EGUsphere, author comment AC4
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Reply on AC3

Nagham Tabaja et al.

Author comment on "Seasonal variation of mercury concentration of ancient olive groves of Lebanon" by Nagham Tabaja et al., EGUsphere, https://doi.org/10.5194/egusphere-2022-174-AC4, 2022

Please disregard the previous response and check instead the below.

Response to the comment on EGUsphere-2022-174 by Anonymous Referee on the article " Seasonal variation of mercury concentration of ancient olive groves of Lebanon" by Tabaja et al. https://doi.org/10.5194/egusphere-2022-174-RC1, 2022

Thank you very much for the pertinent revision of our manuscript. Your input to this study is much appreciated and of great help to this work in order to improve it and make it better for publication. Your recommendations were taken into account and the English and grammar were revised by the help of a scientific English editor.

In this paper we did not combine the results and discussion, following the journal mostly used way of dividing the different parts of the article. The repetition that can be found in the discussion is minimal and is to make it easier for the reader to relate more directly without having to go back to the results part which is much smaller in comparison to the discussion.

The repetition between the text and figure and the table have been minimized.

The speculations made have been revised. We removed the comparison made with data of other countries far from our region. In our study, the main suggestion of the source of the Hg concentration is the atmosphere while only a minimal source from the soil was considered as reflected in the manuscript.

In this study three different generations of foliage were mixed and studied. We are aware that this certainly affected the seasonality in foliar mercury. This has been discussed following the rev 1 comments. We included in the text "For each olive tree, both sun exposed and shaded foliage (olive tree bears foliage from three different years -age classes current+2 (C+2) was collected during the same year) and stems (terminal portions of 20 cm) with no evidence of pathogens were randomly taken and merged from the upper, middle, and lower canopy position of the olive trees on a monthly basis using a manual pruner."

Line 38-39: The term heavy metals is a poor descriptor and one that has been suggested multiple times to be made redundant (Duffus,

2009: https://doi.org/10.1515/ci.2001.23.6.163; Pourrett and Hursthouse, 2019: 10.3390/ijerph16224446). I would suggest changing the terminology throughout with a less ambiguous descriptor like "potentially toxic metals". This phrase is corrected as follows: "Mercury (Hg) is among the most widely distributed potentially toxic metals polluting the Earth (Briffa et al. 2020)".

Lines 44-45: change to "Hg(0) is primarily transferred through the atmosphere by air mass movement and can undergo long-range transport". This phrase is corrected as suggested: "Hg(0) is primarily transferred through the atmosphere by air mass movement and can undergo long-range transport".

Lines 45-47: This is incorrect as written. Hg(0) does not "covalently bond with organic groups to forming… MeHg". It must first be oxidized (either in the atmosphere or in terrestrial matrices after deposition), transferred to anoxic or poorly oxic conditions and it can then be methylated. It is corrected by "Because of its high volatility and susceptibility to oxidation, elemental Hg(0) is the predominant form of Hg in the atmosphere. This highly diffusive Hg can easily pass biological barriers (i.e. cell membranes, foliage, skin). Mercury has three oxidation states, namely, Hg(0) (elemental mercury), Hg(I) (mercurous), or Hg(II) (mercuric), although Hg(I) mercurous form is not stable under typical environmental conditions and, therefore, is rarely observed. It is likely that the Hg(II) high binding affinities bind covalently with organic groups to forming the widespread toxic methylmercury (MeHg, CH_3Hg^+) (Du and Fang, 1983; Clarkson and Magos 2006; Pleijel et al., 2021)."

Lines 47-48: These descriptions about legacy mercury are extremely vague and need to be improved. It is also a bit out of place with the rest of the story and I think these two sentences could be deleted without effect. These sentences were deleted.

Lines 48-50: Needs grammatical correction. It was revised by an English scientific editor.

Lines 51:Delete "in the ecosystem". This word is deleted.

Lines 51-63: This paragraph needs grammatical and structural (and English language) work. It is a bit disjointed and jumps from one thought to another continuously. This paragraph was checked and revised by an English scientific editor.

Lines 67-69: This ignores one of the most critical fluxes of Hg back to the atmosphere from forests: wildfires. Please add a statement on this and include references such as: McLagan et al. (2021) 10.5194/acp-638 21-5635-2021; Dastoor et al. (2022) 10.1038/s43017-022-00269-w; Friedli et al. (2009) 10.1021/es802703g. This phrase is added "Though variable from year to year, Hg emission to the atmosphere from biomass burning is considered as an important driver of the global Hg biogeochemical cycle (Friedli et al., 2009; De Simone et al., 2015; McLagan et al., 2021; Dastoor et al., 2022)".

Lines 73-76: I disagree with this statement. Tree ring Hg (dendrochronology) is predominantly used as an archiving tool for atmospheric Hg(0) (Hg(0) oxidised in leaves, transferred in phloem to bole wood, and generally considered to be stored long-term). It has been established for decades (Beauford et al., 1977: 0.1111/j.1399-3054.1977.tb01880.x; Lindberg et al. (1979) 10.2134/jeq1979.00472425000800040026x) and re-confirmed many times since that Hg in woody materials is derived from atmosphere. Please correct these statements accordingly. The studies of the Hg cycle in forest ecosystems show that gaseous elemental Hg(0) is the main source taken up by plants

(Bishop et al. 2020; Zhou et al. 2021). Analysis of long term atmospheric Hg(0) and CO2 concentrations are very informative to understand the role of the vegetation in the global Hg cycle (Jiskra et al. 2018). Emission reduction measures adopted in Europe and North America since the 70s are corroborated by Hg dendrochemistry analysis showing a declining Hg concentration trend from the older to newer tree rings (Yanai et al., 2020). Indeed, tree ring Hg (dendrochronology) is a powerful archiving tool for atmospheric Hg(0). After Hg(0) oxidation inside the leaves, Hg(II) bind to organic compounds and then is transported fo the bole wood via the phloem (Beaufort et al., 1977; Lindberg et al., 1979). This is corroborated by the recent study of McLagan et al. (2022) showing the benefit of the stable Hg isotope analysis on dendrochrmistry.

Lines 76-77: I would suggest to add McLagan et al., (2022: https://doi.org/10.5194/bg-2022-124, recently accepted) to this reference on Hg dendrochemistry (using stable Hg isotopes). Some of the findings in this recently accepted study may be highly beneficial to this manuscript. We thank you for the reference. We added it as shown in the previous section.

Lines 102-103: I cannot agree with this statement that roots are the primary source of Hg in contaminated areas. (1) This is unpublished work and judging from the abstract it appears they state the atmosphere as the source not the roots; (2) This is at a former Hg mine – there is MASSIVE legacy emissions of Hg(0) to the atmosphere continuing to this day at these sites, which is readily available for stomatal assimilation; (3) as previously mentioned there is countless studies during the past 50 years that show root uptake in tree ubiquitously is an very minor, if not insignificant uptake pathway. This statements needs correcting. This statement is removed.

Lines 107-108: How does this compare to recommended soil guidelines? Please state this. This phrase is corrected as follows "Adding to that, soil samples collected from different areas in southern Lebanon showed values of Hg concentration ranging between 160-6480 ng/g showing a high contamination level as indicated by World reference Senesi et al. 1999, Kabata-Pendias 2001 ".

Lines 144: I really don't see the benefit of making acronyms of the sampling sites. Both a one-word towns and this just confuses readers that are not as closely linked to the study as the authors. I recommend simply writing the town names each time. We agreed and changed the acronyms to town names.

Figure 1: The climate graphs are really ancillary metadata. These are described in the method text and should be moved to the SI. Indeed, even the site map could be move to the supplementary information (SI). There are only two studies sites and again their location, climate and geography and surrounding Hg sources are described in the text. I believe this whole figure would be better served in a SI. On the behalf of all the authors, we believe it is better for the reader to have those sites indicated directly after the text to make it clearer concerning the locations. Concerning the climatic data, it is removed since it is available in the text and also indicated in figure 3.

Line 177: "8-15 m foot circumference". There are obvious errors here. Also I highly recommend using diameter rather than circumference. It is much easier for the reader to comprehend. This sentence has been changed to: "For the Hg concentration analysis, four olive trees (3 to 5 m diameter and an average height of the trees 4-6m) were sampled in each of the two groves"

Line 196-197: While I do not think this is a major problem as I believe there will

be minimal Hg(0) on surfaces or within foliage and stems, it needs to be acknowledge that this heated drying method would likely eliminated any and ALL Hg(0) present in the samples. This statement was amended to the following "Collected foliage and stems were rinsed with distilled water and then dried for 48 hours in an oven at a temperature of 50°C at maximum in order to remove any dust Hg from the surface of the samples following the method of Demers et al. 2013, Li et al. 2017, Pleijel et al. (2021). This procedure likely eliminate any Hg(0) present in the samples".

Line 217: The detection limit should be listed as total mass of Hg, not concentration of Hg. The system does not analyse concentration (that is calculated by the mass of sample input), it is calibrated to determine the mass of Hg in any given sample. This is an important distinction. The calculation yielded the MDL of 0.04ng in units of mass (corresponding to a concentration of 0.7 ng g^{-1}). This value was in the range of our measured Hg concentrations, which ranged from 0.4 ng for stem, 0.7 ng for soil and 0.8 ng for leaves and litter.

Line 261-263: What Hg concentration is being referred to here? Hg(0) Concentration in the air? This needs to be stated. This ambiguity is exactly why the results and discussion should be combined. The Hg concentration referred to here is the Hg content in the foliage and stems and it is the combination of Hg remaining in the foliage and stems after being rinsed and heated.

Lines 312: "the main Hg content" should be changed to "Highest Hg concentration". This phrase is corrected as follows: "Our data corroborates previous studies (Bargagli 1995; Higueras et al. 2016; Naharro et al. 2018) showing that olive foliage has the highest Hg concentration of plant tissue.

Lines 318-322: Once again, I disagree the main source of Hg in the stems of the trees is from the soils. What is the evidence for this? I could reference 10+ papers that have shown Hg in woody materials of trees to be almost exclusively derived from foliage and downward transport in phloem. Higher concentrations in leaves over stems is NOT evidence that Hg in stems is derived from the roots. Not all Hg taken up by foliage is transferred to woody materials, which leads to an enrichment of Hg in foliage compared to Hg in woody materials. The phrase was amended to the following "Since normally the main source of Hg into the foliage is atmospheric and minimally through the soil, this explains the higher Hg concentration in the foliage, while in the stems the main uptake is from the foliage and transported through the phloem and soil, and it seems to be much lower levels of Hg concentration are found in the stems than that in the foliage (Pant et al., 2010; Tomiyasu et al., 2005)."

Lines 323-324: The downward transport of Hg in phloem eventually into roots and potential release into soils may also be contributing to Hg accumulation in soils. This phrase is added: "The downward transport of Hg in phloem eventually into roots and potential release into soils may also be contributing to Hg accumulation in soils."

Lines 333-335: This concept of soil properties driving Hg concentrations and uptake in soils was not something introduced by O'Connor et al., 2019. This is not a new idea and again has been known of for decades. I agree, but I am giving here an updated reference.

Line 336: What does nitrogen content have to do with Hg sorption and uptake in soils? Nitrogen can also be a factor affecting the Hg content in soil depending on its characteristics. Nitrogen supply prevents oxidative stress in roots, but also can improve root development and increase the uptake of Hg from the soil (Carrasco-Gil et al. 2012).

Lines 339-341: Did the authors measure wet and dry deposition of Hg? For wet

deposition to occur, there would need to be considerable Hg(II) in the atmosphere. I also see no reason as to why dry deposition would occur more in a higher temperature region. Higher temperatures favour partitioning of Hg(0) back into the gas phase, which would be suggestive of less dry deposition. The author discussed dry deposition and indicated the effect of higher temperature on higher dry deposition.

Lines 342-344: Foliage accumulates Hg(0) over time. Naturally older leaves that eventually die and senesce will be more enriched in Hg than younger leaves growing on the trees. I agree with your statement, that is why we indicated that older leaves have higher Hg concentration than younger leaves.

Lines 348-404 and Figure 3: This is far too speculative. These data are for Europe (the Authors use a site from Germany for Hg(0) in Figure 3). Lebanon is a long way from Europe and in a totally different climatic zone without typical northern temperate/boreal deciduous/conifer dominated forests. To make any sort of statement about atmospheric Hg zero concentrations this should have been measured or data taken from a long-term monitoring station in this climatic region/ecological biome. I see this whole (and very long discussion) on correlations between foliage and atmospheric Hg(0) to be too speculative to the point it is invalid. I also agree with the other reviewer that the emergence of foliage in olive trees in spring/early summer is the major driver here.

In the process of the reply to the review we rechecked the papers available on the atmospheric mercury closer to our region. We were not able to find any information in the region on atmospheric mercury data, but we passed across an interesting newly published paper by Martino et al. 2022 that is the only atmospheric gaseous elemental mercury (GEM) measurement near an olive site that is comparable to our study. Martino et al. 2022 publication shows the factors affecting the GEM values are mainly the factories, sea emissions, fires, and vegetation. Even though this paper is not in the same area as that of our sites, we take profit to compare with same years studied (2019-2020). We used their data from table 1 representing the monthly median GEM values and compared it to our data. Our values of the foliage in Bchaaleh and Kawkaba show higher values of Hg concentration in winter and lower in summer, were seasonality is clear the same as that of Martino et al. 2022. This seasonality can change due to many factors such as wind, fires, industrial surroundings and other factors. At the same time we decided to remove the northern Hemesphere data upon your feedback. We will change the discussion and narrow it to the Mediterranean region with the data mentioned in our comments.

Other data was done on Total Gaseous Mercury (TGM) in the French coastal Mediterranean site which showed higher values in winter/spring and lower values in summer in the Mediterranean region. This studies also showed seasonality with the atmospheric mercury due to dispersion of pollutants in the troposphere and high TGM values that are due to air masses from regional and local sources (Marusczak et al. 2015).

Mastromonaco et al. 2017 Showed also that the main source of mercury occurs from the Mediterranean Sea water and is affected by wind speed with higher values of GEM concentration registered in autumn in comparison to summer, with higher evasion rates found in summer in comparison to the autumn season. Another study that includes countries closer to Lebanon by Kotnik et al. 2014 found a seasonal variation in Hg in the Mediterranean region near Spain, Italy, Turkey and Israel (1998-1999) with the highest Hg average concentration during winter and the lowest during autumn.

Concerning the emergence of foliage in olive trees in spring/early summer being a major driver, this is shown through the seasonality registered during the different seasons due to the merging of three different years of the foliage in our study.

Lines 417-448: These paragraphs need grammatical and English language corrections. It is very hard to follow and from what I can derive it again seems highly speculative and to contradict the state of the science without data to support that. These paragraphs were checked by a scientific English editor. Some data was given to support our scientific point of view, but we tried to give our point of view in regards to the Hg cycling in stems, litter and soil system.