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Source characterisation of atmospheric platinum group element deposition into an ombrotrophic peat bog

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Platinum, palladium, rhodium, iridium and osmium were found to be enriched relative to their expected natural concentrations in peat samples from Thoreau's Bog, an ombrotrophic peat bog in Concord, Massachusetts. The source of osmium into the bog was determined from its isotopic composition ($^{187}Os/^{188}Os$). Osmium is composed of 4% lithogenic osmium from atmospheric soil dust, 41% of anthropogenic osmium and 55% of osmium from a non-lithogenic, non anthropogenic source, with rain being a likely candidate for the latter. Significant anthropogenic and rain contributions are also expected for iridium. In contrast, platinum, palladium and rhodium are almost exclusively anthropogenic. The larger enrichments of platinum, palladium and rhodium indicate that automobile catalysts are the source of platinum group elements to Thoreau's bog. The bog is located approximately 300 m from a major road and, therefore, the occurrence of platinum elements is evidence for regional dispersion of these metals. The absence of a clear trend following the introduction of catalysts indicates that platinum group elements are not quantitatively conserved in peat with downward leaching and plants playing an important role in the accumulation of platinum group elements.

Introduction

The release of platinum group elements (PGE) from automobile catalysts[1–3] has resulted in elevated PGE concentrations in the urban and roadside environment.[4–10] However, little is known concerning the environmental behaviour of PGE and the recent finding of increasing PGE concentrations in Greenland snow[11] has raised concern over the lack of knowledge regarding the transport of these metals. While the occurrence of PGE in fine airborne particles[4–6,12] argues that their transport over long distances is likely to occur, there is no clear evidence that automobile catalysts are the source of PGE in Greenland ice, and smelters from northern Russia have been suggested as another potential source for arctic PGE contamination.[13]

An increasing deposition of PGE has recently been reported for Upper Mystic Lake, an urban lake in Massachusetts,[8,9] and nearby Boston Harbor.[10] Platinum deposition in Upper Mystic Lake in 1992–2002 was 16-fold higher than the deposition rate prior to the introduction of catalysts;[9] the source of PGE into the lake and the harbour derives from both atmospheric deposition and stormwater runoff in unknown proportion. Thus, knowledge of atmospheric deposition of PGE can provide further understanding of both regional transport and global dispersion of PGE.

The study presented here investigates changes in PGE deposition onto the Thoreau Bog, an ombrotrophic peat bog located near Concord, Massachusetts.[14] Ombrotrophic peat bogs exclusively receive nutrients and trace elements from atmospheric deposition and peat cores from ombrotrophic bogs have therefore been used to investigate historical changes in atmospheric trace metal concentrations and determine rates of atmospheric deposition.[14–22] Our main objectives are to estimate the source of, and rates of deposition of atmospheric PGE and to study profiles of PGE accumulation.

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Experimental

Sampling site

Two peat cores were collected from Thoreau's bog, also known as Gowing's Swamp, in Concord, Massachusetts (latitude 42°27′43″N and longitude 71°19′42″W). The vegetation of the bog has been described in detailed by Thoreau[23] and its biogeochemistry has been studied by Hemond.[14,24]

Thoreau's bog is a floating-mat *Sphagnum* bog which covers a 3800 m^2 area. The bog is part of a larger swamp complex located within an area of glaciolacustrine deposit formed upon the retreat of the ice front at the end of the last glaciation by the melting of a large buried ice mass.[14] The floating mat includes at least two species of *Sphagnum*, *S. rubellum* Wils. and *S. magellanicum* Brid. Additional vegetation in the bog includes ericaceous shrubs and a sparse tree cover. The dominant shrub, *Chamaedaphne calyculata* (L.) Moench (leatherleaf), covers 25–50% of the bog mat.

No surface drainage into the bog has been observed. Surface drainage out of the bog occurs almost exclusively through a constructed stone drainage at the south east of the bog when bog stage is high in late winter and spring.[14] The water table was at a depth of approximately 20 cm during sampling. Hemond[14] reported that the moss surface is typically 10–20 cm above the water table.

Concord has an average yearly temperature of 9 °C with −4 °C in January and 22 °C in July. Precipitation is spread throughout the year with an average yearly precipitation of 1200 m^3 (rain) km^{-2} and snow in winter.[25] Average wind speed in nearby Boston is 20 km $hour^{-1}$ with prevalent northwest direction in winter and southwest direction in summer and occasional gusts.[26]

The bog is surrounded by residential and forested areas and there is no industry in close proximity. The nearest road is located approximately 250 m from the bog and has traffic

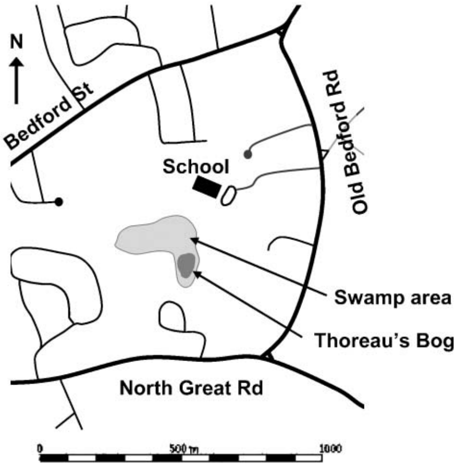

Fig. 1 Street map of the area surrounding Thoreau's bog with major roads (thick lines, $>$10000 vehicles day^{-1}) and minor roads (thin lines, $<$500 vehicles day^{-1}).

$<$500 vehicles day^{-1}. North Great Road (Route 2A), with traffic of 26000 vehicles day^{-1}, is located approximately 300 m south of the bog (Fig. 1).

Sample collection and preparation

Peat cores of approximately 12 × 12 × 25 cm were collected from Thoreau's bog approximately 20 m from each other in October 2002. Squares were cut into the mat with a serrated stainless steel knife and the cores were lifted out by hand and placed in polyethylene boxes. Upon return to the laboratory, the cores were frozen and cutting was performed on the frozen core. To remove any disturbances that might have been created during sampling, a layer of approximately 1 cm was removed from the sides of the frozen cores using a saw to obtain a 10 × 10 × 25 cm core. The frozen cores were then sectioned into horizontal 2 cm and 1 cm slices for core 1 and core 2, respectively with a 6 cm slice for the top of core 1. Volume and wet weight were measured for each slice. Slices were dried overnight in an oven at 103 °C. Dried samples were then weighed, and homogenized using a pestle and mortar. The samples were kept in PE containers until analysis.

Dating

Dry peat samples were dated using accumulation rates calculated from excess ^{210}Pb activities. Activities were determined by γ-counting (GL2020 detector with Series 40 multi-channel analyzer, Canberra Instruments, Meriden, CT) using the 47 keV γ-ray of ^{210}Pb at 9 and 12 different depths for core 1 and 2, respectively. Accumulation rates were calculated using the constant rate of supply model which is based on the radioactive decay of ^{210}Pb assuming a constant atmospheric input of ^{210}Pb and immobility of Pb in peat. The depth of a plastic tubing, which was placed on the bog in 1977 and is now buried as a result of peat accumulation, was used as a marker of known age.

XRF analysis

Profiles of Al, Ca, Fe, K, Mg, Mn, P, Pb, S, Si and Ti in Peat Core 1 were obtained by X-ray fluorescence (XRF). For XRF analysis, approximately 3 g of peat were milled in polyethylene containers with a polyethylene bead for 5 minutes. A binding additive (X-Ray Mix Powder, Chemplex Industries, Inc., Palm City, Fl) was added and the samples were further milled for 1 minute. The samples were then pressed using a hydraulic press under a load of 18 tons. The obtained pellets were analyzed by XRF (X-Lab 2000, Spectro, St. Lawrence, PQ, Canada with Turboquant data-processing) using a calibration database. The concentration profiles were normalized to Al to compensate for variation in peat density and therefore accuracy of the Al data is particularly important. Calibration for Al was performed using a homogenised peat sample with standard additions of a NIST soil reference material (Montana Soil, CRM 2710, NIST, Gaithersburg, USA).

ICP-MS analysis

Peat samples (0.7–1.3 g) were ground in an agate mortar, weighted and spiked with a mixed PGE tracer solution enriched in ^{105}Pd, ^{190}Os, ^{191}Ir, and ^{198}Pt. Samples were prepared by NiS fire assay,[27,28] which uses the high affinity of PGE for sulfide, resulting in the preconcentration of PGE and the removal of most interfering elements. The sulfide bead is then dissolved under reducing conditions in 6.2 M HCl at ~150 °C. The solution containing insoluble PGE-rich particles is filtered through a 0.45 μm cellulose filter. The filter paper is then transferred to a Teflon vial and digested in 1 ml concentrated HNO_3. In order to fully dissolve the PGE-rich particles and oxidize Os to volatile OsO_4 the closed Teflon vial is heated to ~100 °C for about 90 minutes. After chilling the vial in ice water and diluting the solution five-fold with Millipore water, the Teflon lid is replaced with a two-port cap, one end of which is connected to the Ar supply and the other to the ICP-MS torch. When Ar is bubbled through the solution, volatile OsO_4 is carried with the Ar stream into the plasma, allowing the determination of Os and its isotopic composition.[27] Complementary PGE concentrations are determined by ICP-MS in the liquid residue after the solution is taken to dryness and redissolved in 5% HNO_3. Analysis was done on a single collector, magnetic sector ICP-MS (ELEMENT 2, Thermo-Finnigan, Bremen, Germany) equipped with a desolvating nebulizer (ARIDIUS, Cetac, Omaha, USA). Osmium, Pt and Pd concentrations were calculated using two isotope ratios each to check for consistency. Concentrations generally agree within a few percent of each other and are not listed when the standard deviation of the two results is larger than 20%. Rhodium is mono-isotopic and, therefore, isotope dilution analysis is not possible for this element. Rhodium concentrations were calculated by first normalizing Rh count rates to Pt and Pd count rates based on standard solutions and secondly by converting normalized Rh count rates to concentrations using Pt and Pd concentrations determined by isotope dilution. Four Rh concentrations were obtained (two each from Pt and Pd) and Rh concentrations are reported only if their standard deviation was smaller than 30%. Uncertainties are presented in the text as 2× standard deviations.

As there is no available peat or plant reference material with certified PGE concentrations, the concentration of a tunnel dust material (BCR-723) with certified Pt, Pd and Rh concentrations was analyzed after NiS fire assay providing results within 20% of the certified concentrations (results published in Rauch *et al.*[9]).

Results and discussion

Characterization of Thoreau's bog

Peat bogs can receive nutrients and trace contaminants from atmospheric deposition or groundwater inflow and knowledge of the source of metals into a bog is therefore important when peat cores are used as environmental archives of atmospheric metal deposition. Hydrologic studies at Thoreau's Bog have demonstrated the absence of groundwater recharge[14] and, therefore, metal input is expected to be purely atmospheric. It has been hypothesized that for ombrotrophic peat bogs Ca/Mg (presented here as weight ratios) should be similar to or lower than the ratio in rainwater, whereas a higher ratio is expected in minerotrophic bogs owing to non-atmospheric sources of Ca^{2+}.[15,29] Rain in Concord, Massachusetts, is expected to be of continental origin with occasional oceanic storms. Average Ca/Mg in the range 2–6 and 0.5–1 have been estimated for continental and coastal rainwater, respectively.[30] Average Ca/Mg in precipitation at a site in East Massachusetts (latitude 42°38′39″N and longitude 71°21′47″W) was 2.2 in 2002.[31] An average Ca/Mg of 2.4 in peat from Thoreau's bog is therefore further evidence of the ombrotrophic character of the bog. The Ca/Mg ratio is increasing from the bottom to the top of the profile, possibly due to Ca uptake by vegetation at the top of the core.

The profiles of nutrients essential to plant growth, *i.e.* Ca, Mg, K, P and S, provide an estimate of the depth to which the peat is influenced by the overlaying vegetation. Aluminium-normalized profiles show an enrichment, relative to atmospheric soil dust, of essential elements for the uppermost part of the core and indicate that the top 6.5 cm of the core are primarily composed of live vegetation (Fig. 2B and 2E), in agreement with visual observation, while Ca and K enrichment indicate that biological influence reaches 13.5 cm (Fig. 2B). While XRF analysis has only been performed on Peat Core 1, visual observation, density and ^{210}Pb activity indicate a thicker vegetation cover for Peat Core 2.

Aluminium is present at a concentration of 0.11 ± 0.05% with a 2-fold decrease from the bottom to the top of the core (Fig. 2A). The relatively good correlation between Al concentration and density ($n = 9, r^2 = 0.67, p < 0.01$), except for a high concentration at 7.6 cm which was not used for the correlation (Fig. 2A and 3A), indicate that the peat is not significantly affected by decomposition processes such as loss of organic carbon. Both Si and Ti have a relatively constant profile relative to Al (Fig. 2C), indicating no or limited post depositional processes that may affect elemental profiles. Both

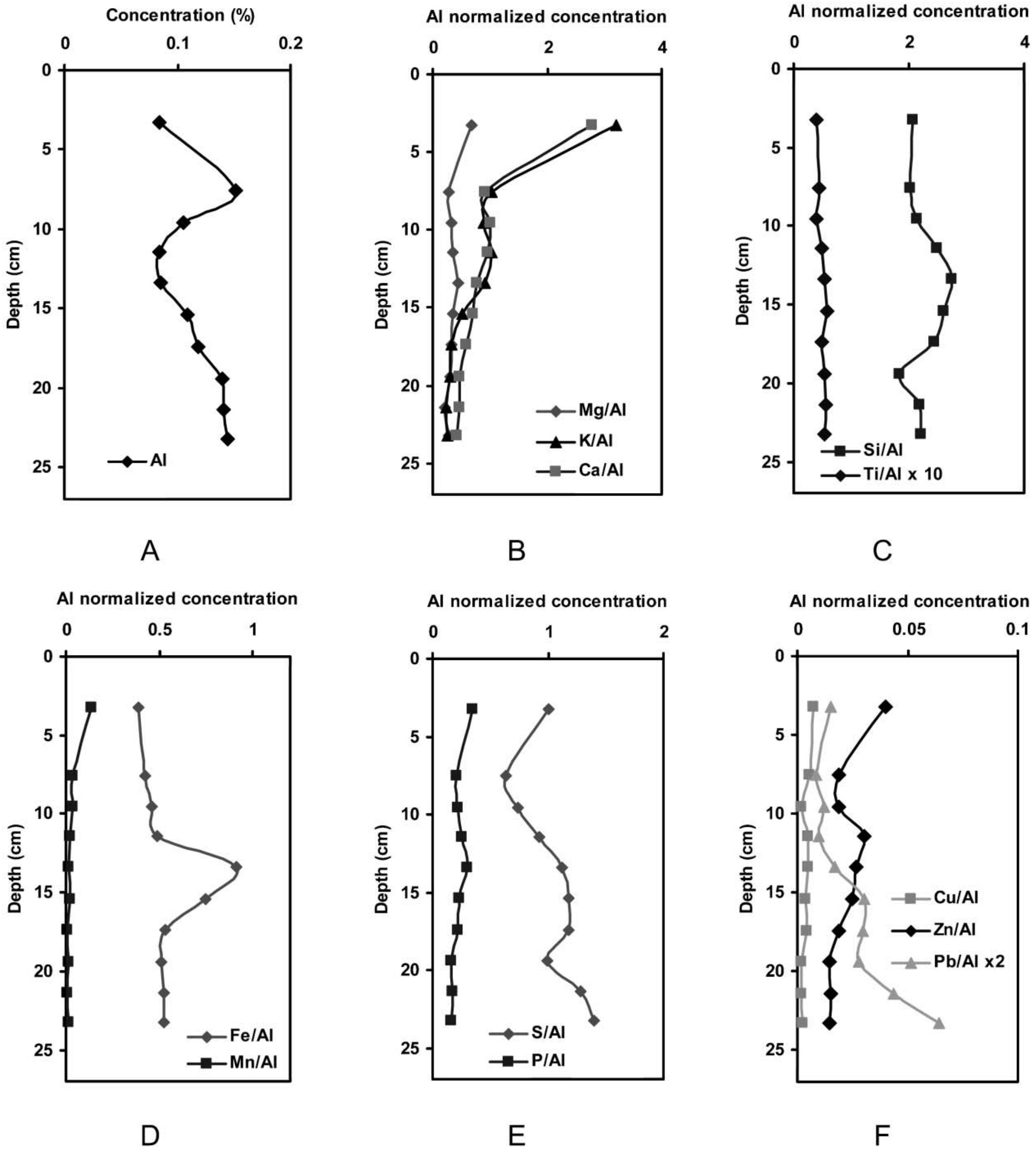

Fig. 2 (A) Al concentration profile and Al normalized concentration profiles of (B) Ca, Mg, K; (C) Ti, Si; (D) Fe, Mn; (E) S, P; (F) Pb, Cu and Zn in Peat Core 1.

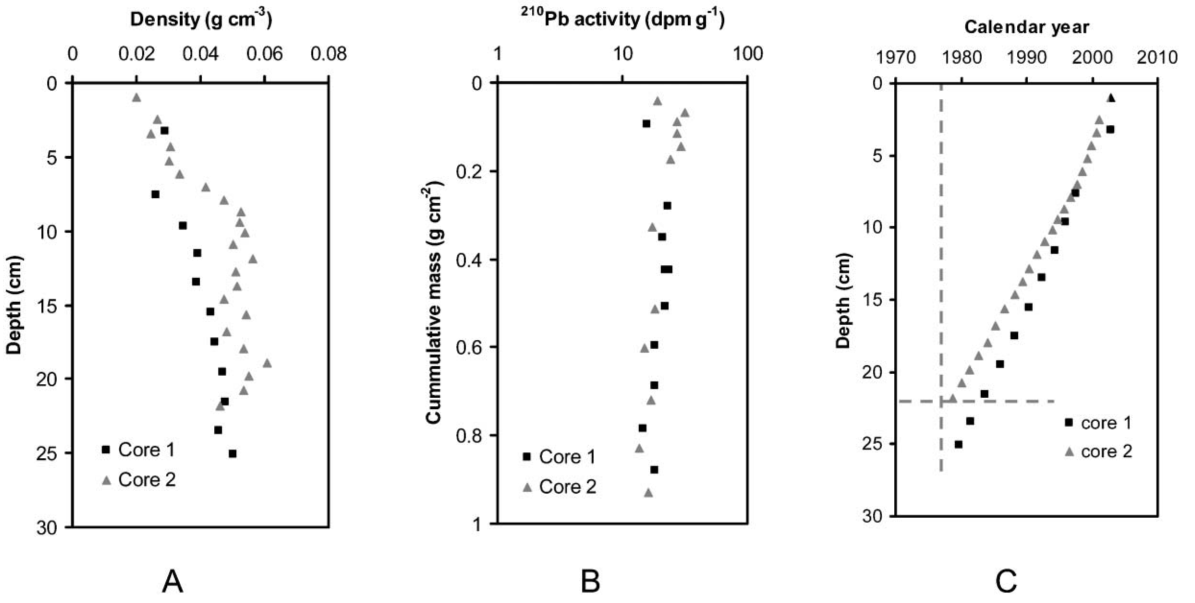

Fig. 3 (A) Peat density *vs.* depth; (B) Correlation between cumulative mass and excess ^{210}Pb activity; (C) Date estimates *vs.* depth. The dashed lines in (C) correspond to the plastic tubing placed in the bog in 1977.

Al/Ti and Si/Ti are approximately 2.5 times lower than expected from Upper Continental Crust (UCC) concentrations,[32] possibly due to preferential loss of Al and Si during weathering of the UCC.[29] The ratios are closer to ratios in soil indicating that soil dust is the main source of minerals to the bog.[33] The Fe peak at 13.5 cm suggests the occurrence of oxic conditions in the top 13.5 cm of the core and anoxic conditions below this depth (Fig. 2D). Changes in redox conditions might affect the profiles of redox sensitive metals. Copper and especially Zn are enriched in the biologically-influenced part of the core (Fig. 2F). Copper is relatively constant below 6 cm, while a maximum is found at 11 cm for Zn. Lead decreases from 46.3 µg g^{-1} at the bottom to an average of 6.4 µg g^{-1} in the top 10 cm of the core (Fig. 2F). The decrease matches results from Hemond[14] and may be the result of the ban of leaded gasoline as well as lower industrial emissions. Profiles of trace metals show an influence of the biologically-influenced zone in the top 6.5 cm of the core for essential elements, but no effect of changes in redox conditions.

The age of the analyzed peat sections was estimated from excess ^{210}Pb activities in Peat Cores 1 and 2 assuming insignificant mobility of Pb.[34] The deposition rate of ^{210}Pb was ~1 dpm cm^{-2} yr^{-1}, as expected for the northeastern USA.[14,35] The logarithm of ^{210}Pb activity was found to decrease linearly with cumulative mass ($n = 20$, $r^2 = 0.75$, $p < 0.001$), but with two outliers corresponding to the top sections of each core. These two outliers, corresponding to the overlying vegetation, were not used for the determination of peat accumulation rates and were considered as 2002. Similar activities were found for both cores (Fig. 3B). An average accumulation rate of 0.041 g cm^{-2} yr^{-1} was obtained assuming a constant rate of supply and age of the peat sections was calculated using the decay of ^{210}Pb (Fig. 3C). A depth of 22 cm corresponds to 1983 for Peat Core 1 and 1979 for Peat Core 2, in good agreement with reported dating of Thoreau's Bog. Different ages were found as a result of differences in peat density (Fig. 3A), with average densities of 0.038 g cm^{-3} for Peat Core 1, 0.045 g cm^{-3} for Peat Core 2 and 0.049 g cm^{-3} on top of the plastic tube, and core chronologies are in good agreement with the buried tube marker.

Enrichment and source of PGE

Platinum group element concentrations in peat samples and corresponding age dates are presented in Table 1. Platinum is the most abundant PGE with an average concentration of 0.05 + 0.16–0.05 µg g^{-1}. Mean Pt concentration is affected by a skewed distribution with a few high concentrations and, therefore, median Pt concentration is a more representative estimate of Pt distribution. The median Pt concentration is 5 ng g^{-1}, approximately 10 times lower than the mean. The high variability in Pt concentration is the result of high variability in core 1, elevated concentrations in the top sections of both cores and different Pt concentrations in the two cores (Fig. 4A). The other PGE have similar concentrations in the two cores (Fig. 4). Palladium and Rh have median concentrations 3.6 and 12 times lower than median Pt concentration, respectively, and Ir and Os are the least abundant PGE with median concentrations 3 orders of magnitude lower than Pt (Table 2).

Lithogenic atmospheric soil dust, which has a composition similar to that of the upper continental crust (UCC), is the major source of naturally-occurring particles to ombrotrophic bogs. Enrichment factors (EF), a comparison of measured concentrations with concentrations expected from lithogenic dust deposition, were inferred using eqn. 1[19,22,29,36,37] with UCC concentrations in Peucker-Ehrenbrink and Jahn[38] for Pt, Pd, Ir and Os, Wedepohl[39] for Rh and McLennan[40] for Al and assuming that lithogenic dust is the major source of Al (Table 2). For comparison, Pb was enriched 29 times compared with atmospheric soil dust.

$$\mathrm{EF(A)} = ([\mathrm{A}]/[\mathrm{Al}])_{\mathrm{peat}}/([\mathrm{A}]/[\mathrm{Al}])_{\mathrm{UCC}} \qquad (1)$$

Lithogenic and non-lithogenic PGE concentrations in peat were inferred using eqn. (2) and (3). In this calculation it is assumed that the behaviour of an element, *i.e.* with respect to mobility or accumulation by vegetation, is independent of the source of the element, *e.g.* lithogenic Pt has the same mobility as non-lithogenic Pt.

$$[\mathrm{A}]_{\mathrm{lithogenic}} = [\mathrm{Al}]_{\mathrm{peat}} \times ([\mathrm{A}]/[\mathrm{Al}])_{\mathrm{UCC}} \qquad (2)$$

$$[\mathrm{A}]_{\mathrm{non\text{-}lithogenic}} = [\mathrm{A}]_{\mathrm{peat}} - [\mathrm{A}]_{\mathrm{lithogenic}} \qquad (3)$$

All elements are enriched relative to atmospheric soil dust, and the calculated lithogenic fraction represents 4% of total Os concentration and less than 1% for the other PGE (Table 2). The occurrence of non-lithogenic PGE may be the result of

Table 1 Reported PGE concentrations and ^{187}Os/^{188}Os in cores from Thoreau's bog

Sample	Depth/cm	Age estimate/ Calendar year	Al (% wt.)	Os/pg g^{-1}	^{187}Os/^{188}Os	Pd/ng g^{-1}	Pt/ng g^{-1}	Rh/pg g^{-1}	Ir/pg g^{-1}
Core 1 01	0–6.5	2002	0.084	9.7	0.559	1.35	289	486	21
Core 1 02	6.5–8.7	1997	0.151	8.6	0.642	1.07	86	522	31
Core 1 03	8.7–10.6	1996	0.105	8.0	0.657	0.84	131	—	25
Core 1 04	10.6–12.5	1994	0.084	8.8	0.622	0.99	3.45	363	46
Core 1 05	12.5–14.5	1992	0.085	6.9	0.771	1.15	16	276	43
Core 1 06	14.5–16.5	1990	0.108	23.9	0.361	1.12	—	398	44
Core 1 07	16.5–18.5	1988	0.119	9.4	0.766	1.40	5.97	—	43
Core 1 08	18.5–20.5	1986	0.139	9.0	0.741	1.35	43	699	97
Core 1 09	20.5–22.6	1983	0.141	15.7	0.577	1.36	205	365	32
Core 1 10	22.6–24.3	1981	0.144	14.3	0.662	1.60	—	—	27
Core 1 11	24.3–25.8	1979	nd[a]	12.1	0.657	1.36	18	444	44
Core 2 01	3.9–4.8	2000	nd[a]	23.5	1.067	2.46	144	464	65
Core 2 02	5.7–6.6	1998	nd[a]	20.9	0.963	1.37	3.72	546	35
Core 2 03	7.5–8.3	1996	nd[a]	11.3	0.814	1.77	3.70	296	65
Core 2 04	9.1–9.8	1994	nd[a]	10.3	0.895	2.09	5.43	372	208
Core 2 05	10.5–11.4	1992	nd[a]	45.6	0.227	3.14	—	—	57
Core 2 06a	12.3–13.3	1990	nd[a]	9.2	0.737	1.10	3.97	547	47
Core 2 06b	12.3–13.3	1990	nd[a]	—	—	1.17	4.87	—	46
Core 2 07	14.1–15.1	1988	nd[a]	11.5	0.722	2.01	4.68	711	22
Core 2 08	16.2–17.5	1985	nd[a]	10.4	0.772	1.31	4.11	290	25
Core 2 09	18.4–19.4	1982	nd[a]	27.7	0.394	1.39	3.79	—	25
Core 2 10	20.3–21.2	1980	nd[a]	24.2	0.580	1.18	2.71	333	33

[a] Not determined.

anthropogenic deposition and/or an additional non-lithogenic, non-anthropogenic source such as rain.

The anthropogenic contribution of Os deposition is reflected in the isotopic composition of the bulk peat. Due to the production of ^{187}Os by the β^--decay of ^{187}Re (half life of ~42 Gyr) the isotopic composition of Os in a sample depends on its initial ^{187}Os/^{188}Os, its Re/Os concentration ratio and its age. The high (*i.e.* radiogenic) ^{187}Os/^{188}Os of ~1.40 characteristic for the continental crust reflects its old age and relatively high Re/Os compared to the Earth's mantle. Loess, a proxy for the eroding continental crust, has a ^{187}Os/^{188}Os of 1.05 ± 0.23.[38] In contrast, commercial Os is mined from mantle-derived PGE deposits with a low Re/Os concentration ratio and, consequently, low (*i.e.* unradiogenic) ^{187}Os/^{188}Os of ~0.1–0.2.[41–44] Osmium emission from automobile catalysts is expected to have an isotopic composition similar to that of mantle-derived Os and a ^{187}Os/^{188}Os of 0.271 has been reported for tunnel dust with an elevated Os concentration.[9]

Given that the lithogenic fraction of Os, with an assumed ^{187}Os/^{188}Os of 1.05, represents only 4% of the total Os in peat, the relatively low ^{187}Os/^{188}Os of bulk peat is definitive evidence for the deposition of naturally occurring non-lithogenic Os in the bog. Using the estimated lithogenic fraction (LF = 4%) of Os (Table 2) and assuming that lithogenic Os has the same isotopic composition as the eroding continental crust (ECC),[38] it is possible to estimate the non-lithogenic ^{187}Os/^{188}Os using eqn. 4.

$$\left(^{187}\mathrm{Os}/^{188}\mathrm{Os}\right)_{\mathrm{non-lithogenic}} = \frac{\left(^{187}\mathrm{Os}/^{188}\mathrm{Os}\right)_{\mathrm{peat}} - \left(^{187}\mathrm{Os}/^{188}\mathrm{Os}\right)_{\mathrm{ECC}} \times \mathrm{LF}}{1-\mathrm{LF}} \quad (4)$$

Non-lithogenic Os was estimated to have an average ^{187}Os/^{188}Os of 0.66 ± 0.36. The relatively high ratio compared with anthropogenic Os indicates that non-lithogenic Os is composed of at least two components: (1) anthropogenic Os with a low ^{187}Os/^{188}Os of 0.1–0.2 and (2) non-lithogenic, non-anthropogenic Os with a higher ^{187}Os/^{188}Os. A significant correlation was found between 1/(^{188}Os concentration) and ^{187}Os/^{188}Os for samples with unradiogenic Os concentrations > 1.4 pg g^{-1} (1/^{188}Os < 0.7) indicating that elevated unradiogenic Os concentrations correspond to low isotopic ratios and therefore to an anthropogenic input (Fig. 5). The intercept, which corresponds to a purely anthropogenic source of Os, is 0.15 with a standard error of 0.07 in relatively good agreement with the ^{187}Os/^{188}Os expected in South African and Russian ores,[43] but is lower than for nearby Upper Mystic Lake, possibly due to uncertainty in the correlations. The anthropogenic source of Os is 0.31 for Upper Mystic Lake with a standard error of 0.07. Samples with Os concentrations <1.4 pg g^{-1} (1/^{188}Os > 0.87) have a relatively constant ^{187}Os/^{188}Os of approximately 0.71 ± 16.

Rain is a likely candidate for the second non-lithogenic component of Os to the bog. While a fraction of anthropogenic Os can be deposited in the form of wet deposition, we refer to "rain" here to indicate solely non-anthropogenic Os deposition. As there is little data on Os concentration and isotopic composition in rainwater,[45] we suggest that continental and oceanic rain have ^{187}Os/^{188}Os similar to that of the eroding continental crust, *i.e.* 1.05, or that of seawater, *i.e.* 1.06. Assuming an anthropogenic ^{187}Os/^{188}Os of 0.14[46] and a rain ^{187}Os/^{188}Os of 1.05, it is possible to estimate the amount of Os originating from rain and from anthropogenic sources (AF = anthropogenic fraction) using eqn. 5. Small differences in the atomic weight of the endmembers[47] affect the results by less than 0.5% and have therefore been neglected in the mass balance calculations.

$$\mathrm{AF} = \frac{\left(^{187}\mathrm{Os}/^{188}\mathrm{Os}\right)_{\mathrm{non-lithogenic}} - \left(^{187}\mathrm{Os}/^{188}\mathrm{Os}\right)_{\mathrm{rain}}}{\left(^{187}\mathrm{Os}/^{188}\mathrm{Os}\right)_{\mathrm{anthropogenic}} - \left(^{187}\mathrm{Os}/^{188}\mathrm{Os}\right)_{\mathrm{rain}}} \quad (5)$$

The anthropogenic fraction represents, on average, 43% of non-lithogenic Os, while rainwater accounts for 57% of non-lithogenic Os with concentrations of 0.005 and 0.006 ng g^{-1}, respectively. Therefore, total Os is composed of 4% lithogenic Os from atmospheric soil dust, 55% of Os from rain and 41% of anthropogenic Os. Lithogenic Os in Peat Core 1 ranged from 0.32 to 0.58 pg g^{-1} with a standard deviation of 22%. Rain-derived Os concentrations (standard deviation of 22%) increased from 4.4 pg g^{-1} near the surface to 8.0 pg g^{-1} below the redox boundary, consistent with the redox sensitive behaviour of dissolved Os. Anthropogenic platinum ranged from 2.0 to 17.6 pg g^{-1} with a standard deviation of 80%. Lithogenic-derived and rain-derived Os are relatively constant in comparison with anthropogenic Os possibly due to the expected constancy of natural Os deposition over the period

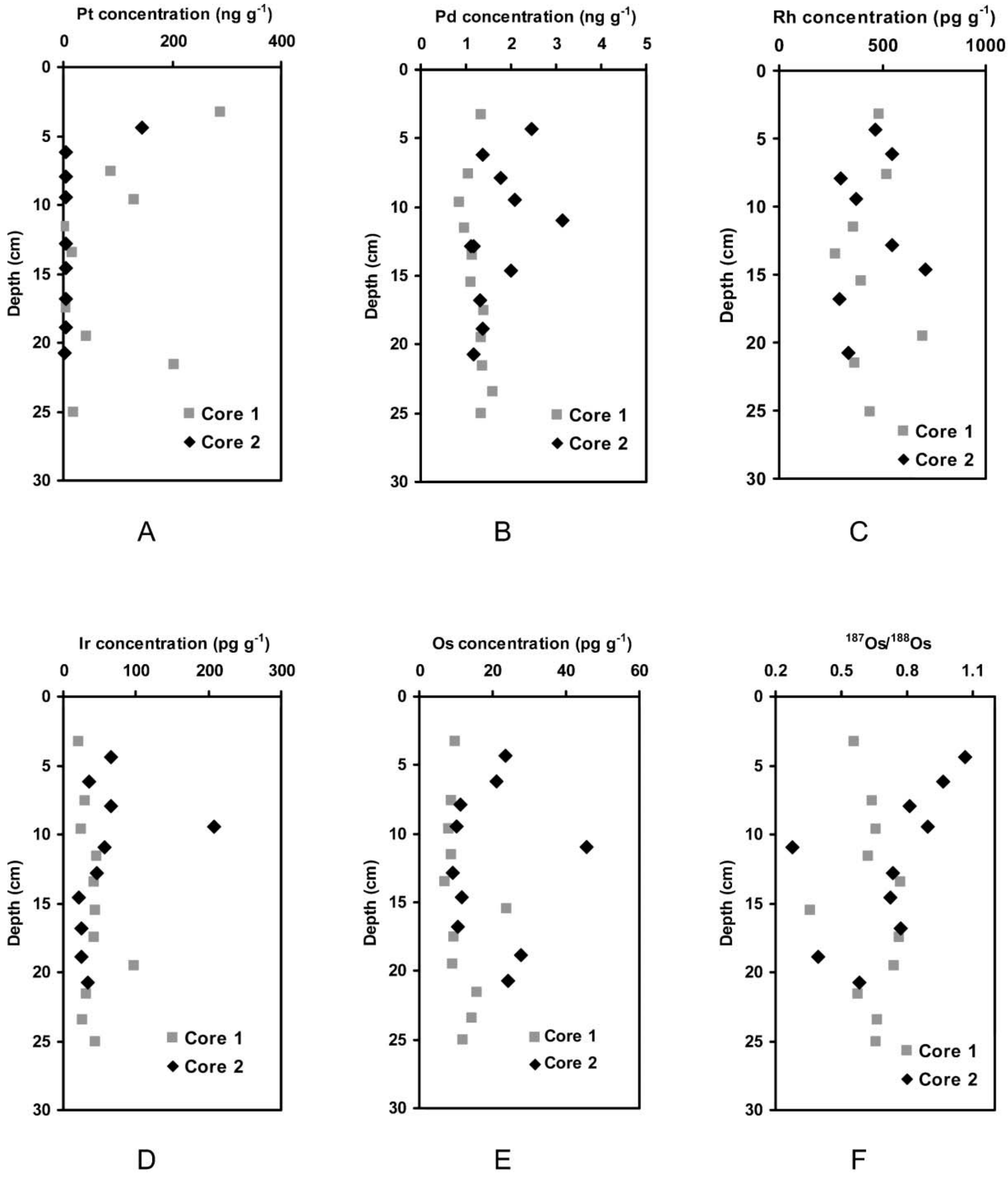

Fig. 4 Concentration profiles of (A) Pt; (B) Pd; (C) Rh; (D) Ir and (E) Os, and (F) the isotopic composition of Os in Peat Cores 1 and 2.

Table 2 Average and median concentrations, enrichment factors and lithogenic and non-lithogenic fractions of PGE in Thoreau's bog

	Concentration				
	Mean (2σ) ng g^{-1}	Median ng g^{-1}	Enrichment factor^{a} —	Lithogenic fraction^{a} ng g^{-1} (%)	Non-lithogenic fraction^{a} ng g^{-1} (%)
Pt	51 (166)	5.0	694	0.007 (0.1)	5.0 (99.9)
Pd	1.5 (1.0)	1.4	191	0.007 (0.5)	1.39 (99.5)
Rh	0.44 (0.3)	0.42	496	0.0009 (0.2)	0.42 (99.8)
Ir	0.05 (0.08)	0.04	129	0.0003 (0.8)	0.04 (99.2)
Os	0.015 (0.018)	0.011	25	0.0004 (4.0)	0.011 (96.0)

[a] Calculated based on median PGE concentration for Peat Cores 1 and 2 and Al concentration in Peat Core 1 with Pt, Pd, Ir and Os in Peucker-Ehrenbrink and Jahn,[38] Rh in Wedepohl[39] and Al in McLennan[40] for the UCC.

represented by Peat Core 1. Published data on Os in rainwater is sparse with only two samples from oceanic islands.[45] Minimum Os concentrations in rain can be calculated using the fraction of the total Os concentration in peat derived from rain according to the above mass balance calculation and the average annual rainfall. The estimated Os concentration in rainwater is 3.8 pg l^{-1}, approximately 3-fold lower than rain concentrations measured over two oceanic islands,[45] indicating

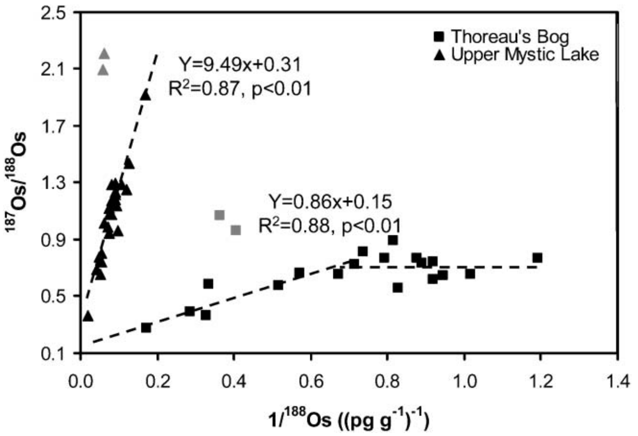

Fig. 5 Plot of ^{187}Os/^{188}Os *vs.* 1/(^{188}Os concentration) for Thoreau's Bog and Upper Mystic Lake sediments. The dashed lines show the linear regressions. In each case, two points did not fit the general trend (in grey) and were considered outliers.

either non-quantitative scavenging of rain-derived Os during peat accumulation or a lower Os concentration in continental *vs.* oceanic rain.

Fig. 5 clearly illustrates differences in the sources of Os into Thoreau's Bog and Upper Mystic Lake. While Thoreau's Bog only receives atmospheric deposition, the lake integrates deposition in the Aberjona watershed resulting in higher Os concentrations. Additional sources of radiogenic Os are also likely for Upper Mystic Lake as result of the weathering of bedrock minerals and transport of soil dust, as indicated by a 13-fold higher Ti flux. The flux of Os is approximately 10 times higher for Upper Mystic Lake than for Thoreau's Bog with 0.045 µg m^{-2} yr^{-1} and 0.005 µg m^{-2} yr^{-1} in 1992–2002, respectively, and therefore the watershed/lake surface area ratio of ~115 implies that a fraction of Os that deposits in the watershed does not accumulate in Upper Mystic Lake sediments, possibly due to retention in the watershed.

The relative importance of non-lithogenic, non-anthropogenic Os in peat may be the result of its low concentration (Table 2). Composition of the UCC[38] and seawater[46,48] indicates that Pt, Pd and Rh input to the bog from rain is relatively small (estimated based on Os concentrations) and it can therefore be assumed that the non-lithogenic component corresponds to anthropogenic input for these elements, which are characterized by higher concentrations (Table 2), while rainwater may provide a significant fraction of the total Ir. Catalysts are a major source of atmospheric PGE in the urban and roadside environment[4–6,49] and the only known source of PGE in the surroundings of the bog. Median PGE ratios in the anthropogenic fraction (Pt/Pd, Pd/Rh, Pt/Rh of 3.6, 3.3 and 11.9, respectively) agree with automobile catalysts composition, although a number of samples had elevated Pt concentrations. Platinum group element ratios in automobile catalysts have recently been estimated to be in the range 1–2.5, 4–9, and 5–16 for Pt/Pd, Pd/Rh and Pt/Rh, respectively.[50] While PGE deposition is expected to decrease sharply with increasing distance from the road, the occurrence of PGE in fine particles, *i.e.* <2 µm, facilitates transport of PGE away from roads.

Platinum group element profiles

The analyzed cores correspond to peat accumulation from 1980 to 2002. Catalysts were introduced in the US in the mid 1970s and their number increased sharply until approximately 1990.[8] It has recently been demonstrated that Pt, Pd and Rh deposition into Upper Mystic Lake increases with the number of cars equipped with catalysts.[8,9] Increasing deposition has also been observed for Ir and Os and it has been suggested that these elements are present as impurities in catalysts. In contrast, PGE concentrations in Thoreau's bog do not follow a similar trend (Fig. 4) and Al-normalized profiles, which represent the trend of PGE in atmospheric dust, do not fit with the increasing number of cars in the 1980s (Fig. 6).

The only published results on PGE in peat bogs investigates the occurrence of elevated PGE concentrations in peat as a result of the Tunguska event in Siberia in 1908.[51,52] Elevated Pd, Rh, Ru and Ir concentrations at depths below the estimated event layer demonstrate post-depositional downward transport of PGE. The absence of vertical trends for Pt, Pd and Rh despite relatively high enrichments and recent historical increases in deposition is evidence for post-depositional mobility in the bog. The enrichment of Pt, Pd and Rh in the top section of the peat cores (Fig. 4 and 6) suggests that Pt, and to a lesser extent Pd and Rh, are bioaccumulated by living *Sphagnum*. The top section of Peat Core 1 is principally composed of *Sphagnum* moss with Pt, Pd, Rh and Ir concentrations of 289 ng g^{-1}, 1.35 ng g^{-1}, 0.49 ng g^{-1} and 0.021 ng g^{-1}, respectively (Table 1). Concentrations of 30 ± 2 ng g^{-1}, 2.4 ± 0.3 ng g^{-1}, 5.4 ± 2.5 ng g^{-1} and 0.10 ± 0.03 ng g^{-1} have been reported for Pt, Pd, Rh and Ir, respectively, in urban moss in Germany, higher than in dandelion, plantain and mushrooms.[53] The same study also includes PGE concentrations in several plants collected along German highways. While mosses were not analyzed, PGE concentrations in dandelion and plantain were higher along highways than in the urban area, indicating that PGE concentrations would also be higher for mosses along highways.[53] PGE concentrations in surface vegetation from Thoreau's Bog are lower than for urban mosses, except for Pt. Catalysts are the main source of PGE in the urban and roadside environment and PGE deposition is believed to decrease sharply with increasing distance from traffic. Concentrations of PGE in surface samples from Thoreau's Bog are expected to be lower than for urban mosses and the relatively high Pt concentration in Thoreau's Bog is therefore surprising. Estimation of the number of particles in peat assuming that particles are fine-grained and purely metallic indicate that nugget effect and the resulting heterogeneity are unlikely to be responsible for the high concentrations observed.

A large fraction of PGE in airborne particles is expected to be soluble in weak acid solutions. Alt *et al.*[5] have reported that 30–43% of Pt in airborne dust is soluble. The average solubility of PGE in emissions from two gasoline catalysts was 5% and 16% for Pt and >50% for Pd and Rh.[3] Low pH and the occurrence of organic ligands in *Sphagnum* moss and peat may aid further dissolution of deposited PGE.[54,55] A variety of functional groups capable of chelate formation and ion exchange, such as uronic acids formed during the synthesis of cell walls, are present in *Sphagnum* moss. In general, sorption will also be favoured by heavier metals with higher ionic charge.[56] We suggest therefore that there is a soluble fraction of PGE in particles which deposit onto the bog that reacts with the moss surface by adsorption, chelation and ion exchange. The importance of living moss for Pt, Pd and Rh accumulation is supported by the good correlation between Pt, Pd and Rh and essential elements, *i.e.* Ca, Mg, K and P in Peat Core 1 ($r^2 > 0.5$, $p < 0.05$) due to high concentrations of these elements in the top of the core (Fig. 2 and 6). No correlation was found for sulfur, which is unlikely to be a limiting nutrient, and there was no correlation with the non-essential elements, *i.e.* Al, Si (for most plants) and Pb. Accumulation of PGE below the surface vegetation occurs with the formation of peat from the accumulation and compaction of dead mosses. Long term leaching of peat by rainwater may cause leaching of PGE, resulting in higher concentrations in peat than in *Sphagnum*. The very high Pt concentrations in surface samples and a few deeper samples are still unexplained and could be the result of a recycling of Pt at the surface of the bog, resulting in an enrichment of PGE in *Sphagnum*.

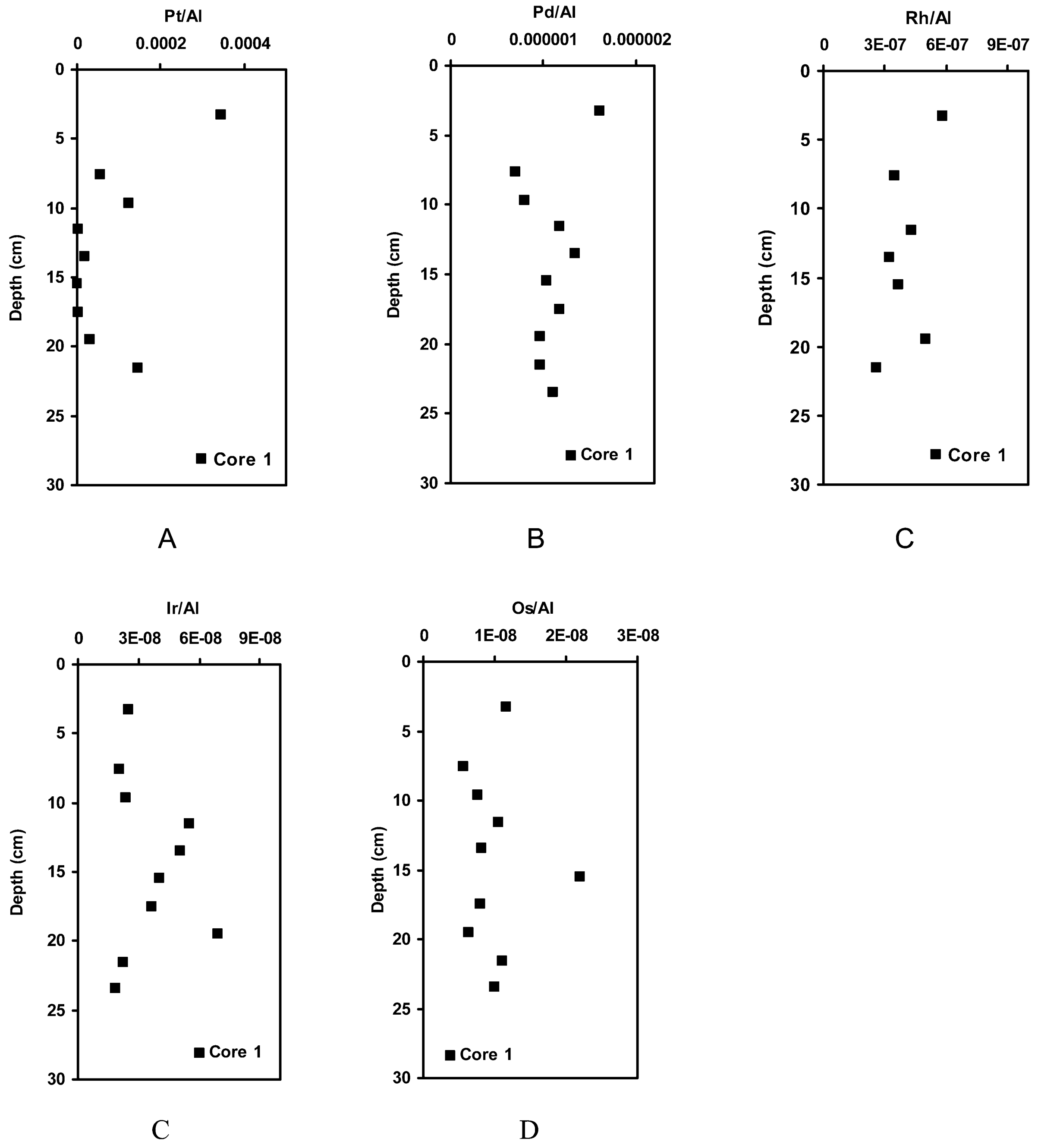

Fig. 6 Aluminium normalised concentration profiles of (A) Pt; (B) Pd; (C) Rh; (D) Ir and (E) Os in Peat Core 1.

Rates of atmospheric PGE deposition were estimated from PGE concentrations in the peat cores for the period 1992–2002 and the mass accumulation rate obtained from ^{210}Pb dating. While the median Pt deposition rate of 8.0 μg m^{-2} yr^{-1} is certainly overestimated owing to high Pt accumulation, deposition rates are expected to be more accurate for the other PGE. Deposition rates were 0.68 μg m^{-2} yr^{-1}, 0.21 μg m^{-2} yr^{-1}, 0.022 μg m^{-2} yr^{-1} and 0.005 μg m^{-2} yr^{-1} for Pd, Rh, Ir and Os, respectively. Deposition is lower than for Upper Mystic Lake, which both collects atmospheric deposition from a larger watershed area and receives terrestrial runoff,[8,9] but is higher than in Greenland (deposition rate estimated from concentrations and snow accumulation rate).[11]

Conclusion

The occurrence of elevated PGE concentrations compared with levels expected from the deposition of atmospheric soil dust provides evidence of non-lithogenic PGE deposition. While the source of Pt, Pd and Rh is believed to be primarily anthropogenic, wet deposition provides an important source of Os and possibly Ir owing to their lower concentrations. Automobile catalysts are the principal anthropogenic source of PGE in the surroundings of the bog and, therefore, catalysts are believed to be the source of anthropogenic PGE into the bog, indicating a regional dispersion of these elements. Thus our study does not contradict possible transport of PGE over long distance that may contribute to increasing concentrations in Greenland ice over the past decades.

Overlaying vegetation was found to play an important role in the cycling of these metals. Platinum group elements do not appear to be sufficiently immobile in peat to support the reconstruction of chronological profiles of PGE deposition using peat cores. Further studies are needed to estimate the importance of diagenesis and provide a better understanding of the mechanisms by which it occurs.

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