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Contemporary Mobilization of Legacy Pb Stores by DOM in a Boreal Peatland

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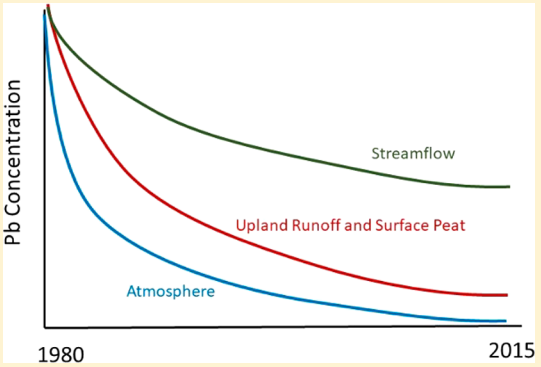
Supporting Information

ABSTRACT: We examined how different landscape areas in a catchment containing a northern ombrotrophic peatland and upland mineral soils responded to dramatic decreases in atmospheric deposition of lead (Pb). Pb concentrations in the outflow stream from the peatland measured from 2009−2015 indicated continued mobilization and export of Pb derived from historic inputs to the bog. In contrast, Pb concentrations in surface peat and runoff from upland mineral soils have declined in response to reductions in atmospheric deposition. Relative to the early 1980s, Pb concentrations in the streamflow decreased only ∼50%, while Pb in surface peat and upland subsurface runoff decreased by more than 90%. Water level fluctuations in the slow-accumulating peat have allowed dissolved organic matter (DOM) to continue mobilizing Pb deposited in the peatland decades earlier. Strong correlations between dissolved organic carbon (DOC) and Pb concentrations in outflow from the peatland and in bog porewaters demonstrate Pb mobility related to DOM production. Peat stores of Pb in 2016 were less than or equal to those reported in the early 1980s despite the dry mass inventory increasing by 60−80%. Much of the loss in Pb stored in peat can be accounted for by stream runoff from the peatland.



INTRODUCTION

The dominant source of Pb to many ecosystems is atmospheric deposition, but Pb deposition rates across North America have dropped dramatically since peaking in the 1970s.[1,2] Removal of Pb from gasoline was the primary driver in reducing Pb deposition in North America.[3] Pb in precipitation is no longer routinely monitored, but atmospheric Pb concentrations monitored in a few select cities in the U.S. have decreased by more than 99% since 1980.[4] While little Pb is currently deposited to northern Minnesota,[2] knowledge of Pb stocks and fluxes decades after dramatic decreases in deposition can give insight into ecosystem response times to changes in deposition for other metals, such as Hg, both of which are commonly transported within and from ecosystems by dissolved organic matter (DOM).[5] Some have considered Pb to be immobile in the large expanses of peatlands of the northern boreal zone based on Pb concentrations and inventories in cores;[2,6,7] however, several studies have reported Pb in peat porewaters and in stream runoff from peat bogs suggesting mobilization and transport.[8,9,10] Pb in the dissolved phase may be small relative to Pb in the solid phase,[11] but mobility and export depend not only on partitioning, but also the flushing rate of the system.[12] Peat systems with high DOM concentrations that can mobilize Pb and are flushed quickly may be particularly susceptible to Pb losses.

A Pb mass balance was developed for a well-studied peat bog (the S2 peatland watershed) at the Marcell Experimental Forest in northern Minnesota for the early 1980s.[9] Urban et al.[9] clearly demonstrated the mobility of Pb in the S2 peatland based on measurements in the dissolved phase and showed that Pb mobilized by DOM and transported out of the peatland represented 30% of measured annual inputs of Pb to the entire peatland. In our study of ecosystem response times to decreased Pb inputs, we revisited the site to measure Pb concentrations over time and in key areas (upland mineral soils that surround the peatland and surface peat) from which Pb may be mobilized to the stream. Peat cores were collected to assess Pb stores in S2 relative to cores collected in the early 1980s. In addition, Pb was measured in porewaters along transects extending from the upland to the lagg (interface between the mineral upland and organic peatland) to the bog to assess the role of DOM in the mobilization of Pb.

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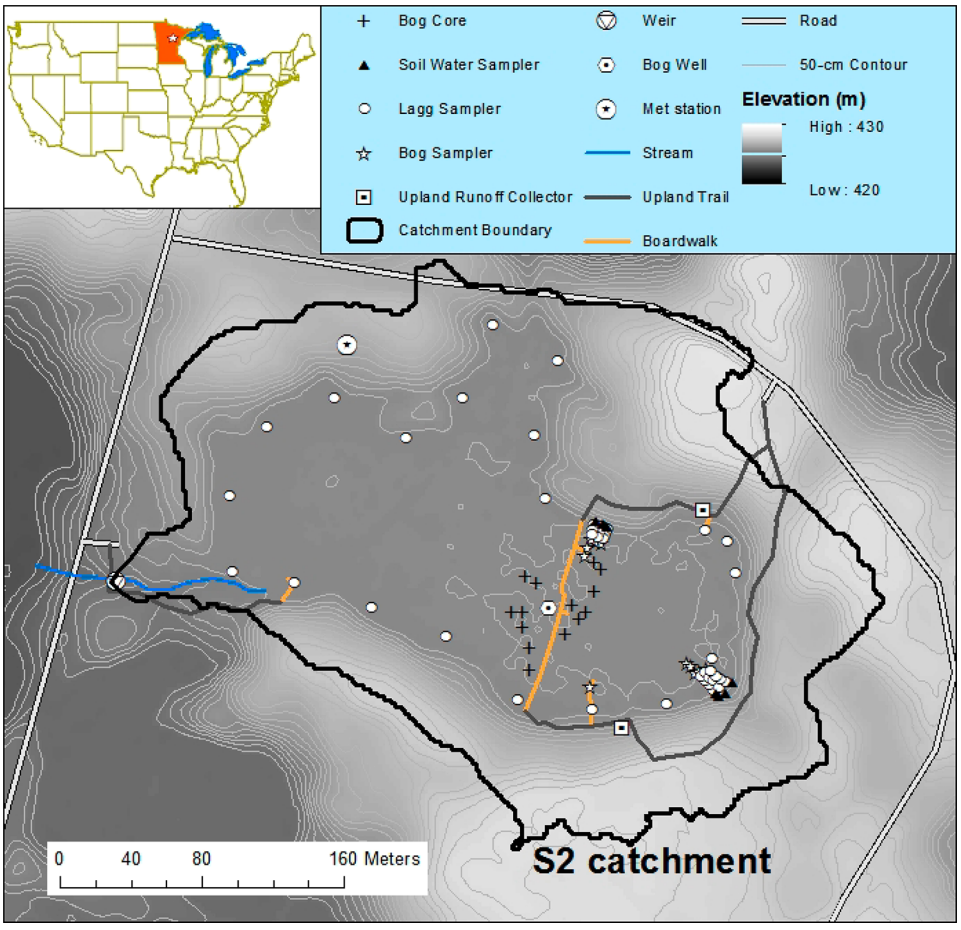

Figure 1. Map of the S2 watershed at the Marcell Experimental Forest and sampling points. The bog, lagg, and soil water samplers are all piezometers, the upland runoff collectors collect subsurface runoff, and water elevation is continuously monitored at the Bog Well and the Weir. Wooden boardwalks are used to access all routine sampling points to minimize disturbance of the peatland. Maps was created using ArcMap software by Esri. ArcGIS and ArcMap are the intellectual property of Esri and are used herein under license. Copyright © Esri. All rights reserved. For more information about Esri software, please visit www.esri.com.

SITE DESCRIPTION

This study was conducted in northern Minnesota, in the S2 watershed at the Marcell Experimental Forest (MEF; 47°32"N. 93°28"W). Hydrology at the S2 site has been studied and monitored since the early 1960s.[13] The 9.7-ha watershed is comprised of a 3.2-ha ombrotrophic peat bog surrounded by a 6.5-ha mineral soil upland. The upland Alfisol soils consist of 2−7 cm of organic matter (O-horizon) and 30−50 cm of thin aeolian, Fe-containing sandy loam (A-horizon) overlaying a low permeability clay loam (B-horizon). Runoff from the upland areas is dominated by subsurface flow above the B-horizon that enters the peatland lagg area.[13] The center of the S2 peatland is a raised-dome ombrotrophic bog which also flows toward the lagg areas of the wetland.[14] Vegetation in the bog is a black spruce-*Sphagnum* (*S. angustifolium*/*S. magallanicum*) community, with the canopy dominated by mature black spruce (*Picea mariana*) that has accumulated since 1864 and ericaceous shrubs in the understory.[15] Alder (*Alnus incana*) grows sporadically in the lagg and the upland is dominated by quaking aspen (*Populus tremuloides Michx.*) and paper birch (*Betula papyrifera Marsh*).[15]

Streamflow from the S2 catchment has been monitored at a 120° v-notch weir since 1961.[14,16] The water level near the center of S2 has been continuously measured since 1961 and subsurface flow from two runoff plots in the uplands was first measured from 1969 to 1973 and again since 1981.[14,17] Streamflow is typically highest during late winter because of snowmelt and flow often stops during summers with low precipitation. The water table is often lowest before snowmelt in late winter (February−March), and at the end of summer (September−October) after a period of prolonged high evapotranspiration. Water level, flow, and precipitation for the study years 2009 to 2015 are plotted in Supporting Information (SI) Figure S1.

MATERIALS AND METHODS

Field Sampling. Water samples were collected from the stream weir (2009−2015), runoff collectors (2009−2015), and peat porewater samplers (2010−2012). Weekly samples were taken at the weir while subsurface runoff was collected when stormflow runoff occurred. Porewater samples were collected approximately monthly (May through September) from two sets of triplicate transects of multiple piezometers extending from the peatland margin to the bog. Each transect had one sampler in upland mineral soil to sample soil water. Upland soil, bog, and lagg water samples were collected from 0 to 10 cm below the soil surface (5 cm diameter PVC piezometers), with lagg and bog samplers located in hollows of the hummock/hollow microtopography.[18] Piezometers were purged with a peristaltic pump and allowed to recharge before sampling.

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Porewater samples were filtered through Whatman 0.7 μm GF/F filters into rinsed PETG 125 mL sample bottles and acidified by adding 0.5% volume/volume 12 M HCl within 2 h of filtering using a modified clean hands/dirty hands protocol.[19] Stream, lagg, and upland runoff water samples were shipped and then filtered and acidified in a clean lab at Gustavus Adolphus College within 36 h of collection. Acidified samples were used for Pb concentration measurement. Filtered samples were collected in glass borosilicate bottles for DOC analysis in 2009 and 2010. Unfiltered samples were collected for general water chemistry and TOC analysis completed at the Forest Service Laboratory in Grand Rapids, MN. DOC and TOC have been shown to be equivalent in this system.[20]

Peat cores from the bog were taken in June 2016. Thirteen cores were taken across the bog within 40 feet from a boardwalk that spans the peatland from north to south (Figure 1). Cores were taken in both hummocks and hollows, and ranged in depth from 70 to 115 cm. The first 20−40 cm were taken with a rotary drill corer (3 in. diameter), and a Macaulay (Russian) corer (5 cm diameter) was used for the remainder of the core. Cores were sectioned in the field (5 cm increments in the peat, 10 cm in the growing/less decomposed surface layer) and stored in plastic specimen cups. Samples were frozen within 4 h of collection, and later freeze-dried prior to analysis.

Analytical Methods. Pb concentrations in filtered water samples and peat were determined by ICP-MS (Agilent 7700 series). Water samples were diluted with 0.32 M nitric acid (HNO_3) prior to addition of internal standard (Inorganic Ventures ICPMS-71D) followed by analysis. Freeze-dried peat samples were homogenized and 0.25 ± 0.03 g were digested in 0.5 M HCl at 80−85 °C for half an hour.[21] An aliquot of the digestate was diluted with 0.32 M HNO_3 and analyzed for Pb in the same manner as water samples. Recovery of Pb from standard reference materials (MESS-3 (marine sediment; 21.1 ± 0.7 μg/g) and SLRS-5 (riverine water; 0.081 ± 0.066 μg/L), National Research Council Canada) were always within the range of certified values. Concentrations of TOC were measured by high-temperature combustion on a Shimadzu TOC V-CPH before October 2014 and a TOC-L after that. Potassium hydrogen phthalate (KHP) was used for reference and check standards.[9] All concentrations in this paper are reported as ± one standard deviation of the mean and all statistical differences were determined with two-tailed t tests using $p < 0.05$.

Dry masses (g/m^2) were summed for each peat core section based on the area of the corer and the dry mass of each section to arrive at a mass inventory. Urban et al.[9] used a stratigraphic marker to estimate the year 1930 in each of their peat cores and report mass and Pb inventories corresponding to 53 years of accumulation (1930−1983). Urban et al.'s mass accumulation rates are consistent with a rate calculated from a single core in another study on S2.[22] Urban et al.'s average mass inventory (M_{1983}) in either hummocks or hollows was extrapolated to 86 years (1930−2016) by multiplying by a factor of 1.62 (86/53). Thus, even if the stratigraphic technique was uncertain, this work replicates their method and is valid if mass accumulation rates have not changed. To calculate Pb inventory in each core, we summed Pb ($\mu g/m^2$) to the closest depth corresponding to $1.62 \times M_{1983}$.

RESULTS AND DISCUSSION

Pb and DOC Relationships in Porewater. Porewater concentrations of Pb were measured over space and time in various parts of the S2 catchment (Figure 1). Pb porewater concentrations in the bog (3.35 ± 2.11 μg/L; n = 155) were higher than concentrations in lagg (2.31 ± 1.20 μg/L; n = 405), upland soil water (1.54 ± 0.82 μg/L; n = 39) and subsurface runoff (0.40 ± 0.43 μg/L; n = 40). The upland piezometers occasionally filled with water but only after rainfall and antecedent wet conditions. Water in these samplers was a mixture of lagg water and upland runoff as evidenced by elevated DOC levels (48.7 ± 20.8 mg/L; n = 30) relative to subsurface runoff (17.5 ± 8.5 mg/L; n = 28).

DOC concentrations were similar in the bog and the lagg (74.8 ± 18.9 mg/L; n = 156 vs 75.1 ± 18.3 mg/L; n = 401) areas of the peatland from 2010−2012,[20] but much lower in subsurface runoff and water collected in upland wells (Figure 2). Lagg areas are nutrient-rich relative to the bog and more

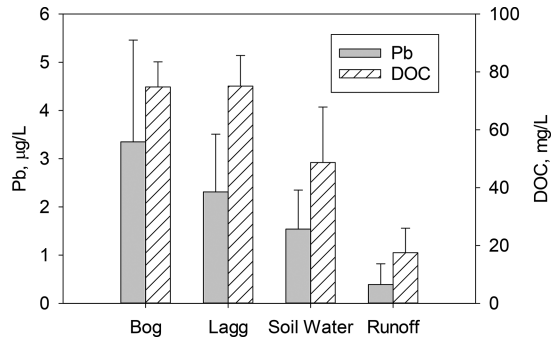

Figure 2. Pb and dissolved organic carbon (DOC) concentrations in bog, lagg, and soil porewaters (2010−2012) and subsurface runoff 2009−2015. The error bars are one standard deviation of the mean. Bog, lagg, and soil waters were collected ~ monthly from piezometers throughout the peatland as shown in Figure 1. The large number of Pb samples (n = 155, 405, 39, 41, respectively, for bog, lagg, soil water, and runoff) results in statistically significant differences ($p < 0.05$) despite wide spatial and temporal variations in Pb concentration. Bog and lagg DOC means are not statistically different ($p = 0.26$).

biologically productive[13,23] leading to similar DOC concentrations despite dilution by lower concentrations of DOC in upland runoff waters. Grouping all bog and all lagg water samples together, Pb and DOC concentrations were correlated in both cases as shown in SI Figure S2, but the relationship is stronger in the bog, particularly at individual sites (SI Figure S3). In addition, the slope, which describes the amount of Pb mobilized per unit DOC (μg Pb/mg DOC), was greater in bogwater (0.047; range 0.037−0.067 at individual sites) than lagg water (0.033; range 0.007−0.050). Pb concentrations followed the pattern Bog > Lagg > Subsurface, suggesting that DOM mobilizes Pb in the lagg and bog, but that upland runoff dilutes Pb in the lagg. Pb losses from the lagg due to water seepage out the bottom of the small lagg area of S2 could also lower the size of the Pb pool in the lagg and lead to lower Pb concentrations relative to the bog.[24]

As shown in SI Figures S2 and S3, the Pb versus DOC relationship was stronger at all but one bog site when compared to lumping all of the bog sites together. Similarly in the lagg, 25 out of 30 sites had stronger relationships than combining all the Pb and DOC lagg water data together. These finding underscore the heterogeneity of peatland systems like S2, but reinforce that DOM production mobilizes available Pb. The key factor is DOM leaching or production leading to Pb redistribution among binding sites in solid peat and the

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dissolved phase as shown by Skyllberg.[25] The magnitude, timing, duration, and pathways of water flow through individual peatlands then dictates how much Pb is transported out of the peatland.

Pb in Subsurface Runoff. Pb can be mobilized by DOM and transported from the upland to the S2 lagg primarily via subsurface stormflow during snowmelt runoff and large rainfall events. Both subsurface and surface runoff were collected at S2, but surface runoff is insignificant to the water balance.[13] Subsurface runoff is estimated to contribute ~42% of the flow at the S2 weir in an average year, but significant uncertainty for any particular year is associated with this average estimate due to the complexity of the overall water budget for S2.

In this study, Pb in subsurface runoff averaged (0.40 ± 0.43 μg/L; n = 40) from 2009−2015, an 86% decline relative to values reported by Urban et al. (1990) from 1982−1983 (2.8 ± 1.7 μg/L; n = 24). The subsurface runoff collectors in the S2 catchment typically flow during spring snowmelt and following major precipitation events resulting in a sparse collection of samples in any given year. One sample from March 2011 (2.57 μg/L) and another from Nov 2015 (1.66 μg/L) contributed to the variation, but 85% of the subsurface samples were below 0.5 μg/L of Pb. In constructing a mass balance for Pb in S2, Urban et al.[9] found that subsurface runoff was a significant input constituting 11−20% of total inputs and averaged 0.45 mg/m^2 yr (relative to the area of the peatland). Following Urban et al.'s method, which assumed 42% of streamflow originates from subsurface runoff,[24] inputs from subsurface runoff ranged from 0.056 to 0.096 mg/m^2.yr and averaged 0.070 mg/m^2.yr from 2009 to 2015.

Pb in Streamflow from the Peatland. Relative to measurements made in the early 1980s, Pb concentration in streamflow decreased less than Pb in upland subsurface runoff, peat (see below), and the atmosphere/precipitation.[4] Pb concentrations in the streamwater averaged 2.38 ± 0.79 μg/L (n = 151) from 2009 to 2015 in this study, a 48% decrease relative to 1981−1983 (4.6 ± 2.3 μg/L (n = 58)).[9] These mean values mask a great deal of interannual variability (Table 1). For example, Pb concentrations during 1983 and 2010 were not different (p = 0.08). Notably, the mean DOC concentration in 2010 of 97.9 ± 21.6 mg/L (n = 35) was the largest on record for S2 and in 1983, DOC was only 41.8 ± 13.0 mg/L (n = 18).

In other recent years, stream Pb concentrations were lower than during the early 1980s, but Pb mobilization increased at higher DOC concentrations (Figure 3). Urban et al.[26] reported an increasing trend in DOC concentration in streamflow from S2 which may enhance Pb export from S2 based on Figure 3. Urban et al.[9] found a significant positive relation between Pb and DOC concentrations in outflow from S2 for the combined years 1981−1983, but correlations were weaker than in recent years as shown in Table 1. Weaker correlations in the early 1980s than now were likely from substantially larger rainfall and upland runoff inputs of Pb as well as a sparser collection of samples. Slopes of Pb and DOC correlations in streamflow (Table 1) show that more Pb was mobilized per unit of DOC from 1981 to 1983 (slopes ranged from 0.047 to 0.070) than from 2009 to 2015 (0.018 to 0.047). The overall slope in Figure 3 is similar to Pb/DOC slopes in lagg water (SI Figure S2) as would be expected since water flows through the lagg before exiting S2.

We estimated annual stream Pb yields by water year (Mar 1 to Feb 28/29 of the next year) from daily flows and linear interpolation between sampling points (Table 2). Urban et al.[9]

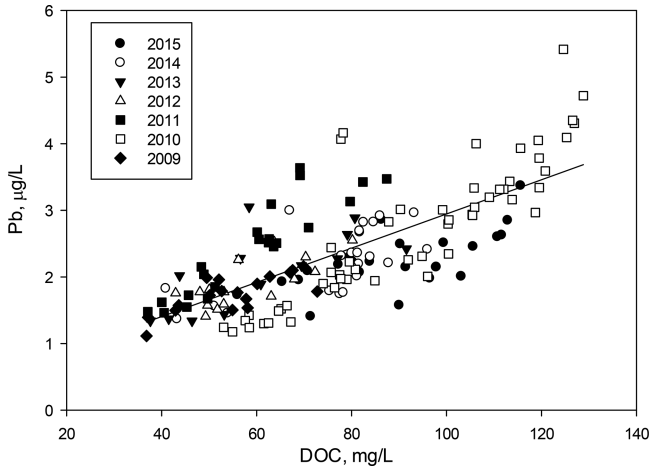

Figure 3. Relationship between Pb and dissolved organic carbon (DOC) concentrations in outflow from the S2 peatland. All samples were collected from the exit stream during times of active flow (see SI Figure S1) which varies each year but typically begins in March or April and can extend into late fall, but often with stoppages during summer months. Slopes for individual years are included in Table 1, as are previous data reported by Urban et al.[9]

Table 1. Pb and DOC Concentrations in the S2 Outlet Stream From 2009−2015 and Historic Data from Urban et al[a]

year	Pb, μg/L ± one std dev (n)	DOC, mg/L ± one std dev	R^2	Pb/DOC slope ± one std dev
2015	2.23 ± 0.27 (25)	88.6 ± 16.1	0.43	0.018 ± 0.0040
2014	2.25 ± 0.27 (22)	75.8 ± 14.8	0.43	0.022 ± 0.0057
2013	2.09 ± 0.27 (13)	61.2 ± 16.4	0.56	0.026 ± 0.0074
2012	1.93 ± 0.27 (16)	59.5 ± 11.4	0.54	0.022 ± 0.0055
2011	2.45 ± 0.27 (22)	59.2 ± 13.7	0.83	0.047 ± 0.0046
2010	3.16 ± 0.27 (35)	97.3 ± 21.6	0.74	0.040 ± 0.0033
2009	1.75 ± 0.27 (18)	55.1 ± 10.4	0.56	0.019 ± 0.0043
1983[b]	3.22 ± 0.97 (18)	41.8 ± 13.01	0.386	0.047 ± 0.015
1982[b]	4.06 ± 1.39 (16)	47.6 ± 12.3	0.306	0.067 ± 0.029
1981[b]	6.18 ± 2.50 (23)	54.6 ± 14.7	0.170	0.070 ± 0.036

[a]The slope represents the amount of Pb per unit of DOC in units of μg Pb/mg DOC. [b]From Urban et al.[9]

Table 2. Fluxes of Pb and DOC Measured in the Stream Exiting the S2 Peatland[a]

water year	Pb flux (mg/m^2.yr)	DOC flux (g/m^2.yr)	[b]water yield (cm)
2015	0.81	30.00	12.90
2014	0.94	28.84	19.42
2013	0.59	17.38	12.78
2012	0.70	20.44	12.31
2011	1.18	30.11	17.34
2010	1.03	33.03	11.40
2009	0.61	17.76	13.20
1983[c]	0.68	10.13	7.6
1982[c]	1.6	20.81	18.4
1981[c]	2.9	27.06	18.8

[a]Fluxes are based on water year from March through the following February. Flux is relative to the area of the peatland (3.2 ha). [b]Water yield relative to whole watershed. [c]From Urban et al.[9]

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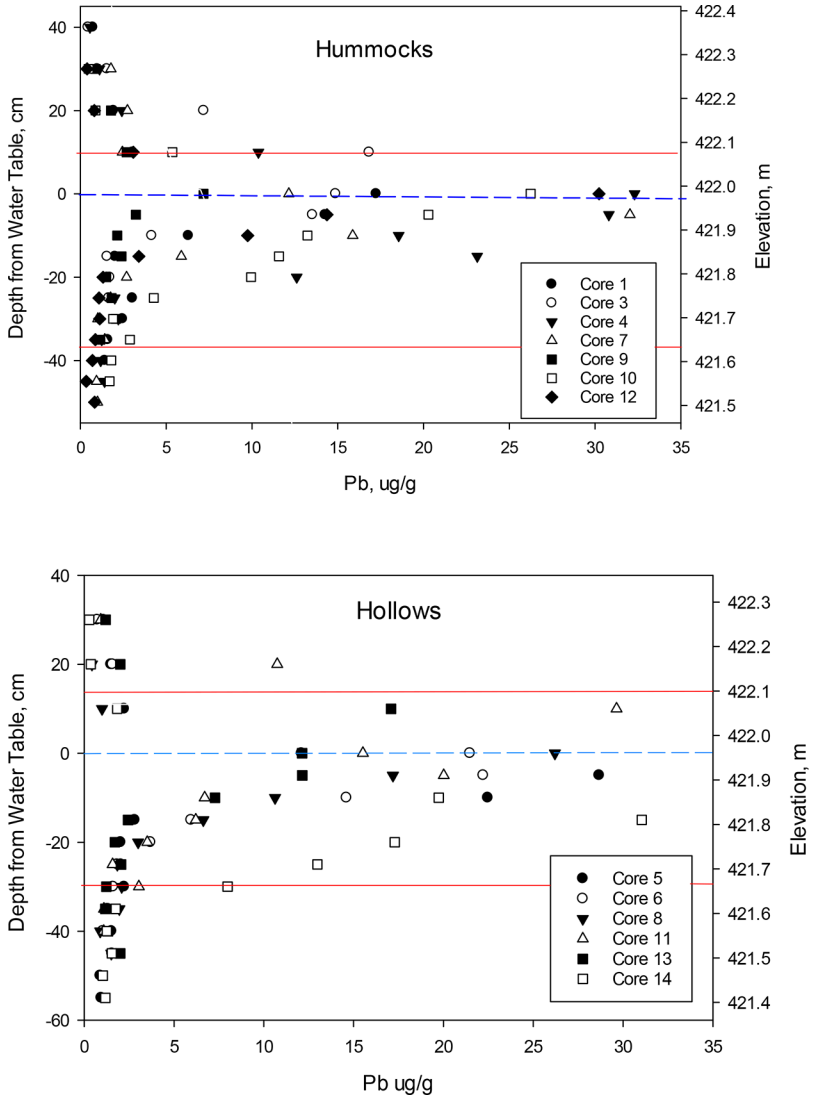

Figure 4. Pb concentrations in peat cores collected from S2. The dashed line is the water table on the date of collection and the solid lines represent typical fluctuation of the water table. The *y*-axis on the right is the actual elevation above sea level, while the *y*-axis on the left is the core depth relative to the water table on the date of core collection.

reported yields of Pb in the S2 stream relative to the area of the peatland (3.2 ha). Yields ranged from 0.68 to 2.90 mg/m^2·yr and averaged 1.73 mg/m^2·yr between 1981 and 1983, while from 2009−2015 Pb yields ranged from 0.59 to 1.18 mg/m^2·yr and averaged 0.84 mg/m^2·yr, a 51% decrease from 1981−1983, similar to the decrease in Pb concentration.

Pb in Sphagnum. Pb concentrations averaged 0.76 ± 0.39 μg/g dry weight (±one std dev; n = 13) in the upper ten cm of peat cores collected in 2016, which consists primarily of living *Sphagnum*.[15] Based on mass accumulation rates from peat cores collected from S2 by Urban et al.,[9] the upper 10 cm corresponds to growth from the past six years (range 2.71−11.57 years, average = 6.02 years). Pb concentrations in living S2 *Sphagnum* were similar to many peatlands across Alberta, Canada (0.71 ± 0.32 μg/g) which have declined from an average of 23 ± 8 μg/g since the 1980s.[27] A range of 5−15 μg/g in living S2 *Sphagnum* in 1983 was reported by Urban et al.[9] Thus, Pb concentrations in living *Sphagnum* in S2 have responded to lower atmospheric deposition, decreasing by 85−95% since the early 1980s. This large decrease in Pb mirrors those of southern Germany where 1970s levels were found to be 22 μg/g and 35 μg/g in two regions. *Sphagnum* in the same regions were found to be 2.1 μg/g and 4.1 μg/g in 2007.[28]

Modeling Pb Declines in S2. To compare response times between ecosystem compartments, simple first-order rate models were constructed between the early 1980s and present day. For example, the Pb decline in the subsurface runoff was modeled from 1982 to 2012 as follows:

$$[\mathrm{Pb}]_{2012} = [\mathrm{Pb}]_{1982} \times e^{-kt} \quad (1)$$

Where $[\mathrm{Pb}]_{2012}$ = 0.40 μg/L, $[\mathrm{Pb}]_{1982}$ is 2.8 μg/L, k is the first-order rate constant, and t is equal to 30 years. The first-order rate constant, k, was determined to be 0.066 yr^{-1} corresponding to a half-life of about 10.5 years. This half-life relates to the response of the mobile Pb in the S2 upland ecosystem to a decrease in Pb deposition. Similarly, from eq 1 and the average concentrations of Pb in surface peat in 1983 and 2016 (10 and 0.76 μg/g; Figure 1 from Urban et al.[9]), we calculated a first order rate constant of 0.078 yr^{-1} describing Pb decline in living *Sphagnum*, which corresponds to a half-life of 8.9 years. Finally, using eq 1 and the average concentrations of Pb in outflow of 2.38 μg/L from 2009−2015 and 4.6 μg/L from 1981−1983, a

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Table 3. Comparison of Mass and Pb Inventories Between 1983 and 2016 in Hummocks and Hollows of S2[a]

	mass inventory (g/m^2)		Pb inventory (mg/m^2)	
	hummock	hollow	hummock	hollow
~1930–1983	$1.33 \pm 0.20 \times 10^4$	$1.06 \pm 0.21 \times 10^4$	420	251 ± 67
	$n = 6$	$n = 18$	$n = 2$	$n = 5$
[b]extrapolated, 1930–2016	2.15×10^4	1.72×10^4	n/a	n/a
[c]actual	$2.17 \pm 0.35 \times 10^4$	$1.91 \pm 0.08 \times 10^4$	221 ± 84	238 ± 29
	$n = 7$	$n = 6$	$n = 7$	$n = 6$
[d]actual +5 cm deeper	$2.93 \pm 0.40 \times 10^4$	$2.65 \pm 0.22 \times 10^4$	245 ± 79	266 ± 29
[e]actual +10 cm deeper	$3.81 \pm 0.63 \times 10^4$	$3.43 \pm 0.30 \times 10^4$	260 ± 77	283 ± 31

[a]1983 inventories date to ~1930 and all errors are one standard deviation of the mean. [b]Calculated assuming mass accumulation rate for 1930–1983 remained constant through 2016. [c]This is the actual average inventory in 2016 peat cores calculated to the depth interval closest to the Extrapolated, 1930–2016 mass inventory. Inventory was determined to depths of 45–65 cm in hummocks (10–20 cm below the water table when cores were collected) and 40–50 cm in hollows (10–15 cm below the water table when cores were collected). [d]This is the Actual inventory plus the next deeper 5 cm core section. Mass inventory more than doubles relative to Urban et al., but Pb inventory is lower (hummocks) or statistically unchanged (hollows). [e]This is the actual inventory plus the next two deeper 5 cm core sections. Mass inventory nearly triples relative to Urban et al.,[9] but Pb inventory is lower (hummocks) or statistically unchanged (hollows).

much lower first order rate constant of 0.022 yr^{-1} was determined which corresponds to a half-life of 30.6 years.

Streamflow response rate was slow in contrast to the atmosphere, upland runoff, and living *Sphagnum*; however, the majority of anthropogenic Pb inputs to S2 are still contained within the acrotelm of the peat (see discussion below). A slow temporal response of streamflow Pb concentrations would be expected if DOM mobilizes available Pb stores in the actrotelm as the water table rises and a small fraction of the Pb inventory is transported out of the bog when the stream flows. On the other hand, upland and living *Sphagnum* respond quicker than the stream because rainwater and DOM flush through the thin soils and living *Sphagnum* transporting mobile Pb out of those compartments. Pb deposited in the early 1980s was likely mobilized by DOM from the uplands,[9] but with less Pb deposition presently, lower Pb concentrations in subsurface runoff and precipitation resulted in generally lower Pb concentrations in streamflow present-day.

Pb in S2 Peat Cores. Low concentrations of Pb in upland runoff (0.40 ± 0.43 μg/L) and comparatively higher levels in bog (3.35 ± 0.17 μg/L) and lagg (2.31 ± 0.06 μg/L) waters and streamwater (2.38 ± 0.79 μg/L) indicate that much of the Pb leaving the peatland was sourced from the bog, which is consistent with the lagg being only 0.2 ha relative to the 3.2 ha bog.[29] Furthermore, since little Pb runs off from the upland currently and atmospheric deposition is quite small, Pb in streamwater mostly comes from historical Pb accumulated in the peat.

Urban et al.[9] examined Pb in peat cores from both hummocks and hollows in S2 and other North American peatlands. They found higher inventories of Pb and ^{210}Pb in hummocks relative to hollows and demonstrated that most Pb in hummocks existed above water table fluctuations, whereas most Pb inventory in hollows was below the water table and susceptible to transport by DOM leading to lower Pb inventories in hollows. Below the water table in S2, Pb in peat can partition to DOM and be mobilized as suggested by Urban et al.[9] or Pb and DOM could be mobilized together during organic matter degradation. DOM is largely mobilized from the acrotelm peat layer[20,30,31] that includes growing plants and roots[32] and extends to the lowest depth of typical annual water table fluctuations.[14] Transient anoxia stemming from the rise and fall of the water table may promote secondary peat decomposition[8,14,31,33,34] which could lead to more DOM. The range in annual water table fluctuations (SI Figure S1) easily encompasses peak Pb concentration in the peat cores (Figure 4).

The situation in 2016 was much different than in 1983 as *Sphagnum* growing in the last few decades was exposed to little Pb deposition and most Pb inventory was within the range of water table fluctuations in both hollows and hummocks (SI Figure S4). As shown in Figure 4, Pb content in peat above the water table fluctuations was generally very low relative to peak Pb content in the acrotelm. The water table in June of 2016 when the cores were collected was at an elevation of 421.97 m, only a few cm above the level where lateral flow ceases.[13] Pb content peaked near the water table, which was about 40 cm below the surface of the peat in the hummocks and between 20 and 30 cm in the hollows. Figure 4 demonstrates that the majority of Pb is contained in the acrotelm within the bounds of water table fluctuations in both the hummocks and hollows. This vertical Pb distribution is the primary reason for the muted response of S2 Pb yields to large reductions in Pb inputs. DOM continues to mobilize historical deposits of Pb in the acrotelm and support Pb concentrations in streamflow. The strong correlations between Pb and DOC concentrations found in porewaters (SI Figures S2–S3) and outflow (Figure 3) support this conclusion.

Based on multiple studies of Pb in peat cores, Shotyk et al.[2] concluded that Pb is immobile in ombrotrophic peat bogs. However, very few studies have measured Pb in the dissolved phase and no other bog has been hydrologically monitored like S2 allowing for accurate determinations of Pb losses via streamflow. Shotyk et al.[11] measured Pb in porewaters of three bogs in Finland and found concentrations ranging from 0.1 to almost 8 μg/L, and noted that the values were a small percentage (<0.01%) relative to the solid phase (~50 μg/g). However, mobility is dependent on the *fraction* of the Pb that exists in the dissolved phase and bulk density should be taken into account. We measured similar concentrations to Shotyk et al.[11] in bog porewaters (mean = 3.35 μg/L) and in the peat (mean peak = 23.6 μg/g from 13 cores). Bulk density at the peak Pb peat concentration averaged 64 mg/cm^3 leading to a fraction of Pb in the dissolved phase of 0.22%. This fraction could be greater near the peat surface where bulk density is lower and Pb concentrations in peat are lower, but Pb concentration in the dissolved phase may be variable with depth.[10] Peat bogs with high DOC concentrations like S2

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would be more likely to have a greater fraction of Pb in the dissolved phase. Hydrologic conditions would then dictate how much of the Pb gets transported out of the bog. Thus, ombrotrophic bogs with high DOC and a short water residence time would be the most susceptible to exporting Pb.

To compare Pb inventories in peat cores collected in 2016 to those in 1983,[9] we extrapolated mass accumulation rates from 1983 to 2016. Urban et al.[9] used an ash stratigraphic method to approximate the year 1930 in peat cores collected from S2 in 1983 and reported average mass inventory down to this time in both hummocks and hollows.[9] At a constant rate of mass accumulation, cumulative masses from 1930−1983 (1.33×10^4 g/m^2 in hummocks and 1.06×10^4 g/m^2 in hollows) would be extrapolated to 2.16×10^4 g/m^2 in hummocks and 1.72×10^4 g/m^2 in hollows from 1930−2016. A single 32 cm core collected in 1989 from a hollow in S2 and dated using ^{210}Pb, pollen, and acid-insoluble ash approaches, reported an average organic matter accumulation rate of 204 g/m^2·yr, which corresponds to 219 g/m^2·yr if insoluble ash content is 7%.[22] Extrapolating 219 g/m^2·yr from 1930 to 216 results in a cumulative dry mass of 1.88×10^4 g/m^2 in hollows, similar to the extrapolated dry mass accumulation (1.72×10^4 g/m^2) estimated from Urban et al.[9] Table 3 shows the Pb inventories from 1930−1983[9] compared to 1930−2016. With only two hummock cores from 1983, the average Pb inventory of 420 mg/m^2 is nearly double that determined in 2016 (221 ± 32 mg/m^2). The hollows average of 251 ± 30 mg/m^2 in the earlier period was no different from 238 ± 12 mg/m^2 in 2016. These results suggest that Pb existing above water table fluctuations in hummocks in 1983 has potentially been redistributed to hollows or lost from the peatland.

Since there is uncertainty in what depth of the peat core to include in the inventory, the Pb and mass inventories were recalculated for the 2016 cores over a longer period of time by including additional 5 cm increments (Table 3 and SI Figure S4). These calculations demonstrate the impossibility of finding an increase in Pb inventory in hummocks and the improbability of demonstrating a change in Pb inventory compared to cores collected in 1983 by Urban et al.[9] At these depths within the catotelm, another 5 cm could easily include another century or more of peat accumulation.[35] With an additional 5 cm of depth, dry mass inventory more than doubled relative to 1983 cores (Table 3) in hummocks and hollows, respectively, while Pb inventory only increased to 245 ± 79 mg/m^2 and 266 ± 29 mg/m^2 in hummocks and hollows, respectively. One more additional 5 cm depth increment nearly triples dry mass inventory relative to 1983 cores and Pb inventory increases further to 260 ± 77 mg/m^2 and 289 ± 31 mg/m^2 in hummocks and hollows, respectively (Table 3). There is still no statistical difference in Pb inventory in the hollows between time periods ($p > 0.33$) and hummocks show a decrease ($p < 0.05$). These deeper core intervals are likely well below the influence of leaded gasoline in the cores and thus have low Pb content and contribute relatively little to the inventory. In fact, none of the 13 cores have a Pb inventory over 400 mg/m^2 using the *complete* core profiles (SI Figure S4), suggesting Pb core inventories must have decreased relative to the 1983 cores.

Assuming equal areas in the peatland for hummocks and hollows, the net loss of Pb between 1983 and 2016 was estimated to be between 80 and 105 mg/m^2 based on the present day Pb inventory ("actual" inventory and "actual plus 5 cm", Table 3). If Pb were immobile in the peat, the Pb inventory in the peat should have increased between 1983 and 2016 as Pb was still elevated in the atmosphere through the 1980s though the overall decrease was over 99% to near zero by 2016.[4]

Stream Pb yields were compared to the loss of Pb in peat from 1983−2016 (~80−105 mg/m^2) based on calculated Pb streamflow yields from 1981−1983 and 2009−2015 and estimates of the intervening time period. First, we applied the first-order rate constant of 0.022 yr^{-1} describing the decline in Pb concentration in outflow to the range of stream Pb yields reported by Urban et al.[9] By this method, total losses of Pb from the peat via streamflow were estimated to range between 43 and 70 mg/m^2 between 1983 and 2016. The second estimation method utilized the more complete annual TOC fluxes (TOC was measured from 1981−1985 and 1992 to present), our expectation that DOC and TOC concentrations are equivalent,[20] and Pb:DOC concentration ratios to define upper and lower bounds for stream Pb yields. Assuming the Pb:DOC concentration ratio remained constant at the average 1981−1983 ratio results in an upper estimate of 66 mg/m^2 lost via streamflow while using the 2009−2015 ratios results in a lower estimate of 30 mg/m^2 lost from 1983 to 2015. Using the first-order rate of 0.022 yr^{-1} describing the decline in Pb concentration in outflow and assuming it applies to the Pb/DOC ratio results in a loss of 52 mg/m^2.

Not all Pb losses from the peat since the early 1980s can be accounted for via streamflow. Losses of Pb from the peat could also occur via water seepage to a deeper, surrounding groundwater aquifer.[24] Water percolates through the shallow peat in the lagg, a process that would transport Pb to underlying mineral soils (a sandy glacial outwash below thin loamy clay lining peatland[15]). Verry et al.[13] estimated deep seepage from the S2 lagg to be ~3800 m^3/yr during an average hydrologic year which is 27.6% relative to average annual streamflow between 2009 and 2015. Seepage through the bog catotelm is negligible where peat is up to 2−7 m deep, hydraulic conductivities decrease exponentially with depth to relative impermeability, and a loamy clay mantle that is thicker under the bog further reduces vertical seepage under deep peats.[36] Using the average Pb concentration in lagg water (2.3 ug/L), the Pb loss from seepage normalized to the area of the whole peatland is 0.30 mg/m^2.yr which is 25−50% of the Pb lost via streamflow. While this estimate has uncertainty associated with the cruder estimate of seepage to groundwater, it demonstrates the plausibility of another Pb loss pathway from the catchment. Summing Pb seepage from the lagg (0.30 mg/m^2.yr) and average Pb streamflow from 2009−2015 (0.84 mg/m^2.yr) yields total annual losses of Pb from S2 peat of 1.14 mg/m^2 or 0.48% of the peat inventory. These losses demonstrate that the peatland is still releasing historical Pb inputs and the peat inventory of Pb should continue to decrease over time.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b06577.

Annual hydrologic graphs, additional Pb vs DOC relationships in grouped bog, grouped lagg, individual bog, and individual lagg sites, Pb inventory versus depth and cumulative mass inventory in hummocks and hollows (PDF)

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