"A 2-year record of atmospheric mercury species at a background Southern Hemisphere station on Amsterdam Island" by H. Angot et al.

Response to referee comments by Referee #2.

We would like to thank the anonymous referee for its time and useful comments towards the improvement of our manuscript. We provide below a point-by-point reply to the comments (points raised by the referee in bold, changes made in the manuscript in italic).

1. A general area for improvement

I would like to see more quantification of the results. For example, how much of your data set (what fraction) was defined as high and low GEM events (and high RGM/PBM). Of these, how many were associated with local surface emissions/long range transport/unknown, based on the radon data? There is no time series for the whole period for radon, so the reader cannot even estimate the number of "radonic storms".

Quantitative statements have been added in the revised manuscript. The occurrence of high GEM events was less than 1% in 2012 and 2013. Based on the Radon data, about 50% of high GEM events were associated with long range transport. Only one event was associated with local surface emissions, and the remaining 50% were of unknown origin. 3% and 18% of RGM and PBM measurements, respectively, were above quantification limit (RGM and PBM events). The occurrence of radonic storms was about 4% in 2012 and 7% in 2013.

I found the paper to be somewhat under-referenced, with a few too many used of "e.g. [single reference]" where the citation was not a review paper.

We agree with the referee. References have been added in the revised manuscript.

2. Specific comments

p. 14440

l. 10-11: From the text I believe the lower end of the RGM and PBM ranges given is actually the estimated detection limit (DL) value that you have replaced the <DL data with. Therefore the range would be better stated as "<DL-4.07" etc. Or just report the maximum.

This has been changed in the revised manuscript: *"mean: 0.34 pg/m^3 [range: <detection limit-4.07 pg/m^3] and mean: 0.67pg/m^3 [range: <detection limit-12.67 pg/m^3]"*.

l. 23: "exposition" should be "exposure"

Corrected.

p. 14442

l. 14: The island is downwind, not upwind, of Africa (based on Fig. 2).

Corrected.

l. 20: "…and carbonaceous aerosol".

Corrected.

p. 14443

l. 1-2: "…in detail by Polian et al. (1986) and relies on…the decrease in alpha radioactivity…"

Corrected.

I would prefer here, since it is relevant to much of your discussion and is not as familiar to the Hg community, a sentence of two describing how 222Rn is differentiated from 220Rn/212Pb.

We have provided additional information in the revised manuscript: "*The method is described in detail by Polian et al. (1986) and Kritz et al. (1990). It is assumed that* ^{222}Rn *and* ^{220}Rn *are in radioactive equilibrium with their short-lived daughters so that* ^{222}Rn *and* ^{220}Rn *concentrations can be calculated by measuring the concentration of their short-lived decay products. Upon formation these short-lived daughters are quickly and irreversibly scavenged by aerosols and sampled by filtration. The detection then relies on the measurement over time of the decrease of alpha radioactivity of these aerosols".*

l. 6: define CRDS acronym.

Definition added in the revised manuscript *("cavity ring-down spectroscopy").*

l. 19-21: "we have monitored…the latter consisting of various oxidized…and hereafter defined as…"

Corrected.

p. 14444

l. 7: clarify that the sodalime trap and 0.2 micron filter are past the RGM and PBM collector in the sample train.

Clarification has been added in the revised manuscript: *"In order to protect the two gold cartridges against deleterious compounds such as acid gases and halogen compounds, and against particulate matter, the sample air stream – after exiting the speciation unit – was pre-filtered through a sodalime trap and a 0.2 µm PTFE filter"*.

p. 14445

Perhaps it is a Northern American bias on our part, but I agree with the first reviewer that I would like to know how your QC criteria compare with AMNet/CAMNet ones that are published (Steffen et al., 2012).

The quality control software used in this study includes a lesser number of automatically generated flags than protocols of AMNet/CAMNet (Steffen et al., 2012; see Annex), requiring additional interpretation before validating/invalidating data. To ensure uniformity across the network, GMOS is currently developing a QC software. An intercomparaison of GMOS and AMNet QC softwares will be undertaken.

l. 18-20: How much does the replacement of your <DL data with the DL change your statistics? It will bias your mean on the high side, and it may be appreciable given the low levels. I recommend you check and report if the mean using the actual measurements is appreciably different.

We agree that this will bias our mean on the high side. In the revised manuscript another method is used to calculate the mean (same result obtained than using the substitution method) and we compare it to the mean obtained using the actual measurements: *"The mean of the distributions was estimated using the Kaplan-Meier cumulative proportion-based method. It provides more reliable results for data sets containing below-detection limit values than the substitution method, i.e. replacement of below-detection limit values by a constant equal to 0, 0.5 DL or DL (Helsel, 2005). 75% and 50% of RGM and PBM measurements, respectively, were below the limits of detection resulting in differences for mean values up to 60% and 15%, respectively, comparing Kaplan-Meier and normally averaged datasets"*.

p. 14446

l. 9-10: "Precipitation was very frequent with total precipitation of 1262…"

Corrected.

l. 13: "peaking…" should be "peaked during winter months when the roaring forties were…"

Corrected.

p. 14447

l. 9-11: "did follow" should be "followed"

Corrected.

l. 20: "where" should be "were"

Corrected.

l. 29: Is there a reference for EBC? Sciare as well? Perhaps reword this sentence so that it is clear which two compounds are "commonly used as tracers for BB".

Yes the reference is Sciare as well. This sentence has been rephrased in the revised manuscript: *"…concomitant seasonal maxima on Amsterdam Island of CO (Gros et al., 1999), equivalent black carbon, non-sea-salt potassium and oxalate (Sciare et al., 2009), the latter two being commonly used as tracers for biomass burning"*.

p. 14448

l. 4-8: Is this defining the question you address in this section? If so, that is not clear as written.

It should be clearer now: *"…the rapid export of air from southern Africa to the subantarctic Indian Ocean could constitute a major source of pollution to southern mid-latitudes. The influence of continental air mass advection on GEM concentrations was thus investigated"*.

l. 21: "a few mBq m-3 only" is unclear. Why not have a threshold like you do with 222Rn? 5 or 10 mBq?

We totally agree. In the revised manuscript we now use a threshold of 3.7 mBq/m^3 (Williams et al., 2001).

p. 14449

Why is the back trajectory for the 13/12/12 event only 4 days instead of 7 like the others? Can you quantify the scale of the transport compared to other events, if you can't draw the 4 maps on the same scale?

The 4-day-trajectory for the 13/12/12 instead of 7 was a misprint. Thank you for noticing. In the revised manuscript the 4 trajectories are now on the same map.

l. 9: "On the contrary" is not used correctly. You can omit and just say "Most high GEM events…"

Corrected.

l.10, 13: again, "only a few" and "low" 220Rn activity is confusing. It would be much clearer if you quantify as you do for 222Rn and wind speed.

Corrected, please see above.

l. 14-15: Was GEM not correlated with 220Rn in this event?

No it was not. Results from the Spearman test have been added in the revised manuscript ($r = -0.27$, p-value = 0.295).

l. 18-21: Discuss the limitations of back trajectory models, i.e. back trajectories are increasingly uncertain as you go further back in time, and you are looking at 7 days back. They are also limited by meteorological measurement density, which is low over oceans. Dispersion models give more information about the region of influence; HYSPLIT does have an online dispersion model as well.

We used back trajectories calculated using the HYSPLIT model as this approach is well established and widely used. We nevertheless agree with the referee that back trajectories are uncertain and a short discussion on the limitations of back trajectory models has been added in the revised manuscript: *"Calculated back trajectories always have some uncertainty arising for example from the possible errors in input meteorological fields and the numerical methods used (Yu et al., 2009), and increasing with time along the path (Stohl, 1998). As suggested by Jaffe et al. (2005) it should be noted that back trajectories only give a general indication of the source region"*.

p. 14450

l. 7-8: How did you determine this? By removing those events and comparing the means? If it is based on the mean=median the "Indeed" is misleading.

l. 8-14: Is there a seasonality to the difference between mean and median? This would suggest that one would have to be aware of the season in order to use the Amsterdam Island concentrations as regionally representative. There isn't enough information here for the reader to answer these questions.

Yes the fact that high and low GEM events do not significantly affect the mean was checked by removing low and high GEM events and comparing the means. The difference between mean and median did not show any seasonal variation (this sentence has been added in the revised manuscript).

p. 14451

l. 1-3: Did you explore the relationship between precipitation events and RGM or PBM levels to test this assumption? Even just dividing the data set between days with and days without precipitation, similar to your seasonal box plot? Or was there precipitation every day?

Yes we explored the relationship between precipitation events and RGM/PBM concentrations. No statistically significant correlation was highlighted, likely due to the very low percentage of RGM/PBM measurements above quantification limit.

l. 5: omit "primary" and "an"

Done.

l. 6: "Due to its short lifetime…"

Corrected.

l. 6-7: add "in the boundary layer"? As mentioned, RGM can be transported further in the free troposphere.

Done.

l. 10-11: I believe it is GEM that evades from DGM, not RGM, and the cited reference supports my interpretation. RGM is far too soluble to come out if solution. It there is another reference that suggests evasion of RGM, please correct the reference.

You are correct. This sentence has been removed in the revised manuscript.

l. 18: remove "at stake"

Done.

l. 22: (next pg): I guess you didn't have radiation data? Did you look at diurnal patterns in RGM? Also, why so much detail about methane and temperature, unless you would like to draw the conclusion that OH is not a significant oxidant of GEM, in which case please be explicit.

No we do not have radiation data. We explored the diurnal pattern in RGM concentrations but no diurnal trend could be highlighted, likely due to the very low quantification frequency of RGM measurements. Similarly, no correlation was found between RGM concentrations and temperature. Our conclusion is not that OH is not a significant oxidant of GEM, but that based on such a scarce dataset of RGM concentrations above quantification limit (n=87) no correlation can be highlighted between RGM and other parameters. We have tried to clarify that in the revised manuscript adding the

following sentence: *"The lack of correlation between RGM concentrations and other parameters may come from the small number of RGM measurements above quantification limit (n=87)"*.

p. 14452

l. 12: I would consider March-April to be fall, not late summer. Also, please clarify the relevance here.

This paragraph has been reorganized in the revised manuscript: *"More frequent RGM events between December and March could also be in line with an enhanced biological activity in summer. The production of halogen species, photochemically oxidizing GEM, could be driven by biological activity (Gschwend et al., 1985). Unlike the oceanic region surrounding Amsterdam Island, an area located in a southwest upwind sector covering the subtropical front (see Figure 8) is highly productive, with a marine productivity (characterizes by chlorophyll-a concentration) peaking from December to January and sometimes in March-April (Sciare et al., 2009), in agreement with peaks of RGM events. Similarly, marine organic aerosol concentrations at Amsterdam Island have been shown to be directly related to the seasonal cycle of chlorophyll-a (Sciare et al., 2009) and dimethylsulfide (DMS) concentrations peaking in summer have been reported on the island, in line with an enhanced biological activity (NGuyen et al., 1990;Sciare et al., 1999)."*

l. 14-15: What point sources would emit PBM, if it originates by adsorption of gaseous species onto particles? I would suggest that PBM may also include crustal minerals that contain Hg. Omit "GEM or" and "primary".

We have corrected this sentence in the revised manuscript: *"PBM is associated with airborne particles – e.g., dust, soot, sea-salt aerosols or ice crystal -, or originates from the adsorption of reactive mercury onto particles (Lu and Schroeder, 2004)"*.

l. 15-17: Agree with reviewer 1, more references needed.

Rutter and Schauer (2007) and Amos et al. (2012) have be included as references in addition to Steffen et al. (2014).

l. 23-25: Were there also twice as many high GEM events in 2013? Did the high GEM and high PBM events coincide?

No the number of high GEM events is quite similar in 2012 and 2013. High GEM events did not coincide in time with high PBM events.

p. 14453

l. 2-4: Please reword this sentence for clarity and grammar.

This sentence has been rephrased in the revised manuscript: *"However, biomass fire counts reached a maximum between June and September while PBM events peaked later, between August and October"*.

l. 9-14: Could the discrepancy between AOD/PBM and emissions be related to dry and/or wet deposition rates? Or particle growth rates? Probably beyond the scope of this paper but I am curious.

We are currently investigating fluxes of mercury in the marine boundary layer around Amterdam island using GEOS-Chem. Our study partly focuses on dry/wet deposition rates and this is definitely something worth investigating.

Fig. 3: Caption indicates "hourly-average…PBM…and RGM", which I believe is incorrect.

Corrected.

Fig. 5: (AND throughout text): "Fire counts" (not "fires counts").

Corrected.

Fig. 6: It is hard to distinguish 222Rn, 220 Rn and wind speed. Please enlarge figure and consider using different colors. Also, I agree with reviewer 1 that dGEM should be aligned on the x-axis.

In the revised manuscript dGEM has been aligned on the x-axis and different colors have been used to distinguish 222Rn, 220Rn and wind speed.

Fig. 7: Why is (a) a 4-day back trajectory and the rest are 7-day? Also, is it possible to fix the output maps such that the reader can see the comparative scale of the four event back trajectories (i.e. have them all on the same map)?

The 4-day-trajectory for the 13/12/12 instead of 7 was a misprint. Thank you for noticing. In the revised manuscript the 4 trajectories are now on the same map.

Fig. 8: Please state how events are defined.

This has been added in the revised manuscript: *"…events, i.e. number of measurements above detection limit"*.

3. References

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4. Annex

Flag comparison for GEM and speciation parameters. NA indicates no common flag for the program.

Flag Code This study	Flag Code CAMNet	Flag Code AMNet	Flag description
GEM parameters			
NA	V01	B2	Baseline voltage change
NA	V02	NA	Hg concentration high
NA	V03	E1	Hg concentration low
E5	V04	E5	Same cartridge difference > 10%
A1	V05	A1	Cartridge A/B difference
A2	I05	A2	Cartridge A/B difference
BL1	V06	B1	Baseline voltage low
NA	NA	B0	Baseline voltage low
BL2	V07	B3	High baseline deviation
NA	NA	B5	High baseline deviation
NA	V08	NA	Below detection limit
NA	V09	M2	Multiple peaks detected
NA	NA	M3	Multiple peaks detected
NA	I09	NP	No peak detected
V1	V10	V5	Questionable sample volume
NA	NA	V7	Sample volume
NA	V19	NA	Time gap in sampling records
NA	V99	NA	Standard addition recovery questionable
NA	NA	F1	Calibration interval
NA	NA	F2	Invalid flag – calibration interval
NA	NA	R_1	Detector sensitivity
NA	NA	R_2	Invalid flag – detector sensitivity
NA	NA	C5	Calibration change
NA	NA	C0	Calibration change
NA	NA	Z1	Calibration blanks
NA	NA	Z2	Invalid flag – calibration blanks
NA	NA	C1	Calibration trap bias
NA	NA	C2	Invalid flag – calibration trap bias
Speciation parameters			
P1	V22	P1	PBM desorption questionable
G1	V23	G1	RGM desorption questionable
NA	V24	S0	High desorption zero value
S1	NA	S1	High desorption zero value
NA	V25	NA	Leak check
NA	V26	P0	No PBM observed
NA	V27	G0	No RGM observed
NA	I98	L1	Invalid desorption cycle
V1	I98	NA	Incorrect sample volume
E0	I19	E0	After desorption