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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Summertime elemental mercury exchange of temperate grasslands on an ecosystem-scale" *by* J. Fritsche et al.

Anonymous Referee #2

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General Comments:

The overall objective of this manuscript is quite worthy: to quantify the magnitude of elemental mercury exchange over temperate grassland ecosystems. This information is important as the community seeks to obtain a better understanding of the magnitudes of mercury stored within a number of environmental compartments and the rates of exchange between these compartments. An accurate description of such exchange rates is critical in that such measurements provide "ground truthing" for various mercury transport and fate models which will be used to study the relative impacts of natural and anthropogenic emissions of mercury on sensitive ecosystems.

It would appear that the authors have performed a carefully planned measurement study. However, there are several sections of the manuscript that trouble me and lead me to believe that the manuscript should not be published in its current form. Please understand that this does not mean that the authors need to "start from scratch". However, there are several serious concerns that need to be addressed and may require a deletion of some of the material presented in the current version of the manuscript.

Specific comments:

Upon reviewing this manuscript, I found several areas of concern which I feel that the authors need to address before this manuscript can be accepted for publication. It is possible that my concerns can be addressed merely by a more complete discussion of the approach or analyses performed by the authors. To be specific:

1) Site descriptions: The authors provide an inconsistent description of the suitability of the sites used for this study. For instance, the authors note that the Neustift site was surrounded by uniform vegetation for around 300 to 900 meters in the directions of the daytime and nighttime winds, and that the footprint maximum was withing these boundaries for more than 90% of all cases. This suggests that this site was probably a good one. Little information is provided for the Fruebuel site, outside of the fact that the largest contributions are within 60m of the covariance tower. Does this mean that 51, 60, 80% of the contributions are within 60m of the tower? Is the vegetation uniform within that 60m? This is information that is necessary to give the reader confidence in the quality of the data. Likewise, we are told that in Oensingen, the "fetch length" is about 70m along the dominant wind sectors. Are the authors referring to the maximum footprint? Are the authors saying that this is the maximum distance that has uniform vegetation or surface traits? A typical rule of thumb for eddy correlation measurements is that one must have uniform surface characteristics for an upwind distance of at least 100-times the height of the sensor in order to insure that the turbulence field is in equilibrium with, and representative of, the underlaying surface over which the local gradient is being measured. The authors never indicate the height of the eddy covariance sensors at each site. Assuming that the sensors are at least as high as the

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highest GEM concentration measurement (1.7m), this would require a uniform fetch of at least 170m. If this is not the case, then the use of these measurements for either the aerodynamic or eddy covarience approaches may not be valid. This information needs to be provided, as a fetch of only 70m at Oensingen would not be adequate and use of the data not valid. I recognize that as a scientific community, we must address environmental issues at locations that are not "ideal" for all types of measurements. There are some assumptions that must be adhered to if a measurement approach is to be validly applied. At the very least, the authors need to address potential uncertainties resulting from these short fetches.

2) Data coverage: In this section, the authors note that they performed a quality assurance step to determine the minimum resolvable gradient (MRG) by placing all five inlets at a height of one meter above the surface at their Fruebuel site and then computing a concentration difference over a three day period. Unfortunately, this reviewer has found that the bias between gradient sampling lines can vary over the course of a given field study, even those of duration of a few weeks. Was this MRG test performed at the beginning and of the field measurement period to insure that no drift in bias was observed during a given study? Was the MRG test performed at each site? Was the same tubing used at each site? While we are told that these studies occurred during the summer of 2006, we are not told if they were performed at the same time or seperately. Each of these issues are important pieces of information in helping the reader to determine potential biases in the results presented. Certainly, they are important in helping the authors interpret their results!

3) CO_2 and GEM Fluxes: In reading this section, I was concerned regarding the discussion of the observed gradients and fluxes. First, the authors note that between days 6 and 10, night-time gradients at Oensingen were negative, suggesting an emission of mercury from the surface during the night. Later in the paper (why not at this point?), the authors attribute this observation to heavy rainfall the previous 48 hours. If the mechanism for this emission was related to soil moisture, why would this effect not be

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seen during the daytime hours, as well? Figure 3 suggests that this was a nighttime phenomenon. Could this have been related to the fetch concerns noted earlier in this review? Certainly, high surface layer stability would be expected at night, which would make advection issues a greater concern during this time of the day.

Also...The authors note at one point that..."Both micrometeorological methods were consistent regarding the sign of the average fluxes". Given that it is the GEM gradient that determines the sign, why would they expect them to be different?

4) Discussion Section:

The authors note that "during several phases the two methods yielded different signs of the GEM flux" and then attribute this to their smoothing process. Now, I completely understand the need to smooth the data, as GEM gradient measurements have some inherent noise in them....I see this, too! However, if the smoothing method results in different signs in the estimated fluxes, then I would suggest that the authors need to reduce the length of their smoothing (9 points, or approximately 8 hours) until such occurrences disappear.

The authors also correctly point out that accurate results of the modified Bowen ratio method can only be expected if the sources and sinks of GEM adn CO2 are equal and the spatial (I believe their word "special" is a typographical error) variability of the fluxes are equal. However, they next go on to say that this was not the case at Fruebuel. The next question should logically be....then how do they propose to report their results as being valid if they tell us that the assumptions that their method is based upon are not generally valid?

The authors also note near Line 27 of page 1967 that ozone oxidation of elemental mercury might explain a lack of GEM emission. If this reaction were to occur at a rate fast enough to impact local scales, I would think that this would lead to a greater decrease in the concentration profile of GEM and thus a greater emissive flux, not a decrease.

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Technical/Editorial comments:

1. Page 1952, line 18: The word "exposition" should probably be replaced by "introduction" or "deposition".

2. Page 1961, lines 7 and 8: What exactly are the values of "atmospheric turbulence" that are being reported? Are these the friction velocity? This should be clarified.

3. Page 1962, line 23: I am assuming that the reported gradient of 20 ng/m3/m is a typo. This should be corrected.

4. Page 1967, line 12: I believe that the Lindberg paper sited pertained to measurements made at a remote, but contaminated site. If this is the case, this point should be mentioned in the manuscript.

5. Page 1968, line 27: The sentence starting with "Nonetheless" is awkward. Perhaps this sentence should be changed to, "Nonetheless, mercury deposition to remote ecosystems could results in a significant loading to these ecosystems if these fluxes....."

Final Comments: There is little question that the authors performed their measurements under challenging conditions. The manuscript suggests that the authors understood the need for careful application of quality assurance protocol and that they also understood that certain assumptions must be met in order for the methods applied to be valid. Unfortunately, it would appear from the manuscript that these protocols were not followed for all sites during the study and that some data is presented despite the fact that not all of the necessary assumptions were met at all of the sites. There are some important pieces of information within this paper and I believe that the authors can make a contribution to the field with the data that was collected. However, the authors need to take a hard look at their dataset and remove data presented in this paper for which QA steps were not followed completely and/or where certain methodological assumptions were violated (namely, insufficient fetch for measurement heights

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applied). At the very least, if this reviewer has misread the completeness of the quality assurance steps taken at each site and/or if all assumptions necessary for application of the micrometeorological techniques were actually met at all three sites, the authors need to do a better job of convincing the reader that the data is valid and complete. Until that time, I do not believe that this manuscript should be published as written.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 1951, 2008.

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