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Atmospheric Chemistry and Physics Discussions

# *Interactive comment on* "Distribution and sources of bioaccumulative air pollutants at Mezquital Valley, Mexico, as reflected by the atmospheric plant *Tillandsia recurvata* L." *by* A. Zambrano García et al.

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Answers to anonymous referee #2

Thank you so much for your very careful review. It was very helpful to improve our work; not to mention the many editing bugs captured in our manuscript.

1. (pp. 5811-5813. The introduction presents useful background on the region of the field study, the biomonitoring species used, and the pollutants analyzed, but it does explicitly state the objective of the research. Rather, it reads, "we report results. . ." (p.



5811, line 15) and summarizes what was done (p. 5813, lines 12-14). It would be useful to state the objectives, which seem to be to describe spatial patterns in concentrations of unregulated pollutants and to detect the major regional sources.

It may be a writing style disagreement. From what you say in your last sentence, you've got our objectives right. So, in this case our text may not need changes. However, we're open to any suggestion for improving our writing.

2. (p. 5815, lines 4-6) Interpretation of the results would be aided if this paragraph also mentioned what fraction of metals and other pollutants in this species have been shown to originate via uptake from the air versus uptake from water through the roots, if any.

For this biomonitor, and because of our sampling provisions ($\geq$ 1m from ground), all pollutants are assumed to derive from atmospheric sources via leaf trapping and absorption. Roots of this plant are vestigial (not functional), except for anchoring purposes. It also obtains water from atmospheric sources via leaves.

3. (p.5815, lines 5-7) "Prior chemical analyses, plant dead parts and extraneous materials like insects, feathers and spider webs were removed manually". What are "prior chemical analyses" that would need to be removed from plants?

It looks like a readability misunderstanding. Samples were not chemically analyzed before the real analyses of metals and PAHs. We mean: samples were cleaned before being chemically analyzed (i.e., too many words. We used the short "Prior chemical analyses",. . .). We would leave this detail to the editor.

4. (p. 5819, line 22) In the description of Figure 2, which shows biomonitoring versus geological source concentrations of various metals, there is no explanation of why the fitted curve is an exponential while it is a line for igneous rocks and limestone. Thus, comparison of goodness-of-fit seems unfair.

Right. We didn't enter into reviewing formal goodness-of-fit aspects for the "fitting"

lines in Fig. 2, and even into discussing this figure further (e.g., is it a linear or power relationship?). Strictly speaking, they are not regression plots between two continuous variables. They rather "relate" single data for several chemical variables between two environmental matrices (biomonitor vs. rocks). The single purpose was to illustrate a regional rock-biomonitor chemical similarity, and we drew those lines quite liberally, using only the R2 criteria as a guide. If you consider those lines as misleading, we would accept eliminating them. That would not affect what we say in the text.

5. (p. 5820, lines 9-12). The explanation of different MV:OC ratios < 1.0 is confusing. The other countries included more urban sites and should therefore have higher concentrations of anthropogenic elements.

We'll modified slightly the text hoping to eliminate such confusion. It will say: "The MV:OC ratio was <1.0 in 11 comparisons (Table 3), indicating lower element concentration in Tillandsia at MV." We do agree with your second comment in this paragraph; that is what we say in lines 9-12.

6. (p. 5820, lines 23-25).The lower amount of high molecular weight PAHs is easily explained by their lower emission factors from sources and lower ambient concentrations compared to low and medium molecular weight PAHs. There are many papers in the literature that the authors can reference on this point.

We do agree with your comment if referred to emission levels of low, medium and high molecular weight PAHs. In abundance, they usually go low > medium > high weight PAHs. However, our intended point in those lines is to compare only our quite low concentrations of high weight PAHs to reported values for other plant biomonitors (e.g., pine needles). We frequently found higher reported absolute concentrations than ours, especially in studies from colder, Northern countries, and wanted to advance a hypothesis about this difference. It is known that PAH degrade faster with increasing light and temperature. Thus, high degradation rates can be reasonably expected at our study region from its high insolation rates and temperature. We clearly failed in telling



it this way, and introduced some confusion. We will try to fix it in the text.

7. (p. 5822, line 16) Indeed, delta C-13 and Ni/V ratio are correlated. The authors should provide an explanation of why Ni/V is chosen for comparison and why it should be correlated with delta C-13.

You're right again. We missed adding some context about it. Niquel and V, and especially this later metal, are two of the most abundant metals in crude oils. It is so that physicochemical specifications of crude oil usually include data on those two elements as indicative of general metallic content. Several environmental studies dealing with metals from petroleum sources often include the Ni/V ratio (sometimes the opposite: V/Ni) as a reliable indicator for such sources. In our case, the Mexican heavy crude oils processed and burned in the study region have average Ni/V ratios roughly within 0.19 to 0.31. Thus we expected the natural Ni/V ratio of the biomonitor to become closer to that of petroleum near the facilities using this fuel. The decline in Ni/V near Km 0 in Fig. 4 shows that. The positive correlation between Ni/V and ïĄd'13C was not surprising because petroleum, due to its biological origin, is depleted in 13C, and so are the C compounds released by combustion and the 13C of plants using this source. Therefore, that correlation confirmed a common emission source. We'll add a couple of sentences on this point in page 5822.

8. (p. 5824, lines 20-22) The coefficients of variation in the text do not agree with those in Table 2.

Thank you for noticing this mistake. The CV values in Table 2 are correct. This text-Table 2 disagreement came from an older table, where regional variability was calculated from average site concentrations (50 sites in most cases), which caused some reduction in regional variability. Values presented in the current Table 2 were calculated from the total number of samples (150 in most cases; i.e., ignoring site averages). We'll correct the text accordingly. This does not alter our interpretation in those lines (20-22).

9. (p. 5825, lines 8-9) It is unclear why the distance of Mixquiahuala is given as both

37 km and -37 km.

It is only to avoid confusion while looking at Fig. 5, where Mixquiahuala lies at -37 km. If you don't mind, we would prefer to leave it that way. Otherwise, it would require changing both Fig. 5 and the text.

10. (p. 5827, line 29) Is it also possible that Factor 5, if it reflects large amounts of N compounds such as ammonium and nitrate, could be associated with secondary aerosol?

Yes, it is completely possible. Deposition of N secondary aerosols; e.g., ammonium nitrate, may have some contribution to N in the biomonitor. However, our discussion was very limited by our complete lack of regional data on these and other air pollution components (gaseous N species). There would be several aspects we need to know before seriously considering secondary aerosols; e.g., are usually very fine particles, and thus subjected to long distance transport, with impact over large areas. We need to know which is the N isotopic signature (if any) of secondary aerosols. Tentatively, we "attached" to the idea that large, nitrate-enriched particles from soil resuspension (subjected to short distance transport) may have the largest impact on the biomonitor's 15N. This survey was our first step to understand what's going on at Mezquital Valley for the studied pollutants. Since it revealed a clear 15N regional pattern, we're planning further research to explain it in terms of specific N compounds.

11. (p. 5840, Table 5) The column showing mean PAH concentrations in Mezquital Valley repeats information shown in Table 4 and is not needed.

Yes, we think so. Because it is a comparison table, we wanted to save some time to the reader by looking at only one table instead of two. What about leaving this point to the editor's judgment?

12. (p. 5841, Table 6) The p-level should appear in its own column or should be associated with the difference, rather than with the south mean.



A preliminary version of this manuscript was reviewed for edition. We formatted Table 6 that way upon editorial advice. We'll see whether further changes are allowed to fulfill your requirement.

13. (p. 5842, Table 7). The numbers in this table contain an excessive amount of significant figures.

OK. We'll reduce figures to three significant ones.

Technical corrections

14. (p. 5813, line 20) The population of "500 thousand" is more easily interpreted as "500,000".

You may be right. Would you mind to leave it to the editor's point of view?

15. (p. 5814, line 12) "tiers" appears where "tires" is intended.

Yes, we'll correct it.

16. (pp. 5814-5817) Minor corrections to the English are needed, especially in the section on PAH analytical methods. Additionally, in this section, concentrations are listed as micrograms/milliliter, whereas elsewhere in the manuscript, engineering notation is used, i.e. exponent of -1 for the divisor.

Thank you for this observation. There were five cases. We'll correct them.

17. (p. 5819, line 27; p. 5820, line 6) The abbreviation for ratio between the Mezquital Valley and other countries is "MW:OT" here but "MW:OC" in the corresponding table.

MV:OC is right. We'll correct it in the text.

18. (p. 5822, line 13) "expected" is usually used in place of "expectable".

OK. Suggestion accepted.

19. (p. 5839, Table 4) The leftmost table header and the bottommost row should read

“PAH” rather than “HAP”

Oh, yes. Sorry, it was a Spanish bug. We’ll correct it.

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Interactive comment on Atmos. Chem. Phys. Discuss., 9, 5809, 2009.