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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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We are grateful for all comments and suggestions that greatly improved the quality of this manuscript. Please find attached a pdf file version of this response in case special symbols may not display properly. Thanks.

1. Page 3 giva sigma 13C values for petroleum signature.

We already cited a ïĂăïĄď13C range (-20‰ to -35‰ valid for fossil fuels in general; i.e., petroleum and mineral carbon. Known ïĂăïĄď13C values for Mexican crude oils

are well within that range (ïĄď13C = -21 to -28.5, being most frequent values around -27, e.g., Prinzhofer et al. 2000. We will change the corresponding sentence in the paper to include this information and add the new reference.

*Prinzhofer, A., Vega, M. A. V., Battani, A., and Escudero, M. 2000. Gas geochemistry of the Macuspana Basin (Mexico): thermogenic accumulations in sediments impregnated by bacterial gas. Marine and Petroleum Geology 17: 1029-1040.

2. Page 4, consider what may be the impact on 15N of atmospheric deposition of NH4NO3 (or trapping of this pollutant by moss). You only discuss on NHy or NOx is influencing moss, but in aerosols these are present usually as ammonium nitrate.

Good points. As first approximation to the complex and scarcely documented air pollution at Mezquital Valley, this survey was not designed to address specific atmospheric compounds. That's why we limited our considerations about ïĄď15N to what is well-established in the plant biomonitoring literature for reduced and oxidized N in general. We clearly need further research to be more assertive in answering your questions; i.e., to connect the well-defined ïĄď15N spatial pattern found at Mezquital Valley to specific N atmospheric compounds. We're now planning to do so by combining biomonitoring techniques with direct measurements of dry deposition for specific atmospheric N compounds. Secondary aerosols such as ammoniun nitrate may be a good case.

Characterizing the impact of the atmospheric deposition of ammoniun nitrate on the biomonitor's 15N is quite challenging, both theoretically and experimentally. Tentatively, we guess it may cause a slightly positive shift in the ïĄď15N of our biomonitor. We cannot say how much at this moment because this will depend on the isotopic signature of this compound at our study region, which in turn depend on that of their atmospheric forming precursors (NH3 and HNO3), the type and size of sources, actual deposition on the biomonitor and fractionation processes, among other factors. Assuming that NH4NO3 is locally formed by the known atmospheric reaction between NH3 and HNO3, its ïĄď15N must relate to the 15NH3/14NH3 and H15NO3 / H14NO3

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ratios in the air. NH3 is usually depleted in 15N (negative to very negative ïĄď15N, down to -40), whereas the tropospheric H15NO3 / H14NO3 is known to be positive, specially when HNO3 derives from NOx emitted by fossil fuel combustion. At the end, the ïĄď15N of ammonium nitrate may be somewhere between the ratios of its precursors. If the NH4NO3 N isotopic ratio were similar, more negative or more positive than that for our biomonitor, its effect will be, depending on the actual amount deposited, null or cause a negative or positive shift in the biomonitor's ïĄď15N, in that order.

Atmospheric ammoniun nitrate aerosols may be abundant at our study area, as it is in other polluted industrial/agriculture areas (e.g., California). Although direct emissions of NH4NO3 from agriculture occur when this compound is used as man-made fertilizer, they can be assumed to be minimal or absent at Mezquital Valley because soil N enrichment is achieved by wastewater irrigation. The conditions are given at MV for secondary formation of ammonium nitrate at MV because of the presence of important ammonia sources (agriculture, vehicle and industrial fuel combustion) and HNO3 precursors (actually NOx from fossil fuel combustion, further oxidized into HNO3).

3. Page 5. 'small and large' by 'different size'; 'electricity' by 'power'; 'open sky mining operations' by 'quarries'; 'tries' by 'tires'.

OK. We'll make those changes.

4. Page 5. How is it possible to pollute moss with natural contributions? Do you mean soil dust? Quarry dust? Wind rock basement dust? The two first are anthropogenic, the third may be natural, but the contribution may be very low compared to the others.

We guess your questions come from this sentence: 'The contribution from natural and agricultural sources to the MV air pollution is still unknown". For our study region, we understand as natural emissions those from wilderness areas (including crustal rocks, soil, biological and natural fire). Those from agriculture (soil, wastewater, crop management) and quarries are rather anthropogenic.

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5. Page 5. How exposure time to pollution is controlled? In the last line of this page you state that this may be one to 2 years. But this may represent a factor of concentration near to x2. It is this considered when comparing results from sampling sites. Would it not be better to grow the moss or to pick it up from very low pollution areas and expose it at the different sites for a similar period of time?

The length exposition period was assumed to be similar among sites and, thus, not taken into account for comparisons; although composite samples were assembled applying rigorous procedure to assure similar exposition time, as explained in the methodology section. According to this, our analysis was rather semiquantitative, meaning that it showed the relative differences among sites in exposition to the measured air pollutants. A quantitative determination of the actual atmospheric deposition would require comparing with concurrent measurements by technological deposition devices at some selected sites.

Controlling this factor is one of the major challenges for air pollution biomonitoring, especially when using in situ plant receptors with unknown age. Some plant receptors or sampling strategies allow for some time control. For instance, you can use pine needles as receptor because the annual production of needles is well defined. However, uncertainty in time of exposition would be still present, ranging from weeks to months. Unfortunately, pines are very scarce at our study region, not allowing us to establish an extensive biomonitoring network to look for spatial patterns (our main purpose in this survey). Transplanting samples from unpolluted into polluted areas certainly allows for some control of time. However, this technique has its own advantages and disadvantages. For instance, it involves more sample handling (risk of undesired sample contamination), it is more time consuming and costly than working with in situ plants, and this usually lowers the number of sampling sites, which may compromise the spatial resolution of a study and the possibility of covering larger or remote areas. Transplanting is more appropriated for studies looking at biological effects of air pollution.

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6. Page 6: clarify what are ‘clean samples’.

Samples without dead parts or materials like insects, feathers and spider webs, etcetera, which are not part of our plant. Samples were not washed with water to avoid losses of pollutants. This is usual practice in plant biomonitoring, especially when there is no interest in biological effects, which may require separating adsorbed vs. absorbed pollutants. We will clarify this expression in the text.

7. Page 9. Take care with igneous rock composition. You have to know if the igneous rocks of your area are acidic or basic and select the mean composition of one or the other type for normalization, otherwise the range of concentrations may be very wide.

You are right. Mezquital Valley has both types of igneous rocks. We used average values from acidic rocks, which characterized for a larger number of elements. We also tried plots for basic igneous rocks, and found no major changes compared to what we already showed.

8. Page 9: ‘Other geochemically major elements’ by ‘Other geological major elements’.

Correction accepted.

9. Page 10: ‘like Ni’ by ‘such as Ni’

Correction accepted.

10. Page 12. r=.7 by r=0.7 and r=.39 by r=0.30 (actually 0.039)

OK, accepted correction.

11. Page 13: apply discussion on previous comment #2 here.

Since we are not providing any data on atmospheric N compound, we avoided to enter deeper in discussing particular compounds. We would like to keep it like that until counting with N measurements at our study area.

12. Page 13: clarify NH4, NO3, NO3+ ??? or NH4+, NO3-???? In different parts of

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the text.

OK. We'll fix it.

13. Page 14. Title 3.4: Distribution of pollutants and identification of major emission sources

Title correction accepted.

14. Page 14, last line: Specify in brackets the values for the north.

OK. We'll fix it.

15. Page 17: Apply previous comment #12 here.

OK. We'll fix it.

16. 'electricity' by 'power'

Correction accepted.

17. Page 17. 64% of the variance explained is not very high. Why you did not get higher explained variance?

It was actually 74% of explained variance, which is quite good for biomonitoring studies. The main reason of why we did not get higher explained variance was our limited number of sampling sites, which lead us to impose some restrictions to FA. One of them was to use only factors with eigenvalues > 1.0 as meaningful. Another was to limit the number of variables, eliminating some of them as explained in the Statistical section. As you may guess, we tried a number of preliminary FAs: for metals or PAHs alone, lowering or increasing the number of variables, different rotations, and so on. In some cases we've got solutions with higher percentages of "explained" variance, usually producing higher number of factors (some of which formed by single pollutants; i.e., no meaningful). In addition, we also decided not to use surrogate values for missing data because they may become significant in such a small data set. Including variables with

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missing data would have sacrificed some sites, making our data matrix even smaller. So, we preferred to keep our sample size (sites) rather that the number of chemical variables.

18. Review using of units: ppm, mg kg-1. The tree types are used in text, figure and tables. Select one and correct along the text, figure axis and figure and table headings, accordingly OK, we'll do it.

19. Why sulfur levels were not analyzed using ICP-OES and presented???? It is very easy!!!! Also the NO3- and Cl- levels would be interesting to be measured in water leachates.

Our survey focused on unregulated and poorly documented air pollutants for Mezquital Valley. The regulated ones (SO2, NOx, O3, and derivatives) were automatically left apart. Some real life restrictions to our project, meaning limited funds and a time deadline to present results internally at our institution, some important toxic elements requiring special sample processing (e.g., Hg) and other, like those you mention, were not addressed. We'll do it after approval of an extension to this project.

20. Table 8: Why local soil does not contain Ca and only Mg, Mn, and Zn?????

Your question refers to Factor 2 (F2), but we need to refer also to F1 to answer it.

In interpreting our FA results, we took as meaningful only loadings $\geq$0.6 because of our small sample size. This left some elements with considerable loading (say between 0.40 and 0.59) apparently out of some factors. This happened for Ca in F1 (loading = 0.49, Table 8) and P (0.42). We interpreted F1 as indicative of crustal sources and considered soil dust as the vehicle (page 5826, line 25-29). Thus, the Ca loading in F1 implies a soil origin. The Mezquital Valley soils are, of course, formed mainly by material from regional crustal rocks. They show higher chemical similarity with the local igneous rocks than with limestone (measured as correlation, not shown in the paper). We did not enter into such considerations because it would take us far from

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our main purpose in this paper.

Our interpretation of F2 as another soil factor was aided by mapping its main elements (Mg, Mn, Zn, and Na) and the F2 site scores (not shown in the manuscript). The site scores were higher at areas with higher elevation, especially at the Mezquital Valley southeast, and were lower (negative scores) at low elevation areas; i.e., at agriculture areas. That is consistent with the spatial distribution pattern of those individual elements (we are only showing the Na pattern in Fig. 8). That suggested the spatial contrast between agriculture soil sources (Na) and natural soil sources (Mg, Mn and Zn). This does not imply a null contribution from other sources to later elements. For instance, Zn was also associated to the industrial factor (0.56 loading in F3). variation of soil chemical composition at Mezquital Valley varies strongly. All FAs contain some soil contribution; i.e., there are no factors responding to pure sources. vary is appears to contribute to several factors.

21. F2 contains high Cu, usually enriched in sludge.

Yes, it does. It also loads high in F1 (0.61). This indicates that Cu in the biomonitor mainly derives from soil sources. There are some studies showing significant amounts of this element at the soils irrigated with wastewater. This may somehow agree with comment on Cu enriched sludges.

22. Give units in headings of Figures 3, 4, 6 and 8

Done

23. Correct sigma in the title of axis Y in figure 4

Done

24. What type of normalization used in Figure 5?? State in Y axis and heading.

Values were normalized to100, which represented the maximum site concentration found within the transect belt. That was included in the corresponding heading.

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25. Figure 9: identify, first, second and third circles. Why Ca is not in the soil? End of report.

First and third circles are already identified in Fig. 9 as F1 (crustal/soil) and F3 (industrial, fossil fuel combustion), and they are defined in heading. The third encircled group does not properly constitute a particular factor; it is formed with elements no significant for F1 and F3, which define this plot. Unfortunately, encircling the elements somehow hides the proximity of Ca to the crustal/soil F1 group (0.49 loading, along the F1 axis). The Ca case is interesting because this soil/crustal element correlated (spatially) better with elements from fossil fuel combustion (F3) than with those from crustal/soil origin. This is a clear anthropogenic effect due to their increased emissions at limestone quarries and cement plants, which use fossil fuels.

Please also note the Supplement to this comment.

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