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Atmospheric deposition and isotope biogeochemistry of zinc in ombrotrophic peat

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Abstract

Zinc isotope ratios were measured in the top sections of dated ombrotrophic peat cores in Finland to investigate their potential as proxies for atmospheric sources and to constrain post depositional processes affecting the geochemical record. The peat deposits were located in Hietajärvi, a background site well away from any point pollution source and representing 'background' conditions, in Outokumpu, next to a mining site, and in Harjavalta, next to a smelter. Measured total concentrations, calculated excess concentrations and mass balance considerations suggest that zinc is subjected to important biogeochemical cycling within the peat. Significant isotopic variability was found in all three peat bogs, with heavier zinc in the deeper and lighter zinc in the upper sections. Isotope ratios and concentrations correlated in the two peats located next to dominant point sources, *i.e.* the smelting and mining site, suggesting that zinc isotopes trace pollution sources. Concentration and isotope peaks were offset from the period of mining and smelting activity, supporting migration of zinc down the profile. The $\delta^{66}Zn_{JMC}$ (where $\delta^{66}Zn = [(^{66}Zn/^{64}Zn)_{sample}/(^{66}Zn/^{64}Zn)_{JMC\text{-}standard} - 1] \times 10^3$) of the top section sample at the remote Hietajärvi site was 0.9‰ and we suggest this represents the regional background isotope signature of atmospheric zinc. The deeper sections of the peat cores show isotopically heavier zinc than any potential atmospheric source, indicating that post depositional processes affected the isotopic records. The large variations encountered (up to 1.05‰ for $\delta^{66}Zn$) and Rayleigh modelling imply that multiple fractionation of zinc during diagenetic alterations occurs and nutrient recycling alone cannot explain the fractionation pattern.

We propose that zinc isotopes are amenable to identify different atmospheric zinc sources, including zinc derived from anthropogenic activities such as mining and smelting, but multiple biogeochemical processes seriously affect the record and they need to be evaluated and assessed carefully if zinc isotopes are used in terrestrial paleorecords.

1. INTRODUCTION

Radiogenic and light stable isotopes applied to terrestrial and marine paleorecords have been key to our understanding of a range of Earth surface processes and the characterisation of past chemical, biological and physical environmental conditions (Dickin, 1995; Alley, 2001; Reuer and Weiss, 2002; Banner, 2004; Hoefs, 2004). Ombrotrophic peats proved particularly for the study of global atmospheric trace element cycling useful as they record exclusively atmospheric deposition and cover approximately 5% of the terrestrial surface area (Bindler, 2006). This enables to gauge trace element deposition at high and low latitudes and thus to address fundamental

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questions with respect to climate change (Pendall et al., 2001; Kylander et al., 2007), global biogeochemical element cycling (Klaminder et al., 2003), atmospheric pollution and long range pollutant transport (Dunlap et al., 1999; Bindler, 2006).

Improvements in inorganic mass spectrometry (Walder et al., 1995) have enabled us to apply stable isotope variations of elements heavier than 40 amu to fundamental problems in earth and environmental science alike, and today, the isotopic variability of Fe, Zn, Cu, Cd, Tl, Se and many other elements is increasingly well known (Johnson et al., 2004; Dauphas and Rouxel, 2006). Field and laboratories studies have helped to constrain biogeochemical controls of isotopic fractionation (Anbar, 2004; Ehrlich et al., 2004; Weiss et al., 2005; Guelke and von Blankenburg, 2007) and applications to ore deposit studies (Wilkinson et al., 2005; Markl et al., 2006), soil and continental weathering (Fantle and DePaolo, 2004; Thompson et al., 2007), past and present biogeochemical cycling (Maréchal et al., 2000; Ellis et al., 2002; Beard et al., 2003a; Beard et al., 2003b; Berquist and Boyle, 2006; Viers et al., 2007) and environmental pollution (Mattielli et al., 2005; Cloquet et al., 2006a,b; Dolgopolova et al., 2006) are promising.

Using zinc isotopes in studies of atmospheric cycling and of paleorecords is of particular interest for two reasons. First, zinc is one of the major global pollutants in the atmosphere (Pacyna and Pacyna, 2001) and significant zinc enrichment from atmospheric deposition was detected even in remote arctic areas (Simonetti et al., 2000). If zinc isotopes could distinguish natural from anthropogenic sources, this would be a major advancement in environmental impact studies. Second, zinc is an essential nutrient in marine ecosystems (Morel and Price, 2003) and changes in the isotopic composition of zinc in seawater during the geological past as recorded in sediments could be linked to paleoproductivity and enable the study of timing and extent of climatic changes.

A number of studies have indeed been conducted to date to explore these potentials. Dolgopolova et al. (2006) measured the zinc isotope signatures in lichen around a mining and mineral processing plant in Russia and showed that the zinc dispersed in the local environmental derived from the anthropogenic activities and not from the local soil dust (Dolgopolova et al., 2006). Luck et al. (1999) reported variations of $\delta^{66}Zn$ in rainwater and potential contributing sources such as rocks (natural) and chemicals (anthropogenic) and found significant correlation between isotope composition and zinc content (Luck et al., 1999). Mattielli et al. (2005) characterised zinc and copper isotopically in two metallurgical plants and found continuous and significant enrichment in light zinc isotopes along the metallurgical process (Mattielli et al., 2005). Cloquet et al. (2006a) found significant variability of $\delta^{66}Zn$ in epiphytic lichens but the signatures were largely indistinguishable from potential sources such as urban aerosols or flue gases from the waste combustor (Cloquet et al., 2006a). Tanimizu et al. (2002) found mass dependent fractionation of up to 0.12% pamu in high purity metal zinc, likely inherited from the purification process, and suggested that industrial zinc could be isotopically very different from natural zinc (Tanimizu et al., 2002). Pichat et al. (2003) measured the zinc isotope composition of the carbonate fraction of sediment core ODP 849, leg 138, and found that $\delta^{66}Zn_{JMC}$ ranged from 0.32 to 1.34‰ with several marked peaks and high frequency variability. Periodicities of 35.2 and 21.2 ka were found and it was suggested that the latter could be linked to the precession of the Earth's axis of rotation (Pichat et al., 2003). And finally, Bermin et al. (2006) presented an isotope profile of dissolved zinc from the NE Pacific and suggested that the observed variability reflected biological recycling (Bermin et al., 2006).

A major concern in applying isotope systems such as zinc in the sedimentary record is the possible effect of diagenetic alteration. Previous work showed or suggested significant fractionation of zinc isotopes in the low temperature environment due to adsorption on organic and inorganic surfaces (Weiss et al., 2005; Pokrovsky et al., 2005b; Gélabert et al., 2006), uptake by micro organisms and higher plants (Stenberg et al., 2004; Weiss et al., 2005; Bermin et al., 2006; Gélabert et al., 2006), variable speciation (Maréchal and Albarède, 2002; Weiss et al., 2005), ion exchange (Maréchal and Albarède, 2002), diffusion (Rodushkin et al., 2004) and primary and secondary mineralization (Mason et al., 2005; Wilkinson et al., 2005).

The aim of the present study was to evaluate the potential of zinc isotopes to identify atmospheric sources and to examine possible post-depositional processes in peat bogs. To achieve this, we analysed the top sections from three bogs in Finland situated in the vicinity of a smelter plant, a mining site and an area isolated from industrial activity to separate possible local point source and background atmospheric contributions.

2. MATERIALS AND METHODS

2.1. Study sites and sampling

Peat cores were taken from undisturbed *Sphagnum* dominated ombrotrophic peat bogs at Hietajärvi (Hj), Outokumpu (Out) and Harjavalta (Har) (Fig. 1). Detailed descriptions of the sampling sites and the geochemical assessments of the cores are given elsewhere (Ukonmaanaho et al., 2004; Rausch et al., 2005a). The Hietajärvi site was located in the Patvinsuo National Park, eastern Finland, with no anthropogenic activities or roads in the vicinity and no point sources of atmospheric metal pollution within a radius of tens of kilometres. The Outokumpu sampling site was located in the Viurusuo mire complex in eastern Finland, 8 km southwest of the town of Outokumpu. A Cu–Ni mine and a concentration plant operated from 1910 until the 1980s, and a small copper refining plant operated from 1913 until 1929 (Kuisma, 1985). At the Harjavalta site, samples were taken from a peat bog in the Pyhäsuo mire complex, 6 km northeast of Harjavalta, south-western Finland, where a copper smelter has been in operation since 1945 and a nickel smelter since 1959 but significant emissions ceased during the 1980s due to stringent emission controls (Nieminen, 2005; Rausch et al., 2005b).

Peat from each site was sampled using a Ti-Wardenaar corer. The cores were immediately frozen and shipped to

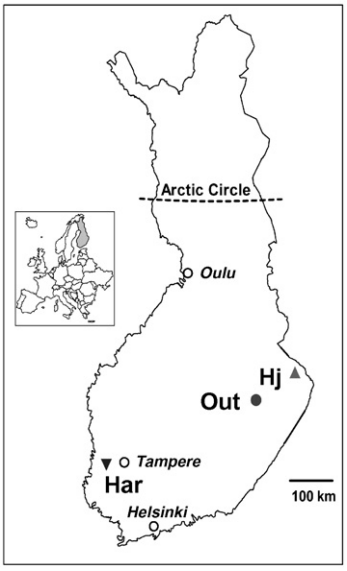

Fig. 1. Map of Finland with locations of sampling sites: Hietajärvi (Hj, background site), Outokumpu (Out, mining site) and Harjavalta (Har, smelting site).

the laboratory, where they were cut into one cm slices with a stainless steel band saw. The edges of each slice were removed and the residual peat was dried at 105 °C in Teflon bowls and milled with a Ti centrifugal mill equipped with a 0.25 mm sieve. The distribution of copper, nickel and zinc in the Outokumpu and Harjavalta cores is similar to the distribution seen in replicate cores (Ukonmaanaho et al., 2004).

Vegetation samples were collected from the different sites during summer 2003. The following plant types were collected: *Sphagnum* sp. (mosses), *Eriophorum vaginatum* (monocotyledons), cloud berry (*Rubus chamaemorus*) and dwarf shrubs (both dicotyledones). Samples were taken randomly, placed into dry plastic bags and returned to the laboratory where they were dried at room temperature. Vegetation samples were powdered to <100 μm particles using a cyclone mill. Representative rocks and ore samples from the Outokumpu ore deposit were selected from the Imperial College London rock archive. Sub-samples were cut from specimens using a diamond saw and crushed to pieces 5 mm in diameter or less using a jaw crusher. Samples were then ground to a fine powder (<100 μm) using a TEMA mill.

2.2. Sample preparation

Peat samples were digested at the University of Heidelberg in duplicate using 250 mg of milled material and a microwave heated high pressure autoclave (ultraCLAVEII, MLS) employing high purity reagents (sub-boiled HNO_3, H_2O_2, and HBF_4). Details are given elsewhere (Krachler et al., 2003). Plant and geological samples, together with in-house reference materials and international standard reference materials (HRM1 HRM 2, NBS2711 for soils; HRM11, HRM14, and GBW07602 for plants), were digested using 250 and 100 mg respectively, in the laboratories at Imperial College London and the Natural History Museum. Samples were digested on a hot block using HNO_3–$HClO_4$–HF (geological material) and HNO_3-$HClO_4$ (vegetation) acid mixtures (Thompson and Walsh, 1989).

2.3. Zinc isotope analysis

2.3.1. Reagents and materials

All reagents were prepared using >18.2 MΩ H_2O from a Milli-Q system (Millipore Corporation, Bedford, MA, USA). Aristar grade reagents (VWR, Poole, UK) or ultra-pure reagents (ROMIL Ltd., Cambridge, UK) were used for sample digestion and ion exchange chemistry, depending on zinc concentrations in the samples, and ultra-pure acids (ROMIL Ltd., Cambridge, UK) were used during mass spectrometry. A 1000 μg Zn/ml metal solution (IMP Zn), gravimetrically prepared from Johnson Matthey Purotronic zinc metal (Batch NH 27040), was used as the in-house zinc isotopic standard. A 1000 μg Cu/ml single element copper solution (IMP Cu) from ROMIL Ltd., Cambridge, UK, was used as internal mass discrimination monitor and to correct for mass bias effects of the matrix during isotope measurements. In addition, a 1000 μg Cu/ml solution prepared from NIST-SRM 976 metal was used for the validation of the mass bias correction procedure (see details below).

2.3.2. Chemical separation using ion exchange chromatography

Matrix components were separated from zinc prior to isotope analysis using anion exchange chromatography (Table 1). Bio-Rad PolyPrep columns were filled with 2.0 ml of the anion exchange resin AG MP-1 (100–200 mesh size) in chloride form. The elution procedure used was based on one described previously (Chapman et al., 2006) but, to reduce the procedural blank, the Fe and Cu fractions were collected together. This cut down the total acid volume from 57 to 38 ml. Recoveries were carefully monitored and yielded >98%. Following the column procedure, recovered Zn fractions were evaporated to dryness and residual chloride and bromide ions driven off by re-evaporating in 10 μl ultra-pure conc. HNO_3. Samples were subsequently dissolved in 0.05% (v/v) ultra-pure HNO_3 and spiked with ROMIL Cu or NIST 976 Cu. Sample and standard solutions were concentration matched to within ±5%. All column separates were analysed using ICP-AES to identify problematic contaminants.

Table 1
Ion-exchange procedure for separating zinc from peat, plant and geological matrices prior to the multi collector-ICP-MS isotope analysis

Step	Fraction	Acid
1	Pre-treatment	6 ml 7 M HCl
2	Sample loading	1 ml 7 M HCl
3	Matrix removal	6 ml 7 M HCl
4	Fe and Cu fraction	15 ml 2 M HCl
5	Zn fraction	10 ml 0.1 M HBr + 0.5 M HNO_3

2.3.3. Instrumentation and measurement protocols

Zinc isotope measurements were made using a former GVi *IsoProbe* at the Natural History Museum, London. Analyses were undertaken using a static measurement protocol at a spectral resolution of M/ΔM = 500, with $^{63}Cu^{+}$, $^{64}Zn^{+}$, $^{65}Cu^{+}$, $^{66}Zn^{+}$, $^{67}Zn^{+}$ and $^{68}Zn^{+}$ being measured on Faraday detectors. Nickel and barium contributions were determined by monitoring mass 60 ($^{60}Ni^{+}$) and mass 67.5 ($^{135}Ba^{2+}$) with a channeltron ion counter and a Faraday collector, respectively. The channeltron ion counter was calibrated to the Faraday array by switching between L2 Faraday and the ion counter during the given measurement session. For all analyses, sample-related nickel and barium contributions were insignificant relative to the reproducibility of the measurements.

A micro-uptake T1-H type nebuliser with an Aridus membrane desolvation system (CETAC Inc., Omaha, NE, USA) was used for sample introduction. The ^{63}Cu and ^{64}Zn ion beams were typically above 4 V. Sample, standard and acid blank analyses comprised 25 consecutive five-second integrations. Instrumental baselines were corrected using an on-peak acid blank correction whereby the average signal for a 0.05% (v/v) ultra-pure HNO_3 solution, analysed prior to each sample, was subtracted from the mass spectrum of the associated sample or standard run. The instrumental settings are given in Table 2.

Mass discrimination effects were corrected using a combined sample-standard bracketing (SSB) and inter-element correction procedure, also termed 'modified SSB' (Mason et al., 2004b). Initially, bracketing standards (IMP Zn + IMP Cu) are used to correct mass discrimination in unknown samples using

$$\delta^{x}Zn = \left[\left(\frac{\left(\frac{^{x}Zn}{^{64}Zn}\right)_{sample}}{\frac{1}{2}\left[\left(\frac{^{x}Zn}{^{64}Zn}\right)_{standard_1} + \left(\frac{^{x}Zn}{^{64}Zn}\right)_{standard_2}\right]}\right) - 1\right] \times 1000 \quad (1)$$

where the subscripts sample and standard denote the unknown sample, and bracketing standards (IMP Zn), respectively, and X represents the mass of the isotope being measured (i.e., 66 or 68).

This procedure does not account for non-linear mass discrimination drift, nor sample matrix induced mass discrimination effects. Consequently, $^{65}Cu/^{63}Cu$ data collected on the copper spike were used for a second correction step, in which a $\delta^{65}Cu$ value was calculated for each unknown sample using an analogous form of Eq. (1) and then subtracted from each associated $\delta^{X}Zn$ value as a multiple of the mass difference between the isotopes in that ratio.

This procedure assumes that different mass discrimination behaviour of copper and zinc per unified atomic mass unit and non linear mass discrimination variations across the copper-zinc mass do not affect the accuracy of the data. To test this, we measured a suite of peat and plant samples spiked with NBS Cu 976 (certified ratio for $^{65}Cu/^{63}Cu$ is 0.4456 ± 0.0021, (Shields et al., 1964)) and corrected the instrumental bias using the external normalization approach (Maréchal et al., 1999; Ohno et al., 2005; Stenberg et al., 2004).

As seen in Fig. 2, the instrumental mass bias (f) of Zn and Cu are not identical (theoretical slope of 0.9840 using ln(65/63) as x-axes) but the relationship of f_{Cu} and f_{Zn} is constant over the analytical measurement session and best described using the exponential law. Using the linear relationship (slope = (f_{Cu}/f_{Zn})[ln(65/63)/ln(66/64)]) and the measured $^{65}Cu/^{63}Cu$ ratios of the NBS Cu 976 in the spiked samples and standards, we corrected the mass bias of the zinc and calculated the corresponding $\delta^{66}Zn_{IMP}$. As Table 3 shows, $\delta^{66}Zn$ (relative to JMC Zn) of peat and plants corrected with the modified SSB or external normalisation approach agree within error. Hence, inaccuracies associated with the assumptions made using the modified SSB approach are smaller than if copper were used directly to correct for mass discrimination using only an inter-element correction, and are deemed insignificant relative to the levels of reproducibility attained during the study.

2.3.4. Data presentation

All results are reported relative to the Lyon group standard JMC 3-0749L Zn. $\delta^{66}Zn_{IMP}$ values relative to the working standard were converted to the widely used Lyon standard using the conventional conversion equation (Hoefs, 2004). The Lyon JMC 3-0749L standard has a $\delta^{66}Zn_{JMC}$ value of −0.087‰ (Mason et al., 2004b). Each solution was measured four times and the error (±2σ)

Table 2
Operation conditions of the *IsoProbe* during the measurement period

Instrument parameters	
Coolant Ar flow	14 l/min
Auxiliary Ar flow	1.0–1.4 l/min
Nebuliser Ar flow	0.69–0.80 l/min
Collision cell Ar flow	1.2–1.4 µl/min
Extraction voltage	−6000 V
Torch power	1336 W
Reflected power	<10 W
Cones	Ni sample cone and Ni skimmer cone
Nebuliser parameters	
Spray chamber temperature	+70 °C
Desolvator temperature	+160 °C
Ar sweep gas flow	2.5–3.5 l/min
Sample uptake rate	ca. 50 µl/min
Sensitivity	ca. 7 V/ppm for Cu and Zn

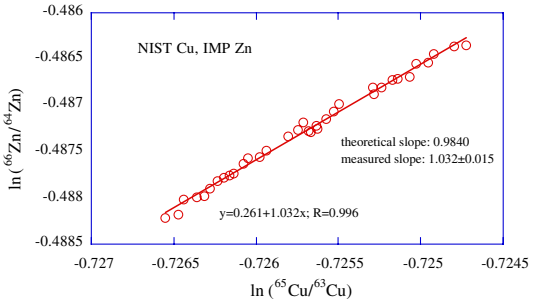

Fig. 2. ln($^{65}Cu/^{63}Cu$) versus ln($^{66}Zn/^{64}Zn$) plot constructed from isotope ratios collected on IMP Zn standards doped with NIST Cu to determine the relationship of f_{Cu} and f_{Zn}.

Table 3
$\delta^{66}Zn_{JMC}$ values (in ‰) for peat, plants and industrial standards and corrected for mass bias using direct sample standard bracketing correction (SSB), post-SSB Cu correction (Mason et al., 2004b) and external normalisation correction (Maréchal et al., 1999)

Sample ID	Sample type	$\delta^{66}Zn_{JMC}$ Direct SBB (‰)	$\pm 2\sigma$	$\delta^{66}Zn_{JMC}$ Modified SSB (‰)	$\pm 2\sigma$	$\delta^{66}Zn_{JMC}$ External normalisation (‰)	$\pm 2\sigma$
Romil Zn	Single element solution	−9.06	0.03	−8.98	0.07	−8.98	0.07
HJ 25 A1	Peat	1.50	0.05	1.54	0.02	1.53	0.02
HJ 32 A1	Peat	1.54	0.09	1.70	0.05	1.69	0.06
Rye grass BCR 281	Plant	0.99	0.08	0.78	0.10	0.81	0.10

was calculated using conventional error propagation. No outlier rejection scheme was applied. Selected peat samples were digested in duplicate to assess sample measurement reproducibility. Long-term instrumental reproducibility was monitored by running in-house single element solutions from Romil (Mason et al., 2004b; Chapman et al., 2006), which over the course of this study yielded a variation of 0.07‰ ($\pm 2\sigma$).

2.3.5. Quality control and assurance

In house and certified reference materials of plant, rock and single element solutions were measured to assess the accuracy of our measurements during the course of the study. We made repeated measurements of the USGS terrestrial basalt BCR-1 ($\delta^{66}Zn_{JMC} = 0.29 \pm 0.12$‰, (Chapman et al., 2006)), the in-house standards Romil and Spec-pure ($\delta^{66}Zn_{JMC} = -9.09 \pm 0.081$‰ and -7.15 ± 0.10‰, (Mason et al., 2004b)) and the in-house rice standard IR64 ($\delta^{66}Zn_{JMC} = 0.63 \pm 0.05$, (Dolgopolova et al., 2006) and $\delta^{66}Zn$ values agreed well within error. The procedural blank, determined from three repeats, was 51 ± 26 ng, with a $\delta^{66}Zn_{JMC}$ ratio of 1.31 ± 0.30‰. The maximum blank contribution was 5% but in general below 1% and mixing calculations showed no significant influence on the final sample data within the analytical reproducibility achieved, even for the small zinc concentration samples. Blank contributions and isotopic composition were in line with previous work on plant and geological material in our laboratories (Weiss et al., 2005; Chapman et al., 2006).

2.4. Trace element analysis

Zinc concentrations in peat samples were determined using the EMMA energy dispersive mini probe X-ray fluorescence multi-element analyser (Cheburkin and Shotyk, 1996). Zinc concentrations in geological and plant materials were determined using a Fison ARL 3508B ICP-AES based at the Natural History Museum (Dolgopolova et al., 2004). Copper and scandium were analysed using ICP-SF-MS and ICP-OES at the University of Heidelberg (Rausch et al., 2005b). Data from repeat samples and reference materials indicated that precision and bias were generally within 10% of the concentrations (reported in Table 4).

3. RESULTS

3.1. Mass spectrometry

Spectral interferences and mass bias effects originating from instrumental and sample matrix components present a major analytical challenge to precise isotope measurements of transition elements (Albarède and Beard, 2004; Mason et al., 2004a,b). Peat and plants have a very resistant organic matrix, which is difficult to break down with digestion techniques. This leads to significant challenges in elemental and isotope analysis (Krachler et al., 2002; Yafa et al., 2004). In view of the difficult sample matrices (peat, whole rocks, plants), a thorough and critical assessment of the impact of interferences and mass bias on precision and accuracy was conducted.

3.1.1. Interferences and mass bias effects

We checked for potential interferences by plotting conventional three isotopes plots using ^{64}Zn, ^{66}Zn and ^{68}Zn from all three cores and vegetation and rock samples (Fig. 3). The regression lines ($R \geqslant 0.99$) intercepted generally within error (95% confidence interval) at $y = 0$ and the slopes varied within error ($\pm 2\sigma$) of the theoretical slope of 2.00096 (Rosman and Taylor, 1998). This suggests that the ion exchange chromatography successfully removed inorganic contaminants in the Cu–Zn mass range that can cause isobaric interferences. Samples that plotted off the three-isotope line were rejected (less than 1%), except samples that had low concentrations and showed $^{68}Zn/^{66}Zn$ measurements with poor precision. It is noteworthy that the slope of vegetation and geological samples are slightly different (1.934 and 2.076) and the intercept of the vegetation is slightly off zero within the calculated 95% confidence interval (0.06 ± 0.04).

Previous work on complex matrices and single element solutions alike (Ehrlich et al., 2004; Mason et al., 2004b; Bermin et al., 2006) has shown that fluctuations in instrumental and matrix-induced mass bias can occur between sample and standard analyses and even during individual standard or sample analyses due to short-term instrumental instability (see Mason et al., 2004b; Fig. 1). Consequently, we carefully monitored the effect of the matrix on mass bias by plotting all zinc and copper ratios for each measurement session and inspecting the copper dopant data.

An example of single analytical runs of two different peat samples (Har 30 A1 and Out 02 A1), which displayed quite different mass bias behaviour is shown in Fig. 4. Sample Har 30 A1 showed perfectly stable Zn and Cu ratios for both standard and sample analyses and the copper ratio did not vary between standards and sample. The calculated $\delta^{65}Cu$ is within error of zero (0.03 ± 0.04‰) so the shift seen in the $^{66}Zn/^{64}Zn$ ratio is considered to reflect a real difference between sample and standard corresponding to a $\delta^{66}Zn$ value of 1.15 ± 0.05‰. By contrast, during the analysis of sample Out 02 A1, the $^{65}Cu/^{63}Cu$ ratio varied

Table 4
Scandium (Sc), total zinc (Zn tot), excess zinc (Zn excess), lithogenic zinc (Zn lith) and total Cu (Cu tot) measured in peat sections at Outokumpu, Harjavalta, and Hietajärvi

Hietajärvi (Hj)								Outokumpu (Out)								*Harjavalta (Har)*												
ID	Depth (cm)	Sc tot (μg/g)	Zn tot (μg/g)	Zn lith (μg/g)	Zn excess (μg/g)	Zn excess (%)	Cu tot (μg/g)	ID	Depth (cm)	Sc tot (μg/g)	Zn tot (μg/g)	Zn lith (μg/g)	Zn excess (μg/g)	Zn excess (%)	Cu tot (μg/g)	ID	Depth (cm)	Sc tot (μg/g)	Zn tot (μg/g)	Zn lith (μg/g)	Zn excess (μg/g)	Zn excess (%)	Cu tot (μg/g)	Cu lith (μg/g)	Cu excess (μg/g)	Cu lith (μg/g)	Cu excess (μg/g)	Cu lith (μg/g)	Cu excess (μg/g)
Hj 01 A		0.02	45.1	0.07	45	100	2.86	Out 01 A	−1	0.04	46.1	0.49	46	99	3.21	Har 01 A	−1.5	0.078	105.1	0.570	104	99	114	0.02	2.84	0.19	3.02	0.22	113
								Out 02 A	0.5	0.05	44.6	0.55	44	99	3.40	Har 02 A	0.5		151.8	0.000	152	100	148	0.05	2.23	0.22	3.18		
Hj 02 A	0.5	0.04	53.8	0.18	54	100	2.29	Out 03 A	1.5	0.06	38.8	0.63	38	98	3.36	Har 03 A	1.5	0.093	150.1	0.677	149	100	163	0.05	2.23	0.24	3.11	0.26	163
Hj 03 A	1.5	0.04	70.5	0.18	70	100	1.84	Out 04 A	2.5	0.06	42.6	0.63	42	99	3.58	Har 04 A	2.5	0.099	169.5	0.724	169	100	172	0.05	1.78	0.24	3.34	0.28	172
Hj 04 A	2.5	0.05	101.0	0.22	101	100	2.18	Out 05 A	3.5	0.06	43.8	0.69	43	98	4.44	Har 05 A	3.5	0.089	148.4	0.649	148	100	149	0.06	2.11	0.27	4.18	0.25	149
Hj 05 A	3.5	0.06	110.8	0.25	111	100	1.90	Out 06 A	4.5	0.06	58.8	0.68	58	99	5.37	Har 06 A	4.5	0.089	161.8	0.648	161	100	166	0.07	1.83	0.26	5.10	0.25	165
Hj 06 A	4.5	0.06	92.6	0.26	92	100	1.94	Out 07 A	5.5	0.06	59.9	0.61	59	99	5.82	Har 07 A	5.5	0.223	187.5	1.625	186	99	359	0.08	1.86	0.24	5.59	0.62	359
Hj 07 A	5.5	0.06	84.5	0.28	84	100	2.44	Out 08 A	6.5	0.06	56.2	0.68	55	99	8.56	Har 08 A	6.5	0.209	162.9	1.526	161	99	380	0.08	2.35	0.27	8.30	0.59	379
Hj 08 A	6.5	0.08	59.1	0.37	59	99	1.95	Out 09 A	7.5	0.07	72.1	0.71	71	99	11.07	Har 09 A	7.5	0.199	137.3	1.455	136	99	430	0.11	1.84	0.28	10.80	0.56	429
Hj 09 A	7.5	0.08	87.8	0.35	87	100	1.93	Out 10 A	8.5	0.08	86.2	0.84	85	99	14.01	Har 10 A	8.5	0.157	134.6	1.150	133	99	512	0.10	1.83	0.33	13.69	0.44	512
Hj 10 A	8.5	0.10	74.0	0.42	74	99	2.03	Out 11 A	9.5	0.07	80.4	0.78	80	99	14.00	Har 11 A	9.5	0.200	161.3	1.462	160	99	585	0.12	1.91	0.30	13.69	0.56	585
Hj 11 A	9.5	0.10	63.7	0.46	63	99	1.94	Out 12 A	10.5	0.10	88.7	1.09	88	99	30.42	Har 12 A	10.5	0.209	141.1	1.523	140	99	575	0.14	1.80	0.42	30.00	0.58	574
Hj 12 A	10.5	0.10	81.9	0.45	81	99	1.84	Out 13 A	11.5	0.12	89.3	1.33	88	99	46.29	Har 13 A	11.5	0.261	132.9	1.904	131	99	413	0.13	1.71	0.52	45.77	0.73	412
Hj 13 A	11.5	0.11	64.7	0.49	64	99	2.14	Out 14 A	12.5	0.08	76.3	0.83	75	99	18.71	Har 14 A	12.5	0.254	96.7	1.856	95	98	257	0.15	1.99	0.32	18.39	0.71	256
Hj 14 A	12.5	0.12	54.9	0.53	54	99	2.48	Out 15 A	13.5	0.11	71.3	1.21	70	98	21.51	Har 15 A	13.5	0.272	83.8	1.986	82	98	109	0.16	2.32	0.47	21.04	0.76	108
Hj 15 A	13.5	0.12	59.6	0.55	59	99	2.93	Out 16 A	14.5	0.12	65.2	1.29	64	98	27.99	Har 16 A	14.5	0.204	83.4	1.486	82	98	48	0.16	2.77	0.50	27.48	0.57	47
Hj 16 A	14.5	0.12	55.5	0.51	55	99	2.15	Out 17 A	15.5	0.12	66.0	1.29	65	98	25.54	Har 17 A	15.5	0.132	76.8	0.961	76	99	11	0.15	1.99	0.50	25.03	0.37	11
Hj 17 A	15.5	0.10	49.5	0.43	49	99	2.13	Out 18 A	16.5	0.07	62.3	0.75	62	99	18.61	Har 18 A	16.5	0.076	83.5	0.557	83	99	6.8	0.13	2.00	0.29	18.32	0.21	7
Hj 18 A	16.5	0.07	42.0	0.32	42	99	1.46	Out 19 A	17.5	0.11	67.6	1.20	66	98	17.07	Har 19 A	17.5	0.093	80.3	0.675	80	99	15.8	0.09	1.37	0.47	16.60	0.26	16
Hj 19 A	17.5	0.05	44.9	0.23	45	99	1.49	Out 20 A	18.5	0.10	76.6	1.11	75	99	13.35	Har 20 A	18.5	0.082	74.3	0.602	74	99	8.9	0.07	1.43	0.43	12.92	0.23	9
Hj 20 A	18.5	0.05	42.6	0.24	42	99	1.36	Out 21 A	19.5	0.07	72.5	0.79	72	99	9.97	Har 21 A	19.5	0.073	63.2	0.535	63	99	4.7	0.07	1.29	0.31	9.67	0.21	4.4
Hj 21 A	19.5	0.06	34.9	0.27	35	99	1.11	Out 22 A	20.5	0.06	72.2	0.70	71	99	10.07	Har 22 A	20.5	0.068	58.0	0.497	58	99	2.8	0.08	1.04	0.27	9.80	0.19	2.6
Hj 22 A	20.5	0.07	30.1	0.29	30	99	1.34	Out 23 A	21.5	0.06	71.6	0.64	71	99	10.04	Har 23 A	21.5	0.069	51.4	0.503	51	99	2.0	0.08	1.25	0.25	9.80	0.19	1.8
Hj 23 A	21.5	0.06	33.9	0.28	34	99	1.05	Out 24 A	22.5	0.06	66.0	0.66	65	99	9.78	Har 24 A	22.5	0.083	43.5	0.607	43	99	2.7	0.08	0.96	0.25	9.52	0.23	2.5
Hj 24 A	22.5	0.07	29.8	0.30	29	99	1.15	Out 25 A	23.5	0.07	68.8	0.71	68	99	10.98	Har 25 A	23.5	0.081	38.9	0.594	38	98	2.1	0.09	1.06	0.28	10.70	0.23	1.9
Hj 25 A	23.5	0.08	27.0	0.36	27	99	1.14	Out 26 A	24.5	0.06	65.3	0.63	65	99	7.91	Har 26 A	24.5	0.081	31.6	0.589	31	98	2.5	0.11	1.04	0.24	7.67	0.23	2.3
Hj 26 A	24.5	0.08	29.3	0.34	29	99	1.15	Out 27 A	25.5	0.08	59.5	0.84	59	99	6.09	Har 27 A	25.5	0.083	25.7	0.606	25	98	1.1	0.10	1.05	0.33	5.76	0.23	0.9
Hj 27 A	25.5	0.07	20.3	0.29	20	99	1.09	Out 28 A	26.5	0.08	63.2	0.83	62	99	5.32	Har 28 A	26.5	0.079	21.9	0.575	21	97	1.4	0.09	1.01	0.32	5.00	0.22	1.2
Hj 28 A	26.5	0.07	18.3	0.29	18	98	1.02	Out 29 A	27.5	0.07	55.7	0.73	55	99	5.60	Har 29 A	27.5	0.108	18.2	0.787	17	96	1.6	0.09	0.94	0.28	5.32	0.30	1.3
Hj 29 A	27.5	0.07	16.4	0.31	16	98	1.07	Out 30 A	28.5	0.06	51.1	0.66	50	99	6.22	Har 30 A	28.5	0.119	14.0	0.868	13	94	1.8	0.09	0.98	0.26	5.96	0.33	1.5
Hj 30 A	28.5	0.10	12.1	0.43	12	96	1.30	Out 31 A	29.5	0.06	50.0	0.63	49	99	5.61	Har 31 A	29.5	0.114	11.7	0.829	11	93	1.8	0.13	1.17	0.24	5.36	0.32	1.5
Hj 31 A	29.5	0.12	14.0	0.53	13	96	1.38	Out 32 A	30.5	0.05	45.3	0.55	45	99	5.38	Har 32 A	30.5	0.113	12.2	0.823	11	93	1.6	0.16	1.22	0.21	5.17	0.32	1.2
Hj 32 A	30.5	0.11	11.2	0.47	11	96	1.31	Out 33 A	31.5	0.07	44.0	0.75	43	98	6.56	Har 33 A	31.5	0.088	9.7	0.641	9	93	1.8	0.14	1.17	0.29	6.27	0.25	1.5
Hj 33 A	31.5	0.12	10.3	0.51	10	95	1.37	Out 34 A	32.5	0.08	47.1	0.83	46	98	4.18	Har 34 A	32.5	0.076	11.1	0.555	11	95	1.5	0.15	1.22	0.32	3.86	0.21	1.2
Hj 34 A	32.5	0.12	9.4	0.54	8.9	94	1.44	Out 35 A	33.5	0.07	46.8	0.76	46	98	3.05	Har 35 A	33.5	0.101	10.2	0.735	9	93	1.1	0.16	1.29	0.30	2.75	0.28	0.8
Hj 35 A	33.5	0.18	9.8	0.80	9.0	92	1.67	Out 36 A	34.5	0.07	42.9	0.74	42	98	2.57	Har 36 A	34.5	0.067	10.6	0.487	10	95	1.3	0.24	1.43	0.29	2.28	0.19	1.1
Hj 36 A	34.5	0.14	7.7	0.63	7.1	92	1.54	Out 37 A	35.5	0.14	40.0	1.53	38	96	2.31	Har 37 A	35.5	0.044	7.8	0.325	7.5	96	0.9	0.18	1.36	0.60	1.71	0.12	0.8
Hj 37 A	35.5	0.15	7.1	0.65	6.5	91	1.59	Out 38 A	36.5	0.12	41.2	1.24	40	97	1.72	Har 38 A	36.5	0.056	6.9	0.407	6.5	94	1.0	0.19	1.40	0.48	1.23	0.16	0.8
Hj 38 A	36.5	0.15	8.8	0.65	8.1	93	1.40	Out 39 A	37.5	0.08	38.6	0.87	38	98	1.29	Har 39 A	37.5	0.052	6.2	0.383	5.9	94	0.9	0.19	1.21	0.34	0.95	0.15	0.8
Hj 39 A	37.5	0.22	11.2	0.99	10	91	1.61	Out 40 A	38.5	0.06	36.4	0.64	36	98	1.23	Har 40 A	38.5	0.026	8.3	0.191	8.1	98	1.2	0.29	1.32	0.25	0.98	0.07	1.1

(*continued on next page*)

Table 4 (*continued*)

Hietajärvi (Hj)								Outokumpu (Out)								*Harjavalta (Har)*													
ID	Depth (cm)	Sc tot (μg/g)	Zn tot (μg/g)	Zn lith (μg/g)	Zn excess (μg/g)	Zn excess (%)	Cu tot (μg/g)	ID	Depth (cm)	Sc tot (μg/g)	Zn tot (μg/g)	Zn lith (μg/g)	Zn excess (μg/g)	Zn excess (%)	Cu tot (μg/g)	ID	Depth (cm)	Sc tot (μg/g)	Zn tot (μg/g)	Zn lith (μg/g)	Zn excess (μg/g)	Zn excess (%)	Cu tot (μg/g)	Cu lith (μg/g)	Cu excess (μg/g)	Cu lith (μg/g)	Cu excess (μg/g)	Cu lith (μg/g)	Cu excess (μg/g)
Hj 40 A	38.5	0.19	9.2	0.85	8.4	91	1.58	Out 41 A	39.5	0.05	41.6	0.53	41	99	1.13	Har 41 A	39.5	0.037	7.0	0.269	6.8	96	1.2	0.25	1.33	0.21	0.93	0.10	1.1
Hj 41 A	39.5	0.18	7.3	0.80	6.5	89	1.14	Out 42 A	40.5	0.05	33.8	0.50	33	99	1.03	Har 42 A	40.5	0.034	7.8	0.251	7.5	97	1.2	0.24	0.90	0.20	0.83	0.10	1.1
Hj 42 A	40.5	0.13	4.5	0.59	3.9	87	1.17	Out 43 A	41.5	0.06	31.3	0.67	31	98	1.25	Har 43 A	41.5	0.026	8.0	0.193	7.8	98	1.0	0.17	1.00	0.26	0.99	0.07	1.0
Hj 43 A	41.5	0.11	2.7	0.48	2.2	82	1.08	Out 44 A	42.5	0.22	46.8	2.39	44	95	**1.22**	Har 44 A	42.5	0.021	5.0	0.153	4.9	97	0.8	0.14	0.94	0.93	0.30	0.06	0.8
Hj 44 A	42.5	0.09	3.7	0.39	3.3	89	1.04	Out 45 A	43.5	0.20	39.7	2.20	37	94	**1.34**	Har 45 A	43.5	0.024	7.0	0.179	6.8	97	1.1	0.11	0.93	0.86	0.49	0.07	1.0
Hj 45 A	43.5	0.05	2.5	0.22	2.3	91	1.01	Out 46 A	44.5	0.18	27.1	1.91	25	93	**1.16**	Har 46 A	44.5	0.029	5.6	0.214	5.4	96	1.0	0.06	0.94	0.74	0.41	0.08	0.9
Hj 46 A	44.5	0.06	2.6	0.27	2.3	90	1.08	Out 47 A	45.5	0.18	30.8	1.97	29	94	1.34	Har 47 A	45.5	0.027	5.7	0.201	5.5	96	1.2	0.08	1.00	0.77	0.57	0.08	1.1
Hj 47 A	45.5	0.05	2.3	0.21	2.1	91	1.13	Out 48 A	46.5	0.12	20.3	1.31	19	94	1.10	Har 48 A	46.5	0.028	5.6	0.207	5.3	96	1.0	0.06	1.07	0.51	0.59	0.08	1.0
Hj 48 A	46.5	0.07	2.3	0.32	2.0	86	1.67	Out 49 A	47.5	0.15	16.0	1.60	14	90	1.19	Har 49 A	47.5	0.028	5.1	0.203	4.9	96	1.1	0.09	1.57	0.62	0.57	0.08	1.0
Hj 49 A	47.5	0.06	1.8	0.26	1.5	85	1.51	Out 50 A	48.5	0.07	12.2	0.73	11	94	0.95	Har 50 A	48.5	0.031	4.5	0.227	4.3	95	0.9	0.08	1.43	0.28	0.67	0.09	0.8
Hj 50 A	48.5	0.06	4.5	0.28	4.2	94	1.57	Out 51 A	49.5	0.04	18.7	0.40	18	98	0.92	Har 51 A	49.5	0.037	4.9	0.269	4.6	94	1.0	0.08	1.49	0.16	0.76	0.10	0.9
Hj 51 A	49.5	0.08	4.0	0.33	3.7	92	1.22	Out 52 A	50.5	0.03	11.0	0.36	11	97	0.89	Har 52 A	50.5	0.043	4.1	0.314	3.8	92	0.7	0.10	1.12	0.14	0.75	0.12	0.5
Hj 52 A	50.5	0.08	3.2	0.36	2.9	89	1.10	Out 53 A	51.5	0.03	9.8	0.33	9	97	0.97	Har 53 A	51.5	0.052	4.0	0.383	3.6	90	0.7	0.11	0.99	0.13	0.84	0.15	0.5
Hj 53 A	51.5	0.10	5.1	0.43	4.7	92	1.14	Out 54 A	52.5	0.04	11.1	0.47	11	96	**1.25**	Har 54 A	52.5	0.075	4.3	0.545	3.7	87	0.7	0.13	1.01	0.18	1.07	0.21	0.4
Hj 54 A	52.5	0.15	6.0	0.64	5.4	89	1.12	Out 55 A	53.5	0.04	13.3	0.47	13	96	1.06	Har 55 A	53.5	0.061	4.5	0.444	4.1	90	0.6	0.19	0.93	0.18	0.87	0.17	0.4
Hj 55 A	53.5	0.22	7.9	0.96	6.9	88	0.87	Out 56 A	54.5	0.07	13.3	0.80	12	94	1.32	Har 56 A	54.5	0.036	4.0	0.261	3.7	93	0.6	0.29	0.58	0.31	1.01	0.10	0.5
Hj 56 A	54.5	0.28	7.2	1.21	6.0	83	0.79	Out 57 A	55.5	0.12	14.6	1.32	13	91	1.44	Har 57 A	55.5	0.029	4.1	0.209	3.8	95	0.6	0.36	0.43	0.51	0.92	0.08	0.5
Hj 57 A	55.5	0.31	8.5	1.35	7.2	84	**1.01**	Out 58 A	56.5	0.06	8.1	0.63	7	92	1.25	Har 58 A	56.5	0.044	3.8	0.321	3	91	0.4	0.40	0.61	0.24	1.01	0.12	0.3
Hj 58 A	56.5	0.25	5.4	1.11	4.2	79	1.06	Out 59 A	57.5	0.04	7.4	0.41	7	94	0.97	Har 59 A	57.5	0.035	5.1	0.252	5	95	0.5	0.33	0.73	0.16	0.81	0.10	0.4
Hj 59 A	57.5	0.13	2.3	0.58	1.7	74	1.57	Out 60 A	58.5	0.14	12.4	1.55	11	88	1.26	Har 60 A	58.5	0.027	5.0	0.194	5	96	1.0	0.17	1.40	0.60	0.66	0.07	1.0
Hj 60 A	58.5	0.14	2.6	0.62	2.0	76	1.24	Out 61 A	59.5	0.12	9.9	1.32	9	87	1.12	Har 61 A	59.5	0.022	9.7	0.161	10	98	0.6	0.18	1.06	0.51	0.61	0.06	0.5
Hj 61 A	59.5	0.17	4.1	0.75	3.4	82	0.92	Out 62 A	60.5	0.14	11.4	1.53	10	87	1.13	Har 62 A	60.5	0.025	5.3	0.186	5	96	1.3	0.22	0.70	0.60	0.53	0.07	1.2
Hj 62 A	60.5	0.29	5.0	1.29	3.7	74	0.74	Out 63 A	61.5	0.12	7.9	1.25	6.6	84	1.04	Har 63 A	61.5	0.016	3.5	0.119	3.4	97	0.3	0.38	0.36	0.49	0.56	0.05	0.3
Hj 63 A	61.5	0.22	3.9	0.96	2.9	75	0.91	Out 64 A	62.5	0.16	9.1	1.74	7.4	81	0.95	Har 64 A	62.5	0.016	17.1	0.116	17.0	99	0.4	0.28	0.63	0.68	0.27	0.04	0.4
Hj 64 A	62.5	0.16	2.2	0.69	1.5	68	1.01	Out 65 A	63.5	0.13	7.9	1.38	6.6	83	1.20	Har 65 A	63.5	0.029	5.0	0.208	4.8	96	1.3	0.20	0.81	0.54	0.66	0.08	1.2
Hj 65 A	63.5	0.11	2.3	0.48	1.8	79	1.49	Out 66 A	64.5	0.11	5.2	1.14	4.1	78	1.23	Har 66 A	64.5	0.021	5.3	0.156	5.1	97	0.4	0.14	1.35	0.44	0.79	0.06	0.3
Hj 66 A	64.5	0.11	3.3	0.50	2.8	85	1.40	Out 67 A	65.5	0.17	8.6	1.79	6.8	79	1.05	Har 67 A	65.5	0.025	15.2	0.180	15.0	99	0.4	0.15	1.25	0.70	0.35	0.07	0.4
Hj 67 A	65.5	0.11	3.6	0.48	3.1	87	1.16	Out 68 A	66.5	0.13	6.2	1.44	4.7	77	1.40	Har 68 A	66.5	0.034	6.9	0.246	6.6	96	1.3	0.14	1.02	0.56	0.84	0.09	1.2
Hj 68 A	66.5	0.14	7.7	0.64	7.1	92	1.22	Out 69 A	67.5	0.20	8.0	2.12	5.8	73	1.14	Har 69 A	67.5	0.024	5.8	0.172	5.6	97	1.5	0.19	1.03	0.83	0.32	0.07	1.4
Hj 69 A	67.5	0.21	5.3	0.93	4.4	83	1.27	Out 70 A	68.5	0.19	8.7	2.09	6.6	76	**1.16**	Har 71 A	69.5	0.020	8.8	0.144	8.6	98	1.8	0.27	1.00	0.81	0.34	0.06	1.7
Hj 70 A	68.5	0.24	4.5	1.05	3.5	77	1.53	Out 71 A	69.5	0.14	10.0	1.53	8.5	85	1.21	Har 73 A	71.5	0.061	23.0	0.445	22.6	98	2.9	0.31	1.22	0.59	0.62	0.17	2.7
Hj 71 A	69.5	0.22	5.6	0.98	4.7	83	1.38	Out 72 A	70.5	0.09	4.9	0.98	3.9	80	1.21									0.29	1.09	0.38	0.83		
Hj 72 A	70.5	0.22	5.1	0.95	4.1	81	1.17	Out 73 A	71.5	0.14	6.9	1.52	5.3	78	1.29									0.28	0.88	0.59	0.70		
Hj 73 A	71.5	0.20	6.3	0.87	5.4	86	1.27	Out 74 A	72.5	0.12	5.6	1.33	4.2	76	1.21									0.26	1.01	0.52	0.70		
Hj 74 A	72.5	0.14	3.9	0.63	3.3	84	1.37	Out 75 A	73.5	0.14	5.4	1.49	3.9	72	1.06									0.18	1.19	0.58	0.49		
Hj 75 A	73.5	0.09	2.1	0.38	1.7	82	1.28	Out 76 A	74.5	0.14	3.8	1.51	2.3	60	1.23									0.11	1.16	0.59	0.65		
Hj 76 A	74.5	0.08	3.4	0.33	3.0	90	1.26	Out 77 A	75.5	0.13	5.2	1.41	3.8	73	1.32									0.10	1.16	0.55	0.77		
Hj 77 A	75.5	0.09	2.0	0.38	1.6	81	1.22	Out 78 A	76.5	0.13	7.5	1.35	6.2	82	1.26									0.11	1.11	0.53	0.73		
Hj 78 A	76.5	0.09	1.9	0.38	1.6	80	1.29	Out 79 A	77.5	0.09	4.6	1.00	3.6	78	1.20									0.11	1.17	0.39	0.81		
Hj 79 A	77.5	0.11	3.6	0.50	3.1	86	1.64	Out 80 A	78.5	0.08	6.6	0.88	5.8	87	0.93									0.15	1.50	0.34	0.59		
Hj 80 A	78.5	0.14	2.8	0.61	2.2	78	1.76	Out 81 A	79.5	0.10	6.2	1.08	5.1	83	0.93									0.18	1.58	0.42	0.51		
Hj 81 A	79.5	0.21	4.9	0.93	4.0	81	1.59	Out 82 A	80.5	0.08	6.3	0.88	5.4	86	0.89									0.27	1.31	0.34	0.54		
								Out 83 A	81.5	0.07	3.6	0.72	2.9	80	1.02											0.28	0.75		

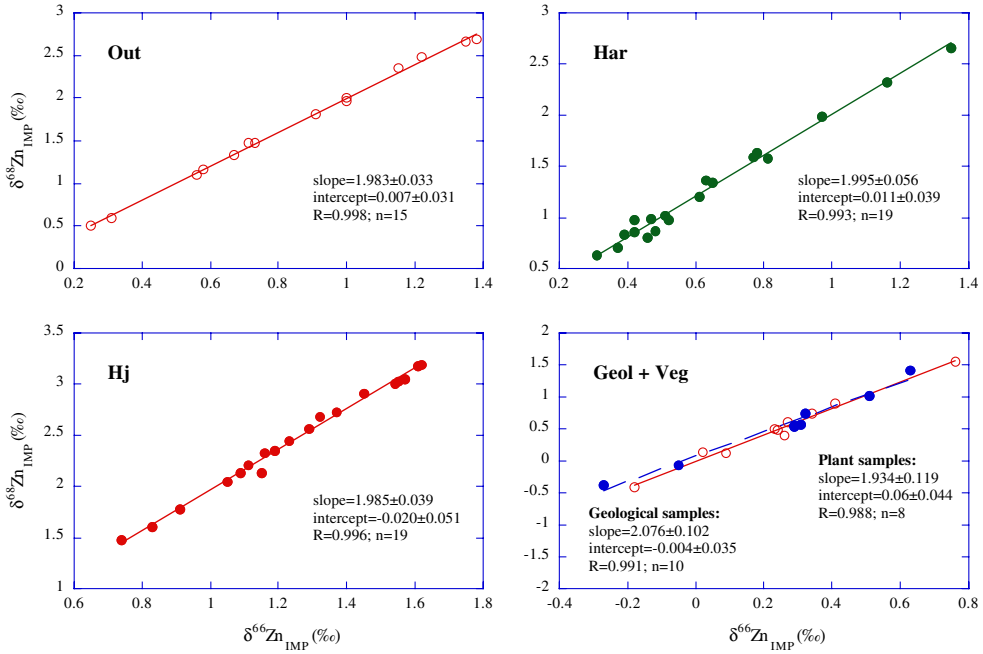

Fig. 3. $\delta^{66}Zn$ versus $\delta^{68}Zn$ shown for the three peat cores (Out, Har, Hj) and the plant (open circles) and geological (closed circles) samples (Veg + Geol). Weighted regressions have been fitted to the data set. Gradient and intercepts estimates for the regression lines are consistent with mass dependent isotopic variability of zinc, indicating spectral interferences were minimal during data collection for the majority of the samples analysed.

significantly between sample and standard measurements ($\delta^{65}Cu = 0.42 \pm 0.05‰$) suggesting that the measured shift in $^{66}Zn/^{64}Zn$($\delta^{66}Zn_{IMP} = 0.69 \pm 0.05‰$) was partly matrix-induced. So, even though the ion exchange chromatography successfully removed inorganic species that could cause interferences, organic components appear to have escaped separation and change the degree of mass bias.

3.1.2. *Precision and reproducibility*

Table 5 lists all the measured $\delta^{66}Zn_{JMC}$ values of the samples from the three peat cores with the analytical error (2σ, 95% confidence interval) for each sample calculated from the four replicate analyses. The average analytical error calculated from samples from all three cores is ±0.14‰, being higher for the Out core (0.2‰) than for the Hj core (0.08‰). As all the peat was digested using the same method, the results suggest that the matrix of different peat sections is significantly heterogeneous (in line the with significant $\delta^{65}Cu$ correction needed for the Out core compared to the Hj core). Selected samples of all three cores were measured in duplicate (two full replicate analyses including dissolution, chromatographic separation and spectrometry, denoted in Table 5 with the suffixes A1 and A2) to assess reproducibility. The overall average reproducibility obtained was ±0.16‰ (2σ, 95% confidence interval), only 8% greater than the analytical error, indicating that the sample heterogeneity was not very significant, similar to observations made during the measurement of zinc isotopes in carbonates (Pichat et al., 2003). Table 6 lists the $\delta^{66}Zn_{JMC}$ data for the geological and plant samples including the analytical error for each sample calculated from the four replicate analyses. The overall analytical error was

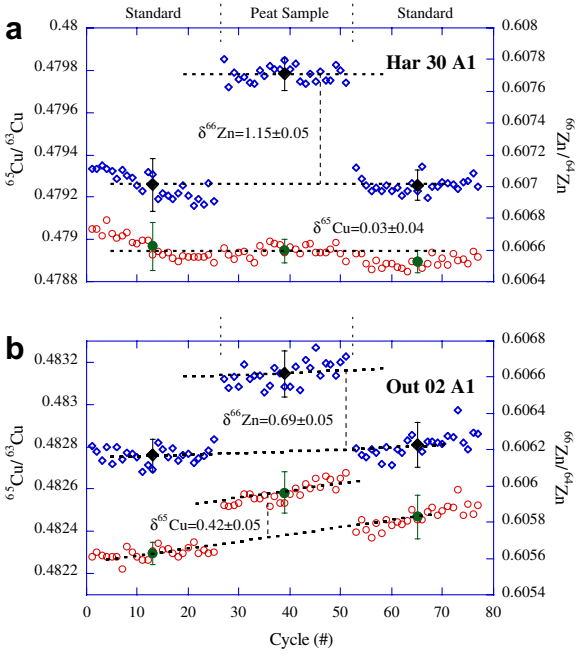

Fig. 4. Sample-standard bracketing (SSB) measurements of the isotopic difference of zinc in two different peat samples, Har 30 A1 (a) and Out 02 A1 (b). Both samples were prepared the same way (digestion, ion exchange chromatography). Samples and bracketing standards (IMP Zn) (open diamonds) were concentration matched and had 1 μg Zn/ml sample. Both sample solutions were spiked with 1 μg Cu/ml using ROMIL Cu (open circles) to act as an internal mass discrimination monitor. Measurements have been on-peak corrected. $\pm 2\sigma$ error bars are given for each analysis of 25 measurements.

Table 5
$\delta^{66}Zn_{JMC}$ (in ‰) determined from four replicate analyses of peat samples at Outokumpu, Harjavalta, and Hietajärvi

Sample location	ID	N	Depth (cm)	Date (year A.D.)	$\delta^{65}Cu_{IMP}$ (‰)	Zn total (μg/g)	$\delta^{66}Zn_{JMC}$ (‰)	$\pm 2\sigma$	Average $\delta^{66}Zn_{JMC}$ (‰)	$\pm 2\sigma$
Hietajärvi (Hj)										
1	Hj 01 A1	2	0	2001	−0.11	45.1	1.00	0.07	0.91	0.25
2	Hj 01 A2				−0.07		0.82	0.08		
3	Hj 05 A1	2	3.5	1992 ± 1	−0.07	110.8	1.14	0.10	1.16	0.06
4	Hj 05 A2				0.00		1.18	0.07		
5	Hj 08 A1		6.5	1985 ± 2	−0.06	59.1	1.25	0.06	1.25	
6	Hj 10 A1	2	8.5	1979 ± 2	−0.04	74.0	1.28	0.07	1.33	0.14
7	Hj 10 A2				−0.12		1.38	0.03		
8	Hj 16 A1	2	14.5	1953 ± 3	−0.09	55.5	1.32	0.04	1.39	0.18
9	Hj 16 A2				−0.12		1.45	0.18		
10	Hj 25 A1	2	22.5	1879 ± 13	−0.07	27.0	1.54	0.07	1.59	0.14
11	Hj 25 A2				−0.21		1.64	0.03		
12	Hj 32 A1	2	30.5		−0.13	11.2	1.70	0.08	1.66	0.11
13	Hj 32 A2				−0.38		1.62	0.31		
14	Hj 37 A1		35.5		0.27	7.1	0.92	0.05	0.92	
15	Hj 39 A1	2	37.5		0.06	11.2	1.20	0.04	1.31	0.29
16	Hj 39 A2				−0.08		1.41	0.05		
17	Hj 52 A1		50.5		0.03	3.2	1.24	0.04	1.24	
18	Hj 57 A1	2	55.5		−0.11	8.5	1.70	0.17	1.68	0.07
19	Hj 57 A2				−0.06		1.65	0.04		
Outokumpu (Out)										
1	Out 02 A2		0.5	1997 ± 4	0.06	44.6	0.32	0.18	**0.32**	
2	Out 10 A1		8.5	1984 ± 5	0.59	86.2	0.40	0.18	0.40	
3	Out 20 A1	2	18.5	1953 ± 11	0.45	76.6	0.64	0.20	0.73	0.24
4	Out 20 A2				−0.04		0.81	0.31		
5	Out 37 A2		35.5		−0.10	40.0	0.67	0.30	0.67	
6	Out 44 A1	2	42.5		0.45	46.8	0.80	0.29	0.78	0.07
7	Out 44 A2				0.02		0.75	0.31		
8	Out 54 A1	2	52.5		−0.15	11.1	1.23	0.15	1.35	0.32
9	Out 54 A2				−0.35		1.46	0.01		
10	Out 57 A1		55.5		0.06	14.6	1.09	0.35	1.14	0.12
11	Out 57 A2		55.5		−0.33		1.18	0.03		
12	Out 68 A1	2	66.5		−0.41	6.2	1.31	0.35	**1.37**	0.17
13	Out 68 A2				−0.10		1.43	0.07		
14	Out 71 A1	2	69.5	1017–1192	0.15	10.0	0.99	0.06	1.04	0.14
15	Out 71 A2				−0.39		1.09	0.22		

Harjavalta (Har)										
1	Har 01 A1		0	2001	−0.13	105.1	0.72	0.17	0.66	0.16
2	Har 01 A2				0.20		0.61	0.20		
3	Har 03 A1		1.5	1992 ± 7	−0.13	150.1	0.70	0.2	0.80	0.28
4	Har 03 A1	2	1.5		0.10		0.90	0.10		
5	Har 07 A2		5.5	1978 ± 11	0.09	187.5	0.60	0.19	0.60	
6	Har 09 A1	2	7.5	1967 ± 15	0.12	137.3	0.51	0.25	0.50	0.04
7	Har 09 A2				0.13		0.48	0.12		
8	Har 11 A1	2	9.5	1954 ± 22	0.31	161.3	0.51	0.22	0.54	0.07
9	Har 11 A2				−0.23		0.56	0.17		
10	Har 13 A1	2	11.5	1931 ± 41	0.15	132.9	0.46	0.16	0.43	0.08
11	Har 13 A2				0.20		0.40	0.18		
12	Har 17 A1	2	15.5		−0.43	76.8	0.55	0.09	0.56	0.03
13	Har 17 A2				0.19		0.57	0.12		
14	Har 18 A1	2	16.5		−0.08	83.5	0.86	0.21	0.80	0.17
15	Har 18 A2				0.22		0.74	0.23		
16	Har 20 A1	2	18.5		0.00	74.3	0.87	0.23	0.97	0.26
17	Har 20 A2				−0.22		1.06	0.13		
18	Har 30 A1	2	28.5		−0.09	14.0	1.25	0.06	1.35	0.26
19	Har 30 A2				−0.22		1.44	0.07		
20	Har 44 A1	2	42.5	older than 1302–1370 (53%), 1381–1435 (47%)	0.10	5.0	1.12	0.10	1.11	0.01
21	Har 44 A2		42.5		0.18		1.10	0.18		
22	Har 58 A1	2	57.5		0.08	3.8	1.08	0.25	1.19	0.15
23	Har 58 A2		57.5		0.07		1.29	0.23		
24	Har 66 A1	2	64.5		0.07	5.3	1.14	0.23	1.21	0.09
25	Har 66 A2		64.5		−0.12		1.27	0.16		

Selected samples were subjected to two full replicate analyses (indicated with A1 and A2) including dissolution, chromatographic separation and spectrometry.

Table 6
$\delta^{66}Zn_{JMC}$ (in ‰) of rock, mineral and surface vegetation derived from four replicate analyses

Sample	ID	Description	Location	Zn (μg/g)	$\delta^{66}Zn_{JMC}$ (‰)	$\pm 2\sigma$
Rocks						
1	Out4	Black schist	Outokumpu	1427	0.85	0.20
2	Out5	Serpentinite	Outokumpu	36.9	0.18	0.07
3	Out6	Dolomite-serpentinite	Outokumpu	25.5	−0.10	0.24
4	Out14A	Wallrock	Outokumpu	2228	0.32	0.27
Minerals						
1	Out10A	cpy/pyr	Outokumpu	26000	0.43	0.10
2	Out11	qtz/cpy/pyr	Outokumpu	4001	0.35	0.25
3	Out13	pyr/sph	Outokumpu	76950	0.33	0.24
4	Out14B	cpy/pyr	Outokumpu	4080	0.50	0.10
5	Out10B	pyr/sph/cpy	Outokumpu	169100	0.35	0.08
6	Out10C	sph	Outokumpu	598910	0.10	0.13
Plants						
1	HjV-1	*Sphagnum* moss	Hietajärvi	22.47	0.38	0.10
2	HjV-4	Cloud berry	Hietajärvi	58.53	0.38	0.23
3	HjV-3	Dwarf shrubs	Hietajärvi	41.52	0.4	0.04
4	HarV-2	*Eriophorum vaginatum*	Harjavalta	58.4	0.03	0.20
5	HarV-1	*Sphagnum* moss	Harjavalta	58.53	0.72	0.28
6	HarV-4	Cloud berry	Harjavalta	73.7	−0.18	0.2
7	OutV-3	Dwarf shrubs	Outokumpu	35.98	0.39	0.24
8	OutV-4	Cloud berry	Outokumpu	73.7	0.59	0.30

Sph = sphalerite (ZnS), cpy = chalcopyrite ($CuFeS_2$), pyr = pyrite (FeS_2), qtz = quartz (SiO_2).

±0.17‰ (2σ, 95% confidence interval) for rocks and plants alike. Here, no full replicate analyses were done.

The errors determined for the peat replicates are approximately twice those reported by Pichat et al. (2003) for deep-sea sediment samples but are in line with the larger errors (0.2‰, 2σ) reported for $\delta^{57/54}$Fe isotope measurements of organic rich sediments (Matthews et al., 2004). We note that the errors on the analytical measurements for plants and rocks during this study are larger (±0.17‰, 2σ) than for lichens (±0.10‰, 2σ) and mineral separates (±0.10‰, 2σ) achieved in previous studies with the same instrument (Mason et al., 2005; Wilkinson et al., 2005; Dolgopolova et al., 2006). Lichens and the plant matrices are arguably similar, thus we would expect similar errors. During this study, however, the plants were digested using an open vessel process, whereas the lichens in the study of Dolgopolova et al. (2006) were digested using a microwave technique. This suggests that microwave digestion is more effective in breaking down the organic matrix of plants, similar to the findings regarding elemental analysis of plants (Papp and Fischer, 1987; Adeloju, 1989). The larger errors for the rock samples can be accounted for by the fact that they were mineralogical complex whole rock samples (schist, dolomites) rather than the relatively 'simple' mineral separates analysed by Mason et al. (2005) or Wilkinson et al. (2005).

3.2. Concentration profiles of total, lithogenic and excess Zinc at the three sites

Fig. 5 shows zinc and copper concentrations measured at all three sites. Zinc concentrations vary between 2.1 and 110.8 μg/g at Hietajärvi, 3.5 and 187.5 μg/g at Harjavalta and 3.6 and 89.3 μg/g at Outokumpu and show similar profiles at contaminated (Outokumpu and Harjavalta) and uncontaminated (Hietajärvi) sites alike, with comparable high concentrations in the top part and low concentrations deeper in the profile. The zinc profile contrasts the copper, which shows higher concentrations only in the top sections at Outokumpu and Harjavalta.

The concentration profiles suggest that biological induced recycling of zinc via plant roots is affecting the element budget in the profile, in line with previous work on nutrient recycling and atmospheric deposition in peats (Shotyk, 1996; Weiss et al., 2002; Steinnes et al., 2005). For plants, zinc is a more important trace element than copper (Lucas, 2001), and this might explain that copper is not concentrated in the surface layers at Hietajärvi.

Several lines of evidences support zinc mobility within the profile. First, the mass balance conducted at the background site at Hietajärvi (Rausch et al., 2005b) found that accumulation is at least an order of magnitude larger than calculated deposition rates. Second, we find significant excess Zn in the deeper peat sections at all the sites compared to zinc derived only from lithogenic sources (>80%, Table 4 and Fig. 5). Excess Zn was calculated using the equation:

$$Zn_{excess} = Zn_{total} - Zn_{lithogenic} \quad (2)$$

Lithogenic zinc concentrations were calculated using the Zn/Sc ratio of local till (4.4 at Hj, 10.8 at Out, and 7.3 at Har) taken from the geochemical atlas of Finland (Koljonen, 1992).

$$Zn_{lithogenic} = Sc_{sample} \times \left(\frac{Zn}{Sc}\right)_{till} \quad (3)$$

While the excess zinc in the top part of the profile at Harjavalta and Outokumpu is likely derived from industrial activities (mining, smelting), only post depositional diagenetic processes such as biological induced recycling can

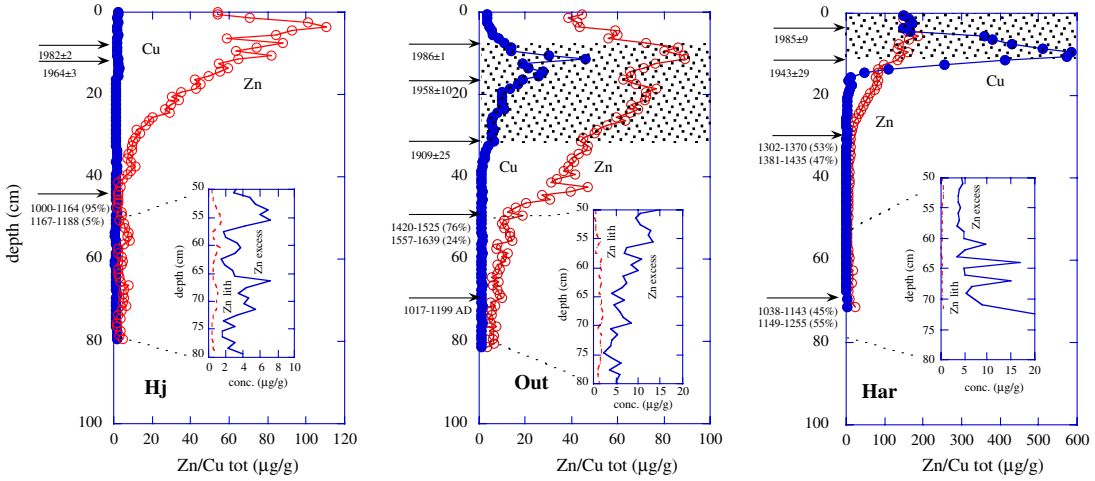

Fig. 5. Depth profiles of copper (in µg/g, closed circles) and zinc (in µg/g, open circles) at Outokumpu, Harjavalta, and Hietajärvi. The insets show lithogenic and excess zinc (Zn lith and Zn excess, respectively) in the deeper section of the core between 50 and 80 cm. Indicated are the peat sections covering the periods of mining (1910 to 1985 at Outokumpu) and smelting (since 1945 at Harjavalta, with significant drop in emission due to stringent environmental controls in the mid 1980) activities. The age dates are derived from ^{210}Pb and ^{14}C (bomb pulse curve) measurements (see Rausch et al., 2005b for details).

account for the excess zinc at the top at Hietajärvi and the lower sections in all other profiles. And finally, the zinc increases at Harjavalta and Outukumpu do clearly pre-date the mining and smelting activity at the sites (Fig. 5), suggesting movement of the zinc down the peat soil column.

3.3. Isotopic variability in peat, rocks and minerals and vegetation

3.3.1. Isotope variations within the peat bog profiles at Hietajärvi, Outokumpu, and Harjavalta

Fig. 6 shows the $\delta^{66}Zn_{JMC}$ profiles of all three peat sections along with the total zinc concentrations. The overall range of $\delta^{66}Zn_{JMC}$ in the three peat cores vary from 0.77‰ at Hietajärvi, and 0.92‰ at Harjavalta to 1.05‰ at Outokumpu. This variability is at least 5.5 times the average reproducibility.

The range of $\delta^{66}Zn_{JMC}$ found in the peat cores falls largely within the previously determined isotopic range of zinc in geological and plant material of −0.5 to 1.5‰ relative to the Lyon Zn standard (Cloquet et al., 2006a). However, three samples measured at Hietajärvi ($\delta^{66}Zn_{JMC}$ up to 1.68‰) are significant heavier than the so far heaviest zinc reported from deep sea carbonates ($\delta^{66}Zn_{JMC} = 1.34$‰; (Pichat et al., 2003), a late stage sphalerite sample from Ireland ($\delta^{66}Zn_{JMC} = 1.33$‰; Wilkinson et al., 2005), and lichens collected at Lake Baikal ($\delta^{66}Zn_{JMC} = 1.36$‰; Dolgopolova et al., 2006).

At Hietajärvi, the background site, $\delta^{66}Zn_{JMC}$ ranges in general between 1.2 and 1.7‰ from the bottom until

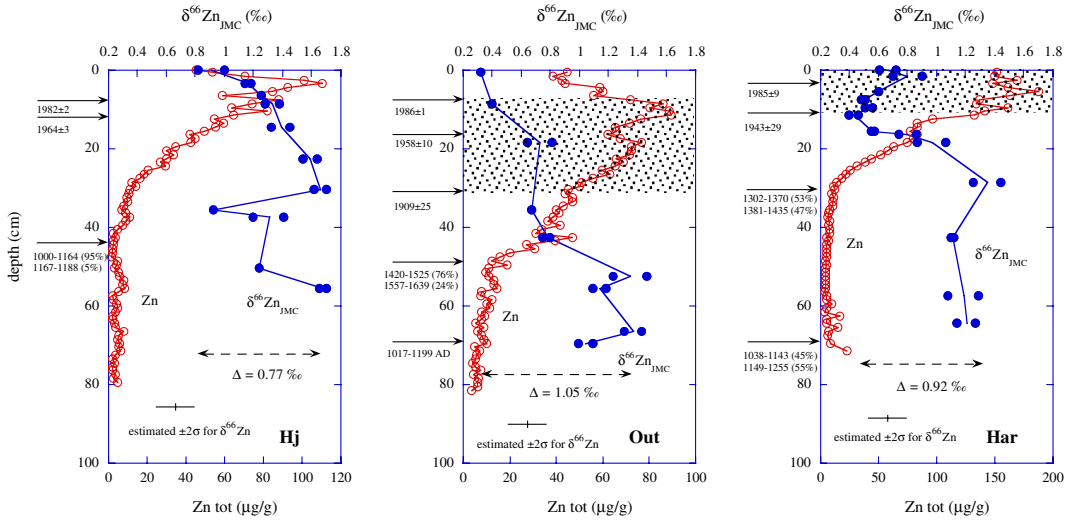

Fig. 6. $\delta^{66}Zn_{JMC}$ (in ‰, filled circle) and zinc concentration (in µg/g, open circles) measured in the peat samples at Outokumpu, Harjavalta, and Hietajärvi. The errors ($\pm 2\sigma$) shown reflect the overall reproducibility of all the peat sample analyses derived from full replicate analyses dissolution, ion exchange, chromatography, and spectrometric measurements. Indicated are the peat sections covering the periods of mining and smelting activities.

approx twenty centimetres below the surface, from where a constant decrease of $\delta^{66}Zn_{JMC}$ sets in towards $\delta^{66}Zn_{JMC}$ of around 0.9‰ at the top. At Outokumpu and Harjavalta, the $\delta^{66}Zn_{JMC}$ in the lower peat section is generally higher than 1.0‰ until approx 50 and 30 cm from the top, respectively, and then decreases towards lighter values, in parallel with a concentration increase. At ten centimetres below the surface, $\delta^{66}Zn_{JMC}$ at Harjavalta increases again towards heavier values (to 0.60‰) while at Outokumpu continues to decrease. Decrease and increase of $\delta^{66}Zn_{JMC}$ are predating the beginning and termination of mining or smelting activities.

The very top samples are always lighter than the sample just below at all three sites (Fig. 6).

3.3.2. Isotope variations within host rocks, minerals and plants at Outokumpu

The range of $\delta^{66}Zn_{JMC}$ values of the mineral samples analysed at Outokumpu ($\delta^{66}Zn_{JMC} = 0.10$ to 0.50‰) is consistent with previously published data for similar mineral types from other ore deposits and hydrothermal vents, mainly between −0.3 and 0.5‰ (Maréchal et al., 1999; Archer and Vance, 2002; Albarède, 2004; Mason et al., 2005; Wilkinson et al., 2005). The range of $\delta^{66}Zn_{JMC}$ values found in the various rock types ($\delta^{66}Zn_{JMC}$ from −0.10‰ in the dolomite-serpentinite rocks to 0.85‰ in schist) agrees with previous measured ranges and values of sedimentary and metamorphic rocks (Maréchal et al., 1999; Maréchal et al., 2000; Archer and Vance, 2002; Ben-Othman et al., 2003; Pichat et al., 2003; Mason et al., 2005; Wilkinson et al., 2005; Dolgopolova et al., 2006).

Although the data set for the Outokumpu deposit is too small to draw firm conclusions, it is noteworthy that the ore minerals plot on a mixing line between putative metal source rocks, the serpentinite, dolomite and the black schist (Fig. 7a), supporting previous geochemical findings with respect to ore deposit genesis at Outokumpu (Peltola, 1978; Loukola-Ruskeeniemi, 1999). It is believed that heavy metal-rich muddy sediments (now metamorphosed into black schists), ultramafic rocks and carbonates (now serpentinites and dolomite) formed the footwall to the ores from which metals were derived by circulating Ca- and Si-rich fluids. The 1/Zn versus $\delta^{66}Zn$ plot (Fig. 7b) shows the dominant, high-Zn content controls in terms of the range of lithologic sources.

The plants analysed – including mosses, monocotyledons and dicotyledones – have $\delta^{66}Zn_{JMC}$ values ranging from −0.18 to 0.72‰ (Table 6). It appears that dicots have lighter zinc compared to the sedges, which would be in line with the varying complexity of the nutrient uptake mechanisms within plants (Gaither and Eide, 2001; Mäser et al., 2001).

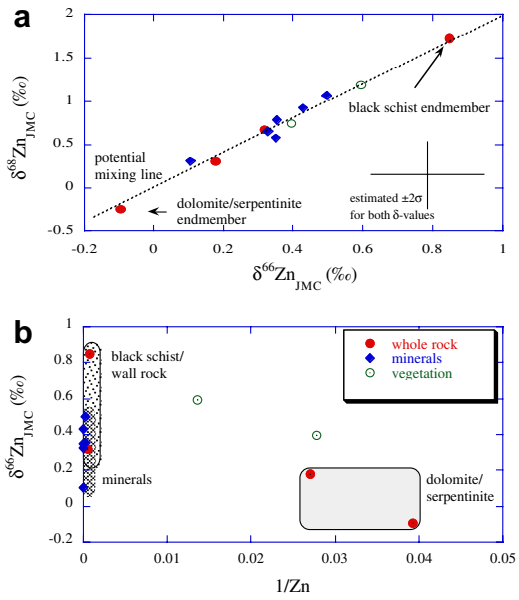

Fig. 7. (a) Three isotope plot including ^{68}Zn, ^{66}Zn and ^{64}Zn of plants, rocks and minerals from the Outokumpu mining site. Shown are the potential fluid end members derived from the host rocks (dolomite/serpentinite and black schist). (b) 1/Zn versus $\delta^{66}Zn_{JMC}$ plot of whole rock, minerals and vegetation.

4. DISCUSSION

4.1. Processes and mechanisms controlling the isotopic composition of zinc in the peat records

4.1.1. Plant uptake

The zinc isotope profiles at all three sites shows distinct lighter zinc in the uppermost sample compared to the samples below (Hj 01 and 05, Out 02 and 10, Har 01 and 03, Fig. 6). This likely reflects the effect of kinetically controlled uptake of light zinc through the living vegetation on the top of the peat, resulting in isotopically heavy zinc in the peat itself and light zinc in the growing vegetation. Previous studies on fractionation of heavy stable isotopes during plant uptake have shown that the lighter isotope is preferentially taken up in the case of zinc (Weiss et al., 2005), calcium (Wiegand et al., 2005), iron (Guelke and von Blankenburg, 2007) and silica (Ding et al., 2005; Opfergelt et al., 2006). Therefore, plant uptake on the peat surface could impart isotopically heavy zinc in the pore water, which then is transported down the profile via advective or diffusive transport and contributes to heavy zinc in deeper parts of the profile (Fig. 6). Although the sample population is small, the surface vegetation at Hietajärvi (the background site) seems to be enriched in isotopically lighter zinc compared to the uppermost peat sample, with $\delta^{66}Zn_{JMC}$ between 0.38 and 0.4‰ measured in the surface vegetation (Table 6, compared to 0.90‰, Table 5) in the uppermost sample.

4.1.2. Atmospheric zinc deposition and its isotopic composition

The Hietajärvi site is located in a national park with no agricultural activities or roads in the vicinity and no point sources of atmospheric metal pollution within a radius of tens of kilometres. The area is forested, which reduces emissions of local soil dust. Consequently, the $\delta^{66}Zn_{JMC}$ of 0.9‰ found in the uppermost part represents likely the zinc isotope signature of present regional background atmospheric deposition for Finland. Long range transport of pollutant zinc seem negligible at this site as typical pollutant

elements such as Cu, Ni and Co do not show any increase in the top part (Rausch et al., 2005a; Rausch et al., 2005b). At Harjavalta, after the effect of emission controls set in, the $\delta^{66}Zn_{JMC}$ is reversing back to a heavier value thus in line with the previously suggested regional atmospheric background signature (Fig. 6). At Outokumpu, the uppermost peat sample is significantly lighter than 0.9‰, but agrees with the isotope range found in the local minerals and host rocks, suggesting that local tailing and waste heaps are the likely sources after closure of the mining site and 'preventing' a return to isotopically heavier zinc. This could explain why the vegetation has a so similar signature to peat.

The findings suggest that the present day 'background' atmospheric zinc isotope signature depends on the geographical location but can be significantly different from loess, estimated to range between 0.2 and 0.38‰ (Ben-Othman et al., 2001; Maréchal et al., 2000). This is in line with observations of Dolgopolova et al. (2006) for zinc who found isotopically heavier zinc in lichens collected around Lake Baikal and of Kylander et al. (2005) who demonstrated a 'local' soil dust control of atmospheric background isotope signature for lead in peat archives (Kylander et al., 2005).

4.1.3. Post depositional effects

Fig. 8 shows $\delta^{66}Zn_{JMC}$ values measured at Outokumpu within the peat profile (divided into top, middle and bottom part with high, medium and low zinc concentrations and representing mining and pre mining periods), the surface vegetation, host rocks and ore minerals.

The bottom peat is significantly heavier than any potential local (represented by minerals and host rocks at Outokumpu, see Table 6) or background atmospheric source (represented by top peat samples at Harjavalta), suggesting that significant diagenetic processes have affected the isotopic composition of zinc after deposition. This is also true for the other two sites, where the deeper peat sections have $\delta^{66}Zn_{JMC}$ signatures well above the estimated background signature of ~0.9‰ (Fig. 6). As there is clear evidence of zinc mobility in the peat, further fractionation of zinc in the pore waters via various biogeochemical processes such as nutrient recycling, adsorption, ion exchange, or diffusion can be invoked to explain the observed variability.

Adsorption onto biological solids is likely selective for heavy isotopes due to covalent binding of the metal with carbonyl groups (Smith et al., 2004). Recent work with two marine planktonic and two freshwater periphytic species (Gélabert et al., 2006) showed an incorporation of zinc leading to enrichment in heavy isotopes compared to growth media ($\Delta^{66}Zn_{solid\text{-}solution} = 0.27 \pm 0.05$‰ and 0.08 ± 0.05‰ for marine and freshwater species, respectively). These observations are in line with the findings of Weiss et al. (2005), who suggested that adsorption of zinc on root surfaces selectively prefers heavy isotopes ($\Delta^{66}Zn_{solid\text{-}solution} \approx 0.2$‰). In addition, adsorption on inorganic surfaces and ion exchange leads to fractionation of up to ca. ±0.2‰ for $\Delta^{66}Zn$ (Pokrovsky et al., 2005b) and was recently suggested to be one of the main processes that governs isotope fractionation during fluid low of iron in the Navajo sandstone (Busigny and Dauphas, 2007). Largest

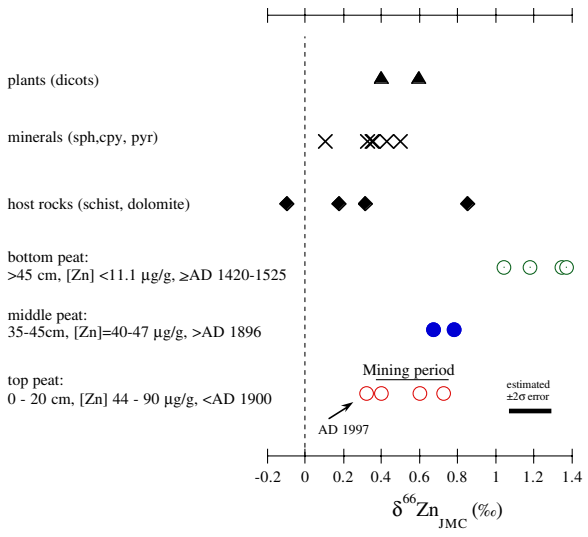

Fig. 8. Variability of $\delta^{66}Zn_{JMC}$ measured at the Outokumpu site including the surface vegetation plants, minerals and host rocks from the deposit, and peat core, divided into bottom (below 45 cm, low zinc concentrations), middle (35–45 cm, medium zinc concentration), and top (above 35 cm, high zinc concentrations, covering the mining period).

fractionations have been observed for zinc adsorption on hematite at pH 5.5 ($\Delta^{66}Zn_{solution\text{-}haematite} = -0.61$‰). Experimental work found isotopic fractionation of zinc towards light isotopes in excess of −0.3‰ during diffusion in pure nitric acid (Rodushkin et al., 2004). In their experimental set up, however, zinc showed only a small degree of hydration, approximately six to twelve water molecules. These conditions are different from peat pore waters where we have high ionic strengths and high concentrations of dissolved organic carbon, which leads to strongly complexed zinc (Smith et al., 2004) and likely decreases the mobility of diffusing ions due to short-range electrostatic forces. In addition, zinc remains largely in dissolved, non-colloidal form in peat soil solutions, concentrating essentially in the <1 kDa fraction (Pokrovsky et al., 2005a), thus decreasing potential transport (and fractionation) via colloids. Although speculative at best, dissolution of the silicate phases deposited in the deeper core (i.e. schist from surrounding host rock) likely leaves heavy isotopes remaining in the altered phases as suggested for iron and calcium (Brantley et al., 2001; Brantley et al., 2004; Fantle and DePaolo, 2004; Wiegand et al., 2005; Berquist and Boyle, 2006; Wiederhold et al., 2006).

It is important to note that the shift in isotopic ratio to isotopically lower values at Outokumpu and Harjavalta clearly predates onset of actual mining and smelting activities, indicating a shift of the isotope signal down the core.

4.1.4. Anthropogenic activities

At Outokumpu and Harjavalta, the peat cores are located close to prominent point sources (mining and smelting) and the observed zinc isotopic variations appear to be linked to zinc concentrations. Plots of 1/Zn versus $\delta^{66}Zn_{JMC}$ (Fig. 9) show significant correlation (R is 0.855

at Outokumpu and 0.741 at Harjavalta, respectively, $p = 0.05$). This relationship is consistent with two component mixing of the atmospheric pollutant source (mining dust and smelting, respectively) and the natural background, although we note that the regression equation presented in Fig. 9c is effectively a two-point line. Samples with the highest zinc concentrations show a weaker relationship.

Even though we have not measured the isotopic composition of zinc emissions from the smelter, our data suggests that light zinc is being released from the smelter at Harjavalta and deposited in the top peat section. This would agree with findings of recent work that characterised samples from two metallurgical plants and found continuous enrichment in light zinc isotopes throughout the metallurgical process with the lightest zinc in the final stage (Mattielli et al., 2005) and with work showing that evaporation and distillation processes enrich significantly light isotopes in the vapour phase (Budd et al., 1999; Marcus and Zevenbergen, 1999; Wombacher et al., 2004).

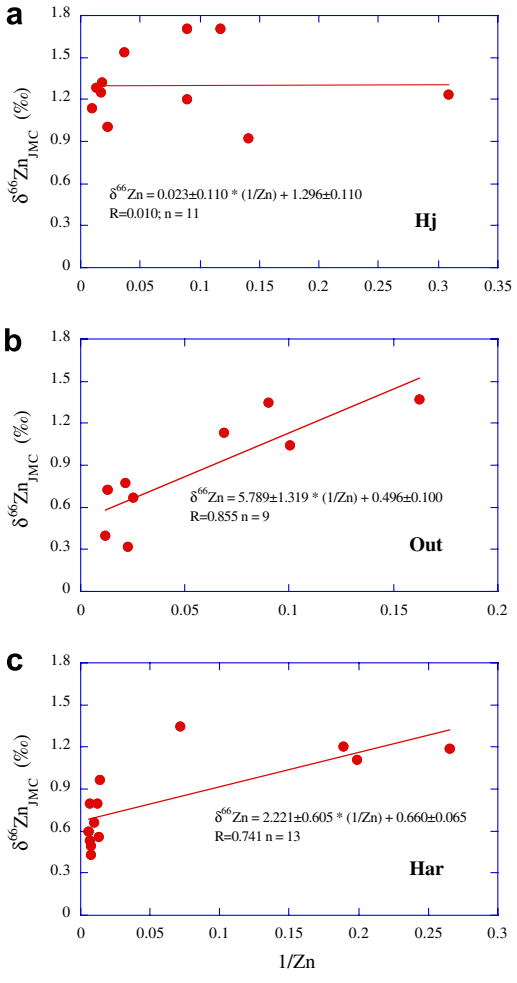

Fig. 9. 1/Zn versus $\delta^{66}Zn_{JMC}$ plots of the three peat cores. The two peat cores next to a dominant point source (mine at Outokumpu and smelter at Harjavalta) show significant correlations.

4.2. Quantifying the diagenetic effect and indication for multiple fractionation processes

We can estimate the magnitude of the diagenetic process ($\Delta^{66}Zn_D$) by taking the isotopic signature of the atmospheric sources (δ_{AS}) and compare with the heaviest value of zinc found in the peat record (δ_{PS}):

$$\Delta^{66}Zn_D = \delta^{66}Zn_{PS} - \delta^{66}Zn_{AS} \quad (4)$$

An ideal location to conduct such an estimate is the Outokumpu site as we can constrain possible end members, being local and regional background aerosol signatures. Assuming that local dust is represented by $\delta^{66}Zn_{JMC}$ of 0.2‰ and background atmospheric aerosols of 0.9‰, we calculate a diagenetic effect $\Delta^{66}Zn_D$ ranging between 1.17 and 0.47‰. These shifts are larger than typical, experimentally determined, fractionations during single biogeochemical equilibrium processes ($\leqslant$0.2‰ for $\Delta^{66}Zn$, see discussion above) and suggest that the isotopic shift observed in the peat is controlled either kinetically, via multiple equilibrium steps or through a Rayleigh type process.

Plant uptake is likely the major process affecting the biogeochemical zinc cycling in nutrient limited ombrotrophic peats (Livett et al., 1979; Shotyk et al., 2002; Weiss et al., 2002). Consequently, in-situ recycling of zinc could produce isotopically heavy zinc in pore waters under a Rayleigh type process and explain the observed isotope pattern.

To test this hypothesis, we calculated theoretical isotopic fractionations invoked by nutrient recycling and consequent depletion of zinc pore water.

Rayleigh fractionation is given as:

$$\frac{(1000 + \delta^{66}Zn_A)}{(1000 + \delta^{66}Zn_{A,0})} = F^{(\alpha_{B-A}-1)} \quad (5)$$

where δ_A is the delta value in phase A, δ_B is the delta value in phase B, α_{B-A} is the fractionation factor between phase A and B (*e.g.*, during plant uptake), F is the fraction of zinc remaining in phase A and $\delta_{A,0}$ is the initial δ_A value at $F = 0$.

The variables α and $\Delta^{66}Zn$ were calculated using $\delta^{66}Zn$ values determined from an experimental hydroponic study by Weiss et al. (2005) conducted with higher plants including rice and tomato and using the following relationships:

$$\Delta^{66}Zn_{plant-solution} = \delta_{plant} - \delta_{solution} \quad (6a)$$

$$\Delta^{66}Zn_{plant-solution} = 1000 \times \ln \alpha_{plant-solution} \quad (6b)$$

Table 7 gives the $\delta^{66}Zn$ of the nutrient solutions, rice and tomato plants and the calculated $\Delta^{66}Zn_{plant\text{-}solution}$ and $\alpha_{plant\text{-}solution}$. Rice represents *Eriophorum vaginatum* and thus monocotyledons, and tomato represents dwarf shrubs and cloud berry and thus dicotyledones. The $\delta^{66}Zn$ signature of the dissolved zinc in the pore water is constrained by the two potential atmospheric sources: local and background (regional), assuming that fractionation during the dissolution of the inorganic phase is insignificant. Any zinc in the pore water derived from

Table 7
Input parameter for the Rayleigh model: $\delta^{66}Zn$ taken from experimental data of Weiss et al. (2005), $\Delta^{66}Zn_{plant\text{-}solution}$ and $\alpha_{plant\text{-}solution}$ were calculated using the equations given in text

	n	$\delta^{66}Zn_{IMP}$ average (‰)	±1SD	$\delta^{66}Zn_{plant\text{-}solution}$	$\alpha_{plant\text{-}solution}$
Nutrient solution	3	0.02	0.04		
Rice/monocotyledones	6	−0.18	0.03	−0.20	0.9998
Tomato/dicotyledones	4	−0.42	0.05	−0.44	0.9996

the dissolution of the sulphides in the upper part of the core fall between the two end members and is covered with the range modelled.

Fig. 10 shows the modelling results for four different boundary conditions: two different fractionation factors α (monocotyledons and dicotyledones) and two initial atmospheric dust signatures (background and local dust). Closed system equilibrium fractionation, calculated using $\delta^{66}Zn_A \approx \delta^{66}Zn_B - \Delta^{66}Zn_{B-A}$ is shown for reference. Closed equilibrium fractionation cannot produce the maximum isotopic shift observed from the experimental data in the Outokumpu peat bog under any boundary

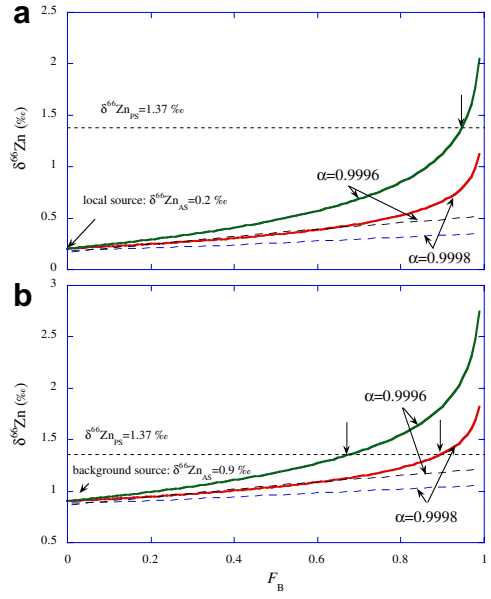

Fig. 10. Isotopic fractionation during zinc uptake of peat bog plants from pore water produced by closed-system equilibrium (dotted lines) and Rayleigh fractionation processes (solid lines). Shown on the *y*-axis is the isotopic composition of the pore water as a function of the proportion of zinc taken up (*x*-axis, denoted as F_B). The initial isotopic composition of zinc at Outokumpu is constrained by aerosols derived from local rocks ($\delta^{66}Zn_{AS}$ of 0.2‰) and background atmospheric deposition ($\delta^{66}Zn_{AS}$ of 0.9‰). This assumes that no or little fractionation of zinc occurs during the dissolution. We used two different fractionation factors ($\alpha_{plant\text{-}solution}$) for the plant uptake, taken from experimental uptake studies of Weiss et al. (2005) and summarised in Table 7: 0.9998 being representative of monocotyledons (*Eriophorum vaginatum*) and 0.9996 being representative for dicotyledones (cloud berry and dwarf shrubs). The horizontal dotted line represents the highest $\delta^{66}Zn_{JMC}$ found in the deeper peat sections ($\delta^{66}Zn_{PS}$ of 1.37‰).

condition. Severe depletion of zinc in the pore waters (>70%) could produce the $\delta^{66}Zn_{JMC}$ found in the deeper core section if all the plants were dicotyledones and all the zinc was derived initially from the background source. Zinc concentrations in the pore waters at Outokumpu, however, are >250 nM (Rausch et al., 2005a) and a depletion of zinc in the pore water reservoir to such extent is deemed unlikely. In addition, the dominant plant species on the peat bogs at Outokumpu is *Eriophorum vaginatum*, a monocotyledon, thus a depletion of over 90% has to occur with this plant species.

Our data suggests that the heavy isotopic signature observed in the lower core sections at the three sites is not simply the product of nutrient recycling/pore water depletion but rather the results of a multiple fractionation including various processes. Multiple isotopic fractionation during diagenetic or biogeochemical cycling has been proposed before for iron (Zhu et al., 2002), sulphur (Canfield and Teske, 1996) or nitrogen (Novák et al., 2005).

5. SUMMARY AND CONCLUSIONS

Zinc isotope ratios were measured in three dated peat cores using multi collector ICP-MS to investigate the potential of isotopes to source atmospheric zinc and to constrain post depositional processes affecting the peat paleo record. We selected three bogs in Finland situated in the vicinity of a smelter plant (Harjavalta), a mining site (Outokumpu) and a background site (Hietajärvi). The main conclusions are:

(1) Variability of $\delta^{66}Zn_{JMC}$ in the three peat cores ranges between 0.77‰ at Hietajärvi and 1.05‰ at Outokumpu, which is at least six times the estimated analytical error.
(2) The large variations in isotope ratios within the profiles and the $\delta^{66}Zn_{JMC}$ values in the lower core sections (which are heavier than potential local or background atmospheric sources) suggest that significant post depositional processes affect the zinc isotope record. Fig. 11 gives a schematic summary of the suggested major processes.
   i. Plant uptake results in isotopically enriched zinc in pore waters which consequently is transported down the profile
   ii. Diagenetic processes such as nutrient recycling, ion exchange and adsorption lead to multiple fractionations. The baseline values in the lower peat sections are significantly different from natural background deposition.

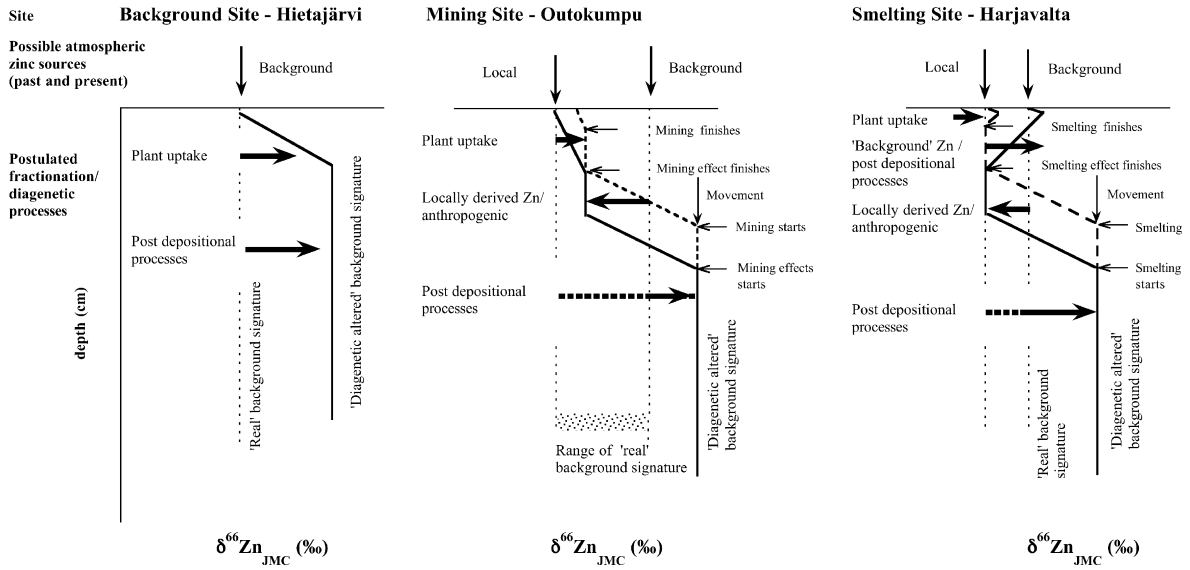

Fig. 11. Cartoon illustrating the processes and mechanisms leading to the observed isotopic variability of zinc at the three different sites. Major mechanisms involved are: plant uptake at the peat surface (enriches pore water with heavy zinc), addition of atmospheric sourced zinc (locally derived aerosols from soil dust/tailings/waste heaps at Outokumpu, from smelter derived aerosols at Harjavalta, and background deposition at all three sites), and post depositional processes including nutrient recycling, adsorption, ion adsorption and dissolution of dust. As a result, the solid peat evolves towards the heavy isotope signature observed, significantly different from the 'true' atmospheric background signature. Also shown are the start and end of the anthropogenic activities and the moment when the effects actually set in (see text for details).

iii. Isotope and concentration spikes found at the smelter and mining sites pre-date the industrial activity periods, suggesting that isotope and concentration signals migrated
iv. Anthropogenic sources from activities such as mining and smelting are detectable, via the addition of light zinc to the peat.

(3) We estimate the zinc isotope signature of the regional atmospheric background aerosols from peat surface measurements at Hietajärvi to approximately 0.9‰ for $\delta^{66}Zn_{JMC}$. This is significantly heavier than loess (ranging between 0.2 and 0.4‰), suggesting that there is significant regional variability in the isotopic signature of background aerosols can occur.
(4) Zinc concentrations at Harjavalta and Outokumpu correlate with isotope ratios, suggesting a two component mixing between atmospheric derived pollutant zinc from smelting and mining and natural background zinc.
(5) Rayleigh models of isotopic fractionation occurring during nutrient recycling cannot explain the magnitude of isotope variability observed in the profile and suggest that multiple post depositional biogeochemical processes are contributing to the observed overall shift.
(6) The peat matrix can affect the mass spectrometric measurements resulting in matrix induced mass bias shifts. Such shifts need to be carefully monitored but can be corrected using the modified standard sample bracketing approach. Average internal precision and reproducibility were 0.14 and 0.17‰, respectively, slightly higher than routinely achieved for MC-ICP-MS on minerals and single element solutions. Future development work focussing on accurate and precise isotope analysis in organic matrix is warranted.
(7) The work demonstrates the contribution that zinc isotope measurements can make in the assessment of atmospheric zinc sources, in particular of anthropogenic impact. In addition, biogeochemical processes are important mechanisms that affect the isotopic fractionation during zinc cycling in the environment.

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