

# Supporting Information for:

## Atmospheric deposition of indium

## in the northeastern United States:

## flux and historical trends

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13 pages, 4 figures, 2 tables

## Methods

### <sup>210</sup>Pb Dating

0.75g (for the upper 15cm) or 3g samples were packaged for gamma counting in polypropylene vials (2oz. and 4oz., respectively) and left for at least 3 weeks before counting, to allow secular equilibrium to be established between <sup>222</sup>Rn production and decay, which translates to secular equilibrium for <sup>214</sup>Pb, which is used to determine supported <sup>210</sup>Pb activity.

Samples for dating were counted for gamma decays on a  $\gamma$ -counter (Canberra Instruments, GL2020 detector with series 40 multi-channel analyzer). Lead-210 was measured at an

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energy of 46.5 keV.  $^{214}\text{Pb}$  was measured as a proxy for supported  $^{210}\text{Pb}$  activity, at 295 and 352 keV.  $^{137}\text{Cs}$  was measured at 662 keV. Energies were calibrated initially using pitchblende (U.S. EPA, Environmental Monitoring Systems Laboratory-Las Vegas, Quality Assurance Division, Standard Pitchblend Ore) and individual gamma sources ( $^{22}\text{Na}$ ,  $^{54}\text{Mn}$ ,  $^{57}\text{Co}$ ,  $^{60}\text{Co}$ ,  $^{109}\text{Cd}$ ,  $^{133}\text{Ba}$ ,  $^{137}\text{Cs}$ , 1  $\mu\text{Ci}$ , The Nucleus, Inc, Oak Ridge, TN), and re-checked periodically with pitchblende.

Background  $^{210}\text{Pb}$  and  $^{214}\text{Pb}$  was measured for an empty plastic vial, and subtracted from the total  $^{210}\text{Pb}$  and  $^{214}\text{Pb}$  counts. (The  $^{210}\text{Pb}$  background was 0.01 counts per minute (cpm), at most 15% of the sample signal. The  $^{214}\text{Pb}$  background was 0.02 cpm, in some cases representing as much as a 100% correction due to the low  $^{214}\text{Pb}$  signal in the samples.) Counting efficiencies for the samples [(counts per minute)/(decays per minute)] were determined by the addition of two pitchblende spikes. The original sample was counted as described above, then 30–65 mg pitchblende was added, mixed, and counted after 3 weeks equilibration time. A second addition of pitchblende was carried out in the same way. This set of additions was done for two samples of each sample size (0.75 g and 3 g samples), since changes in the geometry of a sample can affect the counting efficiency. In this case, the efficiencies for both sample sizes were not distinguishable: 0.5% for  $^{210}\text{Pb}$  and 2% for  $^{214}\text{Pb}$ . For the 3 g sample, relative error on these efficiencies was as much as 17%, determined by the difference between the efficiency calculated for the two 3 g samples. This error is most likely due to both instrumental error, and to slight density differences in the samples that cause the overall volume of the samples to vary slightly. The 0.75 g samples had one point that was seemingly substantially in error, perhaps due to inadequate mixing of the pitchblende with the sample, which can have a significant effect on efficiency. With this point included, relative error on this sample size was 29% and 38% for  $^{210}\text{Pb}$  and  $^{214}\text{Pb}$ , respectively. Without this point, relative error was 2-3%.

Model dates were assigned according to the Constant Rate of Supply (CRS) Model (1–3).  $^{210}\text{Pb}$  is a radioactive decay product in the  $^{238}\text{U}$  series.



Because Rn is volatile and has a several-day lifetime in the atmosphere and widespread sources,  $^{210}\text{Pb}$  is relatively well-distributed on a hemispheric scale, although concentrations may vary depending on geographic location and rainfall (1, 4). The CRS model assumes a constant rate of input of  $^{210}\text{Pb}$  on a year timescale (DPM/(cm<sup>2</sup>-yr)), but allows for variable sedimentation rates (g sediment/(cm<sup>2</sup>-yr)). It therefore allows for any difference in sedimentation rate that may occur each year, based both on changes in *Sphagnum* growth rate from year to year, as well as compaction and decomposition that takes place as the peat ages. After quantification of unsupported  $^{210}\text{Pb}$  (by subtraction of the measured  $^{214}\text{Pb}$  from the total  $^{210}\text{Pb}$ ), a total inventory (dpm/cm<sup>2</sup>) was calculated following Appleby (1), and the age of each sediment layer was determined by

$$A_x = A_0 e^{-\lambda t} \quad (\text{S1})$$

where  $A_x$  is the inventory of  $^{210}\text{Pb}$  below depth  $x$ ,  $A_0$  is the inventory of the full core,  $\lambda$  is the decay constant for  $^{210}\text{Pb}$  of 0.0311 yr<sup>-1</sup>, and  $t$  is the time before present, in years. Cumulative mass (g/cm<sup>2</sup>) can be substituted for depth, and is often a better unit for comparison among cores that may be affected by compression.

Of the 34 core samples analyzed, 25 were dated using this technique. Intervening dates were linearly interpolated or extrapolated for the purposes of plotting indium depth profiles.

Cesium-137 enters the atmosphere from nuclear activity such as bomb testing and nuclear meltdowns. Peaks in  $^{137}\text{Cs}$  can be seen in sediments and peat corresponding to two dates: 1963, the peak year of nuclear bomb testing; and 1986, the nuclear reactor meltdown at Chernobyl (1, 5). The background signal for  $^{137}\text{Cs}$  measured for an empty plastic vial was 0.00 cpm/g. Efficiencies were not calculated for  $^{137}\text{Cs}$ , since only relative activities are needed for determining the 1963 and 1986 peaks.

## Metals Analysis

Homogenized peat samples (0.5–1 g) were digested based on a slightly modified EPA Method 3050B. Samples were refluxed in teflon beakers on a hotplate with 30 mL concentrated nitric acid (Malinckrodt Chemical reagent grade) for approximately 4 hr before adding 10 mL 70% perchloric acid (Alfa Aesar reagent grade) and refluxing for another 4 hr. After sitting at room temperature overnight, another 10 mLs concentrated nitric acid was added before taking the samples to dryness. Perchlorate was driven off finally with the addition of 10 mL nitric acid, which was again taken to dryness. Each sample was resuspended in 10 mL 2% nitric acid, left for 30 minutes, then the acid decanted into a 15 mL polypropylene vial. After addition of indium spikes, samples were filtered using an acid washed Whatman or VWR brand polypropylene 0.45  $\mu\text{m}$  syringe filter, and a non-acid-washed normject 10 mL polypropylene syringe. Reagent blanks and acid blanks were filtered in the same manner and showed no significant indium or lead contamination from this process, and standards showed that neither indium nor lead was lost significantly during filtration.

In order to account for matrix effects and drift of the instrument signal over time, the method of standard additions was used to quantify total indium. Each sample was split in two, one of those samples was spiked with 0.1  $\mu\text{g/L}$  indium, and the samples run back-to-back on the ICP-MS. The concentration of indium in the original sample,  $[In]_{\text{smp}}$ , was then determined by:

$$[In]_{\text{smp}} = ([In]_{\text{spike}} / (CPS_{\text{spiked}} - CPS_{\text{smp}})) \times CPS_{\text{smp}} \quad (\text{S2})$$

where  $[In]_{\text{spike}}$  is the concentration of the indium spike (10  $\mu\text{g/L}$ ),  $CPS_{\text{spiked}}$  is the counts per second of the spiked sample, and  $CPS_{\text{smp}}$  is the counts per second of the unspiked sample.

$^{115}\text{Sn}$  (0.34% of total Sn) is an isotopic interferent for  $^{115}\text{In}$ . It is linear and predictable, and was corrected for by monitoring  $^{117}\text{Sn}$  or  $^{118}\text{Sn}$  and subtracting the corresponding counts that would be attributed to  $^{115}\text{Sn}$  (6). Calculations using the two Sn isotope corrections agree

to better than 1%, indicating that this is a reasonable correction and that there are no other interferences present. The correction for  $^{115}\text{Sn}$  were as high as 50% of the total counts at 115. Samples with a range of concentrations of tin spiked into them showed that indium concentrations could still be analyzed accurately even when  $^{115}\text{Sn}$  counts were high relative to  $^{115}\text{In}$ . Polyatomic interferences ( $\text{RuO}$ ,  $\text{AsAr}$ ,  $\text{ArBr}$ ,  $\text{BrS}$ , and  $\text{MoO}$ ) were ruled out by running pure standards of each of these elements and monitoring for signal at 115.

As discussed in the main text, lead was quantified using indium as an internal standard to account for matrix effects and drift of the instrument signal over time (7).

## Quality Control

All plastic and teflon vessels were acid washed prior to use. During core processing, blanks were tested at all steps of the process, both by exposing the potential contributing surface (saw blade, scissors, homogenization vial, homogenization balls) to acid as a stringent measure of indium content, and by comparing the indium concentrations in two halves of a peat slice — one that was processed normally, and one that was subjected to repetitive exposure to the saw blade or scissors. In all cases the concentration of indium supplied by these surfaces was undetectable; acid blank signals were below detection limits (and  $<1\%$  of sample signal), and the peat that was exposed to saw blade and scissors was within 9% of the non-exposed sample, a difference less than the method uncertainty of 20%. Lead was not tested in the cutting and homogenizing blanks; though contamination from these surfaces is not expected, contamination would be assumed to affect all sample depths equally, potentially affecting the magnitude of lead depositional fluxes, but not affecting the shape of the flux profile, which is what is used for comparison. While metal inputs to the bog may be heterogeneous over the scale of the bog (8), several tests done on indium concentrations in two halves of one vertical core slice indicate that metal inputs are homogeneous on the scale of the core (13 cm).

During digestion and ICP-MS analysis, blanks were tested at all steps of the process,

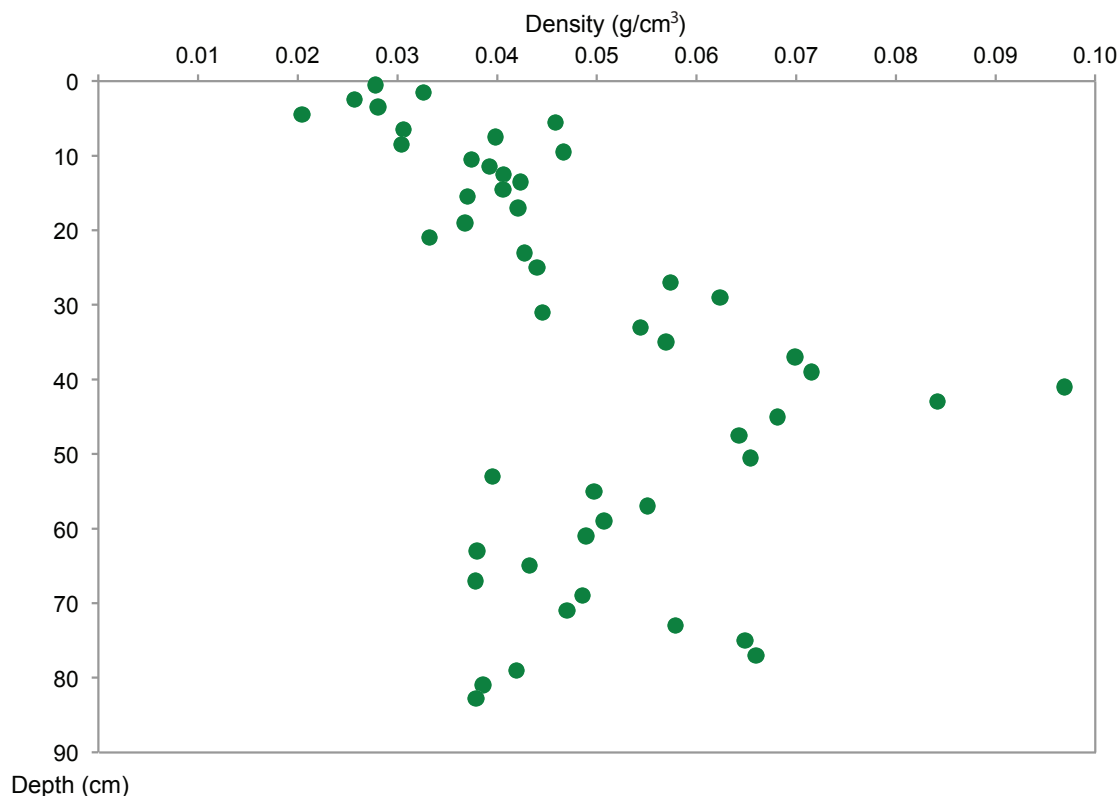


Figure S1: Dry density ( $\frac{\text{dry weight}}{\text{volume}}$ ) of Thoreau's Bog core samples.

including acid blanks, reagent blanks, filter blanks, and standard recoveries. Acid-washed  
teflon beakers and watchglasses were used for these digests, along with acid-washed glass-  
ribbed watchglasses for taking the samples to dryness. Initial digests were done using reagent  
grade acids and a non-laminar flow perchloric acid hood, while subsequent dilutions for the  
measurement of Pb were done using double distilled HNO<sub>3</sub>. Reagent blanks were run with  
each sample set and subtracted from the sample signal; they should reflect any contamination  
during and post-digest, and contributed at most 5% of the sample signal for both In and Pb.

## Data Tables and Figures

The following tables contain the raw data presented in this chapter for <sup>210</sup>Pb dating calcu-  
lations and for the profile of indium concentrations and fluxes in Thoreau's Bog.

Table S1:  $^{210}\text{Pb}$  data used for date calculations.

Depth cm	cumulative mass g/cm <sup>2</sup>	$^{210}\text{Pb}$ dpm/g	$\pm$	Inventory dpm/cm <sup>2</sup>	$\pm$	Age y	$\pm$	Model Date
0	0			38.4	6.2	0	0	2010
1	0.03	21.9	3.4	37.8	1.2	1	1	2009
3	0.09	27.6	2.9	36.2	1.2	2	1	2008
5	0.13	24.4	3.0	35.0	1.2	3	1	2007
7	0.21	21.7	2.8	33.4	1.1	5	1	2005
9	0.28	20.1	2.9	32.0	1.1	6	2	2004
11	0.37	20.3	2.8	30.3	1.1	8	2	2002
13	0.45	17.7	2.7	28.9	1.0	9	2	2001
15	0.53	12.2	2.7	27.8	1.0	10	2	2000
18	0.65	12.6	0.9	26.3	1.0	12	2	1998
22	0.79	9.8	0.8	24.9	1.0	14	2	1996
26	0.96	10.7	0.9	23.1	0.9	16	2	1994
30	1.20	8.2	0.8	21.1	0.9	19	2	1991
34	1.40	10.4	0.9	19.0	0.9	23	2	1987
38	1.65	12.7	1.0	15.8	0.9	29	2	1981
42	1.99	6.9	0.8	13.5	0.8	34	2	1976
46	2.30	7.6	0.8	11.2	0.8	40	3	1970
52	2.68	7.1	0.8	8.4	0.8	49	3	1961
56	2.86	7.1	0.8	7.1	0.7	54	3	1956
58	2.97	9.0	0.9	6.1	0.7	59	4	1951
60	3.07	7.4	0.8	5.4	0.7	63	4	1947
64	3.25	7.6	2.1	4.1	0.5	72	4	1938
66	3.33	6.5	0.8	3.5	0.5	77	5	1933
70	3.51	5.7	0.8	2.5	0.4	87	5	1923
72	3.60	4.6	0.7	2.1	0.4	93	6	1917
76	3.85	4.3	0.7	1.0	0.3	116	9	1894
82	4.14	3.6	0.7	0				

Table S2: Indium depth profile data.

Depth Interval cm	year	In conc ppb	$\pm$	In flux ng/(cm <sup>2</sup> -yr)	sedimentation rate cm/yr	density g/cm <sup>3</sup>
0-1	2009	2	0.4			0.03
2-3	2008	2	0.4	0.06	1.43	0.03
4-5	2007	4	0.7	0.14	1.88	0.02
6-7	2005	3	0.5	0.10	1.28	0.03
8-9	2004	2	0.4	0.09	1.44	0.03
10-11	2002	2	0.4	0.08	1.14	0.04
12-13	2001	2	0.4	0.11	1.30	0.04
14-15	2000	2	0.4	0.14	1.75	0.04
16-18	1998	2	0.3	0.12	1.65	0.04
20-22	1996	2	0.4	0.15	2.31	0.03
24-26	1994	2	0.5	0.18	1.61	0.04
28-30	1991	3	0.5	0.22	1.39	0.06
32-34	1987	5	1	0.33	1.21	0.05
36-38	1981	16	3	0.73	0.67	0.07
40-42	1976	20	4	1.54	0.79	0.10
44-46	1970	34	13	1.54	0.66	0.07
49-52	1961	44	9	1.90	0.66	0.07
54-56	1956	27	5	1.02	0.76	0.05
56-58	1951	50	29	1.15	0.41	0.06
58-60	1947	51	10	1.24	0.48	0.05
62-64	1938	56	12	0.94	0.44	0.04
64-66	1933	45	9	0.82	0.42	0.04
66-68	1926	36	7	0.40	0.29	0.04
68-70	1923	43	9	1.13	0.55	0.05
70-72	1917	69	38	1.08	0.33	0.05
72-74	1908	45	9	0.64	0.24	0.06
74-76	1894	65	16	0.59	0.14	0.06
76-78	1893	41	8	*5.67	*2.09	0.07
78-80	1888	27	5	0.46	0.41	0.04
80-82	1884	30	6	0.51	0.45	0.04
82-83.5	1880	29	6	0.50	0.45	0.04
83.5-84	1879	14	3	0.24	0.28	0.06
84-84.5	1877	13	3	0.22	0.36	0.05
84.5-87	1872	9	2	0.15	0.48	0.04

\*This point was omitted from Figures 4 and 5 because of a calculated sedimentation rate 4x higher than the other calculated sedimentation rates, causing the flux to be 10x higher than surrounding fluxes. See text for discussion.



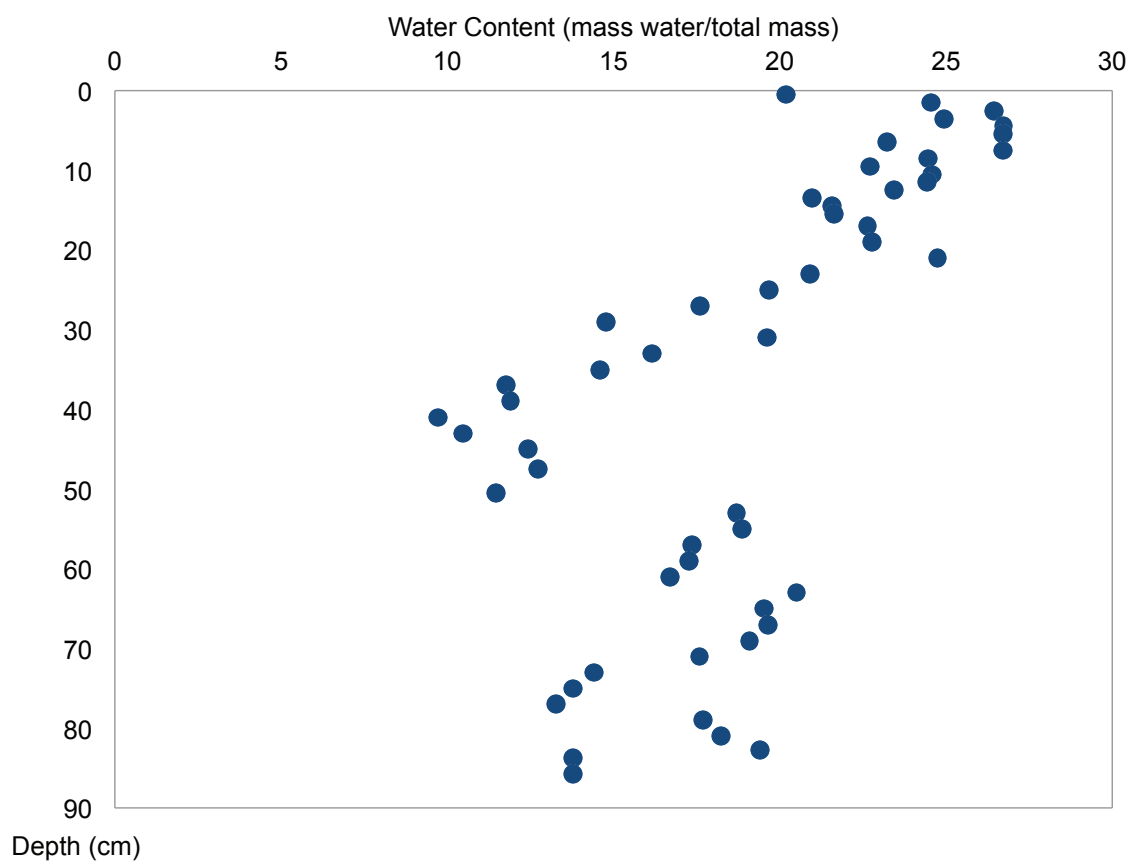


Figure S2: Water content ( $\frac{\text{mass wet weight} - \text{mass dry weight}}{\text{mass wet weight}}$ ) of Thoreau's Bog core samples.

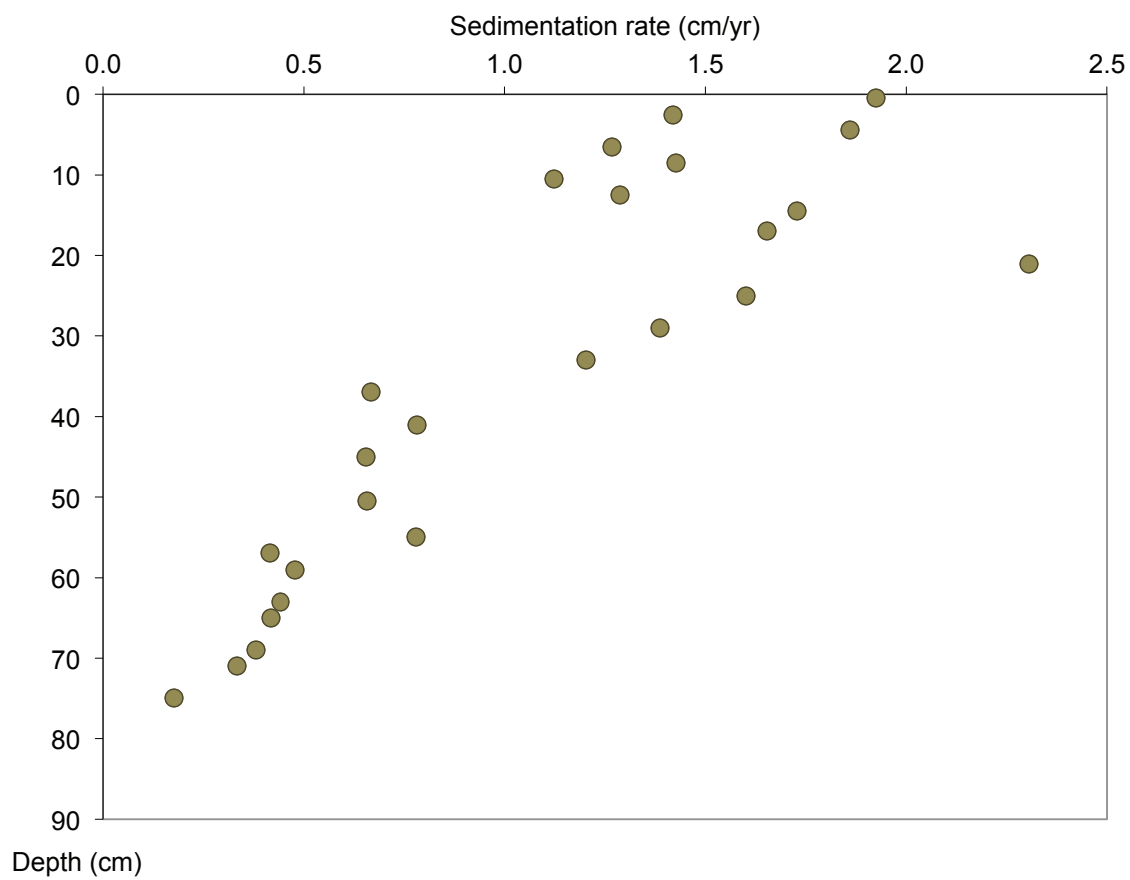


Figure S3: Apparent sedimentation rate of Thoreau's Bog core samples is higher at the surface, where live peat is growing, and lower at depth, where peat is degraded and compressed.

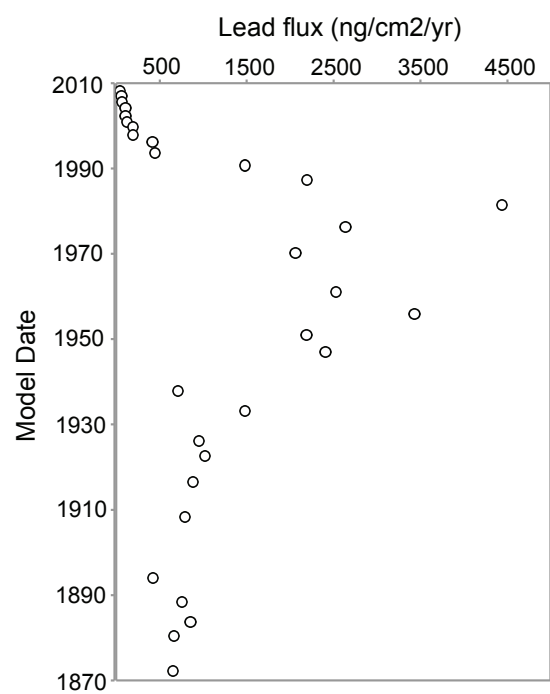


Figure S4: Lead fluxes have been increasing since at least the early 1900s, peak in the 1970s, and decrease to the present. This agrees well with other published flux profiles for lead in the northeastern United States, and serves as a cross-check on the dating and indium analyses for this core.

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