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Atmospheric Chemistry and Physics Discussions

Interactive comment on "^{222}Rn calibrated mercury fluxes from terrestrial surface of southern Africa derived from observations at Cape Point, South Africa" *by* F. Slemr et al.

Anonymous Referee #2

Received and published: 9 April 2013

Overview: The manuscript entitled "222Rn calibrated mercury fluxes from terrestrial surface of southern Africa derived from observations at Cape Point, South Africa", by F. Slemr et al. describes observationally constrained estimates of terrestrial Hg fluxes from southern Africa. The analysis draws upon nearly 5 years (2007–2011) of measurements of gaseous elemental mercury (GEM) and 222Rn made at the Global Atmospheric Watch (GAW) station Cape Point. Estimated terrestrial 222Rn fluxes are combined with correlations between GEM and 222Rn during periods with elevated 222Rn to derive terrestrial GEM fluxes. The derived fluxes are corrected for 222Rn decay using an assumed transport time. As the authors point out, terrestrial Hg fluxes are poorly constrained by existing observations, particularly outside of northern mid-

latitude regions. This study therefore makes an important contribution to understanding regional terrestrial fluxes.

Overall the paper is well written and provides a good review of relevant past work. My main criticisms, described under "Specific Comments", are: (1) some important analytical and methodological details are missing; (2) the true mean Hg flux may not be properly described without weighting each 222Rn "event" by its duration; (3) excluding GEM depletion events may bias the results. Minor issues are identified under "Technical Corrections". I have also included under "Technical Corrections" some suggested grammatical corrections.

Although I have identified some important issues with the manuscript content/organization and with the analysis methodology, I expect my concerns can be addressed without major revisions. I recommend that the paper be published in ACP after the authors address the issues identified below.

Specific Comments

1. Tekran calibrations: The authors make no mention of calibration of the Hg measurements against a Tekran 2505 saturated Hg0 vapor source (or similar primary standard). This information also appears not to have been provided in the preceding work by Brunke et al. (2010). I am assuming the authors did in fact employ a primary Hg calibration standard. Therefore, for completeness, it would be helpful if the authors could include some quantitative data on their primary calibrations. This information is necessary for assessing the overall uncertainty in the measurements. Similarly, further detail on error associated with the 222Rn measurements would be helpful (e.g., quoted from Brunke et al., 2002). As for Hg, only the detection limit is quoted, thereby providing a measure of precision error alone. Here, it is at least clear to the reader that another publication (Brunke et al., 2002) can be consulted for further details on measurement error.

2. Description of data analysis protocol: The paper could be improved by inclusion

of more specific details on how the data were treated. The authors mention that they defined "events" as times periods when 222Rn was >1000 mBq m−3, and that they filtered short duration Hg depletion and pollution events. However, it would be helpful if the authors could define more quantitatively what filter criteria were used (e.g., threshold concentrations of GEM, CO, etc.). It is mentioned that the 15 min integrated GEM concentrations were reduced to 30 min averages prior to merging with other measurements, but the time resolution of the 222Rn measurements is not given. This information also does not appear to be provided in Brunke et al. (2002), while Whittlestone and Zahorowski (1998) indicate a time resolution of 45 min. Some further details need to be included for clarity.

3. Wet deposition measurements: On page 8220, the authors write "the occurrence of precipitation was investigated for 7 of the events with the highest emission and 5 events associated with the highest deposition". Prior to this statement, no mention of deposition measurements at the Cape Point station is made. Only later do the authors reference Gichuki and Mason (2013) when discussing precipitation measurements on page 8221. These measurements should be described, along with any additional relevant meteorological measurements, in the Experimental section.

4. Error in mean values: In some instances it is unclear what is represented by the error values cited for mean GEM/222Rn slopes and intercepts. Standard errors are explicitly noted in some places, but standard deviations are implied in others. For simplicity and clarity it would help if the authors could choose a single metric (e.g., standard error) and describe in the experimental section which metric is to be used, or more clearly identify each quoted error as standard deviation or standard error.

5. Time-weighting of GEM/222Rn correlation slopes during 222Rn events. It seems that a better estimate of the average GEM flux could be obtained by time-weighting each 222Rn event (i.e., weighting the event by duration). If the authors choose not to do this, they should at least provide some mention of this potential source of bias in their discussion of error (perhaps along with discussion of 222Rn decay on page

8220).

6. Contribution of RGM deposition to total Hg flux: On page 8220 the authors cite the measurements of Sorensen et al. (2010) as demonstrating that reactive gaseous mercury (RGM) concentrations in the marine boundary layer around southern Africa are small. Considering that the Sorensen et al. dataset is limited to a short time period in the context of the present dataset, I don't think the Sorensen et al. measurements are fully adequate to support the authors' conclusion that RGM makes a minimal contribution to Hg flux in the region. It seems that the Brunke et al. (2010) analysis is far more relevant to estimating the potential influence of RGM deposition on the overall Hg flux as observed at Cape Point. Brunke et al. indicate that GEM depletion events at Cape Point are "numerous". Presumably these events are associated with enhanced RGM production and deposition. It seems it would be helpful if the authors could test the sensitivity of their results to incorporation of the GEM depletion events into their 222Rn event analysis. I understand this may not be feasible, but if so it would strengthen the analysis.

7. Correction for 222Rn decay: It would be helpful if the authors could provide a brief description to justify the assumed 2 day transport time that was used to correct the derived GEM fluxes for 222Rn decay.

Technical Corrections

1. Title: The authors might want to consider shortening their title. To do so, they could eliminate "derived from observations at Cape Point, South Africa" or "South Africa". I also suggest inserting "the" between "from" and "terrestrial"

2. Abstract; "emission ratio" vs. "flux ratio": The authors refer to the GEM/222Rn "emission ratio" in the Abstract, but use the term "flux ratio" elsewhere. Through their discussion, they demonstrate that the 222Rn flux is always positive. However, since the same is not true for GEM (i.e., the flux is bi-directional), it seems that, in the context of the present analysis, "flux ratio" is more appropriate than "emission ratio". Thus, only

"flux ratio" should be used.

3. Abstract: I suggest the authors replace "with 0.0030 pg mBq–1 being the standard error of the average" with a more shorthand notation.

4. Introduction, page 8214, first sentence: In the second line, as written, "which" refers to the noun "environment" not "methyl mercury" as intended. The sentence should be restructured. Consider "because of its transformation in the aquatic environment to methyl mercury, which. . ."

5. Introduction, page 8214, second sentence: As written here, "which" refers to the noun "atmosphere" not "mercury" as intended. Also, "the" should be inserted between "due to" and "long".

6. Introduction, page 8214: Consider rewriting "with 2880 t yr$-$1" as "(at 2880 t yr$-$1)". Consider inserting "," between "source" and "followed" in the same sentence.

7. Introduction, page 8214: Consider rewording the last sentence. The phrase "more uncertain by about $\pm$50%" is confusing.

8. Introduction, page 8215: I suggest using the term "half-life" rather than "half-time" for consistency.

9. Introduction, page 8216: Consider rewriting "a micrometeorological technique of the modified Bowen ratio" with "the modified Bowen ratio micrometeorological technique".

10. Introduction, page 8216: Consider rewording the second-to-last sentence. It is unclear whether the "discontinuous" GEM measurements continued after September 1995.

11. Section 2, units and conventions: It would be helpful to add that times mentioned throughout the paper are given in UTC. Also, it would be helpful to indicate that upward fluxes are considered positive, while downward fluxes are considered negative.

12. Section 2, page 8217: For clarity, please indicate whether the reported flow rates

and GEM concentrations are scaled to standard temperature and pressure.

13. Section 2, page 8217: In the sentence beginning "It is capable. . .", "It" should be replaced with "The Tekran 2537A" for clarity.

14. Section 2, page 8218: I suggest replacing "orthonormal" with "orthogonal".

15. Section 2, page 8218: In "had been installed at Cape Point", replace "had" with "has".

16. Section 2, page 8218: Although they are fairly common, the agency acronyms (e.g., NOAA ESRL, NILU) should be defined on first introduction for completeness.

17. Section 3, page 8218, first sentence: The phrase "more than a day or more" is redundant and should be truncated to "more than a day".

18. Section 3, page 8218, second sentence: Here, "in agreement with the climatology of Cape Point" is ambiguous, though it can be reasoned that the authors are referring to wind direction. Please clarify.

19. Section 3, page 8218: In the sentence beginning with "56", it would be preferable to write out "Fifty-six".

20. Section 3, page 8218: I suggest rewording the second-to-last sentence since the analysis considers bi-directional terrestrial Hg flux, not just emissions.

21. Section 3, page 8219, first sentence of the last paragraph: I suggest inserting "the other" between "and" and "for 06:00 UTC".

22. Section 3, page 8219: The dates and flux ratios cited here seem to be inconsistent with those presented in Figure 4. Additionally, the panels of Figure 4 are referred to as "upper" and "lower", whereas the panels are published side by side. These discrepancies need to be corrected.

23. Section 3, page 8220: The reference to Griffiths et al. (2010) regarding the terres-

trial 222Rn flux for southern Africa is somewhat confusing as the Griffiths et al. paper considers Australia, not South Africa. Some clarification would be helpful here.

24. Conclusions, page 8222: Shouldn't the end date be December 2011, not "December 2009"?

25. Conclusions, page 8222: I suggest rewriting "was with -0.01 ± 0.34 ng m-2 h-1 (standard error with n = 191, after correcting for 222Rn decay) not..." as "was -0.01 ± 0.34 ng m-2 h-1 (standard error with n = 191, after correcting for 222Rn decay), which is not..."

26. Figure 1: It would help to include the heading "Month" below the x-axis. Also, it seems that the caption should refer to "monthly" event frequency, not "seasonal" frequency. I suggest rewriting "all 222Rn events" as "222Rn events ("all")" and inserting "("significant")" after "correlations". I also suggest adding to the caption a brief description of the event criteria (e.g., 222Rn > 1000 mBq/m3).

27. Figure 2: As it is impossible to achieve a significant slope of 0, the bin for "significant" slopes centered at 0.00 pg mBq-1 in this plot is somewhat confusing. I suggest including the range of slopes included in each bin (or at least in the bin centered at 0). Also, I suggest changing "Signif" to "significant" in the legend, to be consistent with Figure 1.

28. Figure 3: I suggest rewriting "Intersect" as "Intercept".

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 8213, 2013.