Biogeosciences Discussions

Biogeosciences Discuss., author comment AC1
https://doi.org/10.5194/bg-2022-124-AC1, 2022

Reply on RC1

David S. McLagan et al.

Author comment on "Internal tree cycling and atmospheric archiving of mercury: examination with concentration and stable isotope analyses" by David S. McLagan et al., Biogeosciences Discuss., https://doi.org/10.5194/bg-2022-124-AC1, 2022

R1C1: *The manuscript entitled "Internal tree cycling and atmospheric archiving of mercury: examination with concentration and stable isotope analyses." by McLagan and co-authors examine THg concentrations and stable isotopes in two coniferous tree species, Norway spruce and European larch, surrounding a legacy Hg contaminated site in the German Black Forest. The goals of this study are to investigate if historical records of the industrial activities correlate with elevated THg concentrations in tree rings of sampled trees, to examine potential source related variations in MDF and MIF across the tree ring records and physiological processes that may separate pools of Hg in the transport mechanism from atmosphere to foliage to phloem to tree-ring/bole wood, and to investigate if deposition and sorption of Hg to tree bark is the dominant mechanism for bark Hg. For its overall quality and for being of interest to a large audience, this manuscript is worthy of publication to Biogeosciences. I would like to ask a few questions.*

R1AR1: We appreciate the reviewer's feedback and considered all the suggestions and comments this reviewer provided and listed them below (in italics), followed by our replies (in normal text). We also label the comments as follows: *reviewer1 comment1 (R1C1)* and reviewer1 author response1 (R1AR1).

R1C2: *As a research setting, I would like to know why THg concentrations and isotope analysis were not performed for needles and soils as well. I think those data, rather than speculating from the literature, would have allowed us to correctly assess the adsorption and transport of mercury in this type of tree.*

R1AR2: We agree that total Hg and Hg isotope data of needles and soils could be interesting for present day Hg concentrations and also with regards to foliar uptake mechanisms. The original goal of the study was to assess atmospheric Hg emissions from a contaminated legacy site by observing changes in THg concentrations in the tree rings of tree species that have been demonstrated as effective archiving species for atmospheric Hg^0. Tree rings provide an archive for such historical gaseous Hg emissions over several decades, needles and soils on the other hand are not suitable for this archiving purpose; as such they were not sampled. The additional objectives of this study were developed inductively from our initial observations of THg analyses of bole wood extracted using the increment borer cores. These of course were understanding the enrichment of mercury in sapwood and bark (uptake mechanism) samples. After these initial observations, we were eager to explore stable isotope analyses of sapwood, heartwood, and bark samples from trees at this site. Nonetheless, we were aware of the challenges associated with detection limits, which required a substantial amount of material (bole wood from increment borer cores are insufficient). We were fortunate to obtain tree "cookies" from forestry workers that were actively felling trees, but we could neither obtain foliage from these same trees nor soil from where they grew due to their extraction by forest workers and not knowing their exact location within the felled stand. Hg isotopes could be a useful tool to better understand any fractionation that might occur during uptake and downward transport from foliage to bole wood. A closer investigation of the potential fractionation associated with foliage Hg uptake and transformation and subsequent transport to bole wood was not possible in this study, but we agree that this aspect is of great interest for future work.

With regards to soil Hg analysis, we were cognizant to sample only trees that were upslope from the area with contaminated soils and groundwater. Thus, the trees are not situated in contaminated soils; elevated concentrations of THg in tree rings are derived from past atmospheric emissions from the site. Furthermore, root uptake has been demonstrated to have no significant effect on tree tissue Hg concentrations and the dominant uptake route of Hg in several tree species has been shown to be foliar uptake (L62-79). Exploring Hg interactions (potentially with Hg stable isotope analyses) in the rhizosphere is again beyond the scope of this study.

R1C3: *Have you confirmed that mercury does not escape from samples that have been freeze dried, and that Hg isotope does not fractionate during freeze dry? Is it possible to correctly evaluate the original mercury concentration if the moisture content differs between the inside and outside of the wood (top and bottom?)?*

R1AR3: In dendrochemistry, samples are commonly dried before analysis to allow the results to be reported on a dry-weight basis. Freeze-drying is a standard procedure of pretreatment for measuring Hg in various biological samples including tree tissues. The influence of different drying methods (oven, air, freeze drying) for THg in wood samples has been assessed by Yang et al., 2017 and no loss of Hg was found for freeze drying. Similar assessments were made for THg in soils and reference materials (Hojdova et al., 2015) as well as soils and sediments containing MeHg (Kodamatani et al., 2017). Fractionation of Hg isotopes is only possible if there is significant loss, which has not been reported.

R1C4: *L196-197: Apple Leaves and China Soil were used for quality control. Although the major components of those two RMs and trees are very different, is it appropriate to use these two species as a confirmation of the pretreatment method? The same question applies to the RMs used in the isotope analysis.*

R1AR4: The aim of including two RMs was to show good recoveries for the different matrix of these RMs including NIST 1515 apple leaves which is frequently used by studies investigating Hg in wood samples such as tree rings (e.g. Gustin et al., 2022; Scanlon et al., 2020; Yanai et al. 2020). While we acknowledge there are some differences between the matrices (particularly China soil), we deem the differences between bole wood and leaves (tree tissues; apple leaves RM) to be relatively minor, which is supported by the application of this RM (apple leaves) in the other studies assessing mercury archiving in tree growth rings as mentioned in the previous sentence. We are also unaware of any more appropriate and established RMs for woody material with a reference value for Hg.

To assess the recoveries of Hg by the combustion and trap method, additional RMs were assessed in a pervious study by our research group using the exact same instrumentation and method: BCR-482 (lichen): 103 ± 12 %, n =13; CC-141 (loam soil): 95 ± 4 %, n = 16; NIST-3133 (Hg standard solution): 102 ± 4 %, n = 12 (see McLagan et al., 2022).

The goal in this previous and our current study was to demonstrate the efficient trapping for RMs with different matrices. We believe we have done this effectively across this range of matrices that include the most applicable matrix (apple leaves and lichen) that we could find and had ready access to.

Minor comments

R1C5: *L165: "Bole wood (tree ring)…" A description of "Bole wood (tree ring)…" is found in L165, but A first appeared in L57. The explanation in parentheses should be placed in L57.*

R1AR5: The explanation in parentheses will be placed in L57 in the revised manuscript

R1C6: *L167, L172: Why is the height of tree samplings different between the two?*

R1AR6: Sampling with the increment borer was conducted at breast height (standard procedure). The tree cookies were collected on the day of tree felling from the forestry workers. They cut the trees at a lower height and provided the tree cookies from the bottom of the freshly cut bole. Obtaining tree cookies is a much greater challenge than taking increment borer cores as we are not able (nor wanted) to fell trees simply to extract a tree slice/cookie at the appropriate "breast" height.

R1C7: *L180: Heating temperature and duration of THg measurement are written in sample preparation part. Information on combustion should be included in the measurement, not in the preparation.*

R1AR7: We have updated the manuscript accordingly. Additionally, we clarified at which stage of preparation/analysis process samples were freeze dried for the THg and Hg stable isotope analyses (please see the updated manuscript).

R1C8: *The "Spruce" in "Spruce *" and "Spruce ISO*" is better to be capitalized (* is number).*

R1AR8: We have capitalized "Spruce" in the revised version of the manuscript.

R1C9: *L238: Parenthese is not written. It should be "(no larch trees reached the 1stIP),"*

R1AR9: This typo has been corrected in the revised version of the manuscript

R1C10: *L241: It may be necessary to add and between sentences as following; "from tree rings in the BGP, and up to 521…"*

R1AR10: The sentence will be rewritten in the revised version: "The THg concentrations ranged from ≈1—10 $\mu g \cdot kg^{-1}$ in heartwood tree rings from the BGP, and up to 521 $\mu g \cdot kg^{-1}$ in a heartwood sample dated from 1951—1953 during the 1st IP in spruce 1, […]"

R1C11: *L302: saplings => samplings*

R1AR11: The study by Yamakawa et al. 2021 investigated one-year-old spruce shoots (saplings).

R1C12: *L422: "phloem (first layer of bark)…" A description of "phloem (first layer of bark)…" is found in L422, but A first appeared in L91. The explanation in parentheses should be placed in L91.*

R1AR12: The explanation in parentheses will be placed in L91 in the revised manuscript.

R1C13: *L441: Please describe the variation of a GEM concentration (1.49 ng/m3).*

R1AR13: The measurement uncertainty indicated for the EMEP data is indicated to be 0.24 ng·m^3 and the standard deviation of the annual means is 0.12 ng·m^3.

The variation has been included in the revised version of the manuscript.

R1C14: *L466: Delete a space between ISO and 6.*

R1AR14: This typo has been corrected in the revised version of the manuscript.

R1C15: *Table S4.1: "Spruce ISO5 (cont.)" needs to be deleted.*

R1AR15: This has been corrected in the revised version of the SI.