Baya & Van Heyst - Authors' Comments to Anonymous Referee #1

The authors greatly appreciate the time and effort that Anonymous Referee #1 has spent in reviewing our paper. Below are the Authors' Comments in response to the comments and issues raised by Anonymous Reviewer #1. Original reviewer comments are in italics while our Authors' Comments are in normal text.

Anonymous Referee #1
Received and published: 8 March 2010
Review of Assessing the trends and effects of environmental parameters on the behavior of mercury in the lower atmosphere over cropped land over four seasons

General comments
This manuscript addresses the important question of terrestrial surfaces as a source and/or a sink for atmospheric mercury. The authors' study follows the previous work of several other studies but it remains unclear to me why their study is useful to the scientific community and what is the problematic. The data presented here are of good quality though the use of the different abbreviation TGM, Hg(0) or RGM is to my opinion not satisfactory. This should be clearly defined in the experimental section. Due to instrumental failure, there are data missing which I can understand. But I encourage the authors to clarify the period when data are missing. There are several contradictions throughout the manuscript. Moreover it seems to be not convincing to discuss about fall data without a full data set. Overall, the method section is too weak.

The overall impression is that a significant work has to be made on discussing the most important facts and to avoid on long discussion on common admitted facts such as sources. A stronger discussion should be addressed on emission processes.
Then, authors should try to better compare their data with others. No attempt is made to discuss the Hg speciation data, thus I wonder if there are useful for the present study.

If not, they should be removed. Finally, a very important effort has to be made on the figures which are not of suitable quality for several aspects such as readability, scales, printing quality, etc. Some figures are also to my opinion useless and an effort should be made to combine other figures.

I feel that this manuscript could be synthesized a lot by combining different figures, results and discussion and that it should be completely revised.

Specific comments:

I. *Abstract line 10 : a "one year study" : it is wrong*
- Corrected in abstract by referring to a 10 month study

II. *Introduction*

The introduction should introduce much more in detail the state-of the art of Hg fluxes knowledge over soils in particular over agricultural ground covers, snow covers.

p2551

III. *line 7. It is commonly admitted today that the residence time of Hg is around 1 year (e.g. (Lindberg et al., 2007)*
- residence time has been updated from 2 years to 1 year in the text with the Lindberg reference added and the Mason et al (1994) and Schroeder and Munthe (1998) references removed.

IV. *line 22. Do the authors mean RGM and HgP at background sites?*

- the word "background" has been included in the text to describe the RGM and Hg^P concentrations to prevent confusion.

V. *line 25. This sentence is quite evasive and the references are not up to date. Do you mean that 95% of atmospheric mercury accumulates in the soil? "Accumulate" is not the proper word. There are recent model that suggest that a global flux of 33 Mmol/y is deposited on earth with 55% deposited on terrestrial surfaces (Mason and Sheu, 2002). There is confusion between soil and terrestrial ecosystem (that include vegetations that could play a role on the deposition fluxes).*

- References to Lindberg et al (2007), Mason and Sheu (2002) and Mason et al (1994) have been added along with land and ocean Hg flux estimates to indicate that land surfaces are currently believed to be a sink of Hg.

VI. *p2552 line14. "one short-coming..." . I did not go through all the references, but Obrist et al.'study has been conducted over 1 year! The author's statement is therefore wrong. What about your table 3, it seems that there are many other annual studies.*

- the paragraph has been re-written to clear up the confusion between GEM flux experiments versus GEM, RGM and Hg^P concentration experiments. The current study conducted collocated flux and concentrations experiments over the same agricultural soil for the ten month study period.
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Methodology

VII. *p2553 Reading the first line, I realise that the study has started on November 1st, while theabstract says that it started on July! Then November 1st to august 13th cannot be considered as a full year. Almost 1/4 of the year is missing. I am concerned about your definition of the fall season that will be use in the next section. This season, probably defined for the period sept 21st to dec 20th, is reduced to 1 month and the half. The measurements period and missing data have to be clearly defined.*

- the abstract has been changed to reflect the start of the mercury measurements as of November 2006 (other components of the field campaign actually started in July 2006 and hence the confusion in the dates). The reviewer is correct in assuming the Fall period only has 1.5 months of actual data and thus the "fall" aggregate numbers may be biased. Table 2 in the manuscript, however, gives the data for Hg species concentrations and GEM flux on a monthly basis such that readers can get a better idea of the Hg behaviour over the monthly period.

VIII. *The authors do not mention the influence/presence of agricultural work on their station that may disturb their measurements: mechanical tools, important soils disturbance, watering, etc.*

- A description of agricultural work conducted during the study has been added to the manuscript. This work (tilling, manure application, sowing) occurred over several days spanning a three week period. In addition, the crop was not subject to manual irrigation. All natural precipitation events are shown in Figure 10.

IX. *line 15 : "the top soil average (...)" . An average value is presented. I assume that it is a total mercury concentration (it should be mentioned). How is this average calculated? have several samples been collected ? Where, when? Or do the authors assume that the THg content is constant throughout the year ?*

- clarification has been added to give the reader a better understanding of the methods used.

X. *line 16: Acid digestion is not enough to analyse a mercury concentration.*
- included in the edits for the above comment.

XI. *line16: How is calculated ' 0.006 '? What does it represent? You cannot have a better precision for you error (0.006) that for your mean value (0.05). This is not consistent. In that case, you should write 0.05 0.01 or if applicable with your method 0.050 0.006. There are several mistakes throughout the manuscript, and I encourage the authors to check all the values (including their tables)*
- The mean should have been reported to three decimal places (i.e. 0.050). The standard deviation is calculated based on the concentrations of 7 different composite samples collected over three different periods.

p 2554

XII. *have several problems to understand the instrumental set up and I want to make sure that a reader can understand.TGM total gaseous mercury comprises Hg plus a portion of gaseous Hg(II). Usually, if a filter is used (and/or a sodalime trap) at the inlet sample port, Hg(II) would probably not pass the filter and thus the 2537A unit determines the GEM concentration only. The setup is not described enough but I assume that a Teflon or equivalent filters is used at the sample inlet port (or perhaps two as it is usually prescribed: one for the sample inlet and one outside). Unless the authors have done some tests, I think that TGM should be replaced by GEM or Hg .*
- Teflon filters were used in the experimental setup at the inlets of the sample lines as well as at the inlet of the 2537A. As such, the authors agree that the term "GEM" is a better descriptor than "TGM" of what is measured by the 2537A analyzer. As such all "TGM" references regarding measurements made by the 2537A analyzer have been switched to GEM.

XIII. *Are the micromet data available on the tower? Are measurements carried out at a height of 8.5 m?*
- Wind speed and direction were measured at 8.5 m while solar radiation, air temperature and relative humidity were measured at 1.5 m. This has been clarified in the manuscript.

XIV. *A method detection limit for RGM and PHg has to be shown/evaluated to discuss the data presented later. You should evaluate the precision too.*
- The denuder preparation, sampling time and maintenance operations were done as detailed in Landis et al., 2002 and thus the method detection limit is expected to be $3.1 pg m^{-3}$ with a sampling time of 2 hours. This is mentioned in the manuscript.

XV. *Why did you use such a high flow rate whereas the typical flowrate of 2537 is 1.5 lpm?*
- The GEM flux system sampled at a rate of 10 l min^{-1} while the 2537A sampled a sub-volume of this at 1.5 l min^{-1}. This allowed the 2537A to switch between either the upper and lower sample intake without any accumulation or stagnation in the line. When the 2537A was sampling from one intake, a smaller pump would equalize the flow on the other line at 1.5 l min^{-1}. This has been clarified in the manuscript.

XVI. *Where is exactly located the pump? Is it contamination-checked?*
- A Teflon® lined vacuum pump was used and located at the end of the sampling line after the Tekran 2537A sampling intake. Refer to paper

XVII. *Why didn't you try to measure RGM fluxes ?*

- RGM fluxes cannot be measured due to the long sampling time (2 hours) and desorption time (1hr) which prevents to capture variations in concentration. A RGM and Hg^P value is obtained every 3 hrs.

XVIII. *line 25 why don't you use GEM data from the speciation unit???*

- The sampling inlet for the speciation unit was located at 1.5m while for TGM flux measurement, the inlets were at 2 different heights with the lower intake 0.35m above ground cover and the upper intake 0.85m higher.

p2556

XIX. *line 21 I am not sure that the mean GEM value can be really compared to other sites since the other studies show seasonal means, or multiyear averages. Why do the author not include all the data cited in the introduction in their table 3 (Edward 2005;obrist, Engle?)*

XX. *line 24 "the behaviour of TGM (...) displayed diurnal patterns with highest concentrations recorded at midday". From your figure1, this conclusion cannot be drawn. Winter values are: at midday, gem is 0.95, around 0.98 at 9 am, around 0.93 at midnight. You should put error bars. Is it statistically higher?*

- See table below for mean and std values of GEM concentrations in winter.

	Mean	***SD***	***Min***	***Max***
12:00	0.9563	0.2082	0.75	1.16
0:00	0.9332	0.1708	0.76	1.10
9:00	0.9800	0.2629	0.72	1.24

p2557

XXI. *line 3 What is an inverse trend?*

- "inverse" has been replaced by "opposite" in the revised manuscript to avoid confusion

XXII. *line5 What kind of regression analysis? What is the statistical tests used in this manuscript?*

- Details about the statistical method used and p values are given in the revised manuscript.

XXIII. *line 9 "after June (...)" the deviation is not that clear for august and authors do not have any data for September and October. How can they say that TGM is elevated in the fall in compared to the net radiation level? Is it only based on measurement carried out in November? What is the purpose of this paragraph?*

- Addressed in revised manuscript.

p2558

XXIV. *line 6 what about the winter? Is there any industrial influence?*

- The relatively higher GEM concentrations in fall and early winter attributed to higher anthropogenic activities in winter. Furthermore, Figure 5 shows the effect of wind bringing air masses with higher GEM concentrations in fall and winter.

p2559

XXV. *Line 24 : now it is a multiple regression? Please clarify in the methodology section the statistical test that were applied.*

- Details about the statistical method used and p values are given in the revised manuscript.

p 2560

XXVI. *Section 3.3.1 Why is there no data in December-January? Why is there no data in April? from figure 7, I cannot see any evidence of a more pronounced diurnal pattern (how can you derive a diurnal pattern from this graph?)*

XXVII. *line 19: high value of 130 is not visible on the figure*

XXVIII. *line 24 To which extent the soil moisture affect the flux? Does the moisture at 30 cm deep is likely to influence Hg fluxes?*

XXIX. *line 25 where do you see high TGM fluxes during the winter?*

XXX. *The facts that radiation affects the Hg flux seem to be obvious to the authors throughout the manuscript. They should mention what are the mechanisms involved in that irradiation-mediated emission? Is it photochemistry? Is it an effect of increased temperature, and indirect effect of increase microbiological activity?*

XXXI. *p2561*
line 3 that mercury is liberated from one water molecule is physically impossible.

I. *Reading Cobbett and van Heyst, I do not see this hypothesis. That the solubility of Hg*
II. *(which oxidizing state?) is lower in the ice than in the water has to be supported by a reference.*

III. *line 13 I do not see how the soil air may promote aqueous conversion of bound mercuryto elemental mercury. Do you mean that Hg is adsorbed on the soil matter (what kind of molecules) and then desorbed? or is there a chemical reduction of Hg(II) to hg . This part is quite unclear.*

IV. *line21. "A spike of TGM occurred following a major precipitation". How do you explain this phenomenon?*

V. *p2562 The snow might be considered as a source of Hg too ((Lalonde et al., 2002; Lalonde et al., 2003). Why is it not visible? What about the peaks around days 60, 70.*

VI. *line 5 When does the snowmelt occurs ? The snowmelt is known to liberate solutes in a sort of ionic pulses (Bales et al., 1993). This might be applicable to mercury(II).*

Table 1
define the seasons is this table relevant to the article? correct win by wind

- Refer to revised manuscript

Table 2 the first row is incorrect, please revise. why is there no data in march for rgm and pm

- It has been clarified in the revised manuscript that data is not available for some periods (e.g in March for RGM and HgP) due to instrument failures.

Figure 1 and figure 3 there are no error bars Are the figure 4 and 5 really useful?

Figure 7 to 10 the horizontal scale is not acceptable.

- The horizontal scales for the above figures have been changed in the revised manuscript.

Figure 9 is of really poor quality and thus difficult to read
Some typos. 2251 line11. "states" p2552 line2 "compartments. " Instead of "compartments" line 24 : these

Bales, R. C., Davis, R. E., and Williams, M. W.: Tracer release in melting snow: diurnal and seasonal patterns, Hydrolog. Process., 7, 389–401, 1993.
Lalonde, J. D., Poulain, A. J., and Amyot, M.: The role of mercury redox reactions in snow on snow–to–air mercury transfer, Environ. Sci. Technol., 36, 174–178, 2002.
Lalonde, J. D., Amyot, M., Doyon, M. R., and Auclair, J. C.: Photo–induced Hg(II) reduction in snow from the remote and temperate Experimental Lakes Area (Ontario, Canada), J. Geophys. Res., 108, 2003.
Lindberg, S., Bullock, R., Ebinghaus, R., Engstrom, D., Feng, X. B., Fitzgerald, W., Pirrone, N., Prestbo, E., and Seigneur, C.: A synthesis of progress and uncertainties in attributing the sources of mercury in deposition, Ambio, 36, 19-32, 2007.
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