



Supplement of

Quantifying new versus old aerosol deposition in forest canopies: through-fall mass balance with fallout radionuclide chronometry

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S1. Supplemental Methods

S1.1. Preconcentration of FRNs from throughfall precipitation

FRNs in the acidified filtrate were preconcentrated by MnO₂ co-precipitation to determine an operationally-dissolved fraction as follows. The acidified filtrate was first spiked with 500 µg ⁹Be and 250 µg stable Pb yield monitors, and a 20 mL aliquot removed (*a1*). The filtrate was then co-precipitated with MnO₂ by adding sequentially NH₄OH to bring pH to ~9 (3% v/v), 15 µmol MnCl₂ and 70 or 280 µmol KMnO₄ to openfall or throughfall samples. Higher amounts of KMnO₄ are needed for throughfall samples due to the consumption of oxidizing capacity by dissolved organic carbon (DOC). After 24 hours flocculation the MnO₂ precipitate was filtered to quartz fiber (QF) filters. A second aliquot (*a2*) was taken from the filtrate and Be and Pb were measured in both *a1* and *a2* aliquots by inductively-coupled plasma optical emission spectroscopy (ICPOES). Be and Pb yields were then calculated as (*a1-a2*)/*a1* x100%, averaging 88 ±15% for Be and 88 ±16% for Pb (mean ±SD).

Following deployment, collectors were first rinsed in deionized water (DI), scrubbed with cellulose wipes, rinsed 5x in DI, scrubbed with Citranox detergent using a plastic-bristle brush, rinsed 25x and then filled to overflowing with DI. The full collectors were then allowed to sit for a minimum of 7 days before reuse, at which time they were emptied and rinsed a further 10x in DI. Process blanks were routinely measured by deploying collectors, immediately retrieving, and processing them as for samples, and all data are corrected as necessary.

S1.2. Composition and canopy interactions of throughfall

We collected paired openfall (*W*) and throughfall samples (*T*) at either BM or SO sites during 52 storms in the years 2018-2022. Of these, 22 storms were collected at both BM and SO sites. Two trees were sampled per site for a grand total of 156 throughfall measurements. These represented all seasons and precipitation totals ranging from 0.05 to 7.0 cm (geometric mean, GM =1.52 cm). The higher elevation BM site recorded about 5% more openfall precipitation than the SO site but the difference was not significant [*p*=0.34]. The fraction of precipitation intercepted by the canopy decreased with increasing precipitation (Fig. S2). Stemflow was not measured in this study but typically contributes ca. 5% of total throughfall volume. Annual throughfall interception for each species decreased as follows for the leaf-on seasons: spruce (30%) < pine (24%) < SO oak (23%) < BM oak (13%). Spruce retained a greater fraction of incident precipitation due to either higher LAI, canopy architecture, or some combination thereof.

S1.3. FRN and MTE speciation: implications for collection protocols

We distinguished three operational fractions in MTE open and throughfall deposition, an operationally-dissolved water-soluble fraction (*d.*), a weak-acid soluble fraction (*s.*) measured by extracting FPOM filters in 2% HCl, and a refractory fraction that is incorporated in particulate matter (*r.*) and measured by aqua regia extraction of filters. Throughfall collections are typically analyzed only for a water-soluble fraction of MTEs, e.g., Gandois et al., 2010; Hou et al., 2005; Lindberg & Harriss, 1981; Lovett & Lindberg, 1984; Anne W. Rea et al., 2001. Our new protocol provides an operational means of separating long-range aerosols, which are highly soluble, from locally resuspended dust, which is typically insoluble, e.g., Fishwick et al., 2017. This approach also allows further speciation of MTEs by, e.g., filtration or ultrafiltration (Gandois et al., 2010; Hou et al., 2005). In prior approaches samples are acidified for preservation only after filtration or separation from the collector and any particulate fraction. In contrast, FRNs are typically measured following acidification since this is required to recover total deposition of particle-reactive metals (Baskaran et al., 1993). Our previous work with FRNs in bulk atmospheric deposition shows that up to 100% of total ⁷Be or ²¹⁰Pb activity may be found in the >0.5 µm fraction (median 23% and 55%, respectively), depending on the mass concentration of total particulate

matter (p_c) as well as pH and the presence of Mn, Al, and Fe oxides or surface coatings that drive FRN sorption to the particulate fraction (Landis et al., 2021). The FRN activity-fraction particulate (f_p) also increases with aerosol age in what we call a particle age effect (p.a.e.). We previously determined that 20-30% of FRN activity is lost from bulk precipitation if the sample collection train is not rinsed with 2% HCl to recover FRNs that sorb to collector walls (Landis et al., 2021). For these reasons we believe it imperative to measure both operationally dissolved ($d.A$, etc.), acid-soluble ($s.A$, etc.) and refractory ($r.A$, etc.) fractions since many MTEs of interest are, like the FRNs, particle- and surface-reactive. Here the $s.$ and $t.$ fractions were measured following sample filtration by extraction of quartz fiber filters. QFF filters were extracted sequentially, first using 50 mL 2% HCl. The supernatant from this step was separated by centrifugation as the $s.$ fraction, and filters then digested using 12 mL reverse aqua regia (3:1 $HNO_3:HCl$, Optima grade) with addition of 2% v/v BrCl. Digests were allowed to react at room temperature for 15 hours and were then diluted by addition of 30 mL 2% HCl. Final solutions were measured by ICPOES for major elements, ICPMS for trace metals, and purge-and-trap fluorescence for Hg.

Recovery of total FRN activity by 2% HCl was previously established for bulk deposition (Landis et al., 2021). To assess the recovery of FRNs by 2% HCl in throughfall we followed 6 collections with a 6N HCl rinse; these were aggregated to improve detection limits and then pre-concentrated by MnO_2 precipitation. The aggregate yield in the rinse was equivalent to $0.4 \pm 0.2\%$ of total 7Be and $1.4 \pm 0.4\%$ of total ^{210}Pb , indicating near-complete recovery of FRNs by 2% HCl.

S1.4. Partitioning coefficients and behavior of 7Be and ^{210}Pb in throughfall

We use partitioning metrics to assess the solubility behaviors of FRNs and MTEs. We calculate the equilibrium partitioning or distribution coefficient (K_D) as follows:

$$K_D = \frac{A^{>0.5}/M}{A^{<0.5}/V} = \frac{A^{>0.5}}{A^{<0.5} \cdot p_c} \quad \text{Eq. S1}$$

We calculate the activity-fraction particulate according to the following, since at low particulate concentrations a large proportion of FRN activity may remain operationally-dissolved despite K_D values exceeding 10^5 (Landis et al., 2021b):

$$f^{Be} \text{ or } f^{Pb} (\%) = \frac{A^{>0.5}}{A^{>0.5} + A^{<0.5}} \times 100 \quad \text{Eq. S2}$$

We note that f_p is explicitly related to the product $K_D \cdot p_c$ as follows:

$$f_p = 1 - \frac{1}{1 + K_D \cdot p_c} \quad \text{Eq. S3}$$

For both 7Be and ^{210}Pb , $\log_{10}(K_D)$ is significantly lower in TF than in OF. For 7Be , corresponding $\log_{10}(K_D)$ values were 3.86 ± 0.05 and 4.55 ± 0.07 (mean $\pm$ SE), respectively, a decrease by a factor of 5 in TF [$p < 0.0001$]. Corresponding $\log_{10}(K_D)$ for ^{210}Pb in TF and OF were 4.24 ± 0.05 and 5.17 ± 0.08 , a decrease by a factor of 9 in TF [$p < 0.0001$]. At each site the 7Be $\log_{10}(K_D)$ for pine or spruce is significantly lower than oak, but this is not the case for ^{210}Pb [$p > 0.05$]. All species and sites show a significant decrease in $\log(K_D)$ with $\log(p_c)$ for both 7Be and ^{210}Pb , a particle concentration effect (p.c.e.) indicating that FRN solubility is controlled by colloidal phases (Landis et al., 2021) (Fig. S8). This suggests that the speciation of 7Be and ^{210}Pb may be modified in transit through the canopy through sorption to the canopy and complexation by DOC (Gandois et al., 2010; Hou et al., 2005). When corrected for p.c.e using linear regression

against $\log(p_c)$, however, there is no difference in ${}^7\text{Be} \log_{10}(K_D)$ in TF versus OF [$t(217)=-0.32$, $p=0.75$]. That is, the reduction in ${}^7\text{Be} K_D$ in throughfall is attributable to the p.c.e. In contrast, for ${}^{210}\text{Pb} \log_{10}(K_D)$ in TF is significantly lower than OF [$t(217)=-3.3$, $p=0.0013$]; this suggests that ${}^{210}\text{Pb}$ may be solubilized by DOC during residence in the canopy.

S2. Throughfall Chemistry

Precipitation chemistry was modified during transit through the canopy, with DOC increasing from 0.7 mg L^{-1} in OF to 9.2 mg L^{-1} in TF (geometric means, GM). DOC was lowest in winter but not different among spring, summer, or autumn [$p<0.05$]. Mass concentration of fine particulate organic matter (FPOM $0.5 \text{ } \mu\text{m}$ to 1 mm diameter, hereafter p_c) similarly increased from $2.6 \pm 0.5 \text{ mg L}^{-1}$ to $21 \pm 3 \text{ mL}^{-1}$ in throughfall (GM $\pm$ SE). p_c and DOC were strongly, linearly correlated [$R^2=0.55$, $p<0.0001$, $n=156$]. We used multiple regression to identify factors influencing total FPOM loading from the canopy. The effect of each independent factor was quantified as e^* , which is the percent of total variance in the response variable that is explained by each independent explanator. Total FPOM flux per unit area (m_D) was strongly seasonal with a summer maximum [$e^*=26\%$, $p<0.0001$], but also driven by increasing p_D [15% , $p<0.0001$] and longer antecedent dry periods [10% , $p=0.0003$]. Seasonal FPOM concentrations increased in the order: winter ($8 \pm 4 \text{ mg L}^{-1}$)^B < spring (13 ± 3)^B < autumn (16 ± 3)^B < summer (47 ± 9)^A. A p_D threshold = 15 mm to define the antecedent period yielded a stronger effect than either 5 mm or 1 mm , indicating that substantial precipitation is needed to remove susceptible FPOM from the canopy, or that longer periods are required for FPOM to accumulate. There were no differences in p_c by species [$p=0.092$] or site [$p=0.62$]. In contrast to FPOM, export of DOC from the canopy showed no dependence on antecedent period. Significant multiple regression explanators for DOC included season [24%], p_D [10%] and species [5%].

Effect of the canopy on throughfall pH was variable (Fig. S3). The canopy was a net sink for H^+ in summer for each of spruce, pine and oak [$p<0.05$]. On an annual basis, oak was a net sink at both sites but both pine and spruce were net sources of H^+ . Corrected for seasonality, H^+ yields increase in the order: BM oak (44%)^C < SO oak (86%)^{BC} < BM pine (111%)^{AB} < SO spruce (180%)^A [GMs; values connected by the same letter were not different, $p<0.05$]. Corrected for the species effect, throughfall yield of H^+ was significantly lower in autumn and summer: summer (-96%)^A < autumn (-92%)^A < spring (81%)^B < winter (104%)^B. Throughfall mean pH values for the seasons were 5.29, 5.36, 4.98, and 4.86, respectively.

The observed behavior of metals in throughfall can be assessed with the partition coefficient K_D , which quantifies the affinity of metals for particulate matter versus operationally dissolved fraction. Consistent with earlier observations (Landis et al. 2021b), we observe that ${}^7\text{Be}$ has lower K_D than ${}^{210}\text{Pb}$ (Fig. S8). For both ${}^7\text{Be}$ and ${}^{210}\text{Pb}$ throughfall has lower K_D than openfall precipitation, at both sites and all trees studied here. This implies that DOC in throughfall plays an important role in modifying PM metal speciation. The stable isotope counter parts to the FRNs, ${}^9\text{Be}$ and Pb , provide important context to these measurements for the FRNs. The stable isotopes similarly show higher K_D in openfall versus throughfall. While we observe that stable Pb has comparable K_D to ${}^{210}\text{Pb}$, at the same time ${}^9\text{Be}$ has significantly higher K_D than ${}^7\text{Be}$ or indeed than either Pb isotope. We interpret this as evidence of a particle age effect (p.a.e.) whereby the strength of partitioning to a particulate phase increase with the lifetime of the metal in recirculation within the ecosystem.

We constructed multiple regression correlation webs for $\log_{10}(K_D)$ to illustrate the factors that influence partitioning of the FRNs. Multiple regressions are shown in Fig. S9. We began modeling by including environmental factors: season, species, site, pH, $\log(\text{FPOM})$, $\log(\text{precipitation})$, and antecedent dry period. For ${}^7\text{Be} \log(K_D)$ the general model explains 84% of variance [$R^2=0.84$, $n=100$, $p<0.0001$].

Explanators log(FPOM) [61%], season [5.1%], site [4.9%], species [4.7%], pH [4.2%], and log(precipitation) [2.7%] all contributed significant independent effects. Antecedent dry period did not [$p=0.72$]. The general model for ^{210}Pb log(K_D) was similarly strong [$R_a^2=0.78$, $p<0.0001$] with significant effects from log(FPOM) [47%], log(precipitation) [9%], pH [11%], and season [12%]. There were no effects from antecedent [$p=0.70$] or species [$p=0.32$]. Adding log(DOC) [5.8%] superceded both pH and seasonal effects. The importance of pH in ^{210}Pb partitioning in throughfall is a notable departure from its behavior in bulk openfall where no correlation was found for ^{210}Pb (Landis et al., 2021).

From a mass-balance perspective, we stress that while $\log_{10}(K_D)$ is substantially lower in throughfall, the total fraction of ^7Be and ^{210}Pb activities found in the particulate fraction (f^{Be} and f^{Pb}) are either unchanged for ^{210}Pb or actually higher for ^7Be in TF over incident OF. This occurs because decreases in K_D are offset by the large mass of FPOM derived from the canopy. f_{Be} increased from $8.7 \pm 1.1\%$ to $13.7 \pm 1.0\%$ from openfall to throughfall while f_{Pb} was unchanged from $33 \pm 2\%$ to $32 \pm 2\%$.

S3. Bias of conventional mass balance in trace metal cycles

To explain divergence between multiple-regression and filtering mass balance approaches, we review the implicit assumptions in each. The filtering approach assumes that the reference element has no leaching or metabolic contributions. This assumption has been challenged for both Na (Wytttenbach and Tobler, 1988) and Al (Rehmus et al., 2017), and indeed ecosystem mass balances have demonstrated that essentially all trace metals show some degree of metabolic assimilation into long-lived tissues of the tree (Bergkvist, 1987; Landre et al., 2009). The filtering approach further assumes implicitly that apportioning of deposition between wet and dry processes is identical for both reference and target elements. This in turn requires identical aerosol size distributions and thus aerosol sources *vis a vis* secondary aerosol or recycled dust since the removal processes of 1 μm versus 10 μm aerosols are quite different (Jaenicke, 1980). Deposition of crustal elements such as Al, with low concentrations in rainwater and high concentrations in dust, is dominated by dust (Landis et al., 2021). In filtering mass balance, if the reference element is influenced by either canopy leaching (Na) or resuspended dust (Al), the result will overestimate dry deposition for secondary aerosols like ^7Be and ^{210}Pb or other metals in long-range transport.

TMs are typically assumed atmospheric in origin, e.g., Lovett & Lindberg (1984), so the role of resuspended dust in TF is important to resolve since it might create large throughfall EFs without providing new TM deposition. Moreover, soils store enormous reservoirs of legacy pollutants such as Pb and Hg bound to both organic and mineral particles. These larger dust particles (10-100 μm) have lower solubility than secondary aerosol (<1 μm) due to different mineralogy, composition, and surface area (Fishwick et al., 2017). Thus, while secondary aerosol dry deposition may be highly soluble and efficiently rinsed from the canopy, dust particles may require long residence times to be solubilized by production of DOC within the phyllosphere. This process would explain strong DOC associations of Be^T , Pb^T , Al, and Fe in throughfall.

In the multiple regression approach, it is assumed that antecedent dry deposition is fully removed by each rainstorm and incorporated into throughfall (Lovett and Lindberg, 1984). If some fraction of dry deposition remains stored in the canopy (no steady-state at the event scale), the multiple regression antecedent coefficient (β_1) will underestimate dry deposition. This approach may also fail to record the influence of dust deposition if dust constituents are either strongly retained or rapidly removed relative to fine PM. Dry dust deposition may be released subsequently in conjunction with higher rainfall totals and larger fluxes of DOC, as we observe here with TMs in throughfall. In sum, the biases in each mass

balance method can lead their results to diverge. While the filtering approach grossly overestimates deposition of secondary aerosols as shown here with FRNs, it may be better suited for conservative species, e.g., NO_3 , that do not interact and sorb strongly to the canopy as metals do.

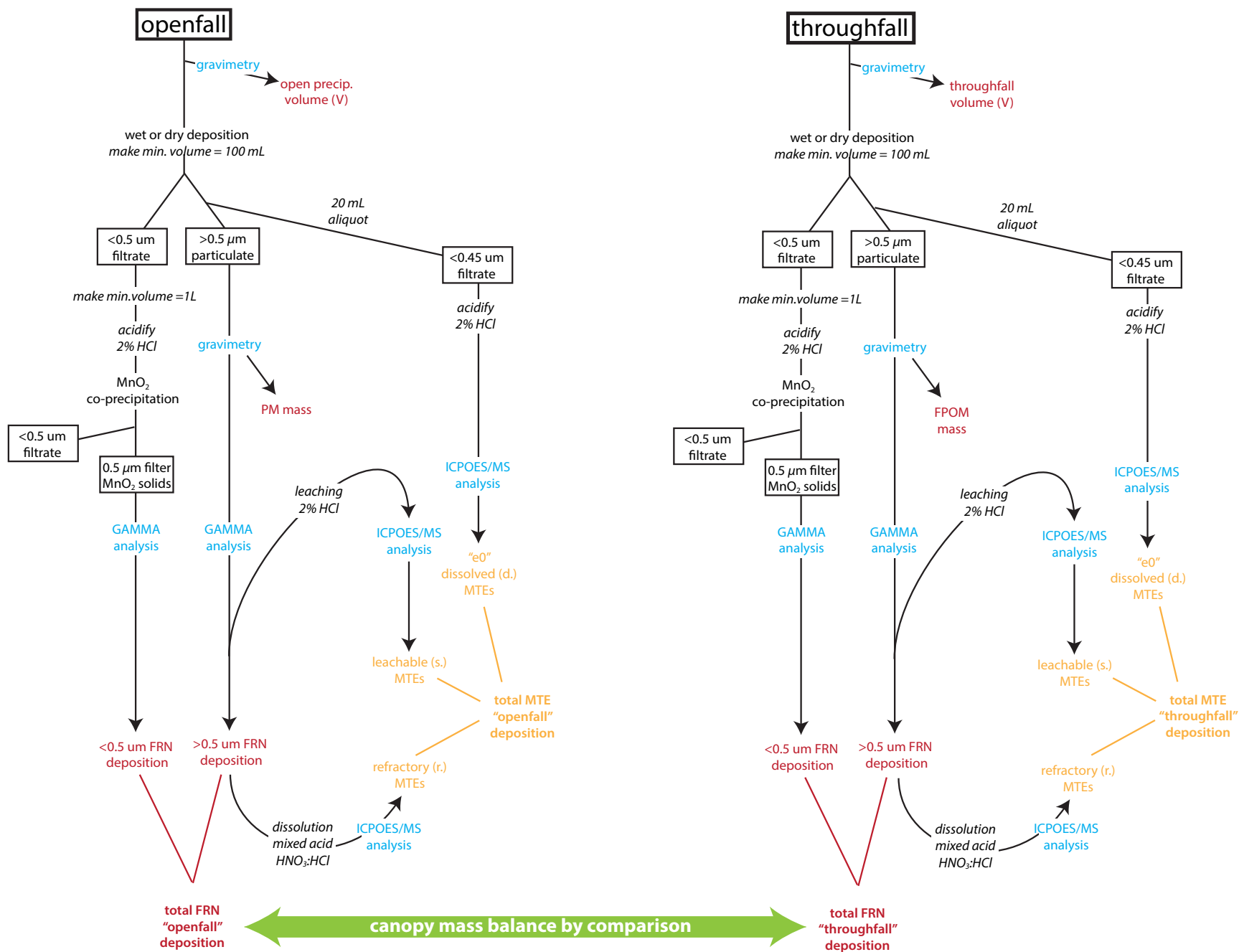


Figure S1: methods flowchart for analysis of fallout radionuclides (FRNs) and major/trace elements (MTEs) in bulk deposition in paired openfall and throughfall collectors.

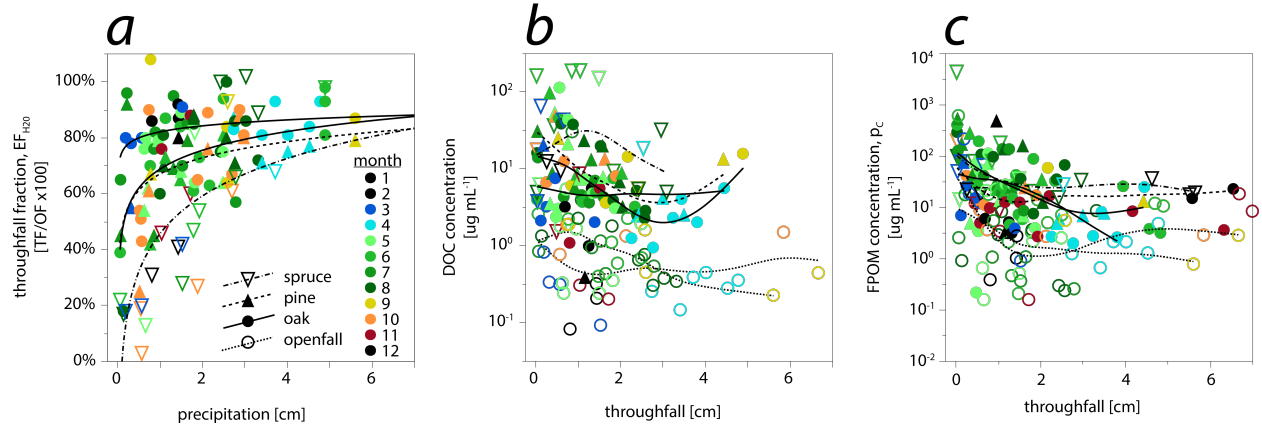


Figure S2. precipitation interaction with tree canopy, (a) interception, (b) DOC concentrations of throughfall, (c) FPOM concentrations.

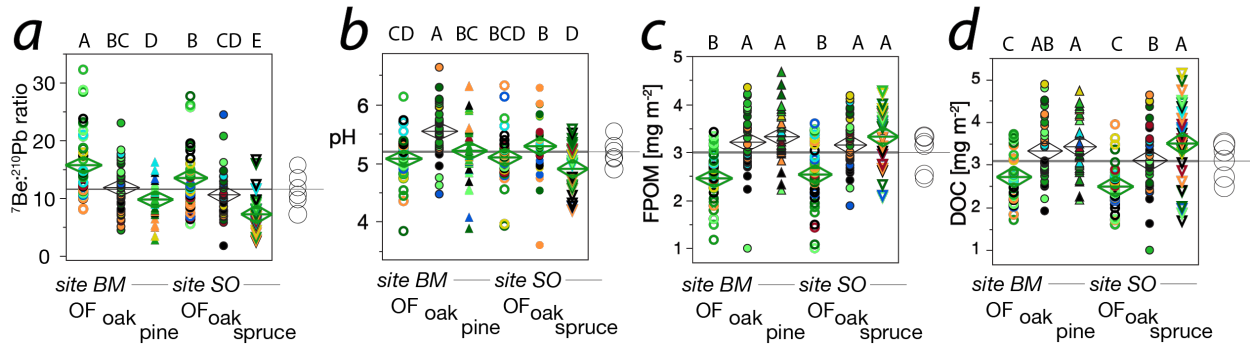


Figure S3. species effects in throughfall on (a) ${}^7\text{Be}:{}^{210}\text{Pb}$, (b) pH, (c) FPOM, (d) DOC.

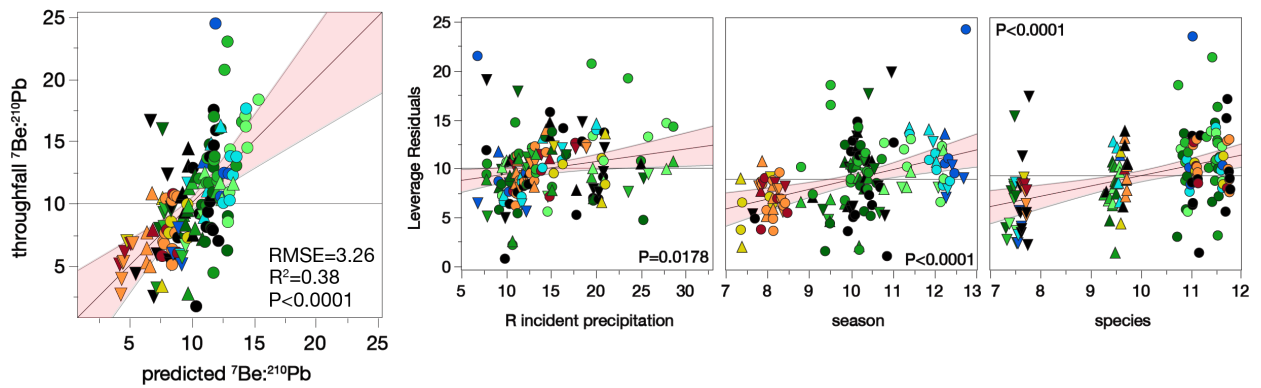


Figure S4. multiple regression for ${}^7\text{Be}:{}^{210}\text{Pb}$ ratios in throughfall. Larger panel shows overall model fit and smaller panels show leverage of individual explainers.

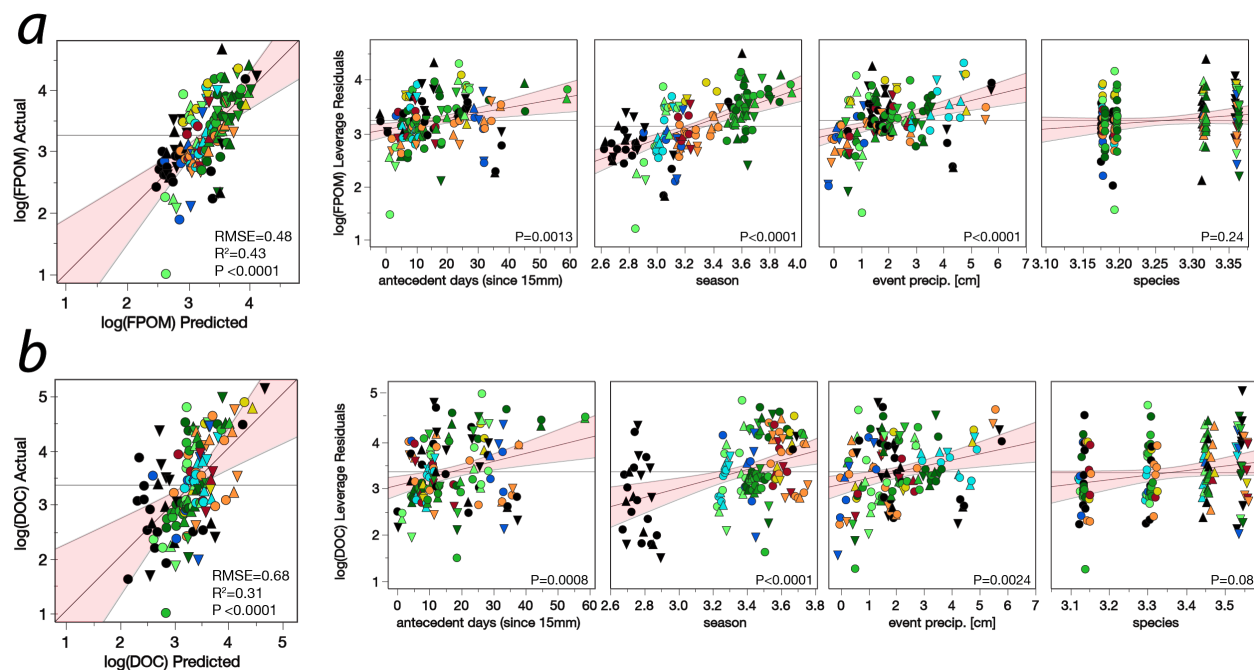


Figure S5. multiple regression for (a) FPOM and (b) DOC fluxes in throughfall. Larger panels show overall model fit and smaller panels show leverage of individual explanators.

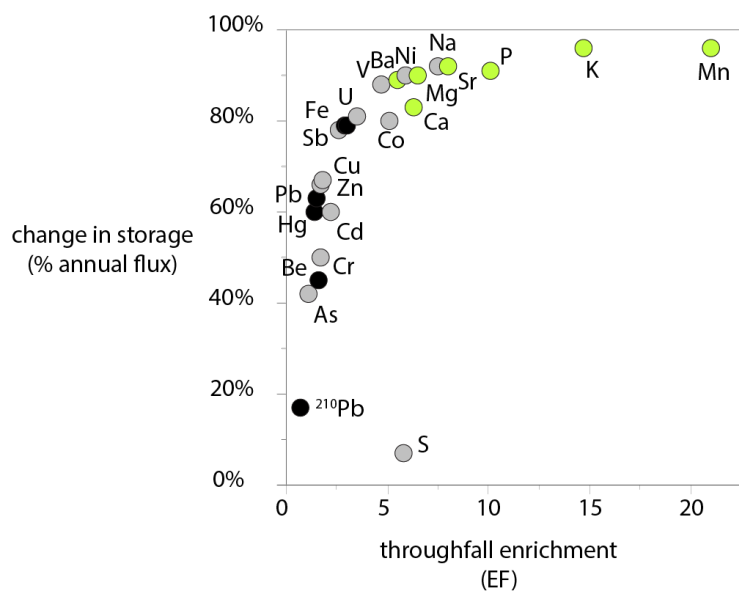


Figure S6. relationship of change in storage to throughfall enrichment for major and trace elements. Note divergence of sulfur which has high EF despite low change in storage due to dry deposition of gaseous SO_2 .

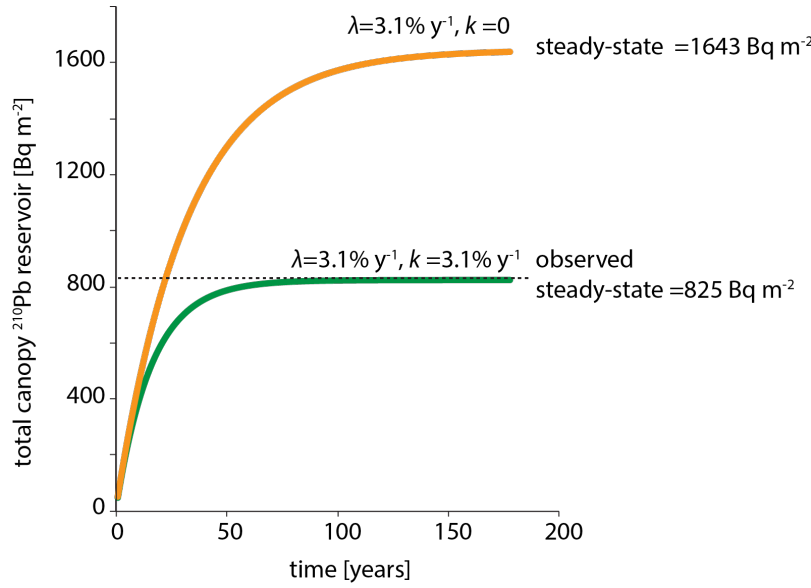


Figure S7. modeling of ^{210}Pb ingrowth for whole-tree canopy with measured wet+dry inputs, minus throughfall and annual litter export. Total year-on-year gain to the canopy totals $51 \text{ Bq m}^{-2} \text{ y}^{-1}$ (Landis 2024). Cases are considered for (1) only radioactive decay (orange) and (2) decay plus physicochemical weathering (green). A loss constant $k=3.1\% \text{ y}^{-1}$ predicts the observed whole-tree inventory of 825 Bq m^{-2} with a corresponding loss of $25 \text{ Bq m}^{-2} \text{ y}^{-1}$ through weathering of the canopy.

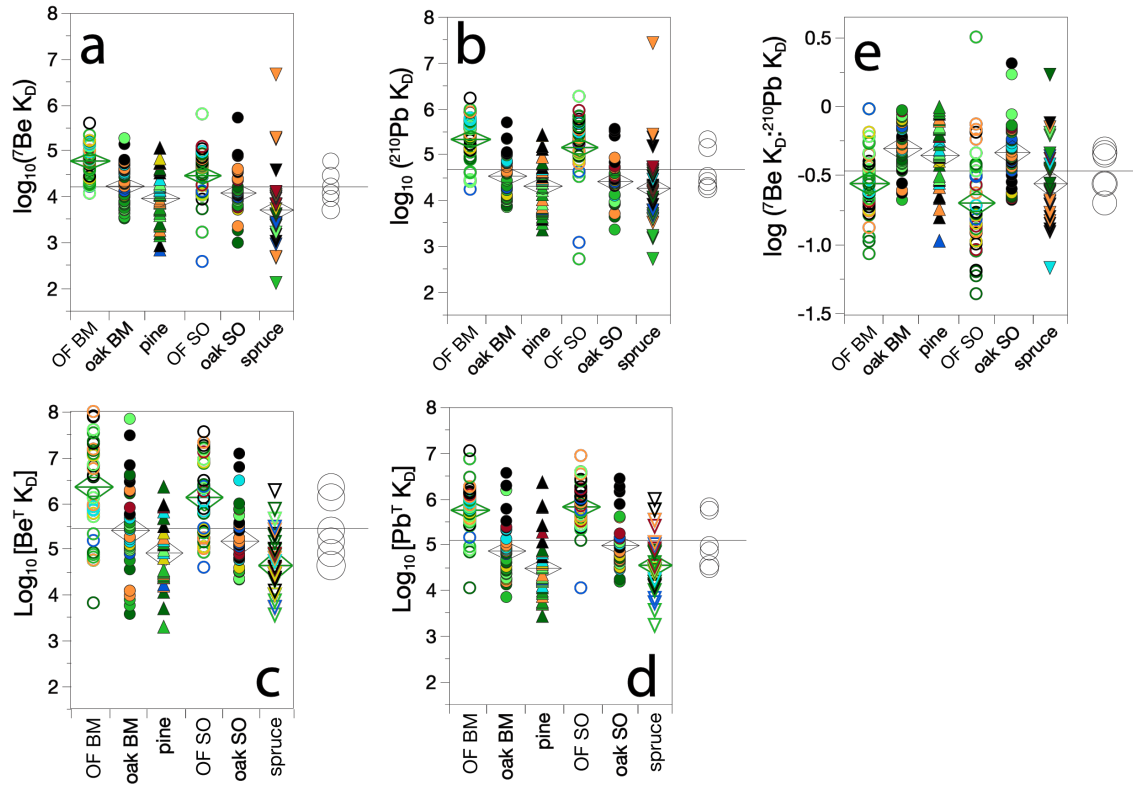


Figure S8. partition coefficients (K_D) for (a) ^7Be and (b) ^{210}Pb , their ratio (c), and (d) Be^T and (e) Pb^T . While ^7Be typically has a lower K_D than ^{210}Pb , the stable isotope ^9Be has higher K_D than observed for either ^{210}Pb or stable Pb. This may indicate a change in speciation with time of PM in circulation (i.e., particle age effect).

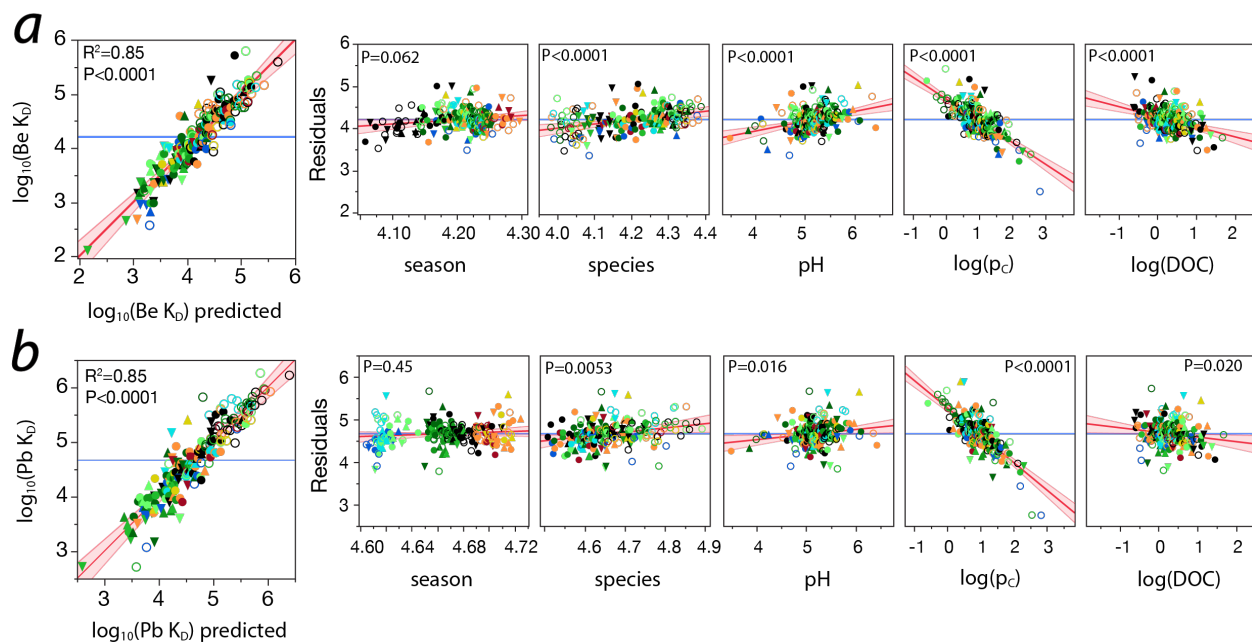


Figure S9. multiple regression for (a) ^7Be and (b) ^{210}Pb partition coefficients (K_D).

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