baseline}}$  is the average Pb concentration in the unpolluted part of the bog. For further calcula-  
 431 tions, the subtracted local geogenic contribution was no longer considered.

432

433 **4.3 Pollution phase 1 (62-25 cm, pre-1900 AD)**

434 Enrichment factors of Cu, Zn, and Pb increase within this segment, which covers the time  
 435 period before the 20<sup>th</sup> century (Fig. 5). Importantly, Pb isotope values do not change substan-  
 436 tially from the composition of the baseline (Fig. 4) and are comparable to the published values  
 437 of the granitic Leinster batholith (Fig. 6a., e.g., Kennan et al., 1987), which is the host rock of  
 438 local Pb-Ag-Zn mineralisation. The increasing heavy-metal input is thus interpreted to reflect

439 the 18<sup>th</sup> and 19<sup>th</sup> century Pb-Ag extractions from the high-grade, low-tonnage galena-rich veins  
440 exposed in the Wicklow uplands (Rynne, 2015; Schwartz and Critchley, 1997). Smelting was  
441 conducted ~15 km NE from LHB (and ~35 NE km from the mining site) at Ballycorus (e.g.,  
442 Callaghan, 2014; Shepard, 1981), which may have additionally contributed to the overall pol-  
443 lution load. The Pb isotope signal argues against a Pb contribution from the clearly distinguish-  
444 able fingerprint of sphalerite-galena mineralisation hosted in the Lower Carboniferous of the  
445 Midland basin (e.g., Wilkinson and Eyre, 2005, Fig. 6a.), subjected to small scale extractions  
446 during the same time period (Rynne, 2015). The synchronous enrichment onset and develop-  
447 ment of Zn and Pb ( $R^2=0.96$ ) in this peat section (Fig. 5c.) suggest pollution from the mining  
448 activity, especially because of Zn co-occurring in most Pb ore bodies, and due to the shared  
449 15% variation of Zn with PC1 (mining and smelting). An important known example of accidental  
450 Zn pollution from Pb mining was the giant Broken Hill deposit in south-central Australia, where  
451 the relative timing of Pb+Ag vs. Zn extraction is accurately reflected in a mire peat core ca.  
452 1,000 km downwind from the mine (Marx et al., 2010). In LHB, the same holds for Cd, which  
453 occurs as major impurity within the mined sphalerite and galena ores.

454         Enrichment patterns of Zn depart from those of Pb towards 25 cm depth, pointing to an  
455 increasing significance of a source other than mining. The continuing amplification of Zn dep-  
456 ositions (EF= 12-23), coupled with subtle elevations in Mo, Ni, V (EF= 0.8-1.6, 1.1-1.8, and  
457 1.1, respectively) in LHB suggests atmospheric depositions from a non-geogenic source. At-  
458 mospheric charging with these particular heavy metals has been long associated with the com-  
459 bustion of liquid and solid fossil fuels (Danihelka et al., 2003; Gallagher et al., 2018;  
460 Hjortenkrans, 2008; Huang et al., 1994; Nriagu, 1989; Pacyna and Pacyna, 2001). In is con-  
461 text, it is well documented that coals were the main fuel source during the entire period of  
462 mining activity in the Wicklow uplands (Rynne, 2015), and can thus be considered a potential  
463 metal emission source at this site.

464

#### 465 **4.4 Pollution phase 2a (25-5 cm, ~1900-2000 AD)**

466 Peak pollution period from local mining is documented between 1900 and 1960's where EF's  
467 of Cu, Ag, Pb, Cd, Sb, and Sn (PC1) reach values of 10, 18, 18, 51, and 14, respectively. Rare

468 Earth element depositions are the highest during this period (*Appendix B.3*), suggestive of an  
469 enhanced atmospheric dust fallout from the mineralisation host rock. Silver, Cu, and Sb en-  
470 richment coincide with early 20<sup>th</sup> century mining for coinage taking place at different sites  
471 around the Wicklow uplands, but also further inland at Silvermines, Co. Tipperary. Stibnite  
472 ( $\text{Sb}_2\text{S}_3$ ) and pyrite ( $\text{FeS}_2$ ) were extracted at Avoca (Fig. 1).

473 The atmospheric load in redox sensitive elements V, Cr, Mo, and other metals such as  
474 Zn and Ni continues to amplify during the second half of the 20<sup>th</sup> century. While there is the  
475 possibility that a minor amount of their atmospheric load relates to the mining, the largest frac-  
476 tion is attributed to the continuing atmospheric pollution resulting from the combustion of UK  
477 sourced coals known to having been extensively used throughout the stages of ore extraction.  
478 Due to the similar Pb isotopic compositions of these coals (e.g.,  $^{206}\text{Pb}/^{207}\text{Pb}=1.181-$   
479  $1.184\pm 0.018$ ; Farmer et al., 1999) compared to the mining-dominated Pb signature (e.g.,  
480  $^{206}\text{Pb}/^{207}\text{Pb}= 1.177\pm 0.011$ ), it is not possible to discern these two sources from the Pb isotopy  
481 of the peat. Thus, in this case, coal pollution can indeed only be inferred from coupled trace  
482 element enrichments.

483 A notable change in the geochemistry of the LHB peat (i.e. element ratios, Fig. 5a-d.),  
484 specifically, a decrease in Pb and Ag (PC 1) and an increase in Zn, Mo, and Ni (PC3), is  
485 evident from ca. 1940 onwards (Fig. 5). This is accompanied by a prominent turn towards a  
486 less radiogenic Pb isotopy (Fig. 3), likely reflecting the transition from mining originated Pb to  
487 pollution from the hemispheric introduction of leaded gasoline. To disentangle the Pb contri-  
488 butions from the two sources, we deployed a binary mixing calculation between the following  
489 end-members: **A**, pollutant 1 ( $^{206}\text{Pb}/^{204}\text{Pb} = 18.30$ ,  $^{207}\text{Pb}/^{204}\text{Pb} = 15.62$ ,  $^{206}\text{Pb}/^{207}\text{Pb}=1.174$ ] min-  
490 ing/industrial signal of the early 20<sup>th</sup> century), and **B**: pollutant 2 ( $^{206}\text{Pb}/^{204}\text{Pb}= 17.20$ ,  
491  $^{207}\text{Pb}/^{204}\text{Pb} = 15.54$ ,  $^{206}\text{Pb}/^{207}\text{Pb}=1.109$ ] average European-Australian leaded gasoline). The  
492 modelled curves (Fig. 7b. and described in *Appendix D*) were calculated using different Pb  
493 concentrations of the respective end-member pollutants ( $10-200 \mu\text{g g}^{-1}$ ). Mixing calculations  
494 expose the increasing influence of leaded gasoline over the course of 20<sup>th</sup> century, becoming  
495 progressively more accentuated only after the decline of the local mining and smelting activity  
496 (post 1940, 18 cm). Quantifying potential contribution of vehicle emissions before 1940s is

497 complicated by the masking from concurrent mining activities which lasted until ca. 1957  
498 (Rynne, 2015). The least radiogenic  $^{206}\text{Pb}/^{207}\text{Pb}$  values of  $1.138\pm 0.011$  recorded in peat from  
499 the 1970-80s represent the peak Pb contribution from leaded petrol documented at this site  
500 (Fig. 7a.). Because of the large variation in the Pb isotopic composition of ores used for the  
501 manufacture of petrol additives ( $^{206}\text{Pb}/^{207}\text{Pb}=1.06-1.12$ , Townsend et al., 1998; Veron et al.,  
502 1999), there is a significant uncertainty of 6 to 78% in the calculated contributions (Fig. 7b.).  
503 Similar findings were made in studies of bogs and freshwater lake sediments from central  
504 Scotland (e.g., Farmer et al., 1997).

505 The decrease in the Pb pollution load as documented by LHB during the main period of  
506 leaded gasoline, 1950-1980 (Fig. 3), is unusual by international comparison (e.g., see Martinez  
507 Cortizas et al., 2002). However, this appears to be an effect caused by previous local mining  
508 that masks the gasoline signal from the first half of the 20<sup>th</sup> century. Only when mining activity  
509 subsided and overall Pb EF dropped, did gasoline become a significant contributor. The at-  
510 mospheric Pb concentrations during the peak Pb gasoline period are, in fact, comparable to  
511 those in other Irish archives (Schell et al., 1997). The high load in Ni, Mo, Cr, V and Zn docu-  
512 mented between 1940 and 1980, support the increasing atmospheric influence of liquid fossil  
513 fuels. Due to their versatile nature, i.e., coals, heating oil, peat, gasoline, used for industrial  
514 and domestic purposes in Ireland, it is not possible to depict exact fingerprints of fuel groups  
515 with the data available.

516

#### 517 **4.5. Pollution phase 2b (5-0 cm, 2000-2015 AD)**

518 Despite continuing Pb-Zn (Tynagh, Navan, Silvermines, Galmoy, and Lisheen) and Cu-  
519 Ag-Hg (Ballynoe and Gortdrum) mining from the 1970's into the 21<sup>st</sup> century at different sites  
520 in Ireland, there is poor correspondence between enrichment of these metals within LHB and  
521 the reported tonnage extractions for the post 1980 AD period (see *Appendix B.4*). This points  
522 to stronger atmospheric influence of other (additional) sources at this site today. Notably, this  
523 is probably because i) metal extraction sites are situated further away in the Midlands, ii) most  
524 ores are extracted underground, and iii) smelting in Ireland has ended, leading to historically  
525 lowest atmospheric Zn-Pb pollution from mining (PC1).

526 Persisting Zn, Ni, Mo, Cr, and V depositions despite international leaded gasoline aboli-  
527 tion corroborate that Pb petrol is just one component of the larger pollutant group controlling  
528 PC3, emissions from fossil fuels. For example, sub-surface enrichments of Cu and Ni and their  
529 ratios including Pb (Pb/Ni= 3-6.7 and Cu/Pb= 0.4-1) are within the experimentally determined  
530 values of the aerosols and particulate matter (PM) resulting from combustion of peat (1.8-14.6  
531 and 0.6-1, Othman and Latif, 2013). Turf (cut and dried peat) is an important heating fuel in  
532 most rural areas of Ireland, and seasonal harvesting for domestic purpose takes place also at  
533 the peripheries of LHB. Although Ireland documents a strong historic and recent dependence  
534 on different kinds of fossil fuels, their atmospheric influence likely became increasingly more  
535 pronounced over the past ca. 60-70 years, i.e., with the introduction of the leaded gasoline  
536 (first half of 20<sup>th</sup> century), and cessation of the mining activity.

537 With the abolition of leaded gasoline in Europe, North America and in 2000 in Ireland,  
538 Pb isotopic compositions of LHB peat progressively returned to more radiogenic values (Fig.  
539 7a.). However, these ratios ( $^{206}\text{Pb}/^{204}\text{Pb}=17.929\pm 0.007$ ;  $^{207}\text{Pb}/^{204}\text{Pb}=15.613\pm 0.007$ ;  
540 [ $^{206}\text{Pb}/^{207}\text{Pb}=1.148\pm 0.007$ ]) are far from the “baseline” signal, implying either, i) a slow post-  
541 gasoline amelioration of atmospheric Pb pollution load; ii) recent pollution from a source with  
542 partially  $^{206}\text{Pb}$  depleted signature; iii) re-suspension of legacy Pb from regional erosion (Clo-  
543 quet et al., 2006); or iv) a combination of these factors. Shotyk and Krachler (2010) attributed  
544 the post-1975 to present Pb isotope variations in the European atmosphere to the growing  
545 importance of modern industrial processes and urbanisation relative to decline of leaded petrol  
546 use. The compilation of Pb-isotope ratios of potential present-day sources shown along with  
547 the LHB values in Figure 6b point towards recent pollution from vehicle exhausts of EU origi-  
548 nated non-leaded petrol (Erel et al., 1997; Hurst et al., 2002) and atmospheric trace metal  
549 release from the use of mineral oil (Chiaradia and Cupelin, 2000). The latter constitutes the  
550 major energy source for domestic heating in Co. Dublin. There is also a strong positive coher-  
551 ence between the increasing amount of private and public vehicles in Ireland ([www.cso.ie](http://www.cso.ie)),  
552 especially around Dublin and the rising dominance of PC3 - fossil fuels fingerprint, in the Irish  
553 atmosphere, supporting the presence of a growing real pollution signal, rather than remobili-  
554 sation of previously deposited pollutants. Lead isotope ratios in the subsurface layer of LHB

555 are consistent with the estimated average composition of what is suggested to be the signal  
556 of the present-day atmospheric Pb pollution ( $^{206}\text{Pb}/^{207}\text{Pb}=1.14-1.16$ , Carignan et al., 2005;  
557 Monna et al., 1997), calculated using the fly ash compositions of waste incinerators in central  
558 Europe. There are thus a variety of recent pollution sources which can explain the Pb isotope  
559 composition of the atmosphere.

560

#### 561 **4.6. Timing of Pb pollution and synthesis of Pb isotope information from other rele-** 562 **vant peat archives**

563 Due to its location at the east coast of Ireland, LHB records processes that are part of broader  
564 regional and hemispheric pollution patterns. In order to facilitate a comparison between the Pb  
565 pollution history recorded by LHB and other Irish archives (Coggins et al., 2006; Schell et  
566 al., 1997), accumulation rates were calculated according to the method described in detail by  
567 Muller et al. (2008). The results are presented in Table 1. In LHB, Pb deposition rates range  
568 between  $0.45-1.8 \mu\text{g cm}^{-2} \text{yr}^{-1}$ , with values  $>1 \mu\text{g cm}^{-2} \text{yr}^{-1}$  observed at different stages through-  
569 out the 20<sup>th</sup> century (Fig. 8). Peak accumulation rates are detected between 1960's and 1980's,  
570 in excellent agreement with the Pb deposition rates in a peat archive situated ca 1-2 km away  
571 to the west, Kippure bog (Schell et al., 1997). Lead accumulation rates are higher in the LHB  
572 peat deposited during the early 20<sup>th</sup> century mining period, which is likely due to its relative  
573 proximity to the mining and smelting sites. Enhanced Pb deposition during the 1980's can be  
574 attributed to the leaded gasoline peak, as it can also be seen from the Pb isotope composition  
575 of LHB. In the Midlands (Clara bog), Pb deposition rates were up to 3 times lower than at the  
576 eastern seaboard (Fig. 8), yet still higher than at all sites investigated so far along the west  
577 coast (Knockroe, Co. Mayo  $0.1-0.3 \mu\text{g cm}^{-2} \text{yr}^{-1}$ , Letterfrack, Co. Galway  $0.4-0.5 \mu\text{g cm}^{-2} \text{yr}^{-1}$ ,  
578 Coggins et al., 2006; and Bellacorick, Co. Mayo,  $0.05-0.4 \mu\text{g cm}^{-2} \text{yr}^{-1}$  Schell et al., 1997). It  
579 appears that historical mining and smelting have not significantly influenced the archives on  
580 the west, although there is also the possibility that the clean Atlantic winds dominating here  
581 contribute to an overall dilution of atmospheric pollution. Peak Pb deposition at the west coast  
582 occurs slightly earlier during the 1960's and has been previously interpreted to render the long-

583 range transport of polluting Pb from the American continent. We suggest that further investi-  
584 gations, such as the Pb isotopy of these westernmost archives are necessary before exact  
585 conclusions can be drawn. A trans-Atlantic Pb gasoline pollution during the 1960's would an-  
586 ticipate the isotope signal of the peat to be close to those of Canadian ( $^{206}\text{Pb}/^{207}\text{Pb}= 1.15\text{-}1.17$ ,  
587 Bathurst) and USA ( $^{206}\text{Pb}/^{207}\text{Pb}= >1.28$ , e.g., Mississippi) ores.

588 In general, the timing of Pb isotopic excursions in LHB core coincide with those in bogs  
589 from Scotland (e.g., Farmer et al., 2002), Sweden (Bindler et al., 2004), or Spain (Martinez-  
590 Cortizas et al., 2012). All these archives commonly report a  $^{206}\text{Pb}/^{207}\text{Pb}$  of 1.16-1.18 in the  
591 lower sections (i.e., geogenic influx, and/or mining), and a rapid change towards less radio-  
592 genic  $^{206}\text{Pb}/^{207}\text{Pb}$  of 1.13-1.14 at peak Pb-gasoline pollution (1970 to 1980 AD). Because of  
593 the different chronology of recent atmospheric pollution in North America (e.g., Bindler et al.,  
594 2001; Pérez-Rodríguez et al., 2018; Weiss et al., 2002), it is very likely that the east coast of  
595 Ireland was, and currently is dominantly influenced by the central- and north-European pollu-  
596 tion circulation rather than trans-Atlantic sources.

597

## 598 **5. Summary and conclusion**

599 We investigated the atmospheric elemental and Pb isotope evolution resulting from local min-  
600 ing, industrial activities and leaded gasoline pollution in eastern Ireland over the last century  
601 from the geochemistry of a bog in the Wicklow Mountains. The elemental cycle associated with  
602 mining of local ores (e.g., Pb, Cu, Ag, Sn, Sb) was highly perturbed during the major period of  
603 mining and smelting in the Wicklow area (19<sup>th</sup> to 20<sup>th</sup> century), showing up to 20-fold, 15-fold,  
604 and 50-fold enrichments (Pb, Ag, and Sb, respectively) with respect to the established baseline  
605 of the core. Element deposition associated with the combustion of fossil fuels (Zn, V, Ni, Cr  
606 and Mo) is detected throughout the polluted section of the core. This pollutant becomes in-  
607 creasingly more pronounced only after the abolition of the mining activity in the area (ca. 1940-  
608 recent). The Pb isotopes precisely document the shift towards less radiogenic  $^{206}\text{Pb}/^{207}\text{Pb}$  val-  
609 ues in response to the introduction of the Pb petrol additives from ca. 1940 (in this archive)  
610 until its complete elimination in 2000 in Ireland. In the most general sense, the observed iso-  
611 topic shift ( $^{206}\text{Pb}/^{207}\text{Pb}=1.138\pm 0.011$  in 1970) is consistent with findings in other records of

612 atmospheric Pb deposition around Europe (e.g., Sweden, Brännvall et al., 1997; Scotland,  
613 Farmer et al., 1997; Spain, Kylander et al., 2005; Switzerland, Weiss et al., 1999). However,  
614 unlike at most other sites, the introduction of leaded petrol is not associated with the highest  
615 atmospheric Pb pollution load at this site, which was instead caused by the historical Pb-Zn  
616 mining and smelting of local ores. Despite a notable decline in the leaded gasoline signal after  
617 2000, the Pb isotopic composition has not quite returned to pre-industrial values, implying input  
618 from modern pollutant sources. Based on combined trace element and Pb isotope investiga-  
619 tions, we suggest that coal, peat, and oil combustion, emissions from unleaded petrol, as well  
620 as trans-regional industrial pollution (e.g., waste incinerators) potentially reaching Ireland on  
621 easterly airstreams are the sources contributing to aerial Pb pollution at this site today. The  
622 strong local control of the bog geochemistry demonstrated in this study emphasises the need  
623 to combine metal concentration and isotopic investigations for reconstructing historic pollution.  
624 Without having investigated the Pb isotopic patterns, the major Pb enrichment peak could have  
625 been erroneously attributed to an early Pb gasoline signal. The decline in most heavy metals  
626 (esp. Pb, Cu, Sb) in the present day *Sphagnum* moss is in line with observations made in bogs  
627 from elsewhere (e.g., Switzerland, Shotyk et al., 2001), and can be attributed to tougher air  
628 pollution prevention policies adopted in Europe over the last three decades.

629

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631

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637

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924

925 **Figure captions**

926

927 **Figure 1:** Map of Ireland showing the geographic distribution of peatlands (brown areas), com-  
928 piled using data from GSI-Ireland ([www.gsi.ie](http://www.gsi.ie)), the sampling site LHB (red dot) along with the  
929 historic Pb-Zn mining and smelting sites in the Wicklow mountains (yellow squares) and the  
930 historic Pb, Cu, S mines at Avoca (purple square). Bog sites discussed in the studies of Cog-  
931 gins et al (2006): Letterfrack (LF) and Knockroe (KN), and Schell et al. (1997): Bellacorick (BL),  
932 Clara (CL), and Kippure (KP) are indicated as green circles. The main Pb-Zn ore deposits  
933 hosted within the Lower Carboniferous of the Midland basin are indicated by blue triangles.  
934 Blue arrows represent the wind directions.

935

936 **Figure 2 a) and b):** Radionuclide ( $^{210}\text{Pb}$  and  $^{241}\text{Am}$ ) activity distribution within the LHB peat  
937 core with errors at  $1\sigma$ . Two additional samples investigated at 72 cm and 95 cm depth dis-  
938 played no  $^{210}\text{Pb}$ - $^{241}\text{Am}$  activity and are not plotted here. Radioactive equilibrium was reached  
939 at 24 cm from the surface. **c)** Density-, and **d)** Percent organic matter content along the LHB  
940 peat core. **e)** Age-depth relationship as received from the  $^{210}\text{Pb}$  CRS model. The 1 sigma un-  
941 certainty in  $^{210}\text{Pb}$  values including error propagation from calibrations is 10-12% (error bars).  
942 A combination of the  $^{241}\text{Am}$  maximum and the  $^{210}\text{Pb}$  inventory was used for the calculation of  
943 the final core chronology as detailed in the text.

944

945 **Figure 3:** Metal enrichment factors along the LHB peat core (grey circles) displayed relative to  
946 the baseline (EF) defined through the lowermost 4 samples (100-62 cm). The chronology (AD)  
947 obtained from the  $^{210}\text{Pb}$ - $^{241}\text{Am}$  activity profiles is indicated in blue.

948

949 **Figure 4:** Pb isotope ratios (black solid circles) together with EF of Cu, Zn and Pb (open dia-  
950 monds) along the LHB peat core. Depth ranges distinguished by colours represent changes in  
951 either Pb isotopic composition, metal concentrations, or both. Radionuclide derived chronology  
952 and contemporaneous historical anthropogenic activities are also indicated.

953

954 **Figure 5:** Bivariate plots of selected metal EF of peat from the LHB core. Samples from the  
955 lower part of the core (prior the introduction of the Pb gasoline from 1940) are shown as solid  
956 black circles. Peat deposited from the 1940s until present day are shown as white open trian-  
957 gles. Grey arrows indicate upward direction from the base of the core to the top, i.e., from local  
958 background through the mining period, Industrial Revolution (IR), Pb gasoline to present day.

959

960 **Figure 6: a)** Common Pb ( $^{207}\text{Pb}/^{204}\text{Pb}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$ ) plot of LHB peat subsamples and liter-  
961 ature values of local mineralisation: [1] Wicklow granites, Kennan et al. (1986), and the Mid-  
962 lands mineralisation [2] Hitzman et al. (1992), and Wilkinson et al. (2005). A sharp change in  
963 the Pb isotopic composition is observed from ca. 1940; **b)** Zoomed out common Pb diagram  
964 with pre-polluted peat samples (black solid circles) and all polluted LHB samples (white dia-  
965 monds) together with the values of the local mineralisation. Also shown are Pb isotope ratios  
966 of pre-pollution at other sites (Klaminder et al., 2003; Kylander et al., 2005; Shotyk et al., 2002;  
967 2010; Rosman et al., 2000) and for different anthropogenically derived pollutants compiled  
968 from Chiaradia and Cupelin, 2000; De Vleeschouwer et al., 2009; Hansmann and Koppel,  
969 2000; Monna et al., 1997; Sudgen et al., 1993; Townsend et al., 1998; Veron et al., 1999;  
970 Walraven et al., 1997). Error bars for all LHB Pb isotope values are smaller than the symbols.

971

972 **Figure 7: a)** Chronology-integrated  $^{206}\text{Pb}/^{204}\text{Pb}$  isotope composition of the upper part of the  
973 LHB peat profile together with areas representative of the local mineralisation (Kennan et al.,  
974 1986) and potential anthropogenic pollution sources during the 19<sup>th</sup> to 21<sup>st</sup> century. **b)** Common  
975 Pb isotope binary mixing model using A: average Pb isotope values of local mineralisation  
976 ( $^{206}\text{Pb}/^{204}\text{Pb}=18.300$ ;  $^{207}\text{Pb}/^{204}\text{Pb}=15.622$ , Kennan et al., 1986), and B: average compositions  
977 representative for aerosols associated with Pb enriched vehicle emissions  
978 ( $^{206}\text{Pb}/^{204}\text{Pb}=17.200$ ;  $^{207}\text{Pb}/^{204}\text{Pb}=15.543$ , e.g., Chiaradia and Cupelin 2000; Monna et al.,  
979 1997; Veron et al., 1999). Lead concentrations range between 10 and 200  $\mu\text{g g}^{-1}$ , correspond-  
980 ing to values measured along the LHB peat profile. For the calculation steps refer to the text  
981 and *Appendix D*. Error bars are smaller than the symbols.

982

983 **Figure 8:** Lead accumulation rates  $\mu\text{g cm}^{-2} \text{yr}^{-1}$  in the upper part of the LHB (this study). Shown  
984 are also accumulation rates calculated in other peat archives from Ireland (Schell et al., 1997).