8/14/25

Dear Professor Stoy,

Thank you for your time in handling this manuscript review. I found the *Biogeosciences* process to be effective. I have made minor revisions following the recommendations of two Reviewers and encountered no difficult in accommodating them. A point-by-point address follows here, and both revised and tracked-changes versions of the manuscript have been submitted,

Best Regards,

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Reviewer #1

I found that this manuscript compellingly addresses a central question for Biogeosciences, (how particulate matter (PM) interacts with forest canopies) by using the contrasting half-lives of fallout radionuclides (FRNs) to tease apart new v old fluxes. The authors' application of 7Be and 210Pb chronometry represents an innovative tracer approach that falls squarely within BGs scope, bridging atmospheric deposition and ecosystem processes with conceptual rigor. Please note that I am not a direct expert in FRN or MTEs (if this means "metal trace elements"... please define this in the manuscript as it might also mean something like "major and trace elements"?).

> Apologies, yes, MTE here is major and trace elements. This is now defined at original line 248.

Here is how I understand the manuscript (and why I like it/recommend minor revisions):

From the outset, the use of differential radionuclide decay in a dual–mass-balance framework constitutes novel contribution. Eq 10 shows how the half-lives of 7Be and 210Pb yield independent constraints on canopy exchange v long-term storage, and the manuscripts logical unfolding through Figs 1 to 5 underscores its clarity and structure. Methods are described in meticulous detail, and assumptions (e.g, cancellation of deposition and resuspension terms in Eq. 9) are transparently stated.

Thought 1. the intro frames PM deposition processes in forests through the lens of radionuclide chronometry, yet:

Recommendation 1: it would strengthen the context to include a brief comparison in Section 1to existing micrometeorological methods for PM flux measurement. Such a paragraph would help readers appreciate quantitatively how this new tracer-based approach complements and extends other inferential studies.

> I appreciate the suggestion! I originally introduced the micrometeorological methods briefly at line 53, and have now expanded this to a full paragraph, thereby separating discussions of the micrometeorological methods and mass balance methods.
>
> I conclude with a statement at line 615 to explicitly link the micrometeorology with FRN mass balance, " We suggest that FRN mass balance and micrometeorological methods for, e.g., Hg deposition, are complementary methods that can verify both PM depositional processes and fluxes (Landis et al. 2024)". The reference is a study using FRN soil mass balance to independently confirm Hg deposition measured by eddy gradient.

Thought 2. The multi-metal application shown in Fig 4 demonstrates that this technique transcends FRN chronometry to illuminate how metals, carbon, and hydrologic cycles converge in forest canopies, yet:

Recommendation 2: I urge the authors to discuss potential biases that may arise if the canopy reservoir of 210Pb is not at quasi-steady state... an issue possibly pertinent given declining industrial lead emissions over recent decades.

Currently there is no evidence to my knowledge for contributions of ^{210}Pb from either tetraethyl lead or fossil fuel consumption that would be significant relative to natural sources, which is good news! Indeed, it is a primary assumption of ^{210}Pb dating originating in the 1970s through to present that ^{210}Pb flux can be assumed constant through time (hence the venerable Constant Rate of Supply model of Appleby and Oldfield (1978)). Nonetheless, this is a topic that has not been looked at vigorously. Certainly, there is year to year variability in ^{210}Pb deposition, and some evidence for decadal-scale changes in flux increasing through 1970-1990s (Germany; Winkler and Rosner 2000), and decreasing 2011-2018 (New Hampshire, USA) that I suggested may be linked to changes in sulfate scavenging that may follow changes in industrial sulfur emissions (Landis et al. 2021).

All of this to say, it is worth discussing implications for the canopy mass balance. This is now acknowledged at line 190, stating " We assume that the ^{7}Be:^{210}Pb flux ratio is constant through time, but acknowledge that short-term variability and long-term decadal trends in ^{210}Pb deposition may require future attention if the age of storage PM is to be determined (Winkler and Rosner 2000, Landis et al. 2021)". The statement is somewhat vague, which I feel is appropriate given that the outcome of this paper is establishing the fundamental process and relationships among elements.

The short answer is that this would not impact our calculation of change-in-storage but does impact the accuracy of PM age determination using 7Be:210Pb ratio. We have not attempted that here, but do so in a forthcoming manuscript on Whole Tree Mass Balance.

Thought 3. The claim that "ΔS represents an emergent ecosystem property through which metal, carbon, and hydrologic cycles converge to determine the fate, reactivity, and timing of metal delivery to underlying soils" is quite sweeping, but well enough supported by consistent correlations of ΔS with DOC and fine particulate organic matter across multiple trace metals (Figs 4 and 5), yet:

Recommendation 3: Because the dataset spans only two temperate sites and four species, a short caveat on the representativeness of those sites (perhaps a sentence on differing pollution regimes or canopy structures) would temper overgeneralization.

Greatly appreciate the care and precision with which you make this point. Agreed, it is a sweeping claim, and therefore in need of careful articulation. I have tried to temper the statement by saying instead "ΔS **may** represent an emergent ecosystem property …", and then "Future work should aim to extend the FRN mass balance to additional biomes and climate gradients so that the importance of phyllosphere storage for PM dynamics can be evaluated on a global scale."

Thought 4. Results section offers clear event-scale insights: Figure 2 shows how net canopy uptake or release depends on precipitation intensity, and Fig3s multiple regressions convincingly parse wet, dry, and depth effects.

Thought 5. Reproducibility is strong, site descriptions, species information, sampler specifications, and filter protocols permit replication, and data deposit aligns with open-science best practices. Minor recommendation 4: To aid readers less familiar with FRN mass balances, a concise workflow schematic in the Supplement illustrating each FRN step would be a welcome addition.

I have added new Fig. S1 which shows the FRN work flow.

In sum, this manuscript offers a robust, novel framework for partitioning PM dynamics in forest canopies. With minor clarifications to contextualize its relation to existing micromet methods, to highlight the steady-state assumption for 210Pb, and to streamline key methodological notes, it is well suited for publication in BG. I look forward to seeing this advance enrich our understanding of canopy-atmosphere exchange!

Thank you for your confidence and help bringing this manuscript out!

Reviewer #2

Deposition to vegetated ecosystems represents a key sink for particulate matter and trace metals globally, however the processes controlling the eventual introduction of these species to soils and the timescales over which these processes act remain poorly constrained. In particular, typical throughfall-based approaches for estimating ecosystem uptake assume that under-canopy measurements of washoff represent the combined input of wet and dry deposition since the previous washoff event, which contradicts growing evidence of trace metal accumulation within forest canopies.

Here, the author presents a novel fallout radionuclide (FRN)-based mass balance approach for evaluating the relative contribution of recent (i.e., since previous precipitation event) and antecedent (i.e., contributions from before the previous precipitation event) components of under-canopy washoff measurements, where the antecedent component is referred to as a storage term. Results show that within-canopy storage contributes a sizable component of the soil inputs measured under the canopy depending on the trace metal considered. The author also finds that the dominant tree species of the canopy has a significant impact on the composition of below-canopy washoff, highlighting the important role of species-specific physiochemical processes. These results offer a key constraint on a process that is overlooked by current atmospheric models of trace metal cycling. The novel methods presented by this paper are thoroughly supported by statistical tests and discussed with respect to potential caveats. To clarify the key points of this paper, I suggest the following edits.

1. *Contextualize particulate matter and trace metals.*
    1. *The introduction of this manuscript seeks to contextualize current methods for quantifying the flux of trace metals and particulate matter in forests and highlight the key issues with these approaches. While many of the trace metals considered do exist almost exclusively as some form of particulate matter, the distinction between particulate matter and trace metal species is more nuanced for semivolitile elements such as Hg. By convention, atmospheric Hg is typically compartmentalized into three primary forms: gaseous elemental*

Hg (GEM), gaseous oxidized Hg (GOM), and particulate bound Hg (PBM). Studies in the region considered by this paper have shown that vegetative assimilation of GEM acts as the dominant sink of Hg, while the direct deposition of GOM and PBM to surfaces exerts a smaller, albeit significant contribution to overall deposition (e.g., Obrist et al., 2021). Given the likely contribution of vegetatively assimilated GEM to the storage term that were remobilized by weathering of the phyllosphere, the complex contribution of different processes should be acknowledged. ***In short, trace metals should not necessarily be conflated with PM.***

2. *Proposed solution: To address the complex processes impacting the abundance and distribution of TMs within canopy and phylosphere media, I recommend that* ***a distinction be made between PM and trace metals in the opening paragraphs of the introduction.*** *While the form of trace metals in washoff may be exclusively PM in a practical sense, the introduction of those constituents to forest canopies may or may not have been in particulate form. This will help clarify reference currently made to Jiskra et al. (2018), Zhou et al., (2021) in the context of PM, despite these papers focusing primarily on the dominant role of GEM.*

I really appreciate this clear recommendation and have added a line "between vegetation and PM and other atmospheric trace metals (TMs)" at line 45 to draw this distinction. I've also included separate reference of both PM and TM at multiple locations throughout, a statement at line 118 "In the case of Hg, although its occurrence in the atmosphere is regulated by gaseous elemental mercury (GEM) rather than by PM, recent measurements nonetheless show that long-lived non-foliar materials of the forest canopy ..."

2. *Define canopy storage earlier in the manuscript.*
    1. *One of the key findings of this manuscript is that a large fraction of the trace metals measured in washoff originate from deposition antecedent to previous washoff event. A comprehensive discussion of these processes is included in the* ***paragraph starting at line 571****, but I wonder if some brief introduction to these processes in the context of "change in storage" in either the introduction of the manuscript or in the methods section could make this key of the study clearer.*

    Another a good recommendation, I added this statement at line 128: " These legacy TM sources remain enigmatic but can include resuspended dust from surrounding soils, roads, or living and dead surfaces of the phyllosphere."

Specific technical considerations:

- *Equations 11 and 12: This may be a convention that I am not familiar with, but at first glance it seems like the left hand side of equation 11 and the storage term on the right hand side of equation 12 are different. Is this intentional*

This was unintentional and now corrected as the Reviewer recommends.

- *Citations to Jiskra et al. (2018), Obrist et al. (2021), and Zhou et al. (2021) are presented in the context of PM, despite these studies focusing primarily on GEM. It should be clearer that while constituents measured below the canopy in washoff may effectively be PM, the introduction of these metals to the phyllosphere may or may not be a PM-like process.*

This is now corrected in the introduction per point 1.2. above.

Typos:

Line 17: Should be ***physiochemical****.*

I believe physiochemical refers to physiology. Physicochemical is accurate, referring to physical and chemical processes or physical chemistry per Wiktionary and Websters'.

Line 172: Instead of canopy exchange, would it make more sense to specify that this is uptake?

Agreed and changed as suggested.

Line 202: ***Species*** *instead of* ***aerosols*** *would more effectively contextualize the range of phases that exist for certain trace metals.*

Agreed and changed as suggested.

Line 209: Storage is introduced as a key term. It may be worth defining this more explicitly somewhere ().

Line 515: ***of*** *for should be* ***for****.*

Corrected.

Overall, this manuscript provides a novel approach for constraining the timescales over which trace metal introduction to soils are mediated by forests. With the minor revisions suggested above, the manuscript will more clearly contextualize the important role that FRN-based mass balance techniques may provide in developing mechanistic models of trace metal cycling and accumulation that are not possible with existing measurement techniques. I recommend that this article be accepted subject to minor revisions.