

# OMBOTROPHIC PEAT BOGS AS NATURAL ARCHIVES TO INVESTIGATE THE HISTORICAL ATMOSPHERIC DEPOSITION OF PERFLUORINATED COMPOUNDS

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## PARTICLE SIZE DISTRIBUTION OF AIRBORNE PERFLUORINATED COMPOUNDS

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### Introduction

Perfluorinated compounds (PFCs), particularly perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) have been described as compounds of increasing environmental concern and numerous studies were conducted to investigate the environmental distribution and fate of these compounds. As result, certain PFCs were found to be toxic, observed to accumulate in humans and wildlife, and detected globally in almost all environmental media from the Arctic to Antarctica<sup>1-3</sup>. Besides their transport with ocean currents, atmospheric transport was identified as important (long-range) transport pathway<sup>1,3</sup>. Laboratory experiments indicated wet and dry deposition to be significant loss mechanisms of certain PFCs from the atmosphere<sup>4</sup> which was confirmed by studies reporting several perfluorinated acids (PFA) in precipitation<sup>5,6</sup>. PFCs in wet deposition have been monitored on short time scales and only few studies investigated longer temporal trends of airborne PFCs using ice cores as archives<sup>7,8</sup>. Studies covering longer time periods were usually conducted using archived biota samples, however, these do not solely account for contamination from the atmosphere<sup>2</sup>. Alternatively, ombotrophic peat bogs can be used to determine the input of airborne contaminants as they get pollution from atmospheric sources, only and accumulation of contaminants is facilitated by a high organic matter content and minimized degradation<sup>9,10</sup>. In contrast to glaciers or ice shields, peatlands are widely distributed in boreal and temperate climate zones as well as in mountainous regions throughout the world allowing for studying the spatial distribution of historical contaminant depositions. Therefore the objective of this study was to analyze PFCs in peatlands in order to evaluate and discuss if ombotrophic bogs are suitable natural archives to reconstruct the historical atmospheric PFC pollution. Therefore, an analytical method was carefully optimized and applied to two peat cores taken in 2009 at Mer Bleue, an undisturbed ombotrophic bog close to Ottawa, Canada.

### Materials and methods

Sampling was performed in October 2009 at Mer Bleue (45.4 °N, 75.5 °W, an ombotrophic peat bog located in the vicinity of Ottawa, Canada. Two peat cores were taken from undisturbed hollows using a steel box sampler (87 x 90.6 x 1000 mm). After sampling, peat cores were cut into 5 cm segments. Coarse root fragments were removed. The first core ('MBI') consisted of nine, the second one ('MBII') of eight segments. The most recent and still active vegetation (mainly *Sphagnum*) was sampled as well ('surface'). Segmented peat samples were freeze-dried and ground after drying. Each segment was extracted and analyzed in duplicate so that PFCs were determined in four sets of samples ('MBI-1', 'MBI-2', 'MBII-1', 'MBII-2') consisting of nine/eight peat segments, the corresponding surface sample, and one analytical blank, each. Dating of the peat segments was applied from a separate core using the <sup>210</sup>Pb method. The peat cores roughly covered the past 100 years. Sample extraction and clean-up was performed by ultra sonication and a QuEChERS method<sup>11</sup> that was modified to suit the need of peat extract clean-up. Mass-labelled internal standards were applied to all samples to account for losses and irregularities. Samples were measured by high performance liquid chromatography – tandem mass spectrometry using electrospray ionization (HPLC-ESI-MS/MS). Details are described elsewhere<sup>12</sup>.

## Results and discussion

Of 25 PFCs determined in the present study, 12 (PFHxS, PFOS, PFBA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTriDA, PFTeDA) were detected regularly in peat core samples. Mean sumPFC concentrations varied between 461 and 1898 ng kg<sup>-1</sup>. PFOS was observed in highest concentrations followed by PFOA, PFNA and PFUnDA. Whereas duplicate PFC concentrations of each peat core differed only slightly, considerable differences were observed between both cores indicating a precise analytical procedure and a less precise sampling (Figure 1). PFC concentrations at Mer Bleue were in the same range as PFC soil concentrations published by Washington et al.<sup>13</sup> for American soil samples. They were 3 orders of magnitude lower than published PAH concentrations for the same site<sup>9</sup>. Calculated average PFOS deposition rates varied between 35 and 250 ng m<sup>-2</sup> a<sup>-1</sup>, those for PFOA were between 50 and 140 ng m<sup>-2</sup> a<sup>-1</sup>. The average overall sum PFC deposition to Mer Bleue Bog (entire peat core) was 28 µg m<sup>-2</sup>. Overall, PFC deposition rates were fairly low compared to those obtained from precipitation<sup>5,6</sup> or ice core analyses<sup>7,8</sup> and were rather in the range of remote or Arctic than of near urban samples. This indicates PFC losses within the peat core, either by leaching or by such a strong adsorption to the peat, that non-extractable bound residues are formed.

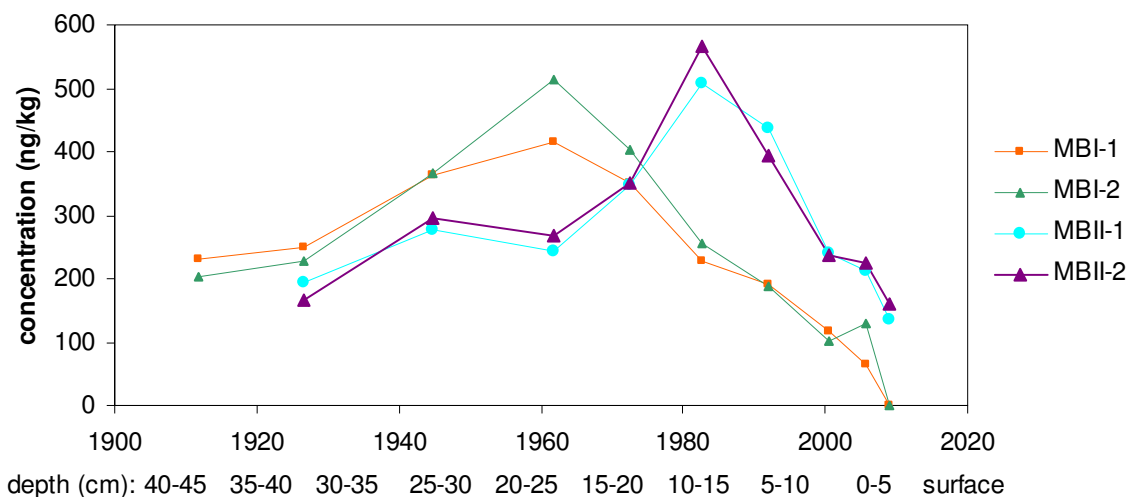


Figure 1: Inter- and intra-core variations of PFC concentrations as exemplarily presented for PFOA.

Overall, total PFC concentrations increased from the most recent samples (surface) towards depths of 10-20 cm (1980ies) and declined afterwards (Figure 2a). Maximum PFC deposition rates were observed in segments of 20-25 cm depth (1970ies; Figure 2b). PFC deposition and concentrations maxima appear 20 to 30 years too early and PFCs were detected even in the oldest samples. This indicates a PFC movement downwards the peat profile and is supported by the occurrence of PFC in samples bog water. Thus our findings do not suggest that peat is a strong PFC-retaining matrix which is in contrast to Rayne and Forest<sup>14</sup> proposing long-chain PFAs to be immobile at the soil organic carbon content of Mer Bleue (46 %).

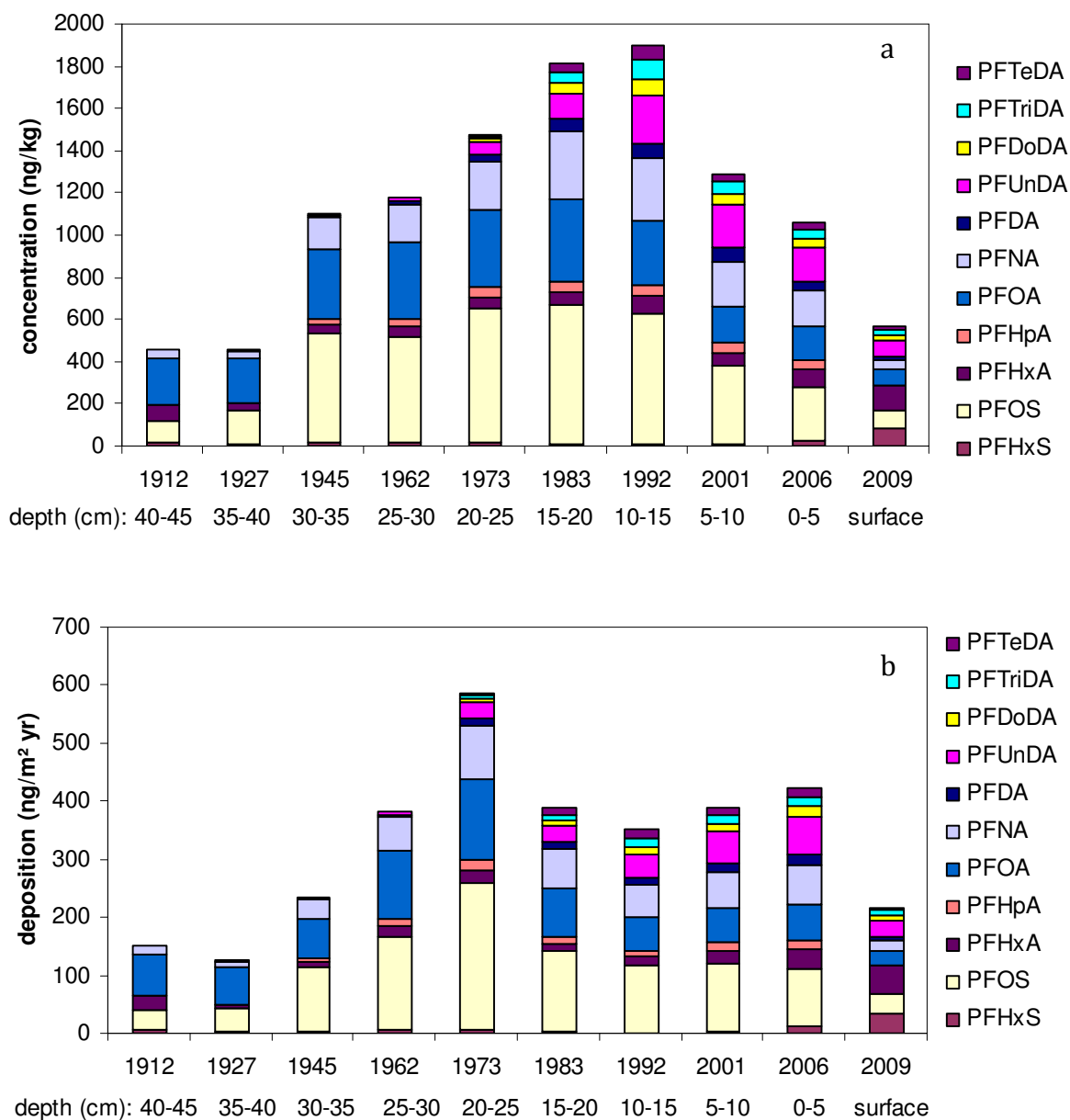


Figure 2: Average PFC concentrations (a) and depositions (b).

Depth-dependent concentration/deposition variations of long-chain PFCAs ( $C_{10} - C_{14}$ ) were quite similar. Their curves were characterized by a distinct and narrow concentration and deposition peak in the upper peat segments. Except for PFDA and PFUnDA, these compounds were not observed in depths below 25 cm. Concentration curves of shorter chain PFCAs and PFSAs ( $\leq C_9$ ) were rather flat and characterized by broad peaks demonstrating the preferential leaching of shorter chain PFCs downwards the peat profile. Contamination of PFCs comprising more than 7 perfluorinated carbon atoms appear to decline recently. These declines appeared to be more distinct than those observed in biota trend studies. In the present study, PFHxS and PFHxA were the only PFCs with increasing concentrations and deposition rates as well as proportions in the most recent samples reflecting a shift from long-chain to short-chain PFCs as result of phase-out, manufacturing restrictions

and/or use regulations<sup>15-18</sup>. These shifts were usually not reported in biota-based trend studies as short-chain PFCs do not bioaccumulate<sup>19</sup>.

Overall, as demonstrated for Mer Bleue in the present study, ombotrophic peatlands are not suited as natural archives to monitor the historical deposition of persistent PFCs, although this is in contrast to findings for other contaminants<sup>9,10,20,21</sup>. As further implication, this study reveals that PFAs are only little retained in soils even if they have high organic matter content.

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