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

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Abstract

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

Key words: anthropogenic pollution, heavy metals, Pb isotopes, ombrotrophic peatland, Ireland

1. Introduction

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

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

²⁰⁶Pb/²⁰⁷Pb values of Greenlandic ice (Rosman et al., 1997), bogs from Spain (Kylander et al., 2005), Switzerland (Shotyk et al., 2001) as well as Sweden (Klaminder et al., 2003) range between 1.19 and 1.25. The temporal and geographic evolution of the Pb pollution fingerprint has helped to discriminate between the impact of mining-smelting and leaded gasoline around the northern hemisphere (e.g., Bindler et al., 2004, Bränvall et al., 1997; Cloy et al., 2008; Kylander et al., 2005, 2009; Le Roux et al., 2004, 2005; Martinez-Cortizas et al., 2012; Shotyk et al., 2002). While often deployed separately, the information obtained from combining trace elements and (Pb) isotopic compositions is more powerful in differentiating between complex multiple sources. To date, there is not a single study reporting Pb isotope chronologies in Irish peatlands, and only two studies which investigated atmospheric depositions of Pb, Cd, and Hg: Kippure bog, Clara bog, Bellacorick bog (Schell et al., 1997), Knockroe bog, and Letterfrack bog (Coggins et al., 2006), which, compared to other European areas is rather scarce. There is thus a strong necessity to geochemically explore the Irish archives in more detail, especially in view of the rich metallurgical history of the island and Ireland's potential subjection to trans-Atlantic metal transport.

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

most of these metals occur as impurities within Irish Cu and Pb-Ag-Zn mineralisation, while also associated with emissions from combustion of fossil fuels, steel and iron manufacture, and refuse incineration (Nriagu and Pacyna, 1988). By combining the information gained from trace element and Pb isotope compositions, our aim is to deconvolute multiple input sources that have influenced the atmospheric metal composition over the last century at this site.

2. Background and methods

2.1. Study area and sample collection

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

A vertical monolith of 115 m in length (10x10x115 cm) was extracted from the LHB in March 2015 from an area with living *Sphagnum* moss growth on top using a stainless steel Wardenaar corer. The core was sampled close to the centre of the bog at its highest

elevation. On site, the core was wrapped in cling film and aluminium foil, placed in a wooden box, brought directly to the laboratory and stored in a dark room at ca. +2°C. Using a thin ceramic knife, the core was cut into 115 one cm slices, each apportioned for individual analyses as described in detail below.

2.2. Radiometric data and analysis

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

2.3. Bulk peat properties

Moisture contents were determined by drying a 2 cm³ subsample (2x1x1 each cm piece of peat) at 105°C for 24 hours. The organic matter contents were defined via the loss on ignition (LOI) by combusting the dried aliquot at 550°C for 6 hours in inert quartz glass crucibles. Bulk density (g cm⁻³) was analysed at 5 cm resolution for the deepest part (40-100 cm) and at 3 cm resolution for the section between 0 and 40 cm following the method of Dean (1974).

2.4. Trace element and Pb isotope analyses

Trace element concentrations in peat samples were acquired at Trinity College Dublin, Ireland via solution quadrupole ICP-MS (SQ-ICP-MS) using a Thermo Scientific iCAP-Qc, and following the method described in Marx et al. (2010). A dedicated ash fraction was prepared for this purpose by combusting a peat aliquot for 6 hours at 450°C. Between 10 and 50 mg of resulting ash was transferred into 15 ml Teflon beakers into which 0.8 ml of a triple sub-boiling distilled conc. HF and 0.2 ml conc. HNO₃ (4:1) was added. The capped beakers were placed into a digestion block at 120°C for 72 hrs and agitated at least once every 24 hrs in a HEPA-filtered fume cupboard. After cool-down, drops were carefully collected before beakers were opened, and the solution was evaporated at 110°C. The residues were then dissolved with 1 ml of 6 M HCl to reduce any remaining organic components, and fluorides were converted by attacking with 2x0.5 ml conc. HNO₃ with evaporation to dryness between each step. Finally, the converted residue was dissolved in 3 ml of 2.5 M HNO₃ and subsequently topped up with additional Milli-Q water to produce 30 ml of 0.3 M HNO₃ solutions. Two blanks were prepared along with the samples throughout all ashing and digestion steps to account for potential contamination.

The ICP-MS analyses followed the procedure of Eggins et al. (1997) with modifications described by Babechuk et al. (2010) and Marx et al. (2010). For analyses, 2 ml solutions containing a small aliquot of each stock solution was diluted with 2% HNO₃ and spiked with an internal standard containing a mixture of ⁶Li, Rh, Re, Bi and ²³⁵U, which is used for

instrumental drift correction, covering the full mass range of ionisation potentials and analysed elements. In some cases, the sample contained so much Bi that this affected the signal from the internal standard, which was then excluded for drift correction (interpolating instead between Re and U). Following Eggins et al. (1997), an additional external drift monitor was employed. Oxide/hydroxide and dimer interferences were corrected according to Ulrich et al. (2010). Multiple digestions of the USGS W-2a reference material were used for calibration, and additional USGS reference materials BCR-2 and BHVO-2 were measured throughout the duration of the study as the quality control standards. One relative standard deviations (rsd) of the mean of multiple measurements of the respective standards were typically <2% for BHVO-2 and BCR-2 and the concentrations were comparable to the GeoReM preferred values (Jochum et al. 2016) demonstrating very good accuracy (low bias) of this dataset (*Appendix A.2*). The elements with poorer reproducibility (>2% rsd) and/or higher bias relative to preferred values are those at very low ng g⁻¹ concentrations or those known to be heterogeneous in the USGS materials (e.g. Kamber and Gladu, 2009; Weis et al., 2006). The concentrations determined for this study also agree well with longer term determinations on the reference materials from similar techniques that applied the same calibration values (e.g., Babechuk et al., 2015; Kamber, 2009).

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

Lead isotope ratios of all peat samples analysed for trace element composition (n=41) were measured on the same quadrupole ICP-MS at Trinity College Dublin. Because trace element analyses consumed only a small fraction of the digest (<1%), the remaining stock solution was used for Pb purification on anion exchange resin (AGX-1x, 200-400 mesh) applying the HBr-HCl method described in Kamber and Gladu (2009). Total Pb yield was between 85-90% for all samples and the purity of the Pb solution was verified with a fast mass scan prior to isotope ratio analysis. Procedural blanks were negligible with amounts less than 0.1% of

the total Pb. The quadrupole ICP-MS Pb analysis technique used followed Ulrich et al. (2010). Accuracy and precision of the Pb isotope ratios were determined from multiple analyses of SRM-NBS 982 standard solution as shown in *Appendix A.3*. Bias was 95 ppm for $^{206}\text{Pb}/^{204}\text{Pb}$, 44 ppm $^{208}\text{Pb}/^{206}\text{Pb}$, and 25 ppm for $^{207}\text{Pb}/^{206}\text{Pb}$, relative to the values of Baker et al. (2004). Lead isotope ratios of the rock-reference materials BHVO-2 (n=2) and BCR-2 (n=2), presented in Table 2 are close to or within the values reported by Woodhead and Hergt (2000) and Baker et al. (2004), demonstrating the good accuracy of this dataset, considering some heterogeneity in Pb isotope composition in these reference materials as a result of their contamination during powder preparation, as discussed elsewhere (e.g., Weis et al., 2006).

We note that in environmental studies, the most commonly used Pb isotope data presentation 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 by a better analytical precision, a normalisation to ^{204}Pb will result in the largest possible variability between reservoirs. Furthermore, as previously pointed by Ellam (2004), an omission to include ^{204}Pb in the data interpretation might result in a limitation of source characterisation. In this study, we performed the source apportionment with the conventional Pb diagram ($^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$) which offers the best dispersion. For ease of reference and comparison to previous studies, the calculated $^{206}\text{Pb}/^{207}\text{Pb}$ values are also included.

3. Results

3.1. Radionuclide chronology reconstruction

The detection limit of ^{210}Pb is located at 23-24 cm from the surface, indicating that almost the entire ^{210}Pb inventory is captured within this peat segment. We find a ^{210}Pb inventory of 4830 Bq/m². The ^{210}Pb profile (Fig. 2a.) is relatively complex and does not show a monotonous decrease with depth thus impeding the use of a constant initial concentration (CIC) approach. The more suitable $^{210}\text{Pb}_{\text{xs}}$ -chronology is therefore a constant-rate-of-supply (CRS)-model (Appleby and Oldfield 1978). The CRS-model can take variations in mass accumulation rates into account, while still relying on a constant supply rate of ^{210}Pb , the

absence of initial penetration (IP) of ^{210}Pb , and a complete assessment of the $^{210}\text{Pb}_{\text{xs}}$ inventory. Such a model for our core is shown in Figure 2e. The possible initial penetration of ^{210}Pb in peat has been described elsewhere and may in principle be modelled, assuming a constant initial penetration and a constant rate of supply of ^{210}Pb (IP-CRS model, Olid et al. 2016). However, this model may still show discrepancies to the record of artificial radionuclides (Olid et al. 2016), in particular ^{241}Am , which is a robust age marker, while not providing a continuous age record. We therefore used constraints based on ^{241}Am together with the distribution of the ^{210}Pb inventory in order to derive the best possible age information.

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

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

Two additional samples investigated at depths of 70-71 cm and 94-95 cm from the surface yielded no ^{210}Pb and ^{241}Am activity, but a small signal of ^{137}Cs (4.4 Bq kg^{-1} , Fig. 2c.). This observation suggests significant down core Cs mobility at our site, as also suggested from the plots in *Appendix B.1*, meaning that ^{137}Cs is of little value in providing precise

chronological information here. Caesium mobility has been demonstrated in several studies of organic, clay-rich, low pH atmospheric and terrestrial archives, limiting its application as a chronologic tool (e.g., Appleby et al., 1991; Kudelsky et al., 1996). Consequently, ^{137}Cs activity was excluded from the chronology reconstruction of the LHB peat profile.

Combined, the activity profiles obtained from ^{210}Pb ($S < 0.27 \text{ cm yr}^{-1}$) and ^{241}Am ($S > 0.21 \text{ cm yr}^{-1}$, with a depth trend) yield an average accumulation of $0.24 \pm 0.03 \text{ cm yr}^{-1}$ for the uppermost 24 cm of the LHB peat core. This result is in agreement with the average values calculated for Irish bogs (Hammond, 1978). The ^{210}Pb - ^{241}Am age-depth relationship for the uppermost 24 cm was derived based on the above information, and the results expressed as AD ages are presented along with element enrichment profiles in Figure 3 and 4.

3.2. Bulk peat properties

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

3.3. Trace element patterns along the extracted LHB peat monolith

3.3.1. Geochemical data treatment

A principal component analysis (PCA) has been suggested as a strategy to minimize the amount of factors governing enrichment in multi-element datasets such as the one presented here (e.g., Küttner et al., 2014; Martínez Cortizas et al., 2013; Muller et al., 2008). The main

advantage of a factor analysis is that it allows the elements to be source-grouped according to their distribution patterns and loadings. We applied such PCA model for our dataset using the statistical software package PAST3 (Hammer et al., 2001). The results and interpretations are shown in *Appendix C*. In brief, three main components are able to explain 99.75% of the total variance. Factor 1 (PC1) accounts for the largest proportion of the variation (92.7%) with the other two factors, PC 2 and PC 3, accounting to 4.4% and 2.7% respectively. PC1 includes the elements Pb, In, Sn, Sb, Ga, Cd, Cu, Zn, Ag, Ti, with Pb showing the highest association of 97%. PC2 groups the elements Ti, Zr, Ta, Ba, Li, As, Tl, Sr, and Rare Earth elements (REE) together, and PC3: Zn, W, Mo, Ni, Ti, Sr, Cr, and Fe. While 77% of Zn is shared with PC3, almost 15% of it is also shared with PC1, pointing to multiple sources controlling Zn enrichment in the LHB peat. Based on their element assemblages, the three element groups can be carefully attributed to dust contributions from the historical Pb-Zn mining and smelting, natural geogenic dust input, and emissions from fossil fuel combustion, respectively (*Appendix C*). The latter is yet to be characterised in more detail. We find that for the LHB dataset, the PCA approach offers a first insight into the major pollutant groups contributing to the element enrichment during the past century. However, in light of complex element apportioning to the respective components from co-occurring pollutants, the information obtained by the PCA is combined with other geochemical tools to better fingerprint sources contributing to metal enrichment in LHB.

3.3.2. Enrichment factors (EF)

When investigating anthropogenic pollution, upper crustal values (UCC) are sometimes used as a reference to extract the natural dust contributions. In doing so, metal enrichments are discussed relative to geogenic element backgrounds with a poorly soluble lithophile element, such as Ti, Sc, Sr, Zr, Al, Si, Y, Ta, or REE as a normalizer (e.g., Espi et al., 1997; Kempter et al., 1997; Marx et al., 2010; Shotyk, 1996). The use of the estimated UCC values as a measure for geogenic input has been, however, intensively debated in several studies (e.g., Martínez Cortizas et al., 2002; Reimann and De Caritat, 2000). The main criticism is that the calculated UCC values represent an average composition that is not necessarily

representative of the local lithological background. This can ultimately result in an under- or overestimation of the natural geogenic budget transported into an archive. To overcome this issue, the interpretation of the element EF's relative to a local "baseline", representative for the area of interest has been proposed (e.g., Martínez Cortizas et al., 2002). This strategy is preferred for this study due to the versatile Irish geology, and trace element patterns are presented as enrichment factors (EF, Table 1) with respect to the average of the least polluted and compositionally most consistent part of the core (62 and 100 cm from the surface). This "baseline" is used to calculate element EF's at shallower depths, as described in [1].

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

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

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

3.4. Excursions of element enrichment

All trace element patterns show well-defined excursions of enrichments along the extracted LHB peat profile (Table 1 and *Appendix A.1* for raw concentrations). In Figure 3 we show a

representative selection of the results. Lead, Cu, and Zn depositions increase jointly from 62 cm depth (Fig. 3 and 4) and peak at different stages during the 20th century (Pb and Cu) until recently (Zn). Enhanced deposition is observed in a number of other metals which asynchronously reach their maxima between 1940 and 1960 (Ag and Sb), 1960 and 1970 (Ni), 1950's and recently (Mo). Rare earth elements (REE) are highest between 10 and 20 cm, i.e., first half of the 20th century, to then decrease again significantly in recently growing *Sphagnum* moss (*Appendix B.3*). A rapid decline in their enrichments is also observed for a number of other elements (e.g., Ag, Pb, Sn, Sb, In, Cd, U; not shown) between 1970 - present, whereas enrichments of Ni and Cu do not quite return to pre-anthropogenic levels and show diminished present-day atmospheric fallout (Fig. 3 and 5). Enrichment factors of Mo and Zn increase more rapidly from ca 1940 and reach highest values of 5 and 39, respectively in the sub-surface level of LHB.

3.5. Lead isotope compositions

Lead isotope ratios are presented together with EF of Cu, Zn, and Pb in Figure 4. Lead isotope composition of the peat is homogenous from the base of the core until ca. 18 cm ($^{206}\text{Pb}/^{204}\text{Pb}$: 18.271-18.429, $^{206}\text{Pb}/^{207}\text{Pb}$: 1.171-1.179). A dramatic change towards unradiogenic Pb signature, coincident with major EF peaks for Cu and Pb is seen between 18 cm and 9 cm, where 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 unradiogenic 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 depth interval between 8 and 4 cm from the surface. This period is followed by a reversal towards more radiogenic Pb isotope signature that extends up to the top of the bog. In detail, 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) does not quite return to the values below 18 cm.

4. Discussion

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

Conservative behaviour of at least some elements within bogs is a prerequisite for their interpretation of atmospheric pollution histories. Experimental studies have demonstrated

that strong complexation and fixation of metals onto the organic matter occurs in acidic environments such as bogs (e.g., Pokrovsky et al., 2005a). The retention of the elements at the depth of deposition is aided by carbon oversaturation within biomass and pore water (Smith et al., 2004). Krosshavn et al. (1993) have shown that metals such as Cu, Zn, Cd, and Pb can sometimes display variable binding capacities, depending on the vegetational background. Yet, the most favourable condition for the successful retention of metals onto the organic matter has been found to be at a pH of 4. The surface of LHB displays pH conditions ranging between 4 and 4.5.

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

In LHB, Cd, Ag, Sn, Sb, In, Co, Mo, Cr, and V are well-correlated with Pb ($R^2=0.71$ to 0.88) which is commonly accepted to be highly immobile in peat (Martínez Cortizas et al., 2012; Shotyk, 1996). Stronger shared variations are observed between Pb-Ag-Sn-Sb-In (e.g., Ag vs. 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 elements into two suites. As suggested from the PCA, these elements correspond to the PC1 and PC3 groups. Further, the temporal deposition patterns of the Zn-Co-Mo-Cr-V (PC3) group differ from those of Pb-Ag-Sn-Sb-In (PC1) by displaying a continuing upward trajectory of their enrichment when PC1 shows a decrease in its pollution load (Fig. 3 and *Appendix C*). The onset of Zn enrichment is coincident with that of Pb pointing towards a simultaneous pollution initiation rather than a down-core mobilisation of Zn. The diverging Pb and Zn enrichment patterns towards the top of the core, i.e., over the last 50 years ($R^2=0.4$, Fig. 4) reflect either i) the decreasing industrial use of the former (PC1) and increased utility of the latter (PC3), or ii) a different source/process responsible for the enrichment of metals in subsurface-layers of the bog. Minor Zn bioaccumulation in the living part of the bog cannot

fully be excluded. However, its relevance to the total Zn budget and source apportioning is rather insignificant as shown from its >95% assignment to PC 1, 2, and 3. In the following chapter, we discuss in detail the complex behaviour of element enrichments in LHB in light of the known records of Irish industrial development. We combine the information obtained by PCA, EF's, and Pb isotopic composition, and discuss the pollution patterns from the base of the core towards the surface, as chronologically subdivided in Figure 4.

4.2. The baseline (100-62 cm)

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

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

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

where the $\text{Pb}_{\text{excess}}$ and ${}^{20x}\text{Pb}/^{204}\text{Pb}_{\text{excess}}$ are the baseline corrected concentration and isotopic composition of Pb in the polluted samples, Pb_{con} and ${}^{20x}\text{Pb}/^{204}\text{Pb}_{\text{measured}}$ are the analysed Pb concentration and isotopic compositions, $\text{Pb}/\text{Ta}_{\text{sample}}$ is the ratio in the polluted part of the bog, $\text{Pb}/\text{Ta}_{\text{baseline}}$ and ${}^{20x}\text{Pb}/^{204}\text{Pb}_{\text{baseline}}$ represent the compositions of the baseline (100-62

cm), and $Pb_{baseline}$ is the average Pb concentration in the unpolluted part of the bog. For further calculations, the subtracted local geogenic contribution was no longer considered.

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

Enrichment factors of Cu, Zn, and Pb increase within this segment, which covers the time period before the 20th century (Fig. 5). Importantly, Pb isotope values do not change substantially from the composition of the baseline (Fig. 4) and are comparable to the published values of the granitic Leinster batholith (Fig. 6a., e.g., Kennan et al., 1987), which is the host rock of local Pb-Ag-Zn mineralisation. The increasing heavy-metal input is thus interpreted to reflect the 18th and 19th century Pb-Ag extractions from the high-grade, low-tonnage galena-rich veins exposed in the Wicklow uplands (Rynne, 2015; Schwartz and Critchley, 1997). Smelting was conducted ~15 km NE from LHB (and ~35 NE km from the mining site) at Ballycorus (e.g., Callaghan, 2014; Shepard, 1981), which may have additionally contributed to the overall pollution load. The Pb isotope signal argues against a Pb contribution from the clearly distinguishable fingerprint of sphalerite-galena mineralisation hosted in the Lower Carboniferous of the Midland basin (e.g., Wilkinson and Eyre, 2005, Fig. 6a.), subjected to small scale extractions during the same time period (Rynne, 2015). The synchronous enrichment onset and development of Zn and Pb ($R^2=0.96$) in this peat section (Fig. 5c.) suggest pollution from the mining activity, especially because of Zn co-occurring in most Pb ore bodies, and due to the shared 15% variation of Zn with PC1 (mining and smelting). An important known example of accidental Zn pollution from Pb mining was the giant Broken Hill deposit in south-central Australia, where the relative timing of Pb+Ag vs. Zn extraction is accurately reflected in a mire peat core ca. 1,000 km downwind from the mine (Marx et al., 2010). In LHB, the same holds for Cd, which occurs as major impurity within the mined sphalerite and galena ores.

Enrichment patterns of Zn depart from those of Pb towards 25 cm depth, pointing to an increasing significance of a source other than mining. The continuing amplification of Zn depositions (EF= 12-23), coupled with subtle elevations in Mo, Ni, V (EF= 0.8-1.6, 1.1-1.8, and 1.1, respectively) in LHB suggests atmospheric depositions from a non-geogenic source.

Atmospheric charging with these particular heavy metals has been long associated with the combustion of liquid and solid fossil fuels (Daniehelka et al., 2003; Gallagher et al., 2018; Hjortenkrans, 2008; Huang et al., 1994; Nriagu, 1989; Pacyna and Pacyna, 2001). In this context, it is well documented that coals were the main fuel source during the entire period of mining activity in the Wicklow uplands (Rynne, 2015), and can thus be considered a potential metal emission source at this site.

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

Peak pollution period from local mining is documented between 1900 and 1960's where EF's of Cu, Ag, Pb, Cd, Sb, and Sn (PC1) reach values of 10, 18, 18, 51, and 14, respectively. Rare Earth element depositions are the highest during this period (*Appendix B.3*), suggestive of an enhanced atmospheric dust fallout from the mineralisation host rock. Silver, Cu, and Sb enrichment coincide with early 20th century mining for coinage taking place at different sites around the Wicklow uplands, but also further inland at Silvermines, Co. Tipperary. Stibnite (Sb₂S₃) and pyrite (FeS₂) were extracted at Avoca (Fig. 1).

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

A notable change in the geochemistry of the LHB peat (i.e. element ratios, Fig. 5a-d.), specifically, a decrease in Pb and Ag (PC 1) and an increase in Zn, Mo, and Ni (PC3), is evident from ca. 1940 onwards (Fig. 5). This is accompanied by a prominent turn towards a less radiogenic Pb isotopy (Fig. 3), likely reflecting the transition from mining originated Pb to

pollution from the hemispheric introduction of leaded gasoline. To disentangle the Pb contributions from the two sources, we deployed a binary mixing calculation between the following end-members: **A**, pollutant 1 ($^{206}\text{Pb}/^{204}\text{Pb} = 18.30$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.62$, $^{206}\text{Pb}/^{207}\text{Pb} = 1.174$] mining/industrial signal of the early 20th century), and **B**: pollutant 2 ($^{206}\text{Pb}/^{204}\text{Pb} = 17.20$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.54$, $^{206}\text{Pb}/^{207}\text{Pb} = 1.109$] average European-Australian leaded gasoline). The modelled curves (Fig. 7b. and described in *Appendix D*) were calculated using different Pb concentrations of the respective end-member pollutants (10-200 $\mu\text{g g}^{-1}$). Mixing calculations expose the increasing influence of leaded gasoline over the course of 20th century, becoming progressively more accentuated only after the decline of the local mining and smelting activity (post 1940, 18 cm). Quantifying potential contribution of vehicle emissions before 1940s is complicated by the masking from concurrent mining activities which lasted until ca. 1957 (Rynne, 2015). The least radiogenic $^{206}\text{Pb}/^{207}\text{Pb}$ values of 1.138 ± 0.011 recorded in peat from the 1970-80s represent the peak Pb contribution from leaded petrol documented at this site (Fig. 7a.). Because of the large variation in the Pb isotopic composition of ores used for the manufacture of petrol additives ($^{206}\text{Pb}/^{207}\text{Pb} = 1.06$ -1.12, Townsend et al., 1998; Veron et al., 1999), there is a significant uncertainty of 6 to 78% in the calculated contributions (Fig. 7b.). Similar findings were made in studies of bogs and freshwater lake sediments from central Scotland (e.g., Farmer et al., 1997).

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

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

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

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

With the abolition of leaded gasoline in Europe, North America and in 2000 in Ireland, Pb isotopic compositions of LHB peat progressively returned to more radiogenic values (Fig. 7a.). However, these ratios ($^{206}\text{Pb}/^{204}\text{Pb}=17.929\pm0.007$; $^{207}\text{Pb}/^{204}\text{Pb}=15.613\pm0.007$; [$^{206}\text{Pb}/^{207}\text{Pb}=1.148\pm0.007$]) are far from the "baseline" signal, implying either, i) a slow post-gasoline amelioration of atmospheric Pb pollution load; ii) recent pollution from a source with partially ^{206}Pb depleted signature; iii) re-suspension of legacy Pb from regional erosion (Cloquet et al., 2006); or iv) a combination of these factors. Shotyk and Krachler (2010)

attributed the post-1975 to present Pb isotope variations in the European atmosphere to the growing importance of modern industrial processes and urbanisation relative to decline of leaded petrol use. The compilation of Pb-isotope ratios of potential present-day sources shown along with the LHB values in Figure 6b point towards recent pollution from vehicle exhausts of EU originated non-leaded petrol (Erel et al., 1997; Hurst et al., 2002) and atmospheric trace metal release from the use of mineral oil (Chiaradia and Cupelin, 2000). The latter constitutes the major energy source for domestic heating in Co. Dublin. There is also a strong positive coherence between the increasing amount of private and public vehicles in Ireland (www.cso.ie), especially around Dublin and the rising dominance of PC3 - fossil fuels fingerprint, in the Irish atmosphere, supporting the presence of a growing real pollution signal, rather than remobilisation of previously deposited pollutants. Lead isotope ratios in the subsurface layer of LHB are consistent with the estimated average composition of what is suggested to be the signal of the present-day atmospheric Pb pollution ($^{206}\text{Pb}/^{207}\text{Pb}=1.14\text{-}1.16$, Carignan et al., 2005; Monna et al., 1997), calculated using the fly ash compositions of waste incinerators in central Europe. There are thus a variety of recent pollution sources which can explain the Pb isotope composition of the atmosphere.

4.6. Timing of Pb pollution and synthesis of Pb isotope information from other relevant peat archives

Due to its location at the east coast of Ireland, LHB records processes that are part of broader regional and hemispheric pollution patterns. In order to facilitate a comparison between the Pb pollution history recorded by LHB and other Irish archives (Coggins et al., 2006; Schell et al., 1997), accumulation rates were calculated according to the method described in detail by Muller et al. (2008). The results are presented in Table 1. In LHB, Pb deposition rates range between $0.45\text{-}1.8\ \mu\text{g cm}^{-2}\ \text{yr}^{-1}$, with values $>1\ \mu\text{g cm}^{-2}\ \text{yr}^{-1}$ observed at different stages throughout the 20th century (Fig. 8). Peak accumulation rates are detected between 1960's and 1980's, in excellent agreement with the Pb deposition rates in a peat archive situated ca 1-2 km away to the west, Kippure bog (Schell et al., 1997). Lead accumulation rates are higher in the LHB peat deposited during the early 20th century mining

period, which is likely due to its relative proximity to the mining and smelting sites. Enhanced Pb deposition during the 1980's can be attributed to the leaded gasoline peak, as it can also be seen from the Pb isotope composition of LHB. In the Midlands (Clara bog), Pb deposition rates were up to 3 times lower than at the eastern seaboard (Fig. 8), yet still higher than at all sites investigated so far along the west coast (Knockroe, Co. Mayo $0.1\text{--}0.3\ \mu\text{g cm}^{-2}\ \text{yr}^{-1}$, Letterfrack, Co. Galway $0.4\text{--}0.5\ \mu\text{g cm}^{-2}\ \text{yr}^{-1}$, Coggins et al., 2006; and Bellacorick, Co. Mayo, $0.05\text{--}0.4\ \mu\text{g cm}^{-2}\ \text{yr}^{-1}$ Schell et al., 1997). It appears that historical mining and smelting have not significantly influenced the archives on the west, although there is also the possibility that the clean Atlantic winds dominating here contribute to an overall dilution of atmospheric pollution. Peak Pb deposition at the west coast occurs slightly earlier during the 1960's and has been previously interpreted to render the long-range transport of polluting Pb from the American continent. We suggest that further investigations, such as the Pb isotopy of these westernmost archives are necessary before exact conclusions can be drawn. A trans-Atlantic Pb gasoline pollution during the 1960's would anticipate the isotope signal of the peat to be close to those of Canadian ($^{206}\text{Pb}/^{207}\text{Pb} = 1.15\text{--}1.17$, Bathurst) and USA ($^{206}\text{Pb}/^{207}\text{Pb} > 1.28$, e.g., Mississippi) ores.

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

5. Summary and conclusion

We investigated the atmospheric elemental and Pb isotope evolution resulting from local mining, industrial activities and leaded gasoline pollution in eastern Ireland over the last

century from the geochemistry of a bog in the Wicklow Mountains. The elemental cycle associated with mining of local ores (e.g., Pb, Cu, Ag, Sn, Sb) was highly perturbed during the major period of mining and smelting in the Wicklow area (19th to 20th century), showing up to 20-fold, 15-fold, and 50-fold enrichments (Pb, Ag, and Sb, respectively) with respect to the established baseline of the core. Element deposition associated with the combustion of fossil fuels (Zn, V, Ni, Cr and Mo) is detected throughout the polluted section of the core. This pollutant becomes increasingly more pronounced only after the abolition of the mining activity in the area (ca. 1940-recent). The Pb isotopes precisely document the shift towards less radiogenic $^{206}\text{Pb}/^{204}\text{Pb}$ values in response to the introduction of the Pb petrol additives from ca. 1940 (in this archive) until its complete elimination in 2000 in Ireland. In the most general sense, the observed isotopic shift ($^{206}\text{Pb}/^{207}\text{Pb}=1.138\pm0.011$ in 1970) is consistent with findings in other records of atmospheric Pb deposition around Europe (e.g., Sweden, Brännvall et al., 1997; Scotland, Farmer et al., 1997; Spain, Kylander et al., 2005; Switzerland, Weiss et al., 1999). However, unlike at most other sites, the introduction of leaded petrol is not associated with the highest atmospheric Pb pollution load at this site, which was instead caused by the historical Pb-Zn mining and smelting of local ores. Despite a notable decline in the leaded gasoline signal after 2000, the Pb isotopic composition has not quite returned to pre-industrial values, implying input from modern pollutant sources. Based on combined trace element and Pb isotope investigations, we suggest that coal, peat, and oil combustion, emissions from unleaded petrol, as well as trans-regional industrial pollution (e.g., waste incinerators) potentially reaching Ireland on easterly airstreams are the sources contributing to aerial Pb pollution at this site today. The strong local control of the bog geochemistry demonstrated in this study emphasises the need to combine metal concentration and isotopic investigations for reconstructing historic pollution. Without having investigated the Pb isotopic patterns, the major Pb enrichment peak could have been erroneously attributed to an early Pb gasoline signal. The decline in most heavy metals (esp. Pb, Cu, Sb) in the present day *Sphagnum* moss is in line with observations made in bogs from elsewhere (e.g., Switzerland, Shotyk et al., 2001), and can be attributed to tougher air pollution prevention policies adopted in Europe over the last three decades.

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- 942

Figure captions

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

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

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

Figure 4: Pb isotope ratios (black solid circles) together with EF of Cu, Zn and Pb (open diamonds) along the LHB peat core. Depth ranges distinguished by colours represent changes in either Pb isotopic composition, metal concentrations, or both. Radionuclide

derived chronology and contemporaneous historical anthropogenic activities are also indicated.

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

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

Figure 7: a) Chronology-integrated $^{206}\text{Pb}/^{204}\text{Pb}$ isotope composition of the upper part of the LHB peat profile together with areas representative of the local mineralisation (Kennan et al., 1986) and potential anthropogenic pollution sources during the 19th to 21st century. **b)** Common Pb isotope binary mixing model using A: average Pb isotope values of local mineralisation ($^{206}\text{Pb}/^{204}\text{Pb}=18.300$; $^{207}\text{Pb}/^{204}\text{Pb}=15.622$, Kennan et al., 1986), and B: average compositions representative for aerosols associated with Pb enriched vehicle emissions

($^{206}\text{Pb}/^{204}\text{Pb}=17.200$; $^{207}\text{Pb}/^{204}\text{Pb}=15.543$, e.g., Chiaradia and Cupelin 2000; Monna et al., 1997; Veron et al., 1999). Lead concentrations range between 10 and 200 $\mu\text{g g}^{-1}$, corresponding to values measured along the LHB peat profile. For the calculation steps refer to the text and *Appendix D*. Error bars are smaller than the symbols.

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

Appendix B: Additional figures

To Rosca *et al.* "Trace element and Pb isotope fingerprinting of atmospheric pollution sources: A case study from the east coast of Ireland"
Carolina Rosca, Emma L Tomlinson, Walter Geibert, Cora A McKenna, Michael G Babechuk, and Balz S Kamber

Appendix B.1: Profiles of Cs/Ta, Cs/Rb, and Cs/Ta vs. organic matter content (%) along the LHB peat core

Appendix B.2: Ta, Ti, Sc and Zr (ppb) vs. organic matter content (%) along the extracted Liffey Head bog peat monolith

Appendix B.3: CI-Chondrite (McDonough and Sun, 1995) normalised REE patterns for LHB samples from selected depths- baseline (73 cm), local mining and smelting (25 cm, 1900 AD), Pb petrol (9 cm, 1970 AD), and recently growing *Sphagnum* moss (1 cm) deposited onto LHB core.

Appendix B.4: Tonnage extractions of the elements Zn, Pb, Cu, and Ag in Ireland between 1960 and 2000 (black lines; source: <http://www.mineralsireland.ie/mining+in+ireland/Current+Mining.htm>, and Department of Communications, Energy and Natural Resources), together with the age-corresponding enrichment factors (EF) of these elements in LHB peat core (blue squares)

Appendix A to:

Rosca et al. "Trace element and Pb isotope fingerprinting of atmospheric pollution sources: A case study from the east coast of Ireland"

Appendix A.1 Trace element concentrations (ng / g) for dry peat samples from LHB core (Wicklow Mountains, east Ireland)

Sample ID		LHB1.3	LHB2.3	LHB3.3	LHB4.3	LHB5.3	LHB6.3	LHB7.3	LHB1.1	LHB1.2	LHB2.2	LHB3.2	LHB4.2	LHB5.2	LHB6.2	LHB2.1	LHB7.2	LHB8.2	LHB9.2
depth (cm)		0 - 1	1 - 2	2 - 3	3 - 4	4 - 5	5 - 6	6 - 7	7 - 8	8 - 9	9 - 10	10 - 11	11 - 12	12 - 13	13 - 14	14 - 15	15 - 16	16 - 17	17 - 18
Element	Li	371	806	352	298	459	740	885	341	256	428	579	688	689	710	543	504	578	540
	Be	17.3	31.8	13.6	16.6	22.4	31.9	43.0	23.7	29.4	47.8	75.7	107	132	152	108	122	143	132
	Sc	85.8	167	69.4	92.5	133	188	250	140	153	266	372	421	441	491	321	411	473	460
	Ti	32120	59450	22870	31670	46970	55030	74480	52700	48350	80350	100300	114300	104300	111500	75580	96720	115600	101900
	V	2087	4568	2015	2784	3752	4697	5644	3847	4535	8089	10420	9870	10040	13530	9175	7088	5852	4856
	Cr	1352	2309	988	1214	1489	2161	3179	1556	2126	3401	5249	6269	4925	5450	2588	2799	2869	2478
	Fe	212	243	258	380	280	337	294	336	355	286	263	293	426	435	304	270	277	540
	Co	195	386	173	172	202	315	416	219	266	457	542	678	738	783	495	579	646	731
	Ni	1494	2645	1243	1487	1922	3039	4092	2385	2620	4469	5332	6417	6152	6470	3700	4053	3972	3979
	Cu	4350	6787	3024	2855	4939	8891	9458	4339	4494	8222	9818	11380	12360	14480	9844	13480	17510	24050
	Zn	45550	81450	36630	32550	37480	59690	70920	43930	45270	72980	66860	84850	92870	99200	62470	64250	65870	83550
	Ga	161	344	158	198	294	487	657	344	488	918	1400	1467	1741	2328	1932	2284	2388	2701
	As	365	819	535	652	599	1179	2077	1170	1141	2128	3075	4133	6111	6153	5752	4778	5557	7696
	Rb	1011	1703	726	718	771	1067	1307	832	724	1193	1261	1490	1461	1453	842	1120	1427	1433
	Sr	19360	34860	14020	13600	15730	24470	34030	13800	13850	23780	21030	28190	31960	34650	23830	26130	26880	34190
	Y	212	422	158	200	267	367	510	269	308	514	616	755	920	1033	771	1027	1039	1068
	Zr	1242	2960	802	1110	1562	1817	2507	1481	1401	2316	2835	3325	3171	3399	1875	2729	3229	2927
	Nb	112	202	75	110	165	196	265	165	171	281	363	419	395	420	241	345	421	366
	Mo	550	849	295	370	401	541	621	347	412	722	830	891	955	1150	836	1031	1045	960
	Ag	35.7	61.7	42.1	41.5	63.7	162	214	109	106	215	271	331	381	423	359	415	498	618
	Cd	95.9	228	134	175	236	426	621	338	425	735	809	1007	1265	1555	1287	996	1033	1359
	In	5.28	11.31	5.09	6.78	9.44	19.6	26.3	12.1	19.6	38.1	60.9	69.3	92.2	109	98.4	180	253	305
	Sn	766	1544	542	703	935	1796	2592	1263	2140	4273	7768	9171	10330	12110	9769	16540	19810	17720
	Sb	413	1018	442	460	543	1545	2175	960	1258	2333	3344	3416	4378	7331	7430	8559	9652	13210
	Cs	66.4	136	63.5	71.1	86.1	117	143	82	72	121	136	166	170	168	91.2	118	148	152
	Ba	9572	17780	7665	8466	10410	14420	18280	9847	9887	16610	16270	21320	23440	24710	16240	20110	21690	23670
	La	325	655	259	312	407	548	772	412	457	755	864	1041	1200	1234	787	1140	1215	1230
	Ce	464	1034	398	517	726	950	1309	750	877	1475	1754	2108	2461	2652	1824	2502	2643	2809
Pr	56.4	121	47.0	65.8	92.0	121	167	92.9	111	188	217	261	310	336	231	314	328	342	
Nd	217	458	174	228	319	431	597	331	399	678	794	956	1148	1262	891	1208	1252	1315	
Sm	40.3	84.8	32.5	42.4	58.6	80.3	110.6	60.8	75.2	127.2	151.8	181.4	222.9	246.4	183.6	251.0	262.6	281.1	
Eu	9.11	16.9	6.92	9.09	12.4	17.3	23.6	12.0	14.9	25.4	30.5	36.6	46.5	51.6	40.0	55.0	59.8	65.7	
Gd	35.2	69.2	28.3	37.0	51.0	69.2	94.5	50.7	65.1	110.0	130.6	157.7	192.6	213.1	158.6	220.2	223.4	237.2	
Tb	5.45	10.5	4.48	5.78	7.93	10.7	14.6	7.50	9.14	15.5	18.6	22.7	27.6	30.9	23.2	31.7	33.1	34.8	
Dy	31.6	59.4	25.8	33.4	45.9	61.1	85.0	45.3	54.2	90.4	110.6	133.8	162.0	181.3	133.7	184.1	192.4	198.4	
Ho	6.48	12.2	5.31	6.87	9.45	12.6	17.3	9.21	11.0	18.5	22.4	27.3	32.6	36.4	26.5	36.4	37.7	38.5	
Er	18.3	33.0	14.6	19.1	26.0	34.5	48.1	25.6	29.5	49.8	60.2	73.0	86.2	96.9	71.0	96.1	98.7	100.3	
Tm	2.74	4.94	2.17	2.84	3.93	5.11	7.08	3.83	4.56	7.66	9.18	11.0	12.9	14.5	10.4	14.3	14.9	15.0	
Yb	17.1	30.8	13.6	18.4	24.9	32.4	45.0	24.3	28.2	47.1	57.2	68.0	79.7	89.2	64.6	88.7	93.7	95.8	
Lu	2.62	4.61	1.99	2.70	3.68	4.78	6.49	3.60	4.07	6.75	8.10	9.60	11.2	12.4	8.95	11.9	12.6	12.5	
Hf	29.9	68.9	19.9	27.9	39.4	45.8	63.0	37.5	36.4	60.8	73.4	85.3	81.8	88.4	47.7	70.4	81.7	75.9	
Ta	11.0	21.0	8.2	7.4	9.0	13.4	19.8	11.6	11.0	18.4	17.9	22.8	27.1	25.4	17.8	22.1	27.0	31.9	
W	118	176	75.1	57.0	75.5	205	158	333	125	183	236	253	290	344	325	327	346	303	
Tl	5.30	12.0	2.33	1.87	2.10	1.78	2.80	21.3	13.1	18.2	16.5	26.2	28.6	25.8	59.5	15.3	12.5	11.0	
Pb	4552	12870	8330	6359	9572	18640	29450	33610	49100	90760	72190	169500	230700	271600	201900	237600	267600	377700	
Th	49.2	107.6	40.7	57.6	87.1	114	150	89.6	98.0	165	220	254	270	278	168	244	263	244	
U	30.1	57.4	27.0	31.7	43.7	66.6	89.2	48.3	54.1	94.6	127	149	163	185	122	162	181	186	

Appendix A.1 (continued)

Sample ID		LHB10.2	LHB11.2	LHB12.2	LHB13.2	LHB3.1	LHB14.2	LHB15.2	LHB16.2	LHB17.2	LHB18.2	LHB19.2	LHB20.2	LHB21.2	LHB22.2	LHB4.1	LHB23.2
depth (cm)		18 - 19	19 - 20	20 - 21	21 - 22	22 - 23	23 - 24	24 - 25	25 - 26	26 - 27	27 - 28	28 - 29	29 - 30	30 - 31	31 - 32	32 - 33	33 - 34
Element	Li	544	697	706	502	481	264	212	243	258	380	280	337	294	336	355	286
	Be	119	128	117	85.3	70.5	42.9	35.2	45.7	50.3	65.0	47.2	59.4	45.1	46.2	39.9	36.9
	Sc	396	466	457	348	235	168	133	148	164	236	177	218	188	212	192	183
	Ti	113000	142200	141600	95730	71300	48820	43140	53080	60030	88420	65530	82950	72870	83360	81910	69850
	V	4075	4338	3838	3060	2274	1342	1108	1259	1364	1799	1330	1705	1446	1612	1468	1377
	Cr	2146	2473	2431	1863	1233	916	727	851	965	1259	935	1146	1032	1246	989	996
	Fe	544	697	652	212	243	258	380	280	337	294	336	355	286	263	293	426
	Co	579	645	638	589	512	281	239	282	326	389	294	383	321	349	322	303
	Ni	3189	3254	2774	2176	2553	966	804	916	978	1155	864	1070	875	932	766	736
	Cu	18430	23230	24590	23680	15640	6339	4326	3306	3117	3316	2418	3036	2366	2594	2058	2456
	Zn	62620	66140	64590	57030	51520	31910	26200	31730	36090	38220	27770	35090	26450	25940	21070	19930
	Ga	1987	2086	1867	1557	1091	544	406	392	380	435	311	387	316	346	288	278
	As	6926	9229	9740	9082	9153	4777	4694	6237	8137	10390	8370	10980	9527	9427	9507	7384
	Rb	1470	1896	1973	1350	919	649	540	643	709	1039	758	907	789	871	754	745
	Sr	27160	30330	29390	25460	22630	16410	15330	20650	25150	29030	22320	29310	23390	24540	21400	21000
	Y	970	1014	974	742	542	373	329	396	436	551	393	495	409	436	357	361
	Zr	3166	3789	3761	2589	2041	1346	1230	1494	1766	2452	1745	2151	1904	2117	1981	1914
	Nb	395	493	487	334	213	177	151	189	216	311	227	284	248	282	241	234
	Mo	833	878	721	667	496	237	167	184	186	216	151	182	151	171	164	154
	Ag	382	386	353	318	177	88	57.0	46.1	44.1	46.1	31.6	37.2	34.3	37.2	31.8	36.0
	Cd	1008	1170	1117	876	885	384	348	425	529	578	422	531	418	390	355	263
	In	291	359	382	340	221	133	100	89.7	85.0	98.6	72.1	86.7	69.0	71.4	53.5	51.8
	Sn	14550	16240	16450	12840	4909	3917	2872	2769	2749	3933	3038	3084	2503	2864	1828	2060
	Sb	8287	7950	6082	4973	2814	1161	869	678	607	618	435	584	440	439	360	337
	Cs	145	184	193	139	103	69.2	54.0	62.4	68.6	100	71.9	88.4	74.8	83.9	73.1	73.5
	Ba	20290	22690	21260	15760	11390	8477	7065	8832	10190	12570	8955	11510	8942	9440	7777	7546
	La	1143	1313	1256	927	624	486	382	469	522	703	515	663	549	616	523	517
	Ce	2467	2757	2573	1927	1286	1013	795	965	1061	1400	1032	1334	1086	1222	1010	1002
	Pr	300	331	309	232	156	123	96.3	119	130	168	124	161	130	144	119	118
	Nd	1152	1255	1169	879	591	474	366	450	491	631	465	615	485	534	439	436
	Sm	241.9	256.8	235.4	179.1	122.4	97.0	73.5	89.7	97.4	122.8	90.3	122.0	94.3	104.4	83.9	83.7
	Eu	55.2	57.3	52.0	40.0	27.5	21.1	16.2	19.1	21.0	25.9	19.0	25.8	19.4	21.3	17.4	17.3
Gd	207.1	218.5	201.9	155.8	107.4	88.5	66.1	79.1	85.4	107.5	78.5	109.7	81.9	88.0	71.3	71.8	
Tb	30.8	31.9	29.9	23.0	15.9	13.2	9.81	11.5	12.7	16.2	11.8	16.4	12.3	13.3	10.7	10.9	
Dy	177.7	187.5	177.0	134.2	93.3	77.9	58.3	69.8	76.7	98.7	70.8	98.4	73.2	79.3	64.0	65.2	
Ho	35.0	36.8	35.5	27.0	18.7	14.2	11.8	14.3	15.8	20.4	14.5	18.9	15.0	16.2	13.1	13.4	
Er	92.4	98.5	95.0	71.9	50.6	42.5	32.2	39.2	43.2	56.1	39.7	56.6	41.2	44.9	36.6	37.2	
Tm	13.9	15.0	14.6	10.8	7.51	6.37	4.72	5.80	6.35	8.44	5.96	8.51	6.20	6.75	5.47	5.61	
Yb	90.2	96.8	92.8	68.8	47.3	40.6	29.8	36.6	40.2	52.7	37.1	53.7	38.7	42.6	34.3	35.2	
Lu	11.9	13.2	12.8	9.44	6.63	5.71	4.25	5.13	5.72	7.58	5.34	7.75	5.59	6.07	5.15	5.15	
Hf	82.2	100.3	99.7	70.6	59.5	45.3	34.0	42.3	49.5	68.6	48.2	69.0	52.3	58.2	53.6	52.0	
Ta	26.1	33.2	32.7	27.2	23.5	13.8	9.9	12.6	14.4	21.3	15.7	22.8	16.8	19.3	16.1	15.9	
W	229	237	209	184	171	78.2	97.6	56.0	51.4	61.2	44.2	62.4	44.4	52.5	61.4	53.2	
Tl	9.90	13.5	15.8	104	84.4	37.8	23.9	36.8	53.3	66.8	52.2	74.4	49.1	50.2	52.6	39.0	
Pb	300300	375600	347700	307200	219400	132500	87820	90520	98190	92270	67340	113600	67970	68960	52910	54070	
Th	237	295	292	219	138	176	90.7	112	123	178	135	205	146	164	141	141	
U	163	183	178	153	110	124	60.1	67.4	75.4	105	76.8	115	81.3	92.7	84.5	81.9	

Appendix A.1 (continued)

Sample ID depth (cm)		LHB24.2 34 - 35	LHB5.1 42 - 43	LHB6.1 52 - 53	LHB7.1 62 - 63	LHB8.1 72 - 73	LHB9.1 82 - 83	LHB10.1 94 - 95
Element	Li	263	293	426	435	304	270	277
	Be	33.2	32.0	42.2	41.5	24.6	21.4	21.9
	Sc	158	201	382	283	209	206	216
	Ti	69870	79020	135600	140000	78770	66110	87760
	V	1241	1489	2349	1799	1390	1238	1121
	Cr	783	935	1381	1238	966	812	805
	Fe	435	304	270	277	540	544	697
	Co	279	311	273	184	221	163	128
	Ni	688	918	991	561	680	814	539
	Cu	1764	1715	2325	1234	1040	1040	852
	Zn	13400	10910	4012	1411	1688	1195	987
	Ga	211	259	337	312	250	204	195
	As	5278	7261	6578	1609	1262	774	444
	Rb	529	615	923	1032	671	518	567
	Sr	20700	23690	23820	19830	21510	17300	12960
	Y	341	387	599	582	368	320	316
	Zr	1657	1857	3170	3713	1888	1824	2287
	Nb	203	229	412	441	237	204	264
	Mo	158	183	261	167	158	183	147
	Ag	24.0	23.7	29.1	20.3	18.0	14.9	7.93
	Cd	223	205	239	90.3	82.1	68.0	53.0
	In	19.7	11.1	10.5	7.55	6.02	3.77	1.90
	Sn	663	754	1719	1596	945	373	95
	Sb	245	278	285	153	173	68	24
	Cs	49.7	54.4	91.3	97.7	74.6	56.9	51.9
	Ba	6936	7901	8991	7166	4596	4317	3929
	La	485	554	843	853	540	530	515
	Ce	1047	1166	1736	1621	1045	946	917
	Pr	111	136	201	192	123	107	106
	Nd	411	493	732	698	458	391	380
	Sm	71.5	93.8	138.3	130.4	86.8	73.9	69.5
	Eu	17.5	19.7	29.4	27.0	18.4	15.7	14.5
	Gd	67.1	79.9	119.1	109.5	73.6	62.3	58.1
	Tb	10.0	11.9	18.1	16.8	11.0	9.39	8.82
	Dy	61.1	69.4	107.6	101.7	65.4	55.8	54.4
	Ho	12.3	14.0	21.9	20.9	13.3	11.9	11.8
	Er	34.0	37.9	59.9	58.4	36.8	31.2	32.0
	Tm	5.09	5.57	8.85	8.84	5.45	4.61	4.89
	Yb	31.5	34.5	54.6	55.5	34.0	28.8	31.0
	Lu	4.56	5.10	8.10	8.23	5.05	4.28	4.62
	Hf	48.8	49.4	83.1	96.6	49.2	46.5	58.5
	Ta	13.0	15.4	21.1	20.2	15.8	14.0	15.2
	W	47.9	67.6	89.8	64.5	48.4	43.2	41.5
	Tl	34.1	38.7	28.4	10.0	4.36	2.07	3.35
	Pb	33250	40010	19940	9952	12380	9812	3757
	Th	123	142	211	209	141	123	129
	U	71.5	78.5	131	108	91.0	90.3	85.4

Appendix A.2: Trace element composition for reference materials (ng / g) of reference materials for QA/QC

BHVO-2									BCR-2										
	d:1,m:1	d:1,m:2	d:1,m:3	d:1,m:4	d:1,m:5	d:2,m:1	d:3,m:1	Mean	RSD	GeoReM	%bias*	d:1,m:1	d:1,m:2	d:1,m:3	d:1,m:4	Mean	RSD	GeoReM	%bias*
Li	4722	4784	4445	4524	4632	4564	4482	4593	2.7	4500	2.1	9535	9408	9288	9274	9376	1.3	9130	2.7
Be	1009	997	974	1046	1107	1016	990	1020	4.4	1076	-5.2	2046	2088	2051	2035	2055	1.1	2170	-5.3
Sc	33230	33120	32330	32840	32720	33570	32560	32910	1.3	31830	3.4	34650	34550	34450	33730	34345	1.2	33530	2.4
V	337040	332500	327500	332600	318600	326100	310200	326363	2.8	318200	2.6	414000	409900	409400	415200	412125	0.7	417600	-1.3
Cr	283100	280900	306300	312700	304800	277300	296630	294533	4.8	287200	2.6	16430	16490	16410	16080	16353	1.1	15850	3.2
Co	45930	45520	46740	47360	45670	45300	44700	45889	2.0	44890	2.2	39410	38260	38740	37750	38540	1.8	37330	3.2
Ni	119100	118700	121100	123700	118300	118100	116700	119386	1.9	119800	-0.3	11830	11980	11890	11860	11890	0.5	12570	-5.4
Cu	127600	128800	127200	128700	123200	124100	123000	126086	2.0	129300	-2.5	16850	14420	16410	15500	15795	6.8	19660	-19.7
Zn	99630	102000	98980	100900	97180	97390	96450	98933	2.1	103900	-4.8	130000	142400	135400	130400	134550	4.3	129500	3.9
Ga	21620	21610	21870	21950	21300	21220	20780	21479	1.9	21370	0.5	22340	22120	22220	21500	22045	1.7	22070	-0.1
As	952	1038	993	1052	1003	941	1003	997	4.1	700	42.5	659	679	661.5	634	658	2.8	860	-23.5
Rb	9375	9341	9555	9596	9333	9203	9175	9368	1.7	9261	1.2	48780	48020	48330	47360	48123	1.2	46020	4.6
Sr	405300	404900	408900	414000	443300	403900	434700	416429	3.8	394100	5.7	346800	346400	346400	335700	343825	1.6	337400	1.9
Y	24950	24950	25300	25700	24940	24430	24320	24941	1.9	25910	-3.7	34430	34320	34320	33020	34023	2.0	36070	-5.7
Zr	177800	179100	176600	179100	173900	173000	170500	175714	1.9	171200	2.6	188900	192200	190300	187900	189825	1.0	186500	1.8
Nb	18940	19060	19260	19570	18900	18510	18640	18983	1.9	18100	4.9	12490	12310	12300	12360	12365	0.7	12440	-0.6
Mo	3824	3236	3682	3453	3233	4588	7000	4145	32.4	4070	1.8	260400	259500	253500	262700	259025	1.5	250600	3.4
Ag	120	113	99	90	119	126	114	112	11.4	89	25.4	84	95	89.74	104	93	9.1	90	3.5
Cd	122	114	104	122	110	111	111	113	5.9	152	-25.5	183	193	174	213	191	8.7	690	-72.3
In	92	92	94	92	90	92	91	92	1.3	117	-21.5	101	99	98	100	99	1.4	70	42.1
Sn	2173	2202	1982	1882	2000	2105	1923	2038	6.1	1776	14.7	2549	2699	2587	2454	2572	3.9	2280	12.8
Sb	89	98	81	88	95	92	107	93	8.9	103	-9.8	289	306	317	279	298	5.7	302	-1.4
Cs	97	96	97	102	96	96	98	97	2.3	100	-2.3	1178	1144	1148	1133	1151	1.7	1160	-0.8
Ba	133000	133100	136340	138040	132600	131900	132800	133969	1.7	130900	2.3	696200	689700	681900	685700	688375	0.9	683900	0.7
La	15440	15400	15840	16060	15330	15330	15260	15523	2.0	15200	2.1	25460	25270	25110	25410	25313	0.6	25080	0.9
Ce	38520	38390	39000	40030	38520	38060	38080	38657	1.8	37530	3.0	52290	53150	53410	53320	53043	1.0	53120	-0.1
Pr	5436	5423	5568	5701	5412	5413	5457	5487	2.0	5339	2.8	7077	6905	6885	6956	6956	1.2	6827	1.9
Nd	24630	24580	25230	25700	24650	24440	24460	24813	1.9	24270	2.2	29870	28780	28790	28670	29028	1.9	28260	2.7
Sm	6159	6161	6278	6438	6042	6098	6045	6174	2.3	6023	2.5	6769	6619	6693	6585	6667	1.2	6547	1.8
Eu	2083	2081	2135	2188	2074	2062	2080	2100	2.1	2043	2.8	1983	1933	1961	1974	1963	1.1	1989	-1.3
Gd	6147	6178	6358	6468	6171	6125	6180	6232	2.1	6207	0.4	6966	6711	6818	6769	6816	1.6	6811	0.1
Tb	942	942	962	986	934	930	933	947	2.1	939	0.8	1080	1062	1064	1075	1070	0.8	1077	-0.6
Dy	5315	5335	5450	5487	5264	5260	5262	5339	1.8	5280	1.1	6572	6527	6633	6741	6618	1.4	6424	3.0
Ho	1006	1007	1032	1048	1001	997	996	1012	1.9	989	2.4	1368	1326	1357	1314	1341	1.9	1313	2.2
Er	2548	2553	2593	2653	2519	2508	2531	2558	2.0	2511	1.9	3738	3680	3599	3623	3660	1.7	3670	-0.3
Tm	343	343	348	355	340	336	339	343	1.8	335	2.5	548	543	529	534	538	1.6	534	0.8
Yb	1969	1965	1995	2054	1972	1950	1953	1980	1.8	1994	-0.7	3486	3377	3374	3365	3401	1.7	3392	0.3
Lu	276	277	283	284	273	270	271	276	1.9	275	0.5	518	508	496	507	507	1.7	505	0.4
Hf	4415	4412	4460	4543	4400	4356	4381	4424	1.4	4470	-1.0	4973	4913	4859	4833	4895	1.3	4972	-1.6
Ta	1145	1133	1194	1223	1168	1146	1159	1167	2.7	1154	1.1	770	764	762	766	765	0.4	785	-2.5
W	200	200	199	182	199	183	199	195	4.3	251	-22.5	415	418	411	429	418	1.8	465	-10.0
Ti	21	20	21	21	20	20	20	20	2.7	22	-6.9	264	260	255	254	258	1.7	267	-3.4
Pb	1494	1486	1382	1373	1349	1620	1558	1466	7.0	1653	-11.3	10010	10110	9800	9870	9948	1.4	10590	-6.1
Th	1184	1190	1190	1271	1187	1198	1174	1199	2.7	1224	-2.0	5807	5771	5761	5702	5760	0.8	5828	-1.2
U	429	430	431	439	426	425	422	429	1.3	412	4.1	1739	1738	1688	1699	1716	1.5	1683	2.0
Fe	87270	87110	88100	87280	85620	86430	86050	86837	1.0	87500	-0.8	98810	97140	97940	97520	97850	0.7	97700	0.2
Ti	16680000	16620000	16460000	16750000	16470000	16520000	16470000	16567143	0.7	16630000	-0.4	13380000	13820000	13650000	13760000	13652500	1.4	13685000	-0.2

*%bias calculated as $(\mu - x)/\mu \times 100$, where μ is the GeoReM abundance reported in Jochum et al. (2016) and x is the mean for each standard measured for the duration of this study

d: digestion number

m: measurement number

Appendix A.3: Lead isotope composition obtained for the solution standard NBS SRM-982 conducted during the measurements of LHB peat samples

Date	n	$^{208}\text{Pb}/^{206}\text{Pb}$	$\pm$	$^{207}\text{Pb}/^{206}\text{Pb}$	$\pm$	$^{208}\text{Pb}/^{204}\text{Pb}$	$\pm$	$^{207}\text{Pb}/^{204}\text{Pb}$	$\pm$	$^{208}\text{Pb}/^{204}\text{Pb}$	$\pm$
28-Jan-16	1	0.99999	0.00023	0.46701	0.00019	36.772	0.024	17.173	0.011	36.771	0.026
28-Jan-16	2	1.00045	0.00023	0.46701	0.00019	36.767	0.024	17.171	0.011	36.784	0.026
28-Jan-16	3	1.00006	0.00023	0.46735	0.00019	36.718	0.024	17.160	0.011	36.720	0.026
28-Jan-16	4	1.00019	0.00023	0.46691	0.00019	36.751	0.024	17.160	0.011	36.759	0.026
28-Jan-16	5	0.99979	0.00023	0.46732	0.00019	36.715	0.024	17.158	0.011	36.708	0.026
28-Jan-16	6	1.00054	0.00023	0.46716	0.00019	36.710	0.024	17.149	0.011	36.730	0.026
28-Jan-16	7	1.00010	0.00023	0.46708	0.00019	36.736	0.024	17.159	0.011	36.740	0.026
28-Jan-16	8	1.00018	0.00023	0.46680	0.00019	36.709	0.024	17.136	0.011	36.715	0.026
28-Jan-16	9	1.00025	0.00023	0.46687	0.00019	36.734	0.024	17.150	0.011	36.743	0.026
29-Jan-16	10	1.00020	0.00036	0.46714	0.00021	36.710	0.026	17.149	0.012	36.717	0.025
29-Jan-16	11	1.00028	0.00036	0.46716	0.00021	36.765	0.026	17.175	0.012	36.775	0.025
29-Jan-16	12	0.99956	0.00036	0.46679	0.00021	36.746	0.026	17.153	0.012	36.730	0.025
29-Jan-16	13	0.99997	0.00036	0.46697	0.00021	36.716	0.026	17.145	0.012	36.715	0.025
29-Jan-16	14	0.99999	0.00036	0.46707	0.00021	36.715	0.026	17.148	0.012	36.715	0.025
29-Jan-16	15	1.00031	0.00036	0.46701	0.00021	36.711	0.026	17.145	0.012	36.723	0.025
29-Jan-16	16	1.00064	0.00036	0.46761	0.00021	36.706	0.026	17.164	0.012	36.730	0.025
29-Jan-16	17	1.00090	0.00036	0.46727	0.00021	36.712	0.026	17.154	0.012	36.746	0.025
29-Jan-16	18	0.99984	0.00036	0.46681	0.00021	36.765	0.026	17.162	0.012	36.759	0.025
29-Jan-16	19	0.99983	0.00036	0.46717	0.00021	36.778	0.026	17.181	0.012	36.772	0.025
29-Jan-16	20	1.00060	0.00036	0.46704	0.00021	36.766	0.026	17.171	0.012	36.788	0.025
29-Jan-16	21	1.00004	0.00036	0.46690	0.00021	36.764	0.026	17.165	0.012	36.765	0.025
29-Jan-16	22	0.99997	0.00036	0.46724	0.00021	36.747	0.026	17.170	0.012	36.746	0.025
29-Jan-16	23	1.00012	0.00036	0.46701	0.00021	36.723	0.026	17.150	0.012	36.728	0.025
06-Feb-16	24	1.00028	0.00067	0.46728	0.00016	36.668	0.043	17.134	0.017	36.678	0.043
06-Feb-16	25	1.00027	0.00067	0.46707	0.00016	36.695	0.043	17.139	0.017	36.705	0.043
06-Feb-16	26	0.99974	0.00067	0.46724	0.00016	36.752	0.043	17.172	0.017	36.742	0.043
06-Feb-16	27	0.99897	0.00067	0.46689	0.00016	36.775	0.043	17.170	0.017	36.737	0.043
06-Feb-16	28	1.00065	0.00067	0.46724	0.00016	36.754	0.043	17.173	0.017	36.779	0.043
06-Feb-16	29	1.00105	0.00067	0.46700	0.00016	36.747	0.043	17.161	0.017	36.786	0.043
06-Feb-16	30	1.00022	0.00067	0.46693	0.00016	36.786	0.043	17.176	0.017	36.794	0.043
04-Mar-16	31	0.99978	0.00047	0.46723	0.00018	36.736	0.025	17.165	0.015	36.728	0.026
04-Mar-16	32	1.00080	0.00047	0.46716	0.00018	36.710	0.025	17.149	0.015	36.739	0.026
04-Mar-16	33	1.00064	0.00047	0.46699	0.00018	36.717	0.025	17.146	0.015	36.740	0.026
04-Mar-16	34	0.99967	0.00047	0.46709	0.00018	36.735	0.025	17.158	0.015	36.723	0.026
04-Mar-16	35	0.99986	0.00047	0.46683	0.00018	36.716	0.025	17.140	0.015	36.711	0.026
04-Mar-16	36	0.99972	0.00047	0.46694	0.00018	36.732	0.025	17.151	0.015	36.721	0.026
04-Mar-16	37	1.00041	0.00047	0.46690	0.00018	36.773	0.025	17.170	0.015	36.788	0.026
04-Mar-16	38	1.00047	0.00047	0.46731	0.00018	36.760	0.025	17.179	0.015	36.778	0.026
04-Mar-16	39	0.99941	0.00047	0.46704	0.00018	36.772	0.025	17.174	0.015	36.751	0.026
04-Mar-16	40	0.99991	0.00047	0.46736	0.00018	36.769	0.025	17.184	0.015	36.765	0.026
22-Jul-16	41	1.00016	0.00013	0.46698	0.00014	36.764	0.015	17.165	0.005	36.748	0.019
22-Jul-16	42	0.99994	0.00013	0.46727	0.00014	36.734	0.015	17.162	0.005	36.709	0.019
22-Jul-16	43	0.99999	0.00013	0.46714	0.00014	36.753	0.015	17.165	0.005	36.730	0.019
28-Jul-16	44	1.00016	0.00023	0.46725	0.00028	36.734	0.009	17.160	0.008	36.717	0.007
28-Jul-16	45	1.00026	0.00023	0.46733	0.00028	36.744	0.009	17.167	0.008	36.730	0.007
28-Jul-16	46	0.99983	0.00023	0.46681	0.00028	36.752	0.009	17.152	0.008	36.722	0.007
28-Jul-16	47	1.00002	0.00028	0.46691	0.00017	36.724	0.022	17.147	0.014	36.724	0.018
28-Jul-16	48	0.99977	0.00028	0.46696	0.00017	36.729	0.022	17.151	0.014	36.720	0.018
28-Jul-16	49	1.00023	0.00028	0.46720	0.00017	36.729	0.022	17.160	0.014	36.737	0.018
28-Jul-16	50	0.99985	0.00028	0.46714	0.00017	36.748	0.022	17.167	0.014	36.743	0.018
28-Jul-16	51	1.00057	0.00028	0.46721	0.00017	36.710	0.022	17.151	0.014	36.731	0.018
28-Jul-16	52	0.99987	0.00028	0.46741	0.00017	36.752	0.022	17.178	0.014	36.747	0.018
28-Jul-16	53	0.99973	0.00028	0.46729	0.00017	36.775	0.022	17.185	0.014	36.766	0.018
28-Jul-16	54	1.00019	0.00028	0.46706	0.00017	36.762	0.022	17.170	0.014	36.769	0.018
TCD mean	57	1.00012	0.00038	0.46710	0.00018	36.740	0.026	17.161	0.013	36.741	0.026
ppm precision			380		388		698		730		703
ppm accuracy			-44		25		-95		-93		-209
Baker et al. (2004)	59	1.00016	0.00002	0.46708	0.00002	36.743	0.002	17.162	0.002	36.749	0.002

Appendix C: Principal Component Analysis (PCA) for LHB peat core

To Rosca *et al.* "Trace element and Pb isotope fingerprinting of atmospheric pollution sources: A case study from the east coast of Ireland"

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A principal component analysis (PCA) was conducted for the LHB dataset applying the statistical software package PAST 3 developed by Hammer *et al.* (2001). Three components, i.e. factors with eigenvalues >1 explain 99.75% of the total variance. Principal component (PC) 1 accounts for the largest variance (92.7%) and is strongly dominated by Pb, as well as other metals such as Sb, Sn, Cu, Ni, Ag, Cd (Fig. 1a und b). The relative loadings suggest small additional association of Zn and Ti with PC1 (Fig. 2a). The strong association of elements attributed to PC1 with Pb, as well as their occurrence as impurities in the Pb-Zn and Cu mineralisation of the Wicklow uplands point towards a common source, namely the mining and smelting activities in the area. This is supported by the highest abundance of PC 1 observed in the peat segment accumulated during the mining period (first half of the 20th century, Fig. 3a).

Principal component 2 accounts for 4.4% of the total variance and its strongest association is seen with Ti (82%, Fig. 2b). Further elements which fall within this group are Zr, Th, Sc, Ta, Nb, Hf, As, and the REE's (Fig. 1a and b). Apart from As, which can have a i) bacterial, ii) mining dust, or iii) mobility related origin, all these immobile elements are associated with (different) mineralogical phases aerially transported onto the peat. These elements are thus good indicators of geogenic dust transport. PC 2 is successfully detected in the peat accumulated before and after the major mining period (Fig. 3b). It is however highly possible that the strong mining signal present between 1900 and 1964 AD (Fig. 3a) has masked the lower-loaded component 2. The highest loading of Ti within PC2 would suggest that Ti the best dust indicator. However, the strong association of this element with both PC1 (local mining-smelting) and PC3 complicates the deconvolution of its origin. Therefore, a different approach must be followed to select a lithogenic element for the correction of the natural dust input into the investigated bog.

Principal component 3 accounts for 2.7% of the total variance and includes the elements Mo, Ni, V, Cr as well as Rb, Sr, Ba, Fe, and Zn. Associated with 79% of its total load, Zn is the most dominant element (Fig. 2c). It thus appears that the overall Zn load is shared between PC1 and PC3, with a significantly stronger association with PC3. This is an interesting finding which suggests that Zn pollution in LHB peat is not governed by the local mining and smelting of Pb-Zn ores (PC1). The increasing load of PC3 in the upper part of the core, from 1940 AD (CR.2.1) towards present (Fig. 3c) indicates the rising significance of a recent pollution source, enriched not only in Zn, but also in other transition metals listed above. The origin of PC3 is carefully attributed to the emissions from fossil fuels, which are discussed in more detail in the manuscript (section 4.3 to 4.5) by deploying additional tools such as Pb isotopes and element enrichment factors (EF).

Figure 1: Principal component analysis (PCA) **Figure 2:** Dominant element loadings for each component

Figure 2: continued

Figure 3: Loading of principal components: samples-ages (AD)

Appendix D: Continuation of the modelling in section 4.4. Pollution phase 2a (25-5 cm, ~1900-2000 AD)

To Rosca *et al.* "Trace element and Pb isotope fingerprinting of atmospheric pollution sources: A case study from the east coast of Ireland"

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The different theoretical mixing curves (hyperbolas) between the two end-members were weighted by concentrations and calculated using following formulas:

$$[4] \quad (^{206}\text{Pb}/^{204}\text{Pb})_{\text{mix}} = f_b[\text{Pb}_1]_b * (^{206}\text{Pb}/^{204}\text{Pb})_b + (1-f_b)[\text{Pb}_2]_a * (^{206}\text{Pb}/^{204}\text{Pb})_a / f_b[\text{Pb}_1]_b + (1-f_b)[\text{Pb}_2]_a$$

$$[5] \quad (^{207}\text{Pb}/^{204}\text{Pb})_{\text{mix}} = f_b[\text{Pb}_1]_b * (^{207}\text{Pb}/^{204}\text{Pb})_b + (1-f_b)[\text{Pb}_2]_a * (^{207}\text{Pb}/^{204}\text{Pb})_a / f_b[\text{Pb}_1]_b + (1-f_b)[\text{Pb}_2]_a$$

where $[\text{Pb}_1]$ or $[\text{Pb}_2]$ are the concentrations ranging between 10 and 200 $\mu\text{g/g}$, a and b are the Pb isotope values of the respective end-members: pollutant 1 – local mining ($^{206}\text{Pb}/^{204}\text{Pb} = 18.30$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.62$, Kennan *et al.*, 1987), and pollutant 2 – average values for leaded gasoline ($^{206}\text{Pb}/^{204}\text{Pb} = 17.20$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.54$, estimated using values compiled by Komarek *et al.*, 2008). f_b represents the fraction of the end-members (pollutants) involved in the mixing, with $f_a + f_b = 1$.

Eliminating f_b from the mixing equations gives:

$$[6] \quad A(^{206}\text{Pb}/^{204}\text{Pb})_{\text{mix}} + B(^{206}\text{Pb}/^{204}\text{Pb})_{\text{mix}} * (^{207}\text{Pb}/^{204}\text{Pb})_{\text{mix}} + C(^{207}\text{Pb}/^{204}\text{Pb})_{\text{mix}} + D = 0 \text{ where,}$$

$$[7] \quad A = [\text{Pb}_1]_b * [\text{Pb}_2]_a * (^{207}\text{Pb}/^{204}\text{Pb})_b - [\text{Pb}_1]_a * [\text{Pb}_2]_b * (^{207}\text{Pb}/^{204}\text{Pb})_a$$

$$[8] \quad B = [\text{Pb}_1]_a * [\text{Pb}_2]_b - [\text{Pb}_1]_b * [\text{Pb}_2]_a$$

$$[9] \quad C = [\text{Pb}_1]_b * [\text{Pb}_2]_a * (^{206}\text{Pb}/^{204}\text{Pb})_a * [\text{Pb}_1]_a * [\text{Pb}_2]_b * (^{207}\text{Pb}/^{204}\text{Pb})_b$$

$$[10] \quad D = [\text{Pb}_1]_a * [\text{Pb}_2]_b - (^{207}\text{Pb}/^{204}\text{Pb})_a * (^{206}\text{Pb}/^{204}\text{Pb})_b - [\text{Pb}_1]_b * [\text{Pb}_2]_a * (^{207}\text{Pb}/^{204}\text{Pb})_b * (^{206}\text{Pb}/^{204}\text{Pb})_a$$

a = respective composition of pollutant 1 (mining), and b = respective composition of pollutant 2 (Pb-gasoline)

$[\text{Pb}_1]$ = concentration of the 1st pollutant, $[\text{Pb}_2]$ = concentrations of the 2nd pollutant

Term B gives the curvature index

Table 1: Ta concentrations (ppb), Pb isotope ratios and deposition rates, together with enrichment factors (EF) of Pb, Cu, Zn, and Sb along the examined LHB peat core

Sample ID	Depth from the surface (cm)	²⁰⁷ Pb/ ²⁰⁴ Pb	±2σ	²⁰⁶ Pb/ ²⁰⁴ Pb	±2σ	²⁰⁶ Pb/ ²⁰⁷ Pb	±2σ	Pb dep. rates ^a	Pb EF	Cu EF	Zn EF	Sb EF	Ta ppb
LHB1.3	0 to 1	15.613	0.007	17.930	0.007	1.148	0.007	0.08	1	5	39	5	11
LHB2.3	1 to 2	15.601	0.007	17.841	0.007	1.144	0.007	0.25	1	4	36	6	21
LHB3.3	2 to 3	15.581	0.007	17.795	0.007	1.142	0.007	0.10	2	5	42	7	8
LHB4.3	3 to 4	15.581	0.007	17.776	0.007	1.141	0.007	0.07	1	5	41	8	7
LHB5.3	4 to 5	15.603	0.007	17.746	0.007	1.137	0.007	0.15	2	7	39	7	9
LHB6.3	5 to 6	15.570	0.007	17.678	0.007	1.135	0.007	0.37	2	9	41	14	13
LHB7.3	6 to 7	15.546	0.007	17.657	0.007	1.136	0.007	0.58	2	6	33	14	20
LHB1.1	7 to 8	15.548	0.010	17.659	0.012	1.136	0.011	0.46	4	5	35	10	12
LHB1.2	8 to 9	15.556	0.011	17.719	0.013	1.139	0.012	0.23	7	5	38	14	11
LHB2.2	9 to 10	15.560	0.011	17.715	0.013	1.139	0.012	1.20	8	6	37	16	18
LHB3.2	10 to 11	15.566	0.011	17.712	0.013	1.138	0.012	0.78	6	7	35	23	18
LHB4.2	11 to 12	15.575	0.011	17.752	0.013	1.140	0.012	1.16	11	7	35	18	23
LHB5.2	12 to 13	15.573	0.011	17.872	0.013	1.148	0.012	1.17	13	6	32	20	27
LHB6.2	13 to 14	15.601	0.011	17.900	0.013	1.147	0.012	1.83	17	8	36	35	25
LHB2.1	14 to 15	15.584	0.011	18.028	0.013	1.157	0.012	1.40	18	7	33	51	18
LHB7.2	15 to 16	15.610	0.011	18.123	0.013	1.161	0.012	1.38	17	8	27	48	22
LHB8.2	16 to 17	15.601	0.011	18.195	0.013	1.166	0.012	0.70	15	9	23	44	27
LHB9.2	17 to 18	15.611	0.011	18.271	0.013	1.170	0.012	1.73	18	10	24	51	32
LHB10.2	18 to 19	15.621	0.011	18.314	0.013	1.172	0.012	0.71	18	9	22	39	26
LHB11.2	19 to 20	15.624	0.011	18.318	0.013	1.172	0.012	1.25	18	9	19	29	33
LHB12.2	20 to 21	15.631	0.011	18.351	0.013	1.174	0.012	1.16	16	10	18	23	33
LHB13.2	21 to 22	15.622	0.011	18.335	0.013	1.174	0.012	0.80	17	12	20	22	27
LHB3.1	22 to 23	15.631	0.011	18.350	0.013	1.174	0.012	0.43	14	9	20	15	23
LHB14.2	23 to 24	15.610	0.011	18.341	0.013	1.175	0.012	-	15	6	22	10	14
LHB15.2	24 to 25	15.635	0.011	18.379	0.013	1.176	0.012	-	14	6	25	11	10
LHB16.2	25 to 26	15.614	0.011	18.377	0.013	1.177	0.012	-	11	3	23	7	13
LHB17.2	26 to 27	15.618	0.010	18.366	0.012	1.176	0.011	-	11	3	23	5	14
LHB18.2	27 to 28	15.610	0.010	18.354	0.012	1.176	0.011	-	7	2	17	4	21
LHB19.2	28 to 29	15.616	0.010	18.384	0.012	1.177	0.011	-	7	2	16	3	16
LHB20.2	29 to 30	15.602	0.011	18.351	0.013	1.176	0.012	-	8	2	14	3	23
LHB21.2	30 to 31	15.624	0.010	18.383	0.012	1.177	0.011	-	6	2	15	3	17
LHB22.2	31 to 32	15.618	0.010	18.364	0.012	1.176	0.011	-	6	2	12	3	19
LHB4.1	32 to 33	15.605	0.010	18.367	0.012	1.177	0.011	-	5	2	12	3	16
LHB23.2	33 to 34	15.627	0.010	18.366	0.012	1.175	0.011	-	5	2	12	3	16
LHB24.2	34 to 35	15.602	0.011	18.361	0.013	1.177	0.012	-	4	2	10	2	13
LHB5.1	42 to 43	15.603	0.010	18.385	0.012	1.178	0.011	-	4	1	7	2	15
LHB6.1	52 to 53	15.612	0.010	18.385	0.012	1.178	0.011	-	1	1	2	2	21
LHB7.1	62 to 63	15.631	0.010	18.429	0.012	1.179	0.011	-	1	1	1	1	20
LHB8.1	72 to 63	15.633	0.010	18.400	0.012	1.177	0.011	-	1	1	1	1	16
LHB9.1	82 to 83	15.631	0.010	18.378	0.012	1.176	0.011	-	1	1	1	1	14
LHB10.1	94 to 95	15.626	0.010	18.346	0.012	1.174	0.011	-	0	1	1	0	15

Enrichment Factors (EF) for the element are with respect to the baseline in the area.

^a Calculated Pb deposition rates are indicated in $\mu\text{g} / \text{cm}^2 \text{ yr}^{-1}$

Table 2: Lead isotope composition of USGS rock reference materials used for assessing accuracy of measurements

Standard	Reference	²⁰⁷ Pb/ ²⁰⁴ Pb	±2σ	²⁰⁶ Pb/ ²⁰⁴ Pb	±2σ
NBS-982 ^a	<i>this study (av)</i>	17.159	0.011	36.736	0.015
	<i>Baker et al (2004)</i>	17.162	0.002	36.743	0.002
BCR-2 ^b	<i>this study (av)</i>	15.630	0.007	18.768	0.012
	<i>Baker et al (2004)</i>	15.628	0.005	18.765	0.011
	<i>Woodhead and Hergt (2000)</i>	15.615	0.003	18.750	0.011
BHVO-2 ^b	<i>this study (av)</i>	15.542	0.014	18.649	0.013
	<i>Baker et al (2004)</i>	15.540	0.015	18.649	0.019
	<i>Woodhead and Hergt (2000)</i>	15.538	0.009	18.641	0.011

a= the average of the NBS-982 average (av) is based on 54 analyses

b= BLHB-2 and BHVO-2 (av) values are based on 6 individual analyses

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Rosca et al. **Highlights**

- Detailed >100 year reconstruction of atmospheric metal pollution in Ireland
- Combined use of high-precision trace element, Pb-isotope and radionuclide data
- Discovery of severe environmental pollution from mining and smelting
- 20th century recovery from pollution of Pb and certain other metals
- But persisting or increasing atmospheric pollution in many other metals