Long-Term Change of Polycyclic Aromatic Hydrocarbon Deposition to Peatlands of Eastern Canada

ANNEKATRIN DREYER,[†,‡]
MICHAEL RADKE,*,[†]
JUKKA TURUNEN,[§] AND
CHRISTIAN BLODAU[†,‡]

Department of Hydrology and Limnological Research Station, University of Bayreuth, 95440 Bayreuth, Germany, Kuopio Unit, Geological Survey of Finland, Post Office Box 1237 (Neulaniementie 5), 70211 Kuopio, Finland, and Department of Geography and Centre for Climate & Global Change Research, McGill University, 805 Sherbrooke Street West, Montreal H3A 2K6, Canada

To date, studies about historic PAH (polycyclic aromatic hydrocarbons) deposition at a regional scale have rarely been published. To address this research gap, we sampled 17 ombrotrophic peatlands across eastern Canada. The peat cores from hollows were dated with ^{210}Pb for the period of about 1850−2000 and analyzed for their PAH concentration, so PAH deposition could be reconstructed. Peat samples were extracted by accelerated solvent extraction (ASE). The extracts were purified by column chromatography with aluminum oxide and silica gel. PAH were measured by gas chromatography−tandem mass spectrometry (GC−MS/MS). Overall reconstructed deposition rates of Σ-11 PAH ranged from 4 to 1432 μg m^{-2} year^{-1}. Three different long-term trends in PAH deposition could be distinguished: sites with two separated periods of maximum PAH deposition, sites with one period of maximum PAH deposition, and sites with no clearly separated period of maximum PAH deposition. Increasing PAH depositions were caused by rapid industrialization accompanied by extensive use of fossil fuels; decreasing PAH depositions were caused by substitution of these fuels and movements of PAH emitting industry to different regions. At all sites either phenanthrene (20−60%) or benzo[*b+k*]fluoranthene (10−40%) was the predominant PAH. Detailed analysis of three bogs suggested that combustion of coal and vehicle exhausts mainly contributed to the peat PAH burden. The temporal trends of PAH deposition indicated that increases in the PAH deposition rates followed the industrial development in Canada, particularly in the periods 1880−1910 and 1940−1960. Recent abatement efforts were reflected in decreased PAH deposition rates to about 15% of the maximum.

Introduction

Polycyclic aromatic hydrocarbons (PAH) are an important group of organic contaminants that are widespread in the environment. It has long been established that atmospheric PAH are mainly emitted from incomplete combustion processes of carbonaceous materials. Additional PAH sources in soils and sediments can be diagenetic and (micro-)biological processes (*1−3*). Depending on the physicochemical properties of the PAH, aerosol particle size, and atmospheric conditions, transport distances of hundreds to thousands of kilometers have been reported (*4−6*).

Global PAH contamination has mainly resulted from large-scale industrial manufacturing in the northern hemisphere since the Industrial Revolution (*7*). Historic increases in PAH deposition are thus generally explained by the onset of the Industrial Revolution, whereas decreases are related to the substitution of coal as energy source by hydroelectric power, natural gas, or nuclear power, the decline of heavy industry, and the regulation of air pollution (*7, 8*). Today, PAH contamination still originates from anthropogenic sources almost exclusively. However, in sediments and waterlogged soils, (micro-)biological sources might be important for some PAH such as perylene, naphthalene, and potentially phenanthrene (*2, 3, 9, 10*).

Investigations of long-term changes of PAH deposition are scarce and are mostly restricted to control plots in long-term experimental studies such as archived soils from Rothamsted Experimental Station (*11, 12*) and lake sediments (*13−15*). The interpretation of PAH concentration profiles from lake sediments is complicated, however, by transport processes in lake sediments, such as bioturbation, sediment focusing, resuspension, and the delivery of substances from nonatmospheric sources (*16*). Compared to lake sediments, undisturbed ombrotrophic peat bogs offer some advantages for the investigation of historic trends in atmospheric deposition of organic contaminants, mainly because compounds are derived only from atmospheric deposition and degradation and also because postdepositional mobility is limited (*7, 8, 16, 17*).

Few studies have reported PAH deposition histories in peatlands. Sanders et al. (*7*) analyzed 14 PAH in a peat core collected in the U.K. and found the maximum PAH deposition rate (about 3000 μg m^{-2} year^{-1}) in 1932. In this peat core, deposition rates remained high until the early 1970s and declined afterward to about 20% of the maximum. Similar results were obtained for an ombrotrophic bog in Switzerland analyzed by Berset et al. (*8*).

Detailed source apportionment in historical trend studies is also rare. Traffic and coal-related sources have been considered to be the most important PAH source categories in many modern metropolitan areas (*18, 19*). In the 1960s to the 1980s the contribution of motor vehicles to the total PAH emissions in the USA was estimated to be about 36%, aluminum production and forest fires each contributed 17%, followed by residential wood combustion, coke manufacturing, power generation, and incineration, which emitted 12%, 11%, 7%, and 3%, respectively (*20* and references therein). Such estimates strongly vary for different regions, though. Wild and Jones (*21*), for example, estimated that domestic coal and wood combustion contributed >80% to the PAH emissions of the U.K. in the 1990s and attributed only minor proportions to emissions of vehicles, power plants, and waste incineration.

We investigated peat profiles from 17 ombrotrophic bogs along a transect across eastern Canada for their content of 13 PAH from the EPA priority list and also benzo[*e*]pyrene and perylene. The specific objectives were to elucidate PAH deposition in eastern Canada throughout the 19th and 20th century and to relate PAH deposition rates both temporally

* Corresponding author phone: +49/921/552297; fax: +49/921/552366; e-mail: michael.radke@uni-bayreuth.de.
† Department of Hydrology, University of Bayreuth.
‡ Limnological Research Station, University of Bayreuth.
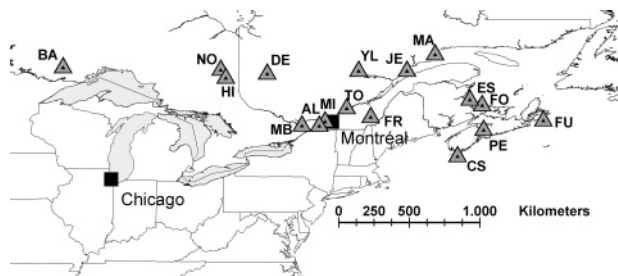§ Geological Survey of Finland and McGill University.

FIGURE 1. Locations of bogs analyzed in this study: Alfred Bog (AL), Baker Bog (BA), Cape Sable (CS), Despinassy Bog (DE), Fourchu (FU), Foxley Moor (FO), Frontenac Bog (FR), Hislop Bog (HI), Ilets-Jeremie Bog (JE), Lac à la Tortue (TO), Mai Bog (MA), Mer Bleue (MB), Mirabel (MI), Norembego (NO), Petite Bog (PE), Point Escuminac (ES), and Yellow Lake (YL).

and spatially to the industrial development of eastern Canada. To these ends, three profiles representing the general deposition patterns are described in detail with respect to their location in the transect, their deposition patterns, potential PAH sources, and correlations to parameters potentially influencing PAH emissions.

Experimental Procedures

Sampling Locations. Fifteen undisturbed ombrotrophic bogs in eastern Canada were sampled in 2000. In 2003, two additional bogs in the Laurentian lowlands were sampled in order to enlarge the number of sites in the developed Ottawa–Montreal region. The locations of the peatlands are shown in Figure 1. A description of the vegetation and characteristics of the peatlands are given by Lavoie and Richard (22) and Turunen et al. (23).

Sampling and Analytical Protocol. Peat samples were taken with a box sampler ($85 \times 85 \times 1000$ mm). At each site cores were taken from undisturbed hollows in the ombrotrophic section of the bog; hollows were selected because of less compaction during sampling compared to hummocks. Peat cores were cut into 5 cm segments, coarse root fragments were removed, and the samples were dried at 70 °C (in 2000) or 30 °C (in 2003). Possible losses of PAH due to sample drying at 70 °C in 2000 were evaluated by comparing the results (Σ11-PAH, see below) of a core taken in 2000 to a core taken from the same location in 2003 but dried at 30 °C. We found no significant influence (t-test, $\alpha = 0.05$) of the drying temperature on the determined PAH concentrations. After drying, the samples were ground with a pebble mill and stored until analysis. All solvents were of picograde quality (Promochem, Wesel, Germany). PAH standards were purchased from Ultra Scientific (North Kingstown, RI), Sigma–Aldrich (Munich, Germany) and Cambridge Isotopes (Andover, MA) at purity >98%. All glassware was machine washed, rinsed with solvent and baked at 280 °C overnight for cleaning. Samples (5 g) were extracted with accelerated solvent extraction (ASE, Dionex 200, Dionex Co., Sunnyvale, CA). An internal standard solution (100 μL) containing six deuterated PAH (acenaphthene-d_{10}, Fluo-d_{10}, Pyr-d_{10}, Pery-d_{12}, Chry-d_{12}, and BghiP-d_{12}; see abbreviations below) were spiked directly onto the peat. Cells were filled with solvent (hexane/acetone 2:1 v:v), pressurized to 14 MPa, and heated to 120 °C within 6 min. Pressure and temperature were held for 5 min (static extraction), followed by rinsing with cold solvent (60% of the cell volume) and purging with argon for 90 s. This extraction cycle was repeated once. Afterward, samples were filtered over Na_2SO_4 and transferred into 250 mL pointed flasks. Three drops of toluene were added as keeper and the solvent was reduced to about 1 mL by use of a rotary evaporator. For extract cleanup, 3 g of aluminum oxide (deactivated with 15 wt % water; alox 90, neutral, 70–230 mesh, Merck, Darmstadt, Germany) upon 5 g of silica gel

(silica 60, 200 mesh, Merck) were filled into glass columns of 1 cm diameter and purged with hexane. The extracts were transferred to the columns and eluted with 35 mL of hexane and 30 mL of hexane/dichloromethane 3:1 (v/v), respectively. Sample volume was reduced by use of a rotary evaporator, and samples were finally evaporated to dryness under a gentle stream of nitrogen. Prior to injection, samples were redissolved in 200 μL of an internal standard solution containing two deuterated PAH (Ant-d_{10} and BaA-d_{12}) in toluene and transferred to glass vials. Samples were analyzed by GC–MS/MS (CP-3800 and Saturn 2000, Varian, Darmstadt, Germany). We quantified 13 EPA-PAH: fluorene (Fluo), phenanthrene (Phen), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chry), benzo[b+k]fluoranthenes (Bb+kF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), dibenz[a,h]anthracene (DahA), and benzo[ghi]perylene (BghiP), and additionally benzo[e]-pyrene (BeP) and perylene (Pery). The following instrumental parameters were used: cool on-column injection; injection volume 1.5 μL; injector program 60 °C held for 1 min, 200 °C min⁻¹ to 320 °C, held for 30 min; column VF-5ms (Varian; 50 m × 0.25 mm × 0.25 μm); carrier gas flow (He) 1.2 mL min⁻¹; temperature program 2 min at 60 °C, 20 °C min⁻¹ to 190 °C, 5 °C min⁻¹ to 325 °C, and held for 7 min. The overall recovery rates of individual internal standards were between 69% ± 14% and 89% ± 16% (number of samples 170). With each set of 10 samples, a laboratory blank was run. PAH were seldom identified in blanks and were never present at concentrations above the analytical limit of detection, which was estimated at 0.02 μg mL⁻¹.

In some peat cores, we observed difficulties with the identification of BaA and Chr because the quality criteria of the mass spectra were not met and so compounds had to be regarded as not detected. To get a comparable database for all bogs, both compounds were not taken into account for data analysis; the sum of the remaining 11 EPA-PAH is referred to as Σ11-PAH below.

The peat cores were dated by use of ²¹⁰Pb ($t_{1/2} = 26.26$ years). Fresh peat samples of 1 cm thickness were taken from each 5 cm peat segment and submitted to Flett Research Ltd., Winnipeg, Canada, for ²¹⁰Pb analysis. Dry 0.5 g subsamples were analyzed for ²¹⁰Pb activity by the measurement of the α-emitting ²¹⁰Po, after spiking with a ²⁰⁹Po yield tracer. To determine the age of the peat samples, the constant rate of supply (CRS) model (24) was applied. Changes of water table, dissolved organic matter (DOM), or diagenetic processes may affect the distribution and/or mobility of the radioisotopes within a profile (7, 25–27). However, Turunen et al. (23) could compare a charcoal horizon resulting from a peat fire (in a bog not analyzed in this study) with the ²¹⁰Pb dating and observed age differences <8 years. Thus age resolution of the ²¹⁰Pb method is estimated to be no better than ±10 years (27). The results of the peat cores' dating, as well as concentrations and deposition rates of carbon, nitrogen, and sulfur, are discussed in detail by Moore et al. (28).

Calculations. PAH concentrations were calculated from the dry weight (dw) of the samples. Taking the exact dimensions of the peat segments and their bulk densities, reconstructed PAH deposition rates in micrograms per square meter per year were calculated. Bogs with similar temporal deposition patterns were grouped together. Out of each group, one profile was chosen for detailed description. For Frontenac Bog and Alfred Bog (both sampled in 2003), no deposition rates could be calculated because dating results were not available; concentrations were used instead.

Statistical analyses were carried out with WinSTAT (version 1999.1; R. Fitch Software, Staufen, Germany). The reconstructed deposition rates were averaged for periods of 10 years and correlated (Pearson correlation) to sulfur

TABLE 1. Published Concentration Ratios of Individual PAH in Emissions of Specific Fuels or Aerosols Affected by Combustion of Specific Fuels

PAH source	Flt/BeP	Pyr/BeP	Bb+kF/BeP	BaP/BeP	Phen/Ant	Flt/Pyr
combustion of brown coal[a]	7.6	5.2	4.0	1.5		
combustion of hard coal[a]	7.1	6.6	3.1	1.2		
diesel engine exhausts[a]	7.0	8.1	2.5	0.4		
gasoline engine exhausts[a]	20.0	30.0	1.5	1.1		
combustion of heating oil[a]	85.0	38.0	3.5	0.2		
mineral oil[b]					50.0	
motor vehicle exhausts[b]				0.2-0.5	4.0	
pyrogenic origin (combustion of fossil fuels or wood)[b]						1.0
petrogenic origin (noncombustion or petroleum derived)[b]						≫1

[a] Data from Jacob et al. (30). [b] Data from Yang et al. (31) and references therein.

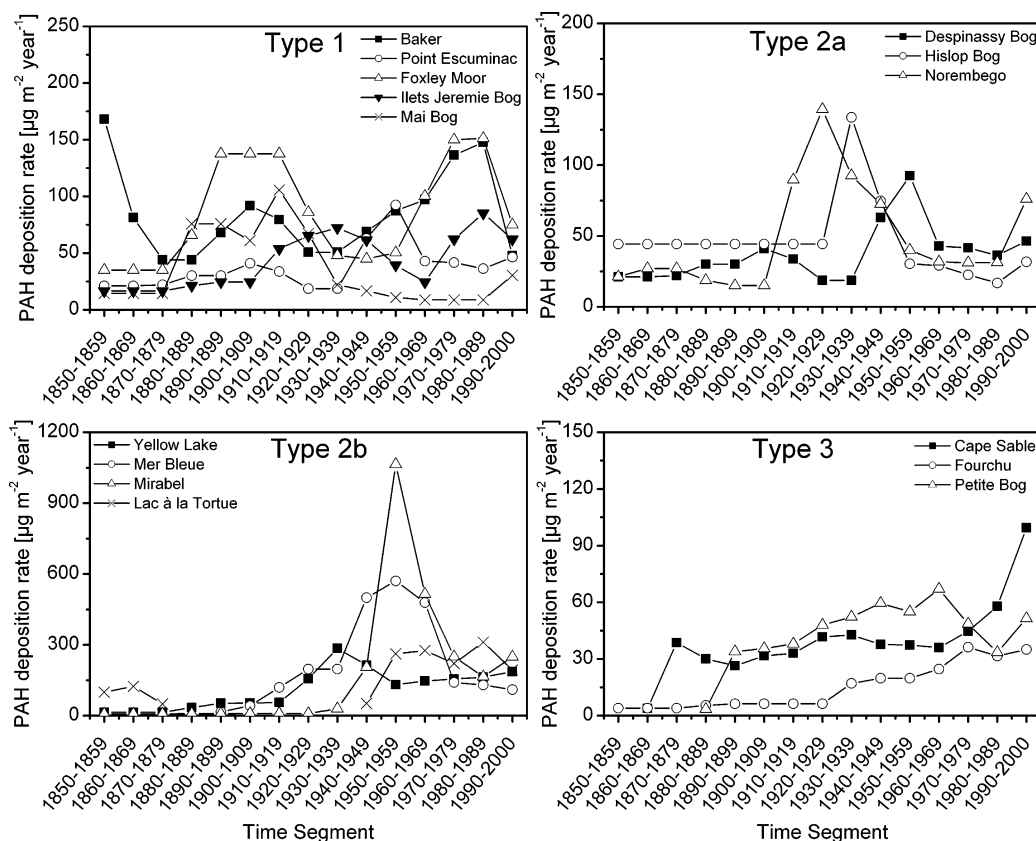**FIGURE 2. Temporal variation in reconstructed Σ11-PAH deposition rate, 1850−2000, in 15 bogs and separation into three groups according to the temporal trends. Type 2 was split into two graphs because of the wide range of deposition rates. Deposition rates were averaged for 10-year periods. At Lac à la Tortue, PAH were not detectable in several time segments. For details see text.**

deposition rates of each bog [data from Moore et al. (28)], total Canadian coal consumption (coal production + coal import − coal export), total Canadian energy production, total Canadian vehicle registrations, total Canadian population, and the total area burned by forest fires (data obtained from Statistics Canada) averaged for the same periods.

Source identification was carried out by dividing concentrations of individual PAH in each segment to corresponding concentrations of BeP, Ant, and Pyr. BeP has been frequently used as reference compound since it is chemically stable and it is found predominantly in the particulate phase of the atmosphere (29). Results were compared to concentration ratios of PAH sources reported and applied in the literature (30, 31) (Table 1).

Results

In the 17 peat cores, Σ11-PAH concentrations of the most recent depth segments ranged from 68 to 363 µg kg⁻¹ dw. Highest Σ11-PAH concentrations of about 2790 µg kg⁻¹ dw

were found at the Mer Bleue bog. Σ11-PAH concentrations of the oldest analyzed sections were in the range of 62−630 µg kg⁻¹ dw. The reconstructed Σ11-PAH deposition rates ranged between 4 and 168 µg m⁻² year⁻¹ in the oldest segments and between 49 and 641 µg m⁻² year⁻¹ in the most recent ones. Maximum Σ11-PAH deposition rates of 1432 µg m⁻² year⁻¹ were reached at Mirabel. Pery was not detected in any sample.

Three types of temporal PAH deposition patterns were distinguished (Figure 2). A first group (deposition type 1), consisting of Baker Bog, Foxley Moor, Ilets-Jeremie Bog, and Point Escuminac, was characterized by two distinct and clearly separated periods of strongly enhanced PAH deposition rates. Generally, the first maximum occurred at the turn of the 19th to the 20th century, and the second one followed in the second half of the 20th century. These bogs were located at the western and eastern fringe of the investigated region (see Figure 1). Another group (type 2) contained bogs with only one peak of the PAH deposition rate in the 20th century.
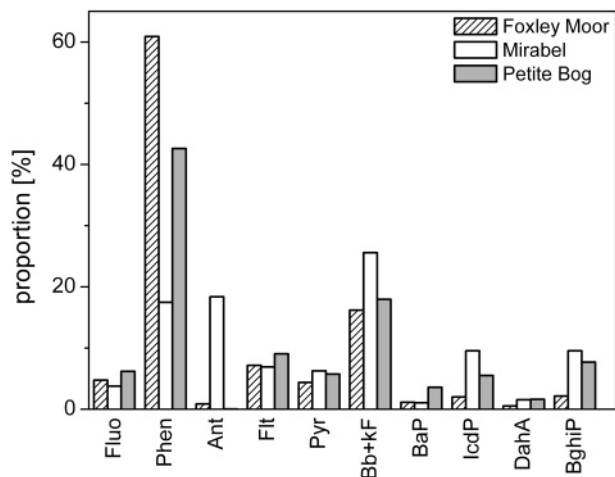
FIGURE 3. Relative contribution of individual PAH to deposition of Σ11-PAH at Foxley Moor, Mirabel, and Petite Bog (average from 1850 to 2000).

This group was characterized by relatively big differences in PAH deposition rates between the individual peatlands (Figure 2, types 2a and 2b) and was located in the center of the investigated region. The two nondated bogs, Frontenac and Alfred Bog, belonged to this group, too, with one clearly separated concentration maximum of 1184 μg kg^{-1} dw at 35–40 cm and 1824 μg kg^{-1} dw at 20–25 cm, respectively (data not shown). In comparison, Mirabel had a concentration maximum of 2155 μg kg^{-1} dw in the 25–30 cm depth segment.

The third group (type 3) consisted of bogs showing no clear maximum in the historical PAH deposition pattern, but with a general increase through time and deposition rates not higher than 110 μg m^{-2} year^{-1}. The bogs assigned to this group (Cape Sable, Fourchu, and Petite Bog) were located in Nova Scotia.

To discuss PAH compositions and identify PAH sources, we selected one bog out of each deposition group (Foxley Moor for type 1, Mirabel for type 2, and Petite Bog for type 3). These sites differed primarily with respect to the relative importance of Phen vs Bb+kF and the occurrence of IcdP and BghiP (Figure 3).

At the remote Foxley Moor site, Phen was the most abundant PAH, contributing on average 60% of the deposited Σ11-PAH, followed by Bb+kF (16%) and Flt (7%). All other PAH contributed 5% or less. In contrast, at the Mirabel site close to Montreal, the spectrum of PAH was more evenly distributed and was dominated by Bb+kF (26%) and Ant (18%), followed by Phen (17%), and Flt, Pyr, IcdP, and BghiP (5–10% each). Petite Bog represented a transition between these two patterns: With 43% on average, Phen was the most abundant PAH there, followed by Bb+kF (18%). All other PAH analyzed were present in proportions of less than 10%.

To elucidate potential sources of PAH emissions, the aforementioned ratios of individual compounds vs BeP, Ant, and Pyr were calculated for each depth segment of the three bogs (Table 2). The concentration ratios were usually quite uniform throughout the profiles, but especially at Petite, changes in several ratios were observable around 1970.

Reconstructed Σ11-PAH deposition rates at Mirabel and Petite Bog were significantly correlated to reconstructed sulfur deposition rates (Table 3), taken from Moore et al. (*28*). At Foxley Moor, the reconstructed Σ11-PAH deposition rate was significantly correlated to Canadian energy production but not to sulfur deposition rates. At Petite Bog a significant correlation was also found between the PAH deposition rates and the utilization of coal in Canada. No other significant correlation was found.

TABLE 2. Concentration Ratios of Individual PAH to BeP, Ant, and Pyr for Identification of Possible PAH Sources at Foxley Moor, Mirabel, and Petite Bog[a]

age	Flt/ BeP	Pyr/ BeP	Bb+kF/ BeP	BaP/ BeP	Phen/ Ant	Flt/ Pyr
Foxley Moor						
1999–2000	0.7	0.4	n.d.[b]	n.d.	3.1	0.2
1992–1999	0.7	0.4	n.d.	n.d.	12.7	0.5
1987–1992	1.0	0.6	4.2	n.d.	5.2	0.5
1981–1987	0.5	0.3	3.6	0.4	4.0	0.3
1965–1981	1.4	1.2	3.5	0.6	10.9	0.6
1946–1965	1.3	1.0	4.0	0.5	8.8	0.6
1933–1946	1.0	0.6	4.2	0.4	11.5	0.7
1923–1833	0.8	0.4	4.1	0.2	10.6	0.9
1830–1923	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Mirabel						
1999–2000	1.7	1.4	4.1	0.5	3.4	0.7
1993–1999	1.1	1.0	4.4	0.5	1.8	0.3
1986–1993	1.6	1.4	5.6	0.3	2.7	0.6
1976–1986	1.2	1.1	4.8	0.6	1.6	0.2
1962–1976	1.1	1.0	4.0	0.8	1.2	0.1
1828–1962	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Petite Bog						
1998–2000	2.7	1.7	2.4	n.d.	14.5	2.8
1988–1998	2.2	1.4	2.5	0.9	14.4	2.9
1980–1988	2.3	1.3	2.5	0.8	12.5	2.2
1970–1980	2.5	1.6	3.3	1.1	14.5	2.0
1961–1970	2.3	1.7	3.2	1.0	11.4	1.6
1951–1961	2.3	1.6	4.1	1.0	9.7	1.3
1938–1951	2.0	1.4	4.8	1.1	8.0	1.1
1922–1938	2.1	1.5	6.3	1.1	7.0	1.0
1906–1922	1.7	1.1	6.7	1.0	7.6	1.1
1889–1906	4.1	2.1	5.9	1.0	20.7	2.6

[a] Age of samples corresponds to the different depth segments. [b] At least one compound was not detected.

TABLE 3. Correlation Coefficients between Reconstructed Σ11-PAH Deposition Rates and Sulfur Deposition Rate, Canadian Coal Consumption, Canadian Energy Production, Number of Registered Vehicles in Canada, Canadian Population, and Total Area Burned by Forest Fires

correlation of PAH deposition rates with	Foxley Moor	Mirabel	Petite Bog
sulfur deposition rate[a]	0.09	0.93[b]	0.89[b]
Canadian coal consumption[c]	−0.03	0.24	0.57[d]
Canadian energy production[c]	0.88[b]	−0.05	−0.63
Canadian vehicle registrations[c]	0.28	0.16	−0.04
Canadian population[c]	0.25	0.43	0.44
forest fires (total burned area)[c]	−0.12	−0.54	0.27

[a] From Moore et al. (*28*). [b] Significant at the $p < 0.01$ level. [c] From Statistics Canada (2004). [d] Significant at the $p < 0.05$ level.

Discussion

Temporal Deposition Trends. The PAH deposition patterns documented in this study confirm earlier findings from sediments of North American lakes but on a much broader regional basis. In North America the occurrence of a double peak in PAH depositions and similar deposition rates as in the Montreal region have been documented for sediments of Lake Michigan (*13*). In these sediments the first period of elevated depositions was between 1900 and 1920, and the second one was between 1950 and 1970. Similarly, an increasing PAH input to sediments was recorded for the past 30 years as seen at some of the Canadian bogs analyzed in this study (Cape Sable, Petite Bog, Fourchu, Hislop Bog, Norembego, Despinassy Bog, Mai Bog, and Mirabel) and can probably be attributed to increased regional PAH depositions (*32*).
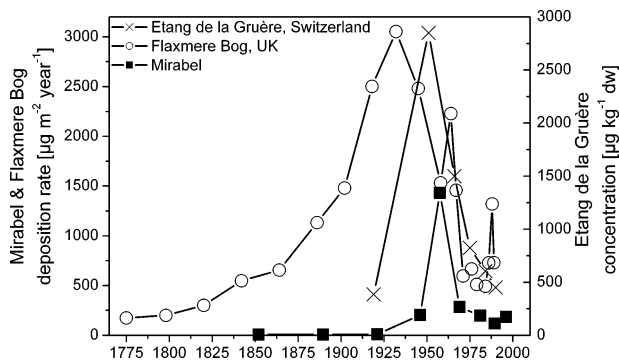
FIGURE 4. PAH deposition rates at Mirabel and Flaxmere Bog, U.K. (data from ref *7*) and PAH concentration at Etang de la Gruère, Switzerland (data from ref *8*).

FIGURE 5. Comparison of coal consumption in Canada and reconstructed PAH deposition at Foxley Moor, Mirabel, and Petite Bog.

These characteristics contrast with European peatlands where just one period of highly enhanced PAH input was found (Figure 4). As expected from the earlier and more intense industrial development in Europe, PAH deposition rates at Flaxmere Bog, U.K. (*7*), started to increase and peak much earlier than concentrations at either the Etang de la Gruère, Switzerland (*8*), or the Canadian sites (Figure 4). Already in 1850 PAH deposition rates at Flaxmere Bog were higher than the maximum deposition rates of many Canadian bogs. The maximum deposition rate was almost twice as high as that of Mirabel, which represents the most highly contaminated Canadian bog analyzed. European sites and almost all Canadian sites were characterized by a sharp decline after the 20th century maximum of PAH deposition rates.

In a study of PAH depositions to sediments of high-altitude lakes in Europe, Fernandez et al. (*14*) also determined two, albeit different, deposition types. Most of the lakes showed one maximum of PAH deposition since the beginning of the 19th century; several lakes in more peripheral regions showed no distinct maximum of PAH depositions. Moreover, no decline of PAH deposition rates during the latest decades was found, probably due to the fact that these lakes were affected more by long-range transport than by regional emissions.

The Industrial Revolution of the 19th century is seen as the main reason for the increasing PAH emissions until the 20th century (*7, 8, 11, 12, 21*). This is supported by the results of this study. The low PAH concentrations found in the first half of the 19th century reflect an economy that was characterized by agriculture and trading of fish, furs, wheat, and lumber (*33, 34*). At the end of the 19th century, deforestation became widespread, and by the early 20th century, classical heavy industries were established in eastern Canada (*33, 34*). In this period early PAH deposition maxima were recorded at Foxley Moor, Point Escuminac, Mai Bog, and Baker Bog and deposition rates also increased at the Mer Bleue site in the Ottawa valley. It is surprising that this early maximum of PAH deposition was not very distinct in bogs of the industrial core regions of Canada, southern Ontario and Québec, despite industrial development preferably occurring close to sites such as Mirabel, Mer Bleue, Lac à la Tortue, Alfred Bog, and Frontenac Bog. PAH depositions to these bogs (as far as dating is available) peak in the 1940s and later. These maxima may be related to increased aluminum and steel production and the developing chemical industry during and after the Second World War (*34*). The postwar decreases in PAH deposition were probably due to reduction of coal combustion, substitution of coal by hydroelectric power, and emission control measures (*7, 8, 21, 35*). Emission data for a large aluminum smelting facility at Lac Saint Louis in the vicinity of Montreal support this
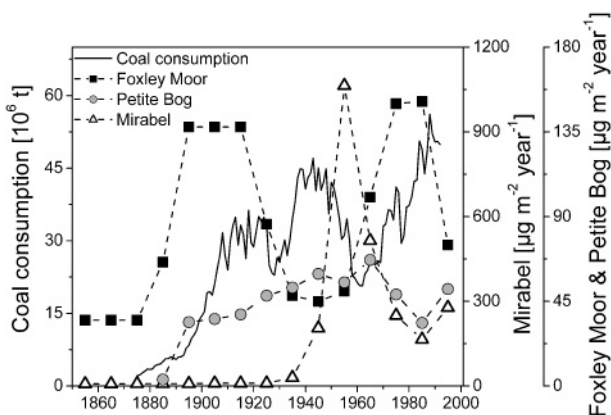
interpretation: the emission rates from this facility were reduced to approximately $1/3$ during the last 20 years (*5*).

PAH deposition trends at Petite Bog in Nova Scotia were low and qualitatively uniform over time with no distinct deposition maximum. This has not been observed in peatlands so far and might be explained by long-distance transport of PAH that was already conjectured by Aamot et al. (*17*) and Bjørseth et al. (*6*), who analyzed PAH in soil and air samples on the European continent and in Norway. The uniform deposition pattern of PAH was explained by mixing processes during transport from central Europe and the U.K. to Norway. For the period 1960−1989, a decrease of the atmospheric deposition was determined at Petite Bog. This coincides with results of Brun et al. (*36*), who directly determined the atmospheric deposition of PAH in Nova Scotia and observed a significant reduction of the deposition for the period 1980−2001. For the latest period from 1990 to 2000, the peat profile seems to suggest an increasing PAH deposition, which has been observed at several other bogs, too (Figure 2). However, this increase should be interpreted with caution, since the uncertainties arising from the dating method are largest in these peat layers and therefore the errors of the deposition rates that are based on the dating are expected to be large, too.

PAH Sources. The exact causes of PAH deposition patterns are not easy to assign, as the number of sources is quite high and the transport distances from the sources to individual bogs may vary substantially, but overall the data suggest that emissions from coal combustion contributed to patterns of PAH deposition in eastern Canada. Taking the dating uncertainties of recent years into account, PAH depositions at Petite Bog matched Canadian coal consumption fairly well, as well as at Foxley Moor at the time of the first maximum and the past four decades (Figure 5). On the other hand, the deposition in the period from 1940 to 1960 did not follow the Canadian coal consumption trend. At the Mirabel site PAH depositions matched the time series of Canadian coal consumption rather poorly. Explanations may be shifts in energy-related PAH sources from coal to other fossil fuels, abatement efforts, and/or substitution of coal by hydroelectric power in recent decades, which was particularly extensive in Québec. In 1990 about 63% of produced energy in Canada (*34*) and more than 90% of that in Québec was hydroelectric power (*37*).

The quantitatively most important PAH at the three bogs were Phen and Bb+kF (Figure 3). Except for Mirabel, Phen dominated the PAH deposition of the bogs, suggesting coal combustion as PAH source (*38*). However, it should be noted that Wilcke and Amelung (*39*) also found predominance of Phen in North American Mollisols that were remote from

major industrial areas. So a high abundance of Phen could also be a common feature of remote locations or even point to biological formation of Phen (1, 2, 9) that is assumed to occur under oxygen-deficient conditions and therefore Phen could be of limited value as an indicator for coal combustion.

The use of different ratios of individual PAH is a common tool for identification of the contribution of general (pyrogenic vs petrogenic) and specific (combustion of coal, wood, etc.) PAH sources in air particulate matter, soils, sediments, or snow (30, 31, 40−47). However, the diagnostic capabilities of compound ratios in peatlands, soils, or sediments might be insufficient and a definitive signature of a source may not exist due to the complexity of combustion processes and conditions, transport distances, physicochemical properties of the compounds, or transformation during transport.

The ratios of Flt/Pyr (Table 2) suggested that PAH in the 20th century at all three peatlands were of pyrogenic origin (fossil fuels or wood), particularly at Foxley Moor (31, 43, 44, 46, 48). Bb+kF/BeP ratios indicated the contribution of coal combustion to the PAH burden of the bogs, suggesting brown coal as predominant PAH source at Foxley Moor and Mirabel and hard coal at Petite Bog (9, 30, 49). At Petite Bog, BaP/BeP ratios also suggested the combustion of coal or gasoline (9, 30, 47, 49). At Foxley Moor and Mirabel these ratios suggested that vehicle exhausts might contribute to a large extent to the PAH burden (9, 30, 47, 49). At Mirabel, which is located in the metropolitan area of Montréal, this was also supported by large quantities of IcdP and BghiP as particular markers for traffic exhausts (29, 50). At the other sites a decreasing ratio of Bb+kF/BeP in the past decades suggested an increasing contribution of vehicle exhausts. The identification of contributing sources with ratios of Flt/BeP and Pyr/BeP did not lead to any results. Probably due to discrimination of the more volatile compounds Flt and Pyr during transport, these ratios were not comparable to those published by Jacob et al. (30) (Table 1).

A significant correlation of PAH deposition rates to Canadian coal consumption and to Canadian energy production could be established at Petite Bog in Nova Scotia, which in 1987 obtained 90% of its electricity by fossil fuel combustion (37). This finding was also supported by the significant correlation between deposition rates of PAH and sulfur, which results mainly from coal combustion. At Foxley Moor and at Mirabel a significant correlation of PAH deposition rates to Canadian coal combustion could not be established, but at Mirabel PAH deposition rates were significantly correlated to sulfur deposition rates. The nonexisting correlation between PAH and sulfur deposition rates at Foxley Moor could be due to its location close to the coast, leading to constant high inputs of sulfur via sea spray. Significant correlations of PAH deposition rates with other variables, such as the number of forest fires, energy consumption, and population figures, could not be established, indicating that these factors were of minor importance or that the global scale of data was not applicable to these locations. Correlation analyses with individual compounds did not lead to further information explaining our data.

Perylene was not present in any of the bogs analyzed in this study. This is in contrast to findings of other studies, where it has been detected in strongly elevated concentrations in sediments (3, 10) and in European peatlands (51). The explanation of this difference would be an interesting question for further research about the formation of Pery, which is thought to be produced biologically under oxygen-deficient conditions (2, 10, 51).

In summary, ombrotrophic peatlands of eastern Canada were characterized by distinct PAH deposition profiles with maximum deposition rates between 60 and 1432 μg m^{-2} year^{-1} occurring either early or in the middle of the 20th century, reflecting the industrial development of Canada.

Even during the first half of the 19th century, there were substantial accumulations of PAH. Maximum depositions of PAH occurred generally later and in smaller quantities at all Canadian sites than at European sites. The strong differences in the magnitude and timing of PAH deposition among sites emphasize the need for regionally detailed investigations of PAH depositions. Due to the complexity of PAH formation, transport, and deposition dynamics, exact origins of the PAH could not clearly be ascertained. However, correlation and source analyses suggested two major PAH sources in the recent history of eastern Canada: coal combustion and vehicle exhausts. Coal combustion seemed to be more important at sites located in peripheral regions of the analyzed transect, while vehicle exhausts seemed to dominate in metropolitan areas.

Literature Cited

(1) Wilcke, W.; Krauss, M.; Amelung, W. Carbon isotope signature of polycyclic aromatic hydrocarbons (PAHs): Evidence for different sources in tropical and temperate environments? *Environ. Sci. Technol.* **2002**, *36*, 3530−3535.

(2) Thiele, S.; Brümmer, G. W. Bioformation of polycyclic aromatic hydrocarbons in soil under oxygen deficient conditions. *Soil Biol. Biochem.* **2002**, *34*, 733−735.

(3) Venkatesan, M. I. Occurrence and possible sources of perylene in marine-sediments − a review. *Mar. Chem.* **1988**, *25*, 1−27.

(4) Halsall, C. J.; Sweetman, A. J.; Barrie, L. A.; Jones, K. C. Modelling the behaviour of PAHs during atmospheric transport from the UK to the Arctic. *Atmos. Environ.* **2001**, *35*, 255−267.

(5) Mackay, D.; Hickie, B. Mass balance model of source apportionment, transport and fate of PAHs in Lac Saint Louis, Quebec. *Chemosphere* **2000**, *41*, 681−692.

(6) Bjørseth, A.; Lunde, G.; Lindskog, A. Long-Range Transport of Polycyclic Aromatic-Hydrocarbons. *Atmos. Environ.* **1979**, *13*, 45−53.

(7) Sanders, G.; Jones, K. C.; Hamilton-Taylor, J.; Dorr, H. PCB and PAH fluxes to a dated UK peat core. *Environ. Pollut.* **1995**, *89*, 17−25.

(8) Berset, J. D.; 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.

(9) Wilcke, W.; Müller, S.; Kanchanakool, N.; Niamskul, C.; Zech, W. Polycyclic aromatic hydrocarbons in hydromorphic soils of the tropical metropolis Bangkok. *Geoderma* **1999**, *91*, 297−309.

(10) Silliman, J. E.; Meyers, P. A.; Eadie, B. J. Perylene: an indicator of alteration processes or precursor materials? *Org. Geochem.* **1998**, *29*, 1737−1744.

(11) Jones, K. C. Observations of long-term air-soil exchange of organic contaminants. *Environ. Sci. Pollut. Res.* **1994**, *1*, 172−177.

(12) Jones, K. C.; Stratford, J. A.; Waterhouse, K. S.; Vogt, N. B. Organic contaminants in Welsh soils − polynuclear aromatic hydrocarbons. *Environ. Sci. Technol.* **1989**, *23*, 540−550.

(13) Christensen, E. R.; Zhang, X. C. Sources of polycyclic aromatic hydrocarbons to Lake Michigan determined from sedimentary records. *Environ. Sci. Technol.* **1993**, *27*, 139−146.

(14) Fernandez, P.; Vilanova, R. M.; Meartinez, C.; Appleby, P.; Grimalt, J. O. The historical record of atmospheric pyrolytic pollutions over Europe registered in the sedimentary PAH from remote mountain lakes. *Environ. Sci. Technol.* **2000**, *34*, 1906–1913.

(15) Simcik, M. F.; Eisenreich, S. J.; Golden, K. A.; Liu, S. P.; Lipiatou, E.; Swackhamer, D. L.; Long, D. T. Atmospheric loading of polycyclic aromatic hydrocarbons to Lake Michigan as recorded in the sediments. *Environ. Sci. Technol.* **1996**, *30*, 3039–3046.

(16) Rapaport, R. A.; Eisenreich, S. J. Historical atmospheric inputs of high molecular-weight chlorinated hydrocarbons to eastern North America. *Environ. Sci. Technol.* **1988**, *22*, 931–941.

(17) Aamot, E.; Steinnes, E.; Schmid, R. Polycyclic aromatic hydrocarbons in Norwegian forest soils: Impact of long-range atmospheric transport. *Environ. Pollut.* **1996**, *92*, 275–280.

(18) Li, A.; Jang, J. K.; Scheff, P. A. Application of EPA CMB8.2 model for source apportionment of sediment PAHs in Lake Calumet, Chicago. *Environ. Sci. Technol.* **2003**, *37*, 2958–2965.

(19) Menichini, E. Urban air-pollution by polycyclic aromatic hydrocarbons – levels and sources of variability. *Sci. Total Environ.* **1992**, *116*, 109–135.

(20) Benner, B. A.; Gordon, G. E.; Wise, S. A. Mobile sources of atmospheric polycyclic aromatic hydrocarbons – a roadway tunnel study. *Environ. Sci. Technol.* **1989**, *23*, 1269–1278.

(21) Wild, S. R.; Jones, K. C. Polynuclear aromatic hydrocarbons in the United Kingdom environment – a preliminary source inventory and budget. *Environ. Pollut.* **1995**, *88*, 91–108.

(22) Lavoie, M.; Richard, P. J. H. The role of climate on the developmental history of Frontenac Peatland, southern Quebec. *Can. J. Bot. (Rev. Can. Bot.)* **2000**, *78*, 668–684.

(23) Turunen, J.; Roulet, N. T.; Moore, T. R.; Richard, P. J. H. Nitrogen deposition and increased carbon accumulation in ombrotrophic peatlands in eastern Canada. *Global Biogeochem. Cycles* **2004**, *18*, GB3002.

(24) Appleby, P. G.; Oldfield, F. The calculation of lead-210 dates assuming a constant rate of supply of unsupported ^{210}Pb to the sediment. *Catena* **1978**, *5*, 1–8.

(25) Biester, H.; Keppler, F.; Putschew, A.; Martinez-Cortizas, A.; Petri, M. Halogen retention, organohalogens, and the role of organic matter decomposition on halogen enrichment in two Chilean peat bogs. *Environ. Sci. Technol.* **2004**, *38*, 1984–1991.

(26) Biester, H.; Kilian, R.; Franzen, C.; Woda, C.; Mangini, A.; Scholer, H. F. Elevated mercury accumulation in a peat bog of the Magellanic Moorlands, Chile (53 degrees S) – an anthropogenic signal from the Southern Hemisphere. *Earth Planet. Sci. Lett.* **2002**, *201*, 609–620.

(27) Urban, N. R.; Eisenreich, S. J.; Grigal, D. F.; Schurr, K. T. Mobility and diagenesis of Pb and Pb-210 in peat. *Geochim. Cosmochim. Acta* **1990**, *54*, 3329–3346.

(28) Moore, T.; Blodau, C.; Turunen, J.; Roulet, N. T.; Richard, P. J. H. Patterns of nitrogen and sulfur accumulation and retention in ombrotrophic bogs, eastern Canada. *Global Change Biol.* **2004**, *11*, 356–367.

(29) Baek, S. O.; Field, R. A.; Goldstone, M. E.; Kirk, P. W.; Lester, J. N.; Perry, R. A review of atmospheric polycyclic aromatic hydrocarbons – sources, fate and behavior. *Water, Air, Soil Pollut.* **1991**, *60*, 279–300.

(30) Jacob, J.; Grimmer, G.; Hildebrandt, A. The use of passive samplers for monitoring polycyclic aromatic hydrocarbons in ambient air. *Sci. Total Environ.* **1993**, *140*, 307–321.

(31) Yang, S. Y. N.; Connell, D. W.; Hawker, D. W.; Kayal, S. I. Polycyclic aromatic hydrocarbons in air, soil and vegetation in the vicinity of an urban roadway. *Sci. Total Environ.* **1991**, *102*, 229–240.

(32) Yunker, M. B.; Macdonald, R. W. Alkane and PAH depositional history, sources and fluxes in sediments from the Fraser River Basin and Strait of Georgia, Canada. *Org. Geochem.* **2003**, *34*, 1429–1454.

(33) Blackbourn, A.; Putnam, R. G. *The industrial geography of Canada*; Croom Helm: London, 1984.

(34) Vogelsang, R. *Perthes Länderprofile: Kanada*; Justus Perthes Verlag: Gotha, Germany, 1993.

(35) Yang, H. H.; Lai, S. O.; Hsieh, L. T.; Hsueh, H. J.; Chi, T. W. Profiles of PAH emission from steel and iron industries. *Chemosphere* **2002**, *48*, 1061–1074.

(36) Brun, G. L.; Vaidya, O. C.; Léger, M. Atmospheric aeposition of polycyclic aromatic hydrocarbons to atlantic Canada: geographic and temporal distributions and trends 1980–2001. *Environ. Sci. Technol.* **2004**, *38*, 1941–1948.

(37) *National Atlas of Canada* (online); http://atlas.gc.ca/, accessed June 2004.

(38) Baird, C. *Environmental chemistry*, 2nd ed.; W. H. Freeman and Company: New York, 2000.

(39) Wilcke, W.; Amelung, W. Persistent organic pollutants in native grassland soils along a climosequence in North America. *Soil Sci. Soc. Am. J.* **2000**, *64*, 2140–2148.

(40) Slater, J. F.; Currie, L. A.; Dibb, J. E.; Benner, B. A. Distinguishing the relative contribution of fossil fuel and biomass combustion aerosols deposited at Summit, Greenland through isotopic and molecular characterization of insoluble carbon. *Atmos. Environ.* **2002**, *36*, 4463–4477.

(41) Stella, A.; Piccardo, M. T.; Coradeghini, R.; Redaelli, A.; Lanteri, S.; Armanino, C.; Valerio, F. Principal component analysis application in polycyclic aromatic hydrocarbons "mussel watch" analyses for source identification. *Anal. Chim. Acta* **2002**, *461*, 201–213.

(42) Khalili, N. R.; Scheff, P. A.; Holsen, T. M. Pah Source Fingerprints for Coke Ovens, Diesel and Gasoline-Engines, Highway Tunnels, and Wood Combustion Emissions. *Atmos. Environ.* **1995**, *29*, 533–542.

(43) Bucheli, T. D.; Blum, F.; Desaules, A.; Gustafsson, Ö. Polycyclic aromatic hydrocarbons, black carbon, and molecular markers in soils of Switzerland. *Chemosphere* **2004**, *56*, 1061–1076.

(44) Budzinski, H.; Jones, I.; Bellocq, J.; Piérard, C.; Garrigues, P. Evaluation of sediment contamination by polycyclic aromatic hydrocarbonds in the Gironde estuary. *Mar. Chem.* **1997**, *58*, 85–97.

(45) Manoli, E.; Kouras, A.; Samara, C. Profile analysis of ambient and source emitted particle-bound polycyclic aromatic hydrocarbons from three sites in northern Greece. *Chemosphere* **2004**, *56*, 867–878.

(46) Macías-Zamora, J. V.; Mendoza-Vega, E.; Villaescusa-Celaya, J. A. PAHs composition of surface marine sediments: a comparison to potential local sources in Todos Santos Bay, B. C., Mexico. *Chemosphere* **2002**, *46*, 459–468.

(47) Simcik, M. F.; Eisenreich, S. J.; Lioy, P. J. Source apportionment aus source/sink relationships of PAHs in the coastal atmosphere of Chicago and Lake Michigan. *Atmos. Environ.* **1999**, *1999*, 5071–5079.

(48) Freeman, D. J.; Cattell, F. C. R. Wood-Burning as a Source of Atmospheric Polycyclic Aromatic-Hydrocarbons. *Environ. Sci. Technol.* **1990**, *24*, 1581–1585.

(49) Wilcke, W.; Lilienfein, J.; Lima, S. D.; Zech, W. Contamination of highly weathered urban soils in Uberlandia, Brazil. *J. Plant Nutr. Soil Sci.* **1999**, *162*, 539–548.

(50) Grimmer, G.; Jacob, J.; Naujack, K. W.; Dettbarn, G. Determination of polycyclic aromatic compounds emitted from brown-coal-fired residential stoves by gas-chromatography mass-spectrometry. *Anal. Chem.* **1983**, *55*, 892–900.

(51) Malawska, M.; Bojakowska, I.; Wilkomirski, B. Polycyclic aromatic hydrocarbons (PAHs) in peat and plants from selected peat-bogs in the north-east of Poland. *J. Plant Nutr. Soil Sci.* **2002**, *165*, 686–691.