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Quantitative Retention of Atmospherically Deposited Elements by Native Vegetation Is Traced by the Fallout Radionuclides ^{7}Be and ^{210}Pb

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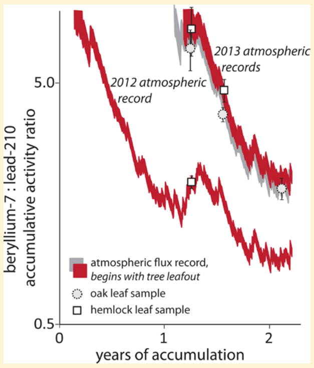
Supporting Information

ABSTRACT: Atmospheric deposition is the primary mechanism by which remote environments are impacted by anthropogenic contaminants. Vegetation plays a critical role in intercepting atmospheric aerosols, thereby regulating the timing and magnitude of both contaminant and nutrient delivery to underlying soils. However, quantitative models describing the fate of atmospherically derived elements on vegetation are limited by a lack of long-term measurements of both atmospheric flux and foliar concentrations. We addressed this gap in understanding by quantifying weekly atmospheric deposition of the naturally occurring radionuclide tracers ^{7}Be and ^{210}Pb, as well as their activities in leaves of colocated trees, for three years in New Hampshire, U.S. The accumulation of both ^{7}Be and ^{210}Pb in deciduous and coniferous vegetation is predicted by a model that is based solely on measured atmospheric fluxes, duration of leaf exposure, and radioactive decay. Any "wash off" processes that remove ^{7}Be and ^{210}Pb from foliage operate with a maximum half-time of greater than 370 days ($P >$ 99%), which is an order of magnitude longer than previously assumed. The retention of both ^{7}Be and ^{210}Pb on leaves is thus quantitative and permanent, coupling the fate of ^{7}Be, ^{210}Pb and similar atmospheric species to that of the leaf matter itself. These findings demonstrate that the long-standing paradigm of a short "environmental half-life" for atmospheric contaminants deposited on natural surfaces must be re-evaluated.



1. INTRODUCTION

Atmospheric deposition of aerosols by wet and dry processes is often the predominant mechanism by which nutrient and contaminant elements are delivered to terrestrial ecosystems.[1−3] Insofar as 70% of the Earth's landmass is vegetated, the deposition and subsequent fate of aerosols is typically mediated by plant surfaces.[4,5] However, processes that regulate the efficiency and time scale of aerosol retention by foliage are not well understood. The long-standing paradigm of aerosol fate was developed from observations of fission radionuclides which were dispersed into the atmosphere by nuclear bomb-testing in the 1960s and 1970s,[6,7] it predicts that various "wash-off" processes remove atmospheric fallout from vegetation, and that the rate of removal can be described using a first-order rate constant (λ_e) and a characteristic "environmental half-life" ($\ln2/\lambda_e$) on the order of weeks.[8,9] These rate constants continue to be published for use in radionuclide and contaminant transfer models[10,11] that are needed in the environmental monitoring of, for example, nuclear reactor disasters and industrial accidents. Such a short time scale of removal is shorter than the radioactive decay of most relevant fission contaminants, and is especially remarkable because it is irrespective of elemental chemistry among relatively mobile elements such as I, Cs, and Sr, and reactive or immobile elements such as Mn and Ce.[10]

Later works[7,12] extended the paradigm of a short "environmental half-life" to the natural cosmogenic radionuclide ^{7}Be (half-life 54 days), which is now widely used in atmospheric[13] and terrestrial tracer applications,[14] often in conjunction with the natural radiogenic tracer ^{210}Pb (half-life 22.3 years).[15,16] However, a short environmental half-life for foliar retention is irreconcilable with contemporary observations of naturally occurring ^{7}Be and ^{210}Pb. When considered as a holistic atmosphere-vegetation-soil continuum, we see that a majority of ^{7}Be inventory typically resides in vegetation rather than in underlying soil,[17−19] this precludes wash-off processes as being important on time scales of ^{7}Be radioactive decay.

A number of factors complicated previous assessments of aerosol-contaminant interaction with vegetation, principally biodilution by ongoing plant growth, but perhaps also the failure of artificial rainwater solutions to reproduce the behavior of natural aerosols.[20] Moreover, the true atmospheric flux was rarely measured,[7] it was widely assumed that the primary mechanism of aerosol deposition was through dry processes, and this error drove a bias toward measuring air concentrations. Wet deposition (where present) is now known to be the

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predominant source of deposition for many atmospheric radionuclides and pollutant metals.[21,1] Earlier interpretations of aerosol behavior may also fail to describe contemporary observations due to a reduction in atmospheric SO_4^{2-} and concomitant increase in rainwater pH which has been observed in some regions of the U.S. over recent decades,[22,23] and which may influence both speciation[21] and sorption behavior[24] of relevant metals.

We now find the concept of a short environmental half-life misleading in our efforts to predict the fate of certain aerosol-derived contaminants. On the contrary, the retention of ^{7}Be and ^{210}Pb by vegetation[25,17−19] is consistent with specific mechanisms of foliar uptake, which have recently been identified[26] and found to be important for accumulation of aerosol metals[27,28] such as Pb, Cd, Zn, and Cu. Atmospheric Hg also accumulates in foliage[29]and is retained to such an extent[30] that leaf fall is the greatest source of Hg input to forest soils.[31]

Here we describe a three-year, ongoing experiment designed to assess the interaction of radionuclides ^{7}Be and ^{210}Pb with natural vegetation. These radionuclides' occurrence in vegetation has historically received little attention because of their low atmospheric fluxes and analytical limitations.[12] This lack of attention belies the value of ^{7}Be and ^{210}Pb as tracers in terrestrial systems, since both are globally ubiquitous, trace atmospheric deposition of aerosols[13] and pollutants,[32,33] and are highly particle-reactive[24,34] such that they trace the subsequent fate of materials, especially organic matter, that sequester aerosols, tracers and contaminants.[17] A full understanding of ^{7}Be and ^{210}Pb depositional behavior and fate provides a critical basis for the evaluation of other atmospheric aerosol constituents and contaminants. To this end, we compare a high-resolution record of ^{7}Be and ^{210}Pb atmospheric deposition with their abundance in the foliage of colocated canopy trees. We find that vegetation accumulates both ^{7}Be and ^{210}Pb efficiently, predictably, and conservatively without evidence for significant wash-off effects or a short environmental half-life. The foliar retention of both radionuclides is quantitative, both predictable and absolute, and is essentially permanent. Furthermore, as a consequence of their shared behavior, the different radio-decay rates of ^{7}Be and ^{210}Pb allow us to construct a chronometer of leaf exposure age. We discuss the implications of our new understanding of ^{7}Be and ^{210}Pb behavior, and its potential for informing us about the behavior of other, environmentally relevant aerosol constituents.

2. BACKGROUND

Both ^{7}Be and ^{210}Pb are naturally occurring radionuclides with strong gamma photoemissions, making them highly traceable at concentrations as low as 10^{-21} gram per gram. ^{7}Be is cosmogenic, produced in the atmosphere by the fission of atmospheric oxygen and nitrogen by cosmic neutrons.[35] ^{210}Pb is a long-lived intermediate in the geogenic ^{238}U decay chain, and is thus a ubiquitous component of all soils worldwide.[36] In the abbreviated decay sequence $^{238}\text{U} \gg {}^{226}\text{Ra} > {}^{222}\text{Rn} \gg {}^{210}\text{Pb}$, volatile Rn outgasses from soils at low, continuous rates.[37] Subsequent decay of ^{222}Rn in the atmosphere (half-life 3.8 days) produces a tropospheric reservoir of ^{210}Pb in excess of that directly supported by the decay of its long-lived precursor ^{226}Ra (half-life 1602 years).

Following their synthesis in the atmosphere both ^{7}Be and ^{210}Pb may be expected to persist as charged ions only very briefly before bonding to atmospheric oxygen or water[38,39,36] and being incorporated into natural aerosols.[36,40,41,13] Their subsequent, efficient removal from the atmosphere primarily by wet deposition[42] sustains a reservoir of both nuclides on vegetation, surface soils, and sediments.[43]

3. EXPERIMENTAL SECTION

All samples were collected on the Dartmouth College campus (Hanover, NH) at the Shattuck Observatory. There a ca. 1 ha field of lawn grass grades into open, managed forest of native hardwoods, softwoods, and ornamental cultivars in mixed growth stages. Beginning in March 2011 and continuing to the present, we collected weekly precipitation samples in an open bucket at ground level. Radionuclide samples were acidified to pH <1 within the collector at the end of the sampling period, allowed to equilibrate for several days and then filtered at 0.5 μm. Daily precipitation totals from a second gauge adjacent to our radionuclide collection were provided by the Shattuck Observatory. These data were supplemented as necessary from nearby automated weather stations in Lebanon, NH and Norwich, VT (at comparable elevations and 10 and 2 km distant, respectively).

Prior to 2013 all ^{7}Be measurements were performed directly on acidified solutions in 1L Marinelli beakers. Subsequent measurements for ^{7}Be, and all ^{210}Pb measurements, were performed on MnO_2 coprecipitates following a method adapted from Benitez-Nelson et al.[44] Coprecipitated MnO_2 solids were filtered onto 0.5 μm glass-fiber filters and presented for gamma counting directly using a Petri-dish geometry. Stable Be and Pb solutions were added to each sample as yield monitors and measured by inductively coupled plasma optical−emission spectroscopy (ICP−OES). Following filtration, the filter apparatus was rinsed with sufficient concentrated HCl which, when combined, acidified the filtrate to pH <1 prior to removing a final yield aliquot. Yields averaged 93 ± 2% (mean ± SD) for both Be and Pb for 168 samples. ^{210}Pb contribution from our lead yield monitor was measured as 0.20 ± 0.07 mBq and is less than 1% of all samples. Gamma instrumental on-peak backgrounds for ^{210}Pb were not neglible. These were measured in count times of $>2 \times 10^{6}$ seconds, and were subtracted from sample measurements. Propagated uncertainties for all measurements follow standard methods[45] and include background subtraction. The total ^{210}Pb background-equivalent for our full atmospheric data set was ca. 9.5% of the estimated real flux.

Leaves were sampled at a site colocated with our radionuclide collections. We sampled leaves of two dominant canopy tree species, deciduous *Quercus rubra* (red oak) and coniferous *Tsuga canadensis* (eastern hemlock) at intervals throughout their growing season(s). Sampled individuals were open-grown, without direct canopy overstorey but in the vicinity of mature trees. The observed leaf-out dates of sampled trees constrains their leaves' ages. Leaves were clipped by hand from the outermost, exposed branch tips of sapling hemlock and from the tops of seedling red oak. Hemlock needles were removed both from apical new growth and from the node immediately behind, the latter we took to be 1-year-old needles from the previous years' growth as hemlock produces a single leaf flush per year. Both trees were sampled in June and October, and oak was sampled again then in April of the following year as it retains some leaves following senescence. By sampling the uppermost or terminal leaves of open-grown trees, we made an explicit effort to avoid shielding effects that occur as trees

Table 1. Depositional Fluxes of ^{7}Be and ^{210}Pb Compiled for Northern Hemisphere Locations

		latitude	rainfall	^{7}Be		^{210}Pb		^{7}Be:^{210}Pb		
location	year	°N	cm	Bq m^{-2} yr^{-1}	σ	Bq m^{-2} yr^{-1}	σ	R	σ	literature source[a]
St. Petersburg, FL	2003	27.77	142	1473		106		13.9		Baskaran and Swarzenski 2007[49]
Galveston, TX	1990	29.28	97	2000		112		17.9		Baskaran 1995[50]
Galveston, TX	1991	29.28	150	3937		285		13.8		Baskaran 1995[50]
College Station, TX	1990	30.60	100	2907		203		14.3		Baskaran 1995[50]
Oak Ridge, TN	1983	36.01	112	1665	62	157	9	10.6	0.7	Olsen et al. 1985[51]
Huelva, Espana	2009	37.00	72	834		59		14.1		Lozano et al. 2011[52]
Norfolk, VA	1983	39.92	131	2002	40	132	7	15.2	0.9	Olsen et al. 1985[51]
Norfolk, VA	1983−1984	39.92	132	2075	106	137	7	15.2	1.1	Todd et al. 1989[53]
Stony Brook, NY	2009	40.91	126	2554	18	147	2	17.4	0.3	Renfro et al. 2013[54]
Woods Hole, MA	1996−1998	41.53	138	2133	33	238	5	9.0	0.2	Benitez-Nelson and Buesseler 1999[55]
Portsmouth, NH	1997	43.08	134	2767	83	158	2	17.5	0.6	Benitez-Nelson and Buesseler 1999[55]
Hanover, NH	2011	43.70	117	2356	24	223	5	10.5	0.2	Landis et al. herein
Hanover, NH	2012	43.70	88	2095	27	218	4	9.6	0.2	Landis et al. herein
Hanover, NH	2013	43.70	115	1963	29	187	5	10.5	0.3	Landis et al. herein
Geneva, Suisse	1982−1983	46.20	ca. 120	2757	11	153	1	18.0	0.2	Dominik et al. 1987[56]
Geneva, Suisse	1998	46.20	97	2087	23	150	3	13.9	0.3	Caillet et al. 2001[57]
Dubendorf, Suisse	1984−1987	47.42	ca. 110	2667	267	138	14	19.3	2.7	Schuler et al. 1989[58]
Esthwaite, Cumbria, UK	1998	54.32	188	3912	120	165	8	23.7	1.4	Short et al. 2007[59]

[a] Empty fields could not be determined from data presented by literature source.

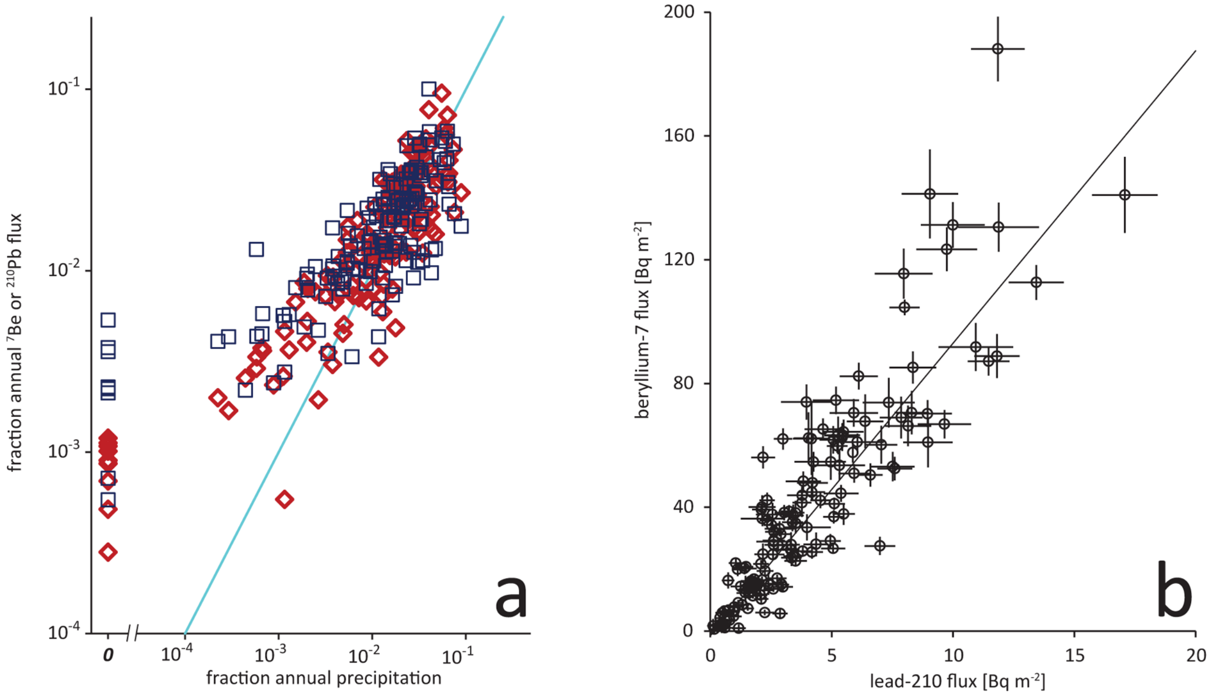

Figure 1. (a) Fluxes of ^{7}Be (red diamond) and ^{210}Pb (square) versus precipitation amount. To allow comparison of the radionuclides, flux and precipitation amount for each collection are normalized to their annual totals, where fractional flux = collection total ÷ by annual total (Baskaran 1995). Deviation from a 1:1 line (solid line) at low fluxes shows the influence of dry deposition. (b) Their common source in precipitation induces a strong correlation between measured ^{7}Be and ^{210}Pb weekly fluxes. Error bars show 1-sigma analytical errors. Robust fit of this relationship is shown by the solid line, where $[^{7}\text{Be}] = [^{210}\text{Pb}]\ (10.09{-}9.04) - (0.60{-}2.00)$. Ranges give 1-sigma confidence interval. Correlation of the log-transformed data gives $r^2 = 0.81$, $n = 168$.

establish their canopy architecture: the superposition of emergent leaves over older ones intercepts and reduces radionuclide flux to those below. Similarly, the threat of bias imposed by altering canopy architecture through sampling limits the number of times a tree may be sampled throughout the year. Sampled leaves were immediately freeze-dried and crushed coarsely as necessary for packing into 110 cm^3 polypropylene cups for direct gamma counting. All gamma measurements were performed in the Dartmouth Short-Lived Radionuclide Laboratory and were decay-corrected to the time of sample collection. Analytical details and data reduction are described by Landis et al.[46]

To allow the direct comparison of leaf radionuclide activities with atmospheric flux, we also estimated the exposed surface area of leaf samples by either measuring whole leaf dimensions with a hand ruler (hemlock) or by taking fixed-diameter punches (oak) of fresh leaves. The dimensioned leaf matter was then oven-dried at 60 °C to allow the calculation of specific leaf area, which is the projected single-sided leaf area per dry mass.[47,48] The quotient of activity-concentration from gamma counting and specific surface area gives radionuclide activity per m^2 leaf area, which is directly comparable to measurements of atmospheric flux.

Some effort must be made to distinguish between two possible sources of ^{210}Pb to precipitation and to plant surfaces: terrigenous (dust) ^{210}Pb which is accompanied by an equilibrium activity of ^{226}Ra, and atmospheric ^{210}Pb which is accompanied by none. No ^{226}Ra was detectable in precipitation; the *maximum* likely ^{226}Ra flux estimated from our own measurements is less than 0.5% of the ^{210}Pb flux. Similarly, ^{226}Ra activities in vegetation are below the detection limits of conventional gamma spectroscopy (measured either directly or indirectly via the ^{222}Rn daughters ^{214}Pb or ^{214}Bi), and the maximum likely ^{226}Ra activities are minor relative to those of ^{210}Pb. In our following discussion we thus assume all measured ^{210}Pb to be atmospheric lead with no meaningful contribution from terrigenous inputs.

4. RESULTS AND DISCUSSION

4.1. Atmospheric Deposition of ^{7}Be and ^{210}Pb. In our record of ^{7}Be and ^{210}Pb atmospheric deposition we find broad trends and descriptive statistics that are consistent with other records (Table 1).[49−59] Our measured ^{7}Be flux is comparable to sites of similar latitude, and our ^{210}Pb flux, while higher than those recorded at other sites, is consistent with regional reference soil inventories.[60,61] Both ^{7}Be and ^{210}Pb depositional fluxes at our site are controlled by precipitation amount, either rain or snow, as demonstrated by their correlation with precipitation amount (Figure 1a). Precipitation events at our locality are frequent, ca. every 3 days throughout the year, and just ten collection periods over three years were free of rain or snow. Collections for these periods were acid-washed and processed as for rainwater samples and from these measurements we estimate that 4.2 ± 0.5% of ^{7}Be and 12.0 ± 2.3% of ^{210}Pb deposition (mean ± SE) was contributed from dry processes.

The common ^{7}Be and ^{210}Pb source via wet deposition induces a strong correlation between weekly ^{7}Be and ^{210}Pb depositional fluxes ($r^2 = 0.81$; Figure 1b) as has been observed elsewhere.[58,50−52,54] An enhancement in ^{7}Be flux beginning in spring and continuing through the summer months is apparent at our site, which may be typical of continental climates[58] but is not universal.[59,14] Variability in the depositional ^{7}Be:^{210}Pb ratio over the event to seasonal time scale converges on a flux-weighted mean of 10.26 ± 0.15 (±SE) over annual cycles.

To reconstruct a high-resolution, daily history of ^{7}Be and ^{210}Pb deposition, we adopted the following method. We first assumed a constant dry deposition as calculated above. Given the strong correlation between precipitation amount and total radionuclide flux, we attributed the remaining measured weekly flux (total minus dry deposition) according to daily precipitation totals.[17] This method allows the interpolation of depositional history between collections without altering the accumulated inventory observed at each weekly collection end date. Wet flux ^{7}Be totals were thus corrected for decay that occurred while our collection bucket was deployed, as even a weekly collection period is somewhat long relative to the ^{7}Be half-life. Weekly ^{7}Be fluxes were thus estimated to be as much as 10% higher than directly measured at the collection end date, and annual ^{7}Be fluxes approximately 4% higher than the amounts summed from weekly measurements. ^{7}Be:^{210}Pb ratios of measured weekly collections and of modeled daily totals are presented in Figure 2a.

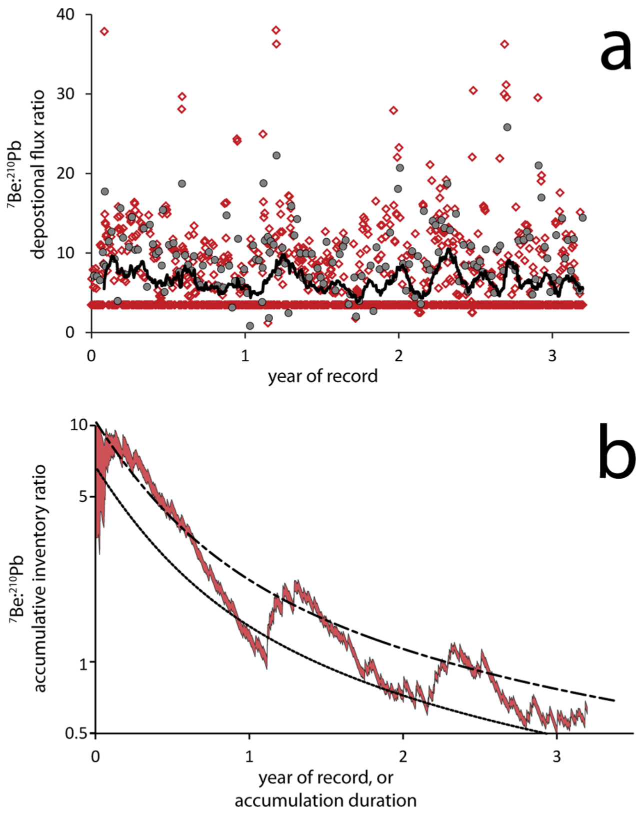

Figure 2. (a) ^{7}Be:^{210}Pb depositional ratio (D^{Be}:D^{Pb}) for measured weekly collections (solid circle) and for modeled daily deposition (open diamond, see text) for a three-year record beginning March 11, 2011. A 30-day running mean for model deposition is shown as a solid line. Daily dry deposition is estimated to have a ratio of 3.4 (see text), and appears as a solid red line due to its high frequency. (b) Accumulative inventory ^{7}Be:^{210}Pb ratio based on the preceding daily flux model. Note log ordinate axis. Shading depicts 1-sigma confidence interval. A model assuming constant flux (see text) is shown using daily average ratio of 6.55 ± 0.14 (mean ± SE; dotted line) or using flux-weighted average ratio of 10.26 ± 0.15 (mean ± SE, dashed line).

4.2. Quantitative Accumulation of Atmospheric ^{7}Be and ^{210}Pb on Vegetation. The accumulating radionuclide inventory on a surface exposed to aerosol deposition can be modeled as

$$\frac{dA}{dt} = \alpha D_t - \lambda A \tag{1}$$

where A is the accumulative inventory [Bq m^{-2}], D is atmospheric flux [Bq m^{-2}], and t is the time between collection periods. The first-order loss constant λ [d^{-1}] incorporates both radioactive decay (λ_r) as well as any environmental removal processes (λ_e, e.g., "wash off") and is equivalent to the sum $\lambda_r + \lambda_e$. In order to compare an atmospheric record with

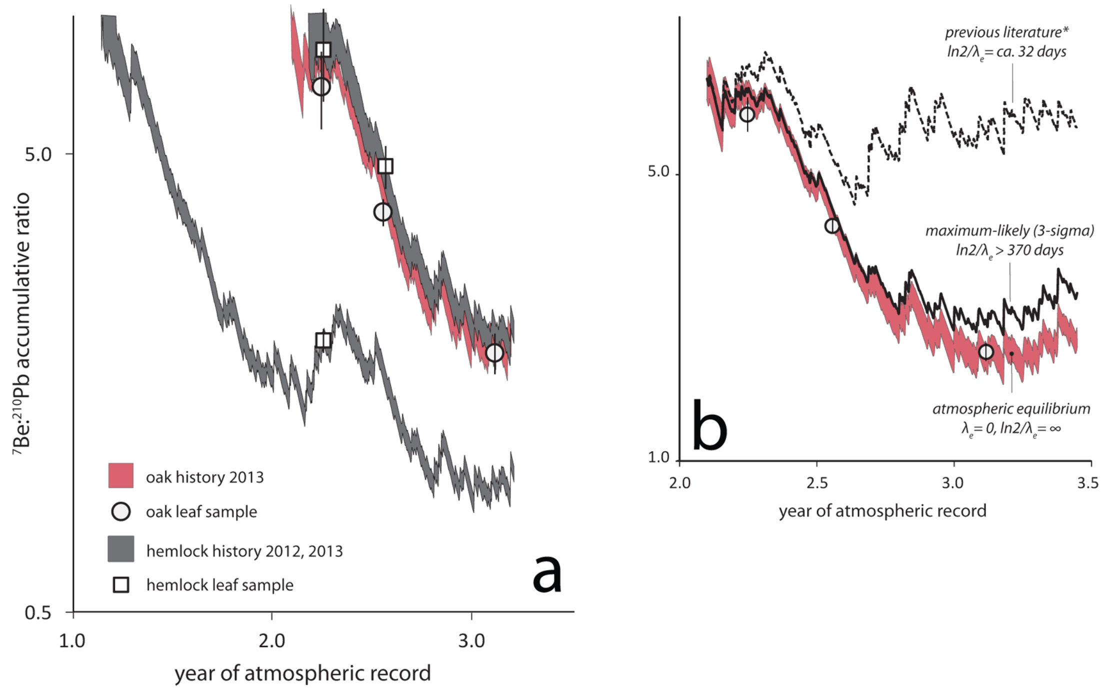

Figure 3. (a) Measured ^{7}Be:^{210}Pb of oak and hemlock leaves compared to their individual histories of atmospheric exposure. Each unique *accumulative atmospheric ratio* history begins with the leaf-out date of the tree and is shown as a shaded 1-sigma confidence interval. For clarity, error bars on leaf symbols for oak (circle, ○) and for hemlock (square, ☐) depict larger 2-sigma propagated uncertainty. Note logarithmic ordinate axis. (b) evaluation of oak leaf and atmosphere record uncertainties to constrain rates of radionuclide "wash off". Here the 2013 record from (a) is rescaled for clarity. In the shaded atmospheric record, radionuclide losses occur only by radiodecay according to their respective decay constants λ_r. Symbols show oak leaf measurements with 1-sigma errors. The heavy black line depicts the hypothetical trajectory of the *leaf accumulative ratio* in the case where "wash off" processes operate with a half-time of 370 days (=ln2/λ_e), the maximum time scale consistent with measurement uncertainties (3-sigma); here the total loss of radionuclides from the leaf surface is modeled as $\lambda_r + \lambda_e$. For comparison, an average literature value[9−11] is modeled and displayed as a dashed line. See Supporting Information for greater detail.

accumulation on a discrete surface we include the dimensionless interception coefficient α, which describes the efficiency with which a surface intercepts (retains) depositional flux. This efficiency is variable among plant species and may vary greatly for different radionuclides based on elemental behavior.[62,63] The case of $\alpha = 1$ describes an "infinite bucket". Importantly, eq 1 distinguishes between two governing processes of atmospheric deposition to a surface, the efficiencies of its initial interception (α) and of its subsequent retention (λ).

Following eq 1 and using our modeled daily fluxes, we calculated *accumulative atmospheric inventories* for both ^{7}Be and ^{210}Pb (i.e., with $\alpha = 1$ and λ = radioactive decay constant). These represent histories of ^{7}Be and ^{210}Pb atmospheric deposition. Because the value of α is difficult to assess a priori, we next considered the ratio of these two records, which, if α is comparable for these elements, is independent of α (but not of λ). The ^{7}Be:^{210}Pb a*ccumulative atmospheric ratio* history—shown in Figure 2b—shows high-frequency, daily variations as well as annual spring-summer excursions. These features are superimposed on a monotonic decline; the latter results from (1) the shortness of the ^{7}Be half-life relative to that of ^{210}Pb and (2) the convergence of the ^{7}Be:^{210}Pb depositional ratio to a long-term mean. In Figure 2b the monotonic decline of our observed record is shown to be bounded by models which assume either a constant *daily average* depositional ratio (dotted line) or a constant *flux-weighted average* depositional ratio (dashed line) as described by eq 2 (below).

To assess the behaviors of ^{7}Be and ^{210}Pb intercepted by tree leaves, in Figure 3 we compare the measured ^{7}Be:^{210}Pb ratios of growing leaves with the *accumulative atmospheric ratio* of their exposure history. As described above, each history is calculated from atmospheric measurements beginning with the leaf-out date of the individual tree following eq 1. We find excellent agreement for both the deciduous *Quercus* and the coniferous *Tsuga*, the latter over two growing seasons. *Quercus* does not drop all leaves in fall, and the retained dead-leaf ^{7}Be:^{210}Pb ratio continues to reflect its known atmospheric exposure history more than one year after leaf emergence. The implications of agreement between leaf and atmospheric records are profound. First, the interception coefficients (α) of ^{7}Be and ^{210}Pb must be approximately the same; whether due to similarities in elemental chemistry (e.g., multivalent metal) or to their persistence in a common physical state (e.g., hosting in aerosol phase) is unclear and requires further study. Second, the fraction of both ^{7}Be and ^{210}Pb that is retained by these leaves is approximately constant throughout the year for deposition via both rain and snowfall.

Comparing our measurements of leaf ^{7}Be and ^{210}Pb activity concentrations, models of atmospheric exposure history, and estimates of exposed leaf area, we estimate that an individual leaf retains on the order of 3−5% of ^{7}Be and ^{210}Pb areal atmospheric flux (Table 2). However, this is a minimum and approximate estimate as it assumes all leaf areas are projected orthogonal to rain direction and that no rain shadow is cast by nearby branches or tree crowns. By comparison, a full canopy cumulatively retains on the order of 40−90% of depositional flux as estimated either by the fraction of standing inventory found in vegetation[51,17,18] or from comparisons of precipitation

Table 2. Leaf Radionuclide Activities and Their Comparison to Atmospheric Fluxes

age[a]		leaf radionuclide activity concentrations						leaf areal activities					atmospheric inventory[b]				interception efficiency[c]			
		^{7}Be:^{210}Pb		^{7}Be		^{210}Pb		leaf area	^{7}Be		^{210}Pb		^{7}Be		^{210}Pb		^{7}Be		^{210}Pb	
sample	yr	R	σ	Bq kg^{-1}	σ	Bq kg^{-1}	σ	cm^{2} g^{-1}	Bq m^{-2}	σ	Bq m^{-2}	σ	Bq m^{-2}	σ	Bq m^{-2}	σ	%	σ	%	σ
new hemlock	0.10	8.5	1.9	18.7	2.0	2.2	0.4													
new hemlock	0.41	4.71	0.51	42.7	1.8	9.1	0.9													
old hemlock	1.10	1.96	0.12	59.6	2.3	30.4	1.4	48.5	12.3	0.5	6.3	0.3	458	25	225	4	2.7%	0.2%	2.8%	0.1%
new oak	0.18	7.04	0.68	85.6	2.2	12.2	1.1													
new oak	0.49	3.75	0.13	331	6	88	3													
old oak (tree)	1.05	1.85	0.09	230	9	124	4	113	20.3	0.8	11.0	0.4	345	23	194	5	5.9%	0.5%	5.7%	0.2%

[a] Absolute leaf age is calculated as sampling date minus flush date. [b] Atmospheric inventory is the accumulative depositional inventory measured during the leaf exposure lifetime. [c] Interception efficiency is the fraction of atmospheric deposition that is retained by the leaf.

in open and throughfall.[25] The retention efficiency of a single leaf as we have measured it scales reasonably well to that of the canopy if we assume a typical leaf-area-index (m^{2} leaf surface per m^{2} ground area) in the range of 5−10: a raindrop touches multiple leaves on its pathway to the ground, each interaction enhancing the role of vegetation in regulating the fate of atmospheric contaminants.

Finally, the agreement between atmospheric and leaf records implies that the radionuclides' inventories in a leaf each behave according to their respective radioactive decay constants (λ_r). Neither Be nor Pb are lost with respect to one another, and no steady-state ^{7}Be:^{210}Pb ratio is reached over a period of weeks to months as would be the case if removal processes (e.g., wash-off) operated at rates on the order of the ^{7}Be half-life of 54 days. This is demonstrated in Figure 3b where we model the accumulative ^{7}Be:^{210}Pb ratio in the hypothetical case of an environmental half-life of 32 days, an average value from previous literature.[9−11] We also model an estimate of the maximum possible (3σ) rate of wash-off consistent with uncertainties of the leaf and atmosphere records; this rate corresponds to a minimum environmental half-life of 370 days (see discussion in Supporting Information). The excellent agreement between our predictive atmospheric model and leaf measurements clearly demonstrates that the short "environmental half-life" model for aerosol fate cannot be applied to these atmospheric constituents.

5. A ^{7}BE:^{210}PB CHRONOMETER OF SURFACE EXPOSURE TO AEROSOL ACCUMULATION

A powerful extension of a ^{7}Be:^{210}Pb normalization scheme is the construction of a two-radionuclide exposure chronometer similar to Lal,[64] which may be expressed as the following:

$$R_{\tau}^{\mathrm{Be:Pb}} = \frac{D^{\mathrm{Be}}}{D^{\mathrm{Pb}}} \cdot \frac{\lambda_{\mathrm{Pb}}}{\lambda_{\mathrm{Be}}} \cdot \frac{(1 - e^{-\lambda_{\mathrm{Be}}\tau})}{(1 - e^{-\lambda_{\mathrm{Pb}}\tau})} \qquad (2)$$

As we have shown, the accumulative ^{7}Be:^{210}Pb ratio $R^{\mathrm{Be:Pb}}$ evolves over a material's exposure time τ due to ongoing atmospheric deposition and the different half-lives of ^{7}Be and ^{210}Pb. Equation 2 applies to a constant-flux scenario and describes the monotonic decline in ^{7}Be:^{210}Pb over time as shown in Figure 2b. Exposure time may be determined explicitly from eq 2 by an error-minimization method, that is, by solving iteratively[65] for an exposure age that yields the measured ratio $R^{\mathrm{Be:Pb}}$. Such a calculation should prove useful for normalizing contaminant accumulation in trees that have multiple flushes of leaves per year, as do some temperate conifers or tropical evergreens, or for long-lived or perennial vegetation of indeterminant age. While ^{7}Be reaches steady state over a period of ca. 1 year, due to ongoing ^{210}Pb accumulation this chronometer in principle extends to decadal time scales, or to the limit of our analytical capacity to resolve the asymptotic slope of eq 2. To the extent that ^{7}Be and ^{210}Pb behave similarly in a given context and their depositional fluxes fluctuate about temporal and spatial means, this chronometer can provide age information on an exposed material without the need for an explicit atmospheric record. In this case the depositional ratio D^{Be}:D^{Pb} could be learned from reference soil cores as is often done for conventional ^{210}Pb dating. A simple measurement of a material's ^{7}Be:^{210}Pb ratio could then be evaluated for exposure age without it having reached steady-state with respect to ^{210}Pb as is required by existing chronometers.

6. IMPLICATIONS FOR OTHER AEROSOL CONTAMINANTS

With the tracers ^{7}Be and ^{210}Pb we are able to describe a continuum from atmospheric deposition to sequestration in leaf matter, and thence to sediment[17] and soil systems,[66] where ^{7}Be and ^{210}Pb are known to track the transport, fate and histories of organic matter and associated contaminants. Other metals such as Cd, Zn, Cu, and Pb have been shown to accumulate similarly in leaves[67,28] and we expect our findings for ^{7}Be and ^{210}Pb will provide direct insights for the fate of these multivalent metals. Important anionic species such as I^-, IO_3^-, SO_4^{2-}, NO_3^-, soluble elements such as Ca^{2+}, Sr^{2+}, or Cs^+, or those with gaseous and/or photoreactive species such as Hg, may behave differently than ^{7}Be or ^{210}Pb upon deposition to vegetation surfaces. In these cases ^{7}Be and ^{210}Pb provide comparators with known, conservative behavior, ubiquitous distribution, and predictable atmospheric fluxes. Irrespective of elemental behavior, we warn that describing the removal of atmospherically deposited elements from vegetation as a rapid wash-off process is misleading, with implications for both elemental cycling and human contaminant exposure. It must be recognized that plant surfaces have specific affinities for atmospheric aerosols; these affinities act to conserve absolute foliar contaminant loads to a much higher degree than previously recognized, even when processes such as biodilution reduce their concentrations. Combined with other recent studies,[68,31] ours predicts that the annual leaf drop of deciduous trees introduces a pulse of many different types of contaminants, be they radioactive fallout or heavy metal pollution, to underlying soils and surrounding streams. The role of vegetation in dictating the fate of aerosol constituents cannot be overlooked in any study of atmospherically deposited elements.[69]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

We estimate the maximum-possible "environmental" losses of ^{7}Be and ^{210}Pb from leaf surfaces. This material is available free of charge via the Internet at http://pubs.acs.org.

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This manuscript includes contributions from all authors, and all have approved its final version.

Notes

The authors declare no competing financial interest.

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