(This is a sample cover image for this issue. The actual cover is not yet available at this time.)

Science of the Total Environment 450-451 (2013) 271–279

Contents lists available at SciVerse ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

How suitable are peat cores to study historical deposition of PAHs?

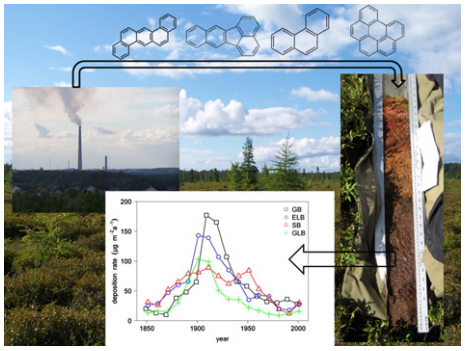
Sabine Thuens [a], Christian Blodau [a,b], Michael Radke [a,c,*]

[a] Department of Hydrology, BayCEER, University of Bayreuth, Bayreuth, Germany
[b] Hydrology Group, Institute of Landscape Ecology, University of Muenster, Muenster, Germany
[c] Department of Applied Environmental Science (ITM), Stockholm University, Sweden

HIGHLIGHTS

- We critically evaluate bogs as natural archives of atmospheric PAH deposition.
- PAHs are not degraded in the peat and there are no signs of their vertical mobility.
- Time trends compared to a sediment core, but deposition rates to peat are lower.
- Bogs are suitable to infer long-term time trends, short events might be missed.
- The low depth resolution of peat sampling methods is a major source of uncertainty.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 19 July 2012
Received in revised form 19 December 2012
Accepted 28 January 2013
Available online xxxx

Keywords:
Polycyclic aromatic hydrocarbons
Deposition time trends
Ombrotrophic bogs
Natural archive

ABSTRACT

Ombrotrophic peat bogs are natural archives of atmospheric pollution, their depth profiles can be used to study the deposition chronology of harmful contaminants. Prerequisites for deriving historical deposition rates from the peat archive are that contaminants are persistent and immobile in the peat and that the applied dating technique is accurate. To examine these requirements and the accuracy of peat archives for polycyclic aromatic hydrocarbons (PAHs) 12 peat profiles were sampled in 4 bogs in Ontario, Canada, as well as surface peat in one bog. Additionally we carried out laboratory incubations; no degradation occurred over a 3-year period in these experiments. The standard deviations of PAH concentrations in surface samples and of PAH inventories in whole cores was approximately 30%, and concentrations in surface peat were on average 50% higher in hollows than in hummocks. No indications for mobility of PAHs were observed in peat. Temporal deposition trends inferred from peat cores were generally in agreement with trends derived from a sediment core sampled close by but deposition rates to the sediment were substantially higher. A major source of uncertainty was the rather coarse vertical sampling resolution of 5 cm which introduced substantial uncertainty in the dating of the individual segments. This caused variations of the deposition rates up to 70% per PAH between three replicate cores, and it also impedes the identification of deposition peaks. Overall, we conclude that peat cores are suitable archives for inferring atmospheric deposition trends, but due to their relatively low temporal resolution short-term events may not be identified and the development of sampling methods that allow a higher vertical resolution would greatly improve the performance of the method. The analysis of more than one core per site is suggested to provide a realistic estimate of the historic deposition and total inventories.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitously present in the environment and were one of the first groups of atmospheric

* Corresponding author at: Department of Applied Environmental Science (ITM), Stockholm University, Sweden. Tel.: +46 86747136.
E-mail address: michael.radke@itm.su.se (M. Radke).

0048-9697/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.scitotenv.2013.01.091

pollutants to be identified as carcinogenic. They are formed by incomplete combustion or high temperature pyrolytic processes of fossil fuels and other organic materials (Wild and Jones, 1995). They are non-polar and have a high affinity to organic matter (Berset et al., 2001).

As the active sampling of environmental pollutants at high temporal and spatial resolution or over extended periods is highly cost and labor intensive, natural archives such as snow and ice, marine and lacustrine sediments, various biological media (corals, tree rings, herbarium specimens), and peat bogs have been used to study atmospheric pollution with organic or inorganic contaminants. For the determination of temporal and spatial trends of atmospheric PAH contamination, the analysis of sediment cores is well established as lake sediments provide a high temporal resolution. Sediment cores have, for example, been used to study historical PAH contamination (Hites et al., 1980; Laflamme and Hites, 1978; Schneider et al., 2001; Simcik et al., 1996; Wakeham et al., 1980). However, the concentration profiles obtained from sediment cores may be disturbed by seasonal mixing processes in the lake, bioturbation, and lake sediment focusing. The latter process considerably influences the sediment deposition rates and depends largely on the lake morphology (Blais and Kalff, 1995). Lake sediments also receive pollutants that are not deposited directly to the lake surface, but elsewhere in the catchment. This might lead to an overestimation of the deposition rates, as for example observed by Sanders et al. for the insecticide DDT (Sanders et al., 1995).

In contrast to sediments, ombrotrophic peat bogs only receive wet and dry deposition from the atmosphere and are not influenced by processes in the catchment. Because of the acidic and anoxic conditions prevailing below the water table, decomposition of biomass is slow. This leads to continuous growth of bogs (Zaccone et al., 2009a). The widespread distribution in the northern wet temperate and southern boreal zone and the similarity of peat bogs with respect to vegetation and hydrology thus provide an opportunity to establish spatial and historical patterns of atmospheric deposition based on this archive.

Organic pollutants are deposited to vegetation from the gaseous phase or bound to particles. From the gas phase they can enter vegetation by deposition onto the waxy cuticle of the leaves or by uptake through the stomata and subsequent translocation by the phloem. Particle-bound pollutants stick to the surface or a partly downwashed by rain, depending on particle size and leaf surface (Hosker and Lindberg, 1982). The pollutants accumulate in the living plants, which are decomposed to peat, an organic residue of varying composition and texture (Holoubek et al., 2000; Johnsen and Karlson, 2007). Due to its high organic matter content peat is a promising archive for atmospheric PAHs. As PAHs are highly sorptive to organic matter, their post-depositional mobility is assumed to be negligible (Sanders et al., 1995). Moreover, because of their low water solubility and the strong sorption PAHs are poorly available for microorganisms (Breedveld and Sparrevik, 2000; Shuttleworth and Cerniglia, 1995). In combination with the acidic and anoxic conditions and consequently a low overall metabolic activity in zones below the water table, the degradation of PAHs in peat is assumed to be very slow. Several studies have previously used peat cores to determine historical deposition rates and concentrations of PAHs (Berset et al., 2001; Dreyer et al., 2005a; Sanders et al., 1995).

A critical factor for establishing depositional records is the accurate dating of the stratified peat deposits. To this end radioisotopes such as ^{210}Pb have been used together with the constant rate of supply (CRS) model. The CRS model has been widely used to determine carbon, nitrogen, and metal accumulation rates in peat (Moore et al., 2004; Norton et al., 1997; Turetsky et al., 2004; Turunen et al., 2004). The slope gives then the accumulation rate (g cm^{-2}a^{-1}) which can be used to calculate the age of the samples. Dating through ^{210}Pb should be verified by independent chronostratigraphic markers (Urban et al., 1990); to this end, the peak of ^{241}Am deposition resulting from the peak of the nuclear bomb testing in 1962/1963 has been proposed as well as pollen records or other characteristic markers.

Although peat cores have been used previously as archives of atmospheric pollutant deposition, to our knowledge the suitability of bogs as archives for organic pollutants and the uncertainties inherent to this archive have not been systematically scrutinized. Such a critical evaluation is the objective of the present study. This study is based on 12 peat profiles sampled in 4 bogs in Ontario, Canada, on samples of surface peat at another bogs, and on one sediment core from a lake in the vicinity of one of the bogs. We studied PAH degradation in peat under aerobic and anaerobic conditions, analyzed the heterogeneity of PAH records within sites and with reference to the microtopography within a bog. Finally, we compared the PAH deposition rates derived from the peat archives to those derived from the sediment core.

2. Materials and methods

2.1. Sampling

In 2007 and 2008 five peat bogs in eastern Ontario, Canada were sampled: Giant Bog (GB, this name was assigned to this site as no previous description and thus no established name was available), Eagle Lake Bog (ELB), Spruce Bog (SB), Green Lake Bog (GLB), and Mer Bleue Bog (MB) (coordinates are given in Table S1, a map is available as Fig. S1 in the Supplementary material). All peatlands had a hummock-hollow microtopography. The vegetation was dominated by Sphagnum with ericaceous scrubs, characteristic for most ombrotrophic bogs in eastern Canada (Turunen et al., 2004). The pore water pH of the sampled bogs ranged from 3.5 to 4.5, which is typical for ombrotrophic bogs (Coggins et al., 2006). Samples were taken at the domed ombrotrophic section of the bogs at the largest possible distance to nearby roads. Triplicate peat cores were sampled with a box corer (87 × 90.6 × 1000 mm) from undisturbed hollows (<10 m distance between sampling locations), avoiding peat compaction as far as possible. Below the living vegetation which was discarded, the cores were cut into 5 cm segments with a knife in the field; each segment was wrapped in aluminum foil, transferred to a plastic bag and stored in a cooler. The box corer and the knife were rinsed with distilled water and ethanol before each sample. At the MB site, we sampled surface peat by cutting it with a knife just below the living vegetation at 5 hollows and hummocks, respectively. Each sample was individually wrapped in aluminum foil and stored in a sealed plastic bag in a cooler.

One sediment core was sampled with a gravity corer at the deepest point of Opeongo Lake (location and details are given in Muir et al. (2009) and in the Supplementary material). It was sectioned in 1-cm intervals. All samples were frozen directly after arrival in the laboratory.

2.2. Degradation experiments

A sufficiently large amount of peat was sampled at Mer Bleue from the layer directly below the active vegetation (aerobic) and from the catotelm (anaerobic peat sampled from approx. 10 cm below the water table), respectively. These samples were homogenized and split into aliquots which were used for the incubation experiments.

Peat samples were incubated under controlled aerobic and anaerobic conditions in the laboratory at optimal degradation conditions to simulate a longer degradation time. For anaerobic incubations, 50 g of fresh wet peat sampled from the catotelm was weighed into crimp vials (120 mL), and the vials were capped with a gas-tight rubber/PTFE septum. The gas phase was replaced by N_2 immediately after capping and subsequently once a week. By this a limitation of degradation by the accumulation of CO_2 and CH_4 in the gas phase was avoided (Goldhammer and Blodau, 2008). The concentrations of oxygen, CO_2, and CH_4 in the headspace were determined regularly by gas chromatography with thermal conductivity and flame ionization detection to

ensure that anaerobic conditions and an active microbial consortium were prevalent (method described by Goldhammer and Blodau (2008)). Rates of CO_2 and CH_4 release were determined by linear regression of the concentration increase over a period of 5 days at 11 sampling events over 2 years.

Aerobic incubations were carried out accordingly with peat from the aerobic zone, but with a permeable filter membrane instead of the rubber septum and without replacing the gas phase. The gravimetric water content was kept constant at around 90%, similar to the original content of fresh aerobic peat; it was controlled regularly by weighing the vials and re-adjusted if necessary by adding distilled water.

Both aerobic and anaerobic incubations were carried out at 15 °C in the dark. Three replicates were sampled after 2, 5, 9, 13, 20, 26, and 33 months and analyzed for their PAH content. All concentrations reported for the aerobic incubation experiments were normalized to the weight of dry peat at the beginning of each experiment. In order to not disturb anaerobic microbial consortia we did not dry the anaerobic peat in the beginning. Therefore, concentrations in the anaerobic peat are normalized to the weight of dry peat at the end.

2.3. Analytical methods

All solvents were of residue analysis quality (nonane and dichloromethane purchased from Promochem, Wesel, Germany; hexane from J.T. Baker, Griesheim, Germany). Native and isotope-substituted PAHs (purity > 98%) were purchased from Ultra Scientific (North Kingstown, USA), Cambridge Isotopes (Andover, USA), and Dr. Ehrenstorfer (Augsburg, Germany). Glassware was machine washed, solvent rinsed, and baked at 280 °C overnight.

Peat and sediment samples were freeze dried, milled to a fine powder in a pebble mill and kept frozen until extraction with pressurized liquid extraction. Extraction cells had glass fiber filters from Whatman (Whatman GF/B, Maidstone, UK) at both ends and were filled with 5 g of dry peat or sediment. A solution containing isotope-substituted PAHs as recovery standards (60 ng each of phenanthrene-*d*10, fluoranthene-*d*10, pyrene-*d*10, chrysene-*d*12, benzo[a]pyrene-*d*12) was spiked directly onto the peat. The cells were filled with diatomaceous earth (Celite545 coarse, Sigma-Aldrich, Munich, Germany) and extracted with pressurized liquid extraction (ASE 200, Dionex Co., Sunnyvale, USA). Cells were filled with hexane, pressurized to 14 MPa, and heated to 120 °C within 6 min. Pressure and temperature were held for 5 min, followed by rinsing with cold solvent (60% of the cell volume) and purging with argon for 90 s. This extraction cycle was repeated once. The extract was reduced to about 1 mL with a rotary evaporator (Büchi, Switzerland). For extract clean-up, 3 g of aluminum oxide (aluminum oxide 90, neutral, deactivated with 15 wt.% water, 70–230 mesh from Merck, Darmstadt, Germany) upon 5 g of silica gel (silica gel 60, 200 mesh; Merck), was filled into glass columns of 1 cm diameter and equilibrated with hexane. The extracts were then quantitatively transferred to the columns and eluted with 35 mL of hexane followed by30 mL of hexane/dichloromethane 3/1 (v/v) as described by Dreyer and Radke (2005). The combined extracts were evaporated to approx. 1 mL by the use of a rotary evaporator and then subjected to size exclusion chromatography for further clean-up. To this end, columns of 2.2 cm diameter filled with Bio-Beads (S-X-3, Bio-Rad, Hercules, USA) equilibrated with hexane/dichloromethane 1/1 were used. The extracts were quantitatively transferred to the columns and eluted with 60 mL of hexane/dichloromethane 1/1. This fraction was discarded. The target compounds were then eluted with 120 mL of hexane/dichloromethane. The column was subsequently rinsed with additional 100 mL of the solvent mixture and re-used. The extracts were evaporated to 1 mL by a rotary evaporator and finally evaporated to dryness under a gentle stream of nitrogen. Prior to injection, samples were redissolved in 200 μL of a solution containing two deuterated PAH (anthracene-*d*10 and benzo[*a*]anthracene-*d*12) in nonane and transferred to glass vials.

We quantified the following 10 out of the 16 EPA-PAHs: phenanthrene (Phen), fluoranthene (Flt), pyrene (Pyr), benzo[*a*]anthracene (B[a]A), chrysene (Chry), benzo[*b*]fluoranthene (B[b]F), benzo[*k*]fluoranthene (B[k]F), benzo[*a*]pyrene (B[a]P), indeno[1,2,3-*cd*]pyrene (Ind), and benzo[*ghi*]perylene (B[ghi]P), and additionally benzo[*e*]pyrene (B[e]P), and benzo[*j*]fluoranthene (B[j]F). However, due to incomplete chromatographic separation of B[b]F, B[k]F and B[j]F in many chromatograms, the sum of the three compounds is reported as B[b + k + j]F. The total concentration of all PAHs is referred to as $\sum_{12}$ PAH throughout the manuscript.

One part of the samples was analyzed by a ion trap GC/MS (CP-3800 and Saturn 2000, Varian, Darmstadt, Germany) and the other part was analyzed on a quadrupole GC/MS (GC 8000 MS, Finnigan, Austin, USA). The chromatographic conditions are listed in the Supplementary material.

PAH calibration solutions (native compounds and recovery standards (see above): 50 ng mL^{-1}–2000 ng mL^{-1}; injection standards anthracene-*d*10 and benzo[*a*]anthracene-*d*12: 200 ng mL^{-1}) were prepared by diluting stock solutions in nonane. They were measured with each set of samples.

The analytical procedure was evaluated by analyzing commercially available certified reference material (IAEA-159, Sediment; n = 5) as well as diatomaceous earth spiked with a known concentration of all native PAHs (n = 5). Laboratory blank samples (n = 13) were analyzed with every set of samples.

Dry-milled subsamples (approximately 1 g from each 5 cm peat segment, 200 mg of each 1 cm sediment segment) were submitted to Flett Research Ltd (Winnipeg, Canada) or to the Institute of Environmental Geochemistry (University of Heidelberg, Germany) for ^{210}Pb analysis. In 4 cores the activity of ^{241}Am was measured as additional chronostratigraphic marker.

2.4. Calculations

All PAH concentrations were normalized to the dry weight (dw) of the peat sample.

The inventories of the PAHs were calculated as the total integrated mass of a compound per unit area as described by Schneider et al. (2001). Only layers younger than 1880 were taken into account so that all peat profiles represent the same time span.

Deposition rates of the individual PAHs (ng m^{-2} a^{-1}) were calculated by dividing the measured mass of PAHs per peat segment by the number of years covered by this segment and the surface area sampled. To derive average deposition rates from the three cores sampled in each bog, the deposition rates derived from each core were averaged to 10 year periods as described by Dreyer et al. (2005b).

Deposition rates determined for Opeongo Lake were corrected by division with a sediment particle focusing factor of 2.66. We obtained this factor by multiplying the excess ^{210}Pb inventory with the decay constant of ^{210}Pb and dividing it by the excess ^{210}Pb atmospheric deposition rate estimated for this longitude by Muir et al. (2009).

Statistical analysis was conducted with the software R (R Development Core Team, 2011).

3. Results and discussion

3.1. Evaluation of the analytical methods

The mean recovery rates of the isotope-labeled internal standards were between 48 ± 27% (Phen-*d*10) and 86 ± 29% (Pyr-*d*10) (n = 126). The operational limit of quantification (LOQ) determined according to DIN 32645 (1994) ranged from 2 ng g^{-1} (Phe) to 11 ng g^{-1} (Chry); details are summarized in Table S2 in the Supplementary material. As concentrations in peat and sediment were generally > LOQ, we did not

determine the limit of detection (LOD). Some blank samples contained individual PAHs at concentrations > LOQ (given in Table S3). However, we did not observe a systematic contamination pattern in the blanks. Except for Chry in one blank sample, concentrations in the blanks were at least one order of magnitude lower than in the field samples. Therefore, the results were not blank corrected.

Recovery of the PAHs spiked to diatomaceous earth ranged from 95% (B[a]A) to 136% (Pyr), and PAH concentrations measured in the reference sediment (IAEA-159, Sediment) were comparable to the concentrations given by the distributor (shown in Fig. S2). Thus, the clean-up procedure was suitable to separate the interfering and complex matrix of peat from the PAHs at acceptable recovery of the analytes, and the overall analytical method can be considered appropriate for the purpose of this study.

3.2. PAH degradation in peat

The CO_2 and CH_4 production rates determined in our degradation experiments (1.37 ± 1.13 ($n = 24$) and 1.06 ± 0.98 ($n = 15$) μmol g^{-1} dw peat d^{-1}, respectively) are within the range of rates determined by Moore and Dalva (1997) in similar incubation experiments. These production rates indicate an active peat degrading microbial community.

In the samples incubated at aerobic conditions, the PAH concentrations did not change significantly ($p \leq 0.1$) over time as shown in Fig. 1 (other compounds are presented in Fig. S3 as Supplementary material). Similarly, in the anaerobic incubations there was no significant concentration trend ($p \leq 0.1$) for any PAH (Fig. 1 and Fig. S4 (Supplementary material)). Although there is some scatter in the data, we consider these interpretations valid based on the large number of samples and replicates they are based on.

Although the incubation period was much shorter than the period covered by the peat cores (up to 200 years) we think that this finding can be extrapolated to somewhat longer time scales as we maintained optimal degradation conditions throughout the incubation period. Therefore, degradation rates in the incubation experiments should be higher than in the field. This is based on the following reasons: i) the time while PAHs are present in the aerobic part of the peat is limited (although still in the range of 50–100 years in the studied bogs); ii) the anaerobic incubation experiments were carried out at relatively high temperature (15 °C) while turnover in the field is limited by colder temperatures (mean annual temperature 6 °C, 4 months a year below 0 °C (Moore et al., 2006)), and iii) the anaerobic incubations were not limited by an accumulation of the decomposition products CO_2 and CH_4, which in undisturbed bogs limits the overall microbial turnover in deeper peat layers (Blodau et al., 2011).

The stability of PAHs against degradation has also been studied in other media. Schneider et al. (2001) reported no degradation of PAHs in sediment cores sampled in the Great Lakes. In contrast to their and our findings, Lei et al. (2005) observed a 50–80% removal of 2- to 5-ring PAHs in field-contaminated sediment during 24 weeks of incubation under aerobic conditions. This discrepancy to our observations can at least partly be explained by the high organic matter content of peat and thus a very high adsorbed PAH fraction, for which degradation should be very slow or does not occur (Eriksson et al., 2000; Johnsen et al., 2005) due to a lack of bioaccessibility (Johnsen and Karlson, 2007). In the experiments by Lei et al. (2005) degradation was inhibited when the pH was below 4.5, and no degradation of PAHs was observed under anaerobic conditions. These two conditions apply to the anaerobic parts of ombrotrophic bogs and thus limit the PAH degradation there. Based on the results of our incubation experiments and these findings, we conclude that post-depositional degradation of PAHs in peat is not significant on the time-scale of our experiments (3 years) and that it is likely that such a degradation is quantitatively of limited importance also on longer timescales.

3.3. Dating

Mean total residual unsupported ^{210}Pb activity in the dated peat cores was 0.64 ± 0.17 Bq cm^{-2}, which is higher than the average activity of 0.35 ± 0.11 Bq cm^{-2} measured by Turunen et al. (2004) in Canadian

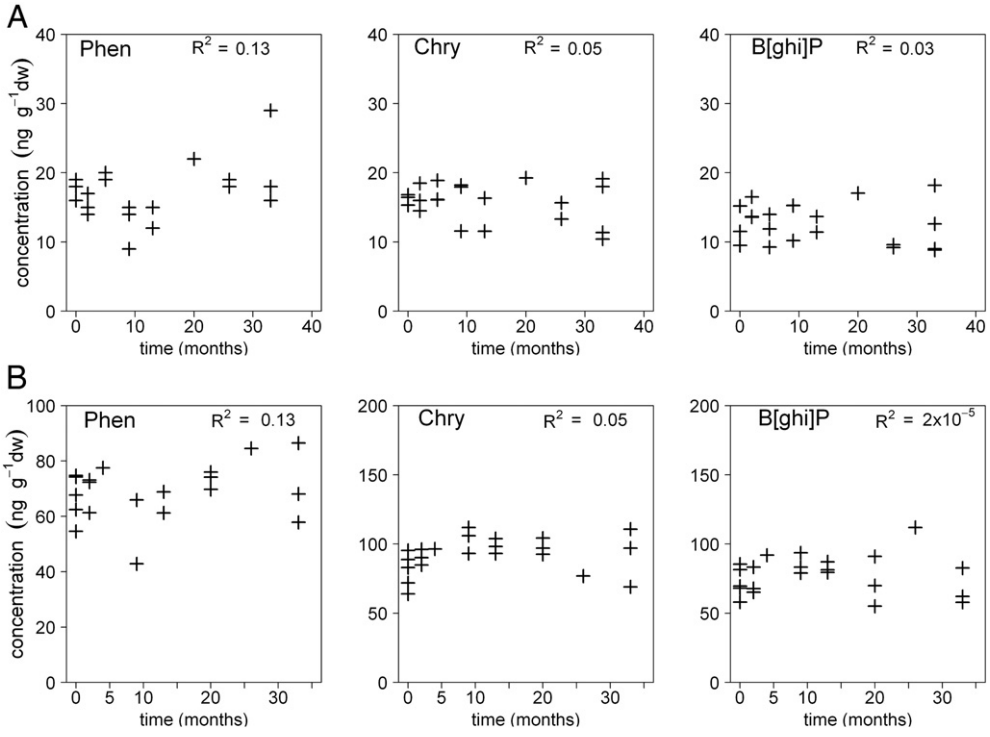


Fig. 1. Concentration time trends of phenanthrene, chrysene, and benzo[ghi]perylene in the aerobic (A) and anaerobic (B) degradation experiments with coefficient of determination for a linear regression.

bogs but in the range of soil inventories reported for North America (0.31–0.84) by Urban et al. (1990). The CRS model was exclusively applied as all cores reached background activities and because it provided reasonable age predictions for each section even though the peat accumulation rate was changing with time.

The ^{210}Pb method is based on the assumption of post-depositional immobility of atmospherically derived constituents (Shotyk et al., 1997; Vile et al., 1999). However, the mobility of ^{210}Pb is discussed controversially in the literature. On the one hand Urban et al. (1990) concluded that ^{210}Pb is mobilized by the organic-rich waters of peatlands and inventories of ^{210}Pb in hummocks are depleted compared to peatland hollows. On the other hand, Vile et al. (1999) and MacKenzie et al. (1997) demonstrated the immobility of ^{210}Pb in peat profiles. One way of assessing the mobility of lead in individual peat profiles is the interpretation of the lead distribution with respect to the water table. Fluctuations of the redox potential caused by water table movements can affect metal solubility and mobility. When lead is dissolved in the pore water, it is mobilized and accumulates in the depth of the water table (Vile et al., 1999). Consequently, the activity of ^{210}Pb should be enhanced in this depth if a substantial relocation of lead occurs at the specific site. However, none of the peat cores sampled in this study showed a maximum of ^{210}Pb activity in the depth of the water table at the time of sampling. Instead, the ^{210}Pb activity in the peat cores as well as in the sediment core decreased exponentially as a function of cumulative dry weight ($R^2 > 0.8$; see Fig. S5 in the Supplementary material), indicating a low mobility of lead in the sampled cores. However, even if post-depositional mobility of ^{210}Pb in peat cannot be excluded, it does not affect the dating results obtained through the CRS model as long as it occurs at a uniform rate from year to year throughout the entire profile (Urban et al., 1990).

In four of our peat cores we measured the ^{241}Am activity to assess the dating accuracy. In core GB 2 the ^{241}Am peak appears in the segment dated to 1944–1962. This coincides with the maximum of the nuclear bomb testing activities in 1963. One core (SB 1) did not show a clear maximum of ^{241}Am activity, although the ^{210}Pb activity in this profile decreased exponentially with depth which indicates an intact core. In the two other cores the ^{241}Am activity peaked in layers dated to 1937–1956 (SB 2) and 1909–1933 (GB 1). Overall, ^{241}Am seems to appear slightly too early in most cores. However, it has to be taken into account that ^{241}Am itself might be somewhat mobile in peat as observed by Mitchell et al. (1992). Moreover, as the temporal resolution of the peat profile is rather low individual segments can cover several decades. This is reducing the temporal resolution necessary to detect a sharp ^{241}Am peak, and depending on the segment borders a peak might even appear in an older peat layer. This possible peak shift is illustrated in the Supplementary material with a synthetic dataset (Fig. S6). Based on these results, we conclude that the findings by Urban et al. (1990) that dates based on ^{210}Pb can be inaccurate by as much as 30 years are likely to be applied to this study. However, other authors have reported a substantially lower dating inaccuracy. Appleby et al. (1997) used Cannabis pollen and ^{241}Am as independent chronostratigraphic maker for ^{210}Pb dating and found good agreement. Turunen et al. (2004) used a charcoal horizon resulting from a peat fire to validate the ^{210}Pb dating and reported a difference of only 4–8 years. Such differences might be due to site- or core-specific factors and are thus difficult to generalize.

The temporal resolution of the segments within individual cores varied considerably, i.e. the 5 cm segments represented very different time spans. While the upper layers can represent as little as 5 years, the lower layers comprised up to 70 years. This can be attributed to the ongoing peat mineralization and compaction of the lower layers. Moreover, the time span covered by segments sampled in identical depths of the three replicate cores per bog was highly variable as shown in Fig. 2A. This can be critical for the analysis of deposition peaks as there is the potential for substantial underestimation of maximum deposition rates during peak periods which are "diluted" by a period of lower deposition rates represented within the same core segment.

One difficulty regarding the interpretation of three replicate cores from one bog arises from the different periods covered by each individual segment. This precludes direct averaging of the three deposition profiles. To alleviate this problem, we generated 10 year average values as described in Dreyer et al. (2005b).

As shown in Fig. 2B, this approach usually preserves the maximum deposition rates while generating somewhat sharper deposition peaks. We examined several modifications of this method. Increasing the aggregation period from 10 to 20 or 30 years did not lower the variation between the deposition rates of the 3 cores, but lowered the maximum deposition rates considerably as shown in Fig. 2C. Decreasing the aggregation period to less than 10 years created sharp deposition peaks that were unrelated to measured data. Therefore, we consider the aggregation to 10 year-periods as most appropriate. To improve the temporal resolution of the method and to allow a better comparability of replicate cores, it would be necessary to sample thinner peat segments. This has been successfully used by Givelet et al. (2004) for the analysis of several elements (mainly metals) in 1 cm sub-sections of peat cores. However, given the dimensions of currently available peat corers, such thin slices will not provide the peat mass which is necessary to meet the detection limits of the analytical method for PAHs in all of the sections, and consequently this higher vertical resolution was not applicable in the current study.

Overall, based on our results we conclude that dating inaccuracies can mainly be attributed to the coarse resolution of the 5 cm segments rather than to a general inapplicability of the ^{210}Pb method in bogs.

3.4. Vertical mobility of PAHs

To use peat cores as archives of atmospheric pollution, the contaminants have to be immobile within the profile. This has been questioned by Malawska et al. (2006) who determined more LMW PAH in deeper

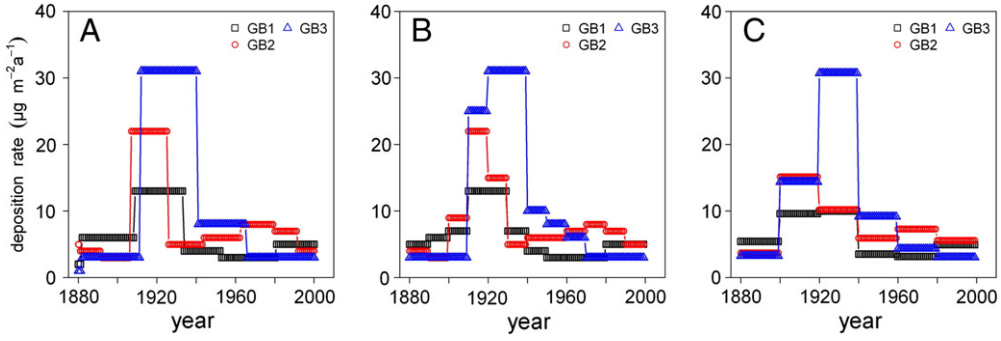


Fig. 2. Deposition time trend of phenanthrene in three replicate cores at GLB presented in original data (i.e., the concentration of each segment is plotted for the entire period covered by this segment) (A) and averaged to segments of 10 years (B) and 20 years (C).

depth than HMW PAHs in peat profiles and therefore assumed a downward movement of LMW PAHs. However, we did not observe such a difference in the distribution of LMW and HMW PAH within the profiles as the deposition rates of all PAHs correlate significantly ($p<0.1$; see Fig. S7 in the Supplementary material). Moreover, the PAH concentration profiles and reconstructed deposition rates show a relatively sharp increase after 1870, which is the time of a substantial increase of industrial emissions (see Section 3.7 for details) in the study region (see Figs. S8 and S9 in the Supplementary material for concentrations of Phen (LMW) and Ind (HMW), and Fig. 3 for deposition rates of Σ_{12} PAH). For compounds undergoing vertical transport in the peat, an apparent increase of deposition rates should be detected before the actual increase of emissions. This indicates that the PAHs were not transported downward along the peat profile to a large extent.

3.5. Reconstructed deposition rates

Statistical analysis did not reveal significant differences between concentrations of the individual PAHs over depth ($p<0.1$). This indicates that the compounds behave similar in all cores. Therefore, analyzing the sum of all compounds does not mask any trends of individual compounds and consequently we present the results mostly as $\sum_{12}$ PAH in the following. The most abundant compounds were Phen, Flt, Chry, Pyr, Ind and B[ghi]P. The maximum $\sum_{12}$ PAH deposition rates ranged from 180 μg $m^{-2}a^{-1}$ in GB to 59 μg $m^{-2}a^{-1}$ in GLB (Table 1). These deposition rates are very similar to those reported by Dreyer et al. (2005a) who determined $\sum_{11}$ PAH deposition rates to 17 bogs in eastern Canada. Except for one subset (group 2b) of their bogs which was characterized by higher PAH contamination they reported deposition rates in the range between 20 and 150 μg $m^{-2}a^{-1}$.

Although the 5 cm sections represent differing time spans, the deposition rates of the 3 cores per bog had similar maxima dated to 1880–1940 (given in Fig. S10 in the Supplementary material). All 3 cores of ELB showed a small secondary maximum. In SB 1 this secondary maximum was higher and in SB 3 even equal to the first one. In SB 2 only one broad peak was observed. In the profile of GLB 1 two small peaks were displayed in contrast to high single ones in GLB 2 and 3. These differences can be caused by different deposition to the individual locations in the bog or more likely by the rather coarse resolution of the peat cores with 5 cm segments (see example for apparent time shift in Supplementary material Fig. S6 and discussion above). By sampling of 5 cm sections or by subsequent averaging of the three cores, the two maxima may be merged into one and the information on these secondary maxima gets lost. The disparity between cores with one and two deposition maxima has also been observed previously. Dreyer et al. (2005b) found two maxima of PAH deposition in four out of fifteen sampled bogs. A difference in the intensity of the secondary peak has also been observed by Givelet et al. (2004) in Pb concentration profiles in peat. Secondary maxima of PAH deposition have also been observed by Schneider et al. (2001) in sediments from the Great Lakes, but not by Simcik et al. (1996). As shown above,

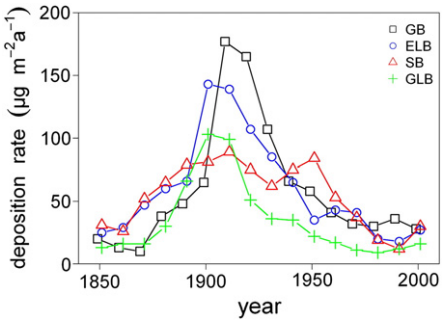


Fig. 3. Deposition rates of $\sum_{12}$ PAHs to the sampled bogs averaged to decades (n = 3).

Table 1
Maximum $\sum_{12}$ PAH deposition rates with years of occurrence and inventory per peat profile and average inventory per bog with standard deviation (s.d.).

	Max. deposition rate		Inventory	Average inventory (s.d.)
	Year	$\sum_{12}$ PAHs (μg $m^{-2}a^{-1}$)	$\sum_{12}$ PAHs (mg m^{-2})	$\sum_{12}$ PAHs (mg m^{-2})
GB 1	1909–1933	180	6.1	7.4 (1.1)
GB 2	1907–1925	176	8.2	
GB 3	1912–1940	172	7.8	
ELB 1	1902–1919	171	9.5	7.5 (1.8)
ELB 2	1875–1911	119	6.3	
ELB 3	1898–1926	137	6.6	
SB 1	1940–1970	95	4.0	5.9 (1.9)
SB 2	1911–1936	115	7.8	
SB 3	1893–1923	85	6.0	
GLB 1	1883–1913	59	5.8	4.6 (1.1)
GLB 2	1893–1920	136	4.2	
GLB 3	1901–1926	120	3.8	
OPL	1961–1968	379	18.4	

a secondary and rather narrow peak of deposition might not be captured in cores with a comparatively low temporal resolution. This should be taken to account when interpreting deposition time trends, and averaging of replicates has also to be used with caution. Deposition trends of each single core prior to any data aggregation should be presented in addition to the average trends per site (see Fig. S10 in the Supplementary material).

The average deposition rates obtained from 10-year aggregated deposition trends of the three replicate cores per site are shown in Fig. 3 (the same figure including error bars is available as Fig. S11 in the Supplementary material). The reconstructed historical deposition trends derived at the five bogs show increasing PAH deposition after 1870. This is consistent with the beginning of smelting operations in Sudbury (SARA, 2008), a city located upwind of the bogs which has been a major source of airborne contaminants to this region, and with the overall steep increase of steel production and industrial coal consumption in Ontario between 1880 and 1900 (Donald, 1915). Other sources such as residential heating or wood burning have certainly also contributed to PAH immissions to the bogs, but these can be assumed to be comparatively small and especially their source strength can be assumed to be rather constant during this period if compared to the industrial emissions. Decreasing deposition rates after 1940 might reflect the installation of filters and replacement of the blast furnaces and roast yards by multi-hearth roasters and reverberatory furnaces for smelting (SARA, 2008) and other measures to reduce industrial emissions.

3.6. Heterogeneity within one bog

Except for Flt, the PAH concentrations in surface samples taken at Mer Bleue were significantly ($p<0.05$; $n=5$) higher in hollows than in hummocks (Fig. 4, data are given in Table S3). The $\sum_{12}$ PAH concentration was 225 ± 34 ng g^{-1} in hollows and 142 ± 31 ng g^{-1} in hummocks. This finding illustrates the influence of microtopography on PAH concentrations in surface peat. A similar observation was made by Martens et al. (1997) at valleys and hills close to streets. Higher contaminant concentrations in hollows could be due to post-depositional transport of deposited particles following the microtopography of the bog during rain and snowmelt events. An alternative explanation is a reduced air velocity in hollows which might lead to an enhanced exchange between the gas phase and plant surfaces as well as to an increased deposition of particles. As it is not possible to determine the age of surface samples it might also be that the samples of hollows represent a longer accumulation period. Therefore, to avoid inconsistencies in the results it is important to exclusively sample either hollows or hummocks in studies that compare PAH inventories.

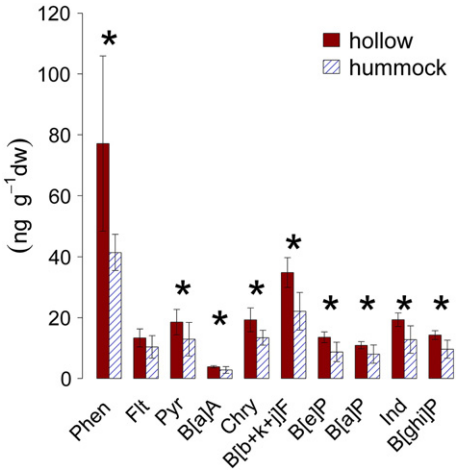


Fig. 4. Mean concentration of PAHs in surface peat samples of hollows and hummocks. Error bars represent standard deviations (n = 5), a star marks compounds with significant difference between hummock and hollow.

A measure for the total historical deposition per surface area is the inventory of contaminants. Such inventories were calculated for the period from around 1880 to present for each individual core. As the age of the lowest peat segment varies somewhat between the cores, the actual lower age is within the range from 1867 (GB 1) to 1901 (GLB 1). The average $\sum_{12}$ PAH inventories of the four bogs ranged from 4.6 mg m^{-2} (GLB) to 7.5 mg m^{-2} (ELB; Table 1). The relative standard deviations of the $\sum_{12}$ PAH inventories at the four bogs with replicate cores were between 15 and 32% which is similar to the deviation of the surface samples. This reflects the heterogeneity of PAH concentrations between different hollows of an individual bog and the combined uncertainty of the sampling and analytical methods. The inventories determined here are comparable to the $\sum_{11}$ PAH inventory of 5.67 mg m^{-2} reported by Zaccone et al. (2009b) for a peat core sampled in the Jura Mountains, Switzerland, and also to the ones that can be calculated from the concentrations published by Dreyer et al. (2005b) for several Canadian bogs. For a peat core spanning the period 1886–1989 that was sampled in comparatively close proximity to large urbanizations in the UK, Sanders et al. (1995) determined a much higher inventory of $\sum_{14}$ PAH of 216 mg m^{-2}.

The relative standard deviations of the maximum deposition rates at the individual bogs, calculated from the three replicate cores, ranged up to 70% per compound and up to 41% for $\sum_{12}$ PAH. This deviation is caused both by differences in the absolute deposition rates and by some differences in the timing of the deposition peaks. The pre- and post-maximum rates also differ as the segments they are obtained from might still represent some years of pollution. Nevertheless they were all below 50 μg m^{-2}a^{-1}. The mean recent deposition rates ranged from 13 to 34 μg m^{-2}a^{-1} for $\sum_{12}$ PAH with relative standard deviations up to 70% (Table S4 in the Supplementary material) while the rates averaged to 10 years have standard deviations from 28 to 140% for $\sum_{12}$ PAH. This high deviation of the rates averaged to 10 years is an example of how averaging of replicate cores might enhance the uncertainty as discussed above. For the metals lead and mercury, Bindler et al. (2004) reported concentrations and inventories to vary in one bog by a factor of 2 and 4, respectively. In the current study, this variation was somewhat lower for PAHs, but we agree with Bindler et al. that a single core may not provide a representative record of atmospheric deposition for one bog as a whole.

3.7. Comparison with sediment core

The $\sum_{12}$ PAH deposition rates derived from the Opeongo Lake sediment core peaked around 1920 with 249 μg m^{-2}a^{-1} and again around 1960 with 379 μg m^{-2}a^{-1}, followed by decreasing rates up to the present time. The drop in deposition rates between the two peaks reflects general economic events such as the Great Depression, for example, or changes in dominant emission sources like the installation of filters. Christensen and Zhang (1993) determined maximum deposition rates of 2.8 mg m^{-2}a^{-1} for $\sum_{12}$ PAH to Lake Michigan for the year 1985, which is one order of magnitude higher than rates determined in remote lakes (Usenko et al., 2007). Schneider et al. (2001) determined $\sum_{33}$ PAH deposition rates in sediment cores of Lake Michigan between 250 and 520 μg m^{-2}a^{-1} and inventories of 21 to 78 mg m^{-2}. They dated maximum rates to the year 1942. Simcik et al. (1996) measured $\sum_{17}$ PAH deposition rates between 700 and 1500 μg m^{-2}a^{-1} and inventories of 50 to 70 mg m^{-2}. The reconstructed deposition rates of their study peaked on a plateau from 1930 to 1975. The latter two studies report inventories and historical trends comparable to the ones determined here for Opeongo Lake (inventory of 18.4 mg m^{-2}). This is surprising as Opeongo Lake is a rural site located in a Provincial Park and thus it should not be strongly impacted by local PAH sources, whereas Lake Michigan is impacted by direct anthropogenic PAH emissions from industry, power plants, households, and traffic. Muir et al. also reported Hg concentrations in surface sediment and the anthropogenic Hg flux to the sediment of Opeongo Lake to be elevated by a factor of 2 to 30 compared to other mid latitude lakes in eastern Canada (Muir et al., 2009). Based on these unexpected contaminant levels in OPL sediment, some historic or recent input of contaminants to the lake catchment from local or direct sources (e.g., forestry or tourism) cannot be completely excluded. On the other hand, atmospheric input stemming from long-range transport has been reported to be an important source of lead (Dillon and Evans, 1982) and other metals (Wong et al., 1984) to lakes in the study region. The uncertainty with respect to contaminant sources to OPL has to be taken into account when comparing OPL and peat data.

Thanks to higher concentrations of PAHs in sediment and a matrix which can be sectioned more easily, thinner sections can be obtained from sediment cores. Therefore, the temporal resolution of the sediment is higher as demonstrated in Fig. 5 for the results of the sediment core and the peat core sampled close by (SB). The distance between Opeongo Lake and Spruce Bog is only 16 km, so it is reasonable to assume that both sites received a similar atmospheric deposition of PAHs in the past. The deposition time trends recorded in the OPL sediment core and in two of the SB peat cores are similar, while core SB2 was substantially different (as discussed above). In cores SB1 and SB3, the deposition peaks and the drop between these peaks appeared some 10–20 years earlier than in the OPL core (Fig. 5). This time shift might be caused by the time lag between deposition to lake and catchment and incorporation to the sediment. But most probably the early appearance of the peaks in SB 1 and 3 is due to the comparatively low temporal resolution of the peat profile. Still, the overall trends of PAH deposition are comparable. Good agreement in the temporal deposition trends between sediment and

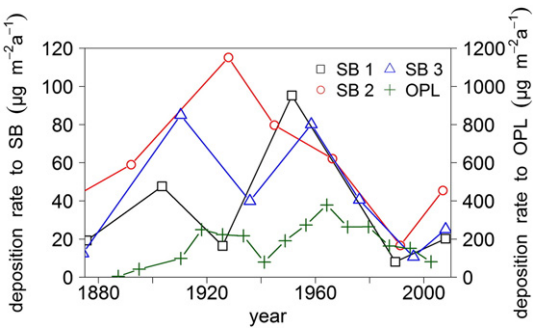


Fig. 5. Deposition rates of $\sum_{12}$ PAHs to the sediment core (OPL) and to SB; deposition to SB is represented on the left y-axis, to OPL on the right y-axis.

peat has already been demonstrated for Pb and Hg (Farmer et al., 1997; Norton et al., 1997).

The deposition rates and the inventory reconstructed from the sediment core were four times higher than those inferred from the SB cores (Table 1) for all compounds. Higher inventories and consequently higher reconstructed deposition rates for lake sediments than for bogs were also reported for Pb and Hg (Farmer et al., 1997; Norton et al., 1997). While Farmer et al. assumed a certain loss within the bog but no mobility, Norton et al. (1997) and Bindler et al. (2004) supposed that a peat core may better reflect atmospheric deposition rates than lake sediments because no watershed is involved in the delivery of the pollutants and because of the greater complexity of lake basins and sedimentation processes. The relative synchronicity of the temporal deposition trends indicates that the differences in quantity are caused by deposition to the catchment and sedimentation, and are not caused by mobility within the sediment. Further studies are necessary to determine the reason for the higher deposition rates reconstructed from sediments and more specifically to investigate whether OPL was contaminated by local sources.

4. Conclusion

Based on the results of this study, we conclude that peat bogs fulfill the criteria for an archive for atmospheric PAH deposition. The results provide evidence that i) PAHs are not degraded over longer periods, ii) PAHs are immobile once they are deposited to the peat, and iii) that the temporal deposition trends inferred from the peat archives are generally in agreement with trends derived from sediment cores and across bogs in the same region. However, this study also shows the limitations of the peat archive, which are mainly related to the temporal resolution that can be achieved. Therefore, peat cores are not suitable to display short-time events as information on these might get lost due to methodological constraints. Moreover, the comparison of three replicate cores at four sites shows that the frequently used approach of analyzing only one core per bog might not provide adequate results, both regarding the absolute magnitude of reconstructed atmospheric deposition and the deposition time trends.

To overcome some of the limitations of reconstructing PAH deposition rates from peat profiles identified in this study, larger samplers could be developed and used to allow sampling of thinner peat slices. However, this might be impaired by logistical problems when sampling in remote areas as there are limits to hand-held operation of such corers.

Acknowledgments

The authors thank the German Research Foundation (DFG; project RA 896/6-1) and the German Academic Exchange Service (DAAD; project 50021462) for the financial support, and the administration of Ontario Parks for the permission to sample in Algonquin Provincial Park. Thanks to Andriy K. Cheburkin for his help with the evaluation of the ^{210}Pb dating and the Analytical Chemistry lab at BayCEER (University of Bayreuth) and the Department of Applied Environmental Science at Stockholm University for GC/MS measurements. We also want to thank Derek Muir for providing the sediment core, Harald Biester for the CNS analyses, and Jutta Eckert for her help with sample preparation. We also thank three anonymous reviewers for their constructive comments on an earlier version of this manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2013.01.091.

References

Appleby PG, Shotyk W, Fankhauser A. Lead-210 age dating of three peat cores in the Jura Mountains, Switzerland. Water Air Soil Pollut 1997;100:223–31.
Berset JD, Kuehne P, Shotyk W. Concentrations and distribution of some polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) in an ombrotrophic peat bog profile of Switzerland. Sci Total Environ 2001;267:67–85.
Bindler R, Klarqvist M, Klaminder J, Förster J. Does within-bog spatial variability of mercury and lead constrain reconstructions of absolute deposition rates from single peat records? The example of Store Mosse, Sweden. Global Biogeochem Cycles 2004;18:GB3020.
Blais JM, Kalff J. The influence of lake morphometry on sediment focusing. Limnol Oceanogr 1995;40:582–8.
Blodau C, Siems M, Beer J. Experimental burial inhibits methanogenesis and anaerobic decomposition in water-saturated peats. Environ Sci Technol 2011;45:9984–9.
Breedveld GD, Sparrevik M. Nutrient-limited biodegradation of PAH in various soil strata at a creosote contaminated site. Biodegradation 2000;11:391–9.
Christensen ER, Zhang X. Sources of polycyclic aromatic hydrocarbons to Lake Michigan determined from sedimentary records. Environ Sci Technol 1993;27:139–46.
Coggins AM, Jennings SG, Ebinghaus R. Accumulation rates of the heavy metals lead, mercury and cadmium in ombrotrophic peatlands in the west of Ireland. Atmos Environ 2006;40:260–78.
Dillon PJ, Evans RD. Whole-lake lead burdens in sediments of lakes in southern Ontario, Canada. Hydrobiologia 1982;91:121–30.
DIN 32645. Chemische Analytik: Nachweis-, Erfassungs- und Bestimmungsgrenze, Ermittlung unter Wiederholungsbedingungen, Begriffe, Verfahren, Auswertung. Beuth: Verlag; 1994.
Donald WJA. The Canadian iron and steel history. A study in the economic history of a protected industry. Dissertation, 1915, University of Chicago, US (http://www.archive.org/details/cu31924021085687, access date 2012-12-10).
Dreyer A, Radke M. Evaluation and optimization of extraction and clean-up methods for the analysis of polycyclic aromatic hydrocarbons in peat samples. Int J Environ Anal Chem 2005;85:423–32.
Dreyer A, Radke M, Turunen J, Blodau C. Long-term change of polycyclic aromatic hydrocarbon deposition to peatlands of eastern Canada. Environ Sci Technol 2005a;39:3918–24.
Dreyer A, Blodau C, Turunen J, Radke M. The spatial distribution of PAH depositions to peatlands of Eastern Canada. Atmos Environ 2005b;39:3725–33.
Eriksson M, Dalhammar G, Borg-Karlson AK. Biological degradation of selected hydrocarbons in an old PAH/creosote contaminated soil from a gas work site. Appl Microbiol Biotechnol 2000;53:619–26.
Farmer JG, Mackenzie AB, Sugden CL, Edgar PJ, Eades LJ. A comparison of the historical lead pollution records in peat and freshwater lake sediments from central Scotland. Water Air Soil Pollut 1997;100:253–70.
Givelet N, Le Roux G, Cheburkin A, Chen B, Frank J, Goodsite ME, et al. Suggested protocol for collecting, handling and preparing peat cores and peat samples for physical, chemical, mineralogical and isotopic analyses. J Environ Monit 2004;6:481–92.
Goldhammer T, Blodau C. Desiccation and product accumulation constrain heterotrophic anaerobic respiration in peats of an ombrotrophic temperate bog. Soil Biol Biochem 2008;40:2007–15.
Hites RA, Laflamme RE, Windsor JG, Farrington JW, Deuser WG. Polycyclic aromatic-hydrocarbons in an anoxic sediment core from the Pettaquamscutt River (Rhode-Island, USA). Geochim Cosmochim Acta 1980;44:873–8.
Holoubek I, Korínek P, Seda Z, Schneiderová E, Holoubková I, Pacl A, et al. The use of mosses and pine needles to detect persistent organic pollutants at local and regional scales. Environ Pollut 2000;109:283–92.
Hosker RP, Lindberg SE. Review: atmospheric deposition and plant assimilation of gases and particles. Atmos Environ 1982;16:889–910.
Johnsen A, Karlson U. Diffuse PAH contamination of surface soils: environmental occurrence, bioavailability, and microbial degradation. Appl Microbiol Biotechnol 2007;76:533–43.
Johnsen AR, Wick LY, Harms H. Principles of microbial PAH-degradation in soil. Environ Pollut 2005;133:71–84.
Laflamme RE, Hites RA. The global distribution of polycyclic aromatic hydrocarbons in recent sediments. Geochim Cosmochim Acta 1978;42:289–303.
Lei L, Khodadoust AP, Suidan MT, Tabak HH. Biodegradation of sediment-bound PAHs in field-contaminated sediment. Water Res 2005;39:349–61.
MacKenzie AB, Farmer JG, Sugden CL. Isotopic evidence of the relative retention and mobility of lead and radiocaesium in Scottish ombrotrophic peats. Sci Total Environ 1997;203:115–27.
Malawska M, Ekonomiuk A, Wiłkomirski B. Polycyclic aromatic hydrocarbons in peat cores from southern Poland: distribution in stratigraphic profiles as an indicator of PAH sources. International Mire Conservation Group, International Peat Society; 2006.
Martens D, Maguhn J, Spitzauer P, Kettrup A. Occurrence and distribution of polycyclic aromatic hydrocarbons (PAHs) in an agricultural ecosystem. Fresenius J Anal Chem 1997;359:546–54.
Mitchell P, Schell W, McGarry A, Ryan T, Sanchez-Cabeza J, Vidal-Quadras A. Studies of the vertical distribution of ^{134}Cs, ^{137}Cs, ^{238}Pu, ^{239,240}Pu, ^{241}Pu, ^{241}Am and ^{210}Pb in ombrogenous mires at mid-latitudes. J Radioanal Nucl Chem 1992;156:361–87.
Moore TR, Dalva M. Methane and carbon dioxide exchange potentials of peat soils in aerobic and anaerobic laboratory incubations. Soil Biol Biochem 1997;29:1157–64.
Moore TR, Blodau C, Turunen J, Roulet NT, Richard PJH. Recent rates of N and S accumulation in peatlands, eastern Canada. Glob Chang Biol 2004;11:356–67.

Moore TR, Lafleur PM, Poon DMI, Heumann BW, Seaquist JW, Roulet NT. Spring photosynthesis in a cool temperate bog. Glob Chang Biol 2006;12:2323–35.
Muir DCG, Wang X, Yang F, Nguyen N, Jackson TA, Evans MS, et al. Spatial trends and historical deposition of mercury in eastern and northern Canada inferred from lake sediment cores. Environ Sci Technol 2009;43:4802–9.
Norton SA, Evans GC, Kahl JS. Comparison of Hg and Pb fluxes to hummocks and hollows of ombrotrophic big heath bog and to nearby Sargent Mt. Pond, Maine, USA. Water Air Soil Pollut 1997;100:271–86.
R Development Core Team. R: a language and environment for statistical computing. Vienna, Austria: R Foundation for Statistical Computing; 2011 [http://www.r-project.org/].
Sanders G, Jones KC, Hamiltontaylor J, Dorr H. PCB and PAH fluxes to a dated UK peat core. Environ Pollut 1995;89:17–25.
SARA. Volume I — chapter 3: historical review of air emissions from the smelting operations. http://www.sudburysoilsstudy.com/EN/media/volume_I.asp. 2008. [access date: 2012-07-03].
Schneider AR, Stapleton HM, Cornwell J, Baker JE. Recent declines in PAH, PCB, and toxaphene levels in the northern Great Lakes as determined from high resolution sediment cores. Environ Sci Technol 2001;35:3809–15.
Shotyk W, Norton SA, Farmer JG. Summary of the workshop on peat bog archives of atmospheric metal deposition. Water Air Soil Pollut 1997;100:213–9.
Shuttleworth K, Cerniglia E. Environmental aspects of PAH biodegradation. Appl Biochem Biotechnol 1995;54:291–302.
Simcik MF, Eisenreich SJ, Golden KA, Liu S-P, Lipiatou E, Swackhamer DL, et al. Atmospheric loading of polycyclic aromatic hydrocarbons to Lake Michigan as recorded in the sediments. Environ Sci Technol 1996;30:3039–46.
Turetsky MR, Manning SW, Wieder RK. Dating recent peat deposits. Wetlands 2004;24:324–56.
Turunen J, Roulet NT, Moore TR, Richard PJH. Nitrogen deposition and increased carbon accumulation in ombrotrophic peatlands in eastern Canada. Global Biogeochem Cycles 2004:18.
Urban NR, Eisenreich SJ, Grigal DF, Schurr KT. Mobility and diagenesis of Pb and ^{210}Pb in peat. Geochim Cosmochim Acta 1990;54:3329–46.
Usenko S, Landers DH, Appleby PG, Simonich SL. Current and historical deposition of PBDEs, pesticides, PCBs, and PAHs to rocky mountain national park. Environ Sci Technol 2007;41:7235–41.
Vile MA, Wieder RK, Novak M. Mobility of Pb in Sphagnum-derived peat. Biogeochemistry 1999;45:35–52.
Wakeham SG, Schaffner C, Giger W. Polycyclic aromatic hydrocarbons in recent lake sediments—I. Compounds having anthropogenic origins. Geochim Cosmochim Acta 1980;44:403–13.
Wild SR, Jones KC. Polynuclear aromatic hydrocarbons in the United Kingdom environment: a preliminary source inventory and budget. Environ Pollut 1995;88:91-108.
Wong HKT, Nriagu JO, Coker RD. Atmospheric input of heavy metals chronicled in lake sediments of the Algonquin Provincial Park, Ontario, Canada. Chem Geol 1984;44:187–201.
Zaccone C, D'Orazio V, Shotyk W, Miano T. Chemical and spectroscopic investigation of porewater and aqueous extracts of corresponding peat samples throughout a bog core (Jura Mountains, Switzerland). J Soils Sediment 2009a;9:443–56.
Zaccone C, Gallipoli A, Cocozza C, Trevisan M, Miano T. Distribution patterns of selected PAHs in bulk peat and corresponding humic acids from a Swiss ombrotrophic bog profile. Plant Soil 2009b;315:35–45.