

“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 #1.

We thank this anonymous referee for very insightful questions and comments. 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

The work needs to include a more critical discussion of the limitations of the RGM and PBM measurements in the context of the identified sampling biases and artifacts (Gustin et al., 2013;Huang et al., 2013;Lyman et al., 2010;Malcolm and Keeler, 2007;Talbot et al., 2011). At this point, the weight of evidence is clear – RGM and PBM suffer from serious biases and interferences (Jaffe et al., 2014). The authors acknowledge that the KCl denuder has problems with collection efficiency, but do not discuss what this means for reliability and interpretation of the Amsterdam Island dataset. There is probably meaningful information embedded in the RGM and PBM that can be defensibly interpreted (e.g., elevated PBM associated with African biomass burning), but not all aspects of the RGM and PBM data are reliable and these need to be more openly acknowledged. For example, the RAMIX intercomparison conclusively demonstrated Tekran RGM concentrations are biased very low (Gustin et al., 2013;Huang et al., 2013). And Rutter et al. (2008), Talbot et al. (2011), and Malcolm and Keeler (2007) have all published studies suggesting PBM is biased as well. All of this work suggests we cannot trust the absolute magnitudes of Tekran RGM and PBM. This then places serious limitations on how useful RGM and PBM data are for model evaluation and development, so I’d like to see the authors be more thoughtful about how exactly they suggest modelers (or policy makers) use the Amsterdam Island data.

We fully agree with the referee that RGM and PBM suffer from serious biases and interferences and that we cannot trust the absolute concentrations. We have added a more critical discussion in the revised manuscript: *“There is growing evidence that RGM and PBM measurements might suffer from significant biases and interferences (Lyman et al., 2010;Gustin et al., 2013;Jaffe et al., 2014). Several studies highlighted the inefficient collection of gaseous oxidized mercury compounds with a KCl-coated denuder in the Tekran technique (Gustin et al., 2013;Huang et al., 2013), leading to an underestimation of reactive mercury concentrations by a factor 1.3 to 3.7 (Huang et al., 2013). Other studies suggested sampling artifacts for PBM measurements due to temperature or sampling duration (Malcolm and Keeler, 2007;Rutter et al., 2008). Moreover, the upper size cut-off diameter at 2.5 μm raises concerns about mercury associated with large ($> 2.5 \mu\text{m}$) particle fractions (Kos et al., 2013), especially in the marine environment where mercury is likely mainly contained in coarse sea salt aerosols (Talbot et al., 2011;Feddersen et al., 2012). There is no robust calibration technique of the Tekran speciation unit and no certified reference material available. The precision of RGM measurements - shown to be of 15% under given conditions (Landis et al., 2002) – should be assessed in various sampling environments (e.g., varying ozone/relative humidity conditions). Given the limitations of the RGM and PBM measurements, data reported in this study should thus only be directly compared with the existing Tekran-based literature, as suggested by Wang et al. (2014). An*

extensive dataset has been gathered worldwide using the Tekran speciation technique, which is the best available automated method. Future interference and calibration tests are fundamental to validate measurements and quantify uncertainties (Kos et al., 2013), and might enable us to correct RGM and PBM data. Until then, orders of magnitude and variability in time and space of Tekran-based RGM and PBM concentrations can be used as first estimates by policy makers or to evaluate atmospheric models.”

2. Specific comments

Title: Should there be a hyphen in “2-year”. If so, please correct here and elsewhere in the text.

Corrected.

Page 14440

Lines 2-3: “Scarcity of mercury species records in the Southern Hemisphere is a critical weak point for the development of appropriate modeling and regulation scenarios”. It is debatable whether or not the lack of Hg speciation measurements in the SH is actually a “critical weak point” for modelers and regulators. For example, I would content that uncertainty in the atmospheric chemistry or anthropogenic emission inventories are more serious weak points. The second half of the sentence is also not helpful because it’s unclear what you mean by “appropriate modeling and regulation scenarios”. I strongly suggest revising or replacing this sentence.

Agreed. In the revised manuscript we have changed that sentence to: *“Although essential to fully understand the cycling of mercury at the global scale, mercury species records in the Southern Hemisphere are scarce”*.

Lines 14-15: “Lowest concentrations of GEM” is grammatically incorrect.

Corrected.

Line 17: I suggest deleting “for further modeling studies”. First, it’s ambiguous what sort of modeling studies the author refer to and, second, the Amsterdam Island don’t are helpful more than just models and so why limit yourself to just supporting model studies?

We agree. “for further modeling studies” has been deleted.

Line 23: “were” should be “have been” and “exposition” should be “exposure”.

Corrected.

Line 26: “However, research gaps for mercury control policies at regional and global scale still remain such as our understanding of mercury sources, atmospheric chemistry or deposition processes (Selin et al., 2007)”. First, the grammar of this sentence needs to be corrected. Second, what’s being said isn’t helpful because it’s so general. What would be helpful is a more specific statement about what knowledge gaps are really limiting Hg regulations? You may find Selin (2011) or Selin (2014) helpful for ideas and references.

We agree with the referee. In the revised manuscript we have changed that sentence to: *“However, research gaps limiting mercury reduction policies at regional or global scale remain. For example, the policy effectiveness at reducing deposition of mercury requires a better knowledge of the chemistry of atmospheric mercury species (Selin, 2014).”*

Page 14441

Lines 5: Ocean upwelling is not a primary source of Hg. Please delete.

Deleted.

Lines 3-8: The 10-30-60 partitioning is an original result from Amos et al. (2013) and not UNEP (2013).

Corrected.

Lines 19-22: “Nevertheless, the cycling of mercury at the global scale is not fully understood and the role of the oceans still remains unclear, mainly due to the lack of long-term records of atmospheric mercury in the Southern Hemisphere (Pirrone et al., 2013)”. This sentence needs to clarify that atmospheric observations place an important constraint on the global Hg cycle, but atmospheric measurements in the SH are not the largest uncertainty in ocean cycling. Uncertainties in air-sea exchange and carbon dynamics/particle scavenging play a much larger role in the ocean.

That is correct. We have changed the text: *“To better understand the cycling of mercury at the global scale a coordinated global monitoring network is needed (Pirrone et al., 2013), along with long-term records of atmospheric mercury species in the Southern Hemisphere and at background sites (Sprovieri et al., 2010).”*

Page 14443

Lines 19: Please rephrase or delete “most relevant”. Tekran GEM, RGM, and PBM are operationally defined and not objectively the most relevant forms to measure, rather they are the forms we can measure current instrumentation.

Corrected.

Page 14444

Lines 10: I'd recommend saying just "4h" instead of "3 to 4h" since you later say that the sampling period is 4 hours.

Corrected.

Lines 22: Is checking the permeation source frequent enough? How does it compare to other long-term measurement sites, such as Alert?

Steffen et al. (2012) recommend calibration of the permeation source at least once per year and Landis et al. (2002) when the permeation rate calibration and standard addition are off by more than 5%. At Amsterdam Island, after one year the manual injections were within 3% of the expected mercury concentrations during the manual injection checks.

Page 14445

Lines 1: How does the GMOS QA/QC protocol compare to the protocols of AMNet/CAMNet? I'm just curious for the sake of intercomparison.

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 intercomparison of GMOS and AMNet QC softwares will be undertaken.

Lines 3-13: It's confusing to state the detection limits as "better than X". If possible, please provide the actual detection limit or your best estimate.

We have provided our best estimate of the detection limit in the revised manuscript.

Lines 10-11: Landis et al. (2002) reported 15% precision for RGM and PBM. Lyman et al. (2010) and Gustin et al. (2013) have suggested that RGM interferences vary with O₃ and RH, which would suggest the precision reported in one sampling environment does not apply to sampling environments with different O₃ and/or RH levels. Please provide a justification for why the Landis et al. (2002) can apply to RGM and PBM at Amsterdam Island.

We agree with the referee that the precision/background noise might be impacted by ozone and relative humidity. However, to the best of our knowledge, the precision of replicated RGM measurements has never been studied under varying ozone/RH conditions. Our statement has been nuanced in the revised manuscript: "*...the precision of RGM measurements – shown to be of 15% under given conditions (Landis et al., 2002) – should be assessed in various sampling environments (e.g. varying ozone/relative humidity conditions)*".

Page 14446

Lines 8: “till” should be “until”.

Corrected.

Section 3.2: It would be appropriate to include a citation to (Sprovieri et al., 2010) for their review on Southern Hemisphere atmospheric Hg data. Also, please provide a rationale for why you directly compare TGM and GEM. Lastly, I suggest providing the months instead of seasons. It will be easier for Northern Hemisphere readers (likely the bulk of your readership) to follow the text.

The citation has been added in the revised manuscript: “*GEM data are lower than concentrations reported in the Northern Hemisphere but well within the expected range for a remote marine site in the Southern Hemisphere (Sprovieri et al., 2010)*”.

RGM concentrations in the marine boundary layer are usually $<10 \text{ pg/m}^3$ (Soerensen et al., 2010). The difference between GEM and TGM concentrations is then less than 1%, which is insignificant when comparing orders of magnitude.

Months have been provided in the revised manuscript, thank you for the suggestion.

Page 14447:

Line 11: “did follow” should be “followed”.

Corrected.

Line 28: Should “this assumption” be “this observation”?

Yes, corrected.

Page 14448: Is Amsterdam Island really representative of background “tropospheric conditions”? Does the marine boundary layer where you’re sampling really represent the free troposphere as well?

You are right, this is not correct. Amsterdam Island is only representative of background marine boundary layer conditions. This has been corrected in the revised version.

Page 14450:

Section 3.2.3: You might consider adding a table with summaries of the data (e.g., monthly mean, median, std dev, max, min, n) to make the Amsterdam Island more accessible for modelers. Alternatively, you could provide the QA/QC's data online as an Excel spreadsheet in the SI.

A table with the monthly means, medians and standard deviation has been added in the revised manuscript.

Based on your analysis, can you comment on the existing estimates for biomass burning Hg emissions (Friedli et al., 2009; Holmes et al., 2010)? Are they consistent with what you're finding?

It would have been interesting to investigate the correlation of Hg⁰ to carbon monoxide during winter months/biomass burning season but CO is no longer monitored at Amsterdam Island. We are currently investigating fluxes of mercury in the marine boundary layer around Amsterdam island using GEOS-Chem. Our study partly focuses on biomass burning mercury emissions from Southern Africa.

Page 14451:

Line 6: Is it a good assumption everywhere that RGM can only be transported <100s kilometers? What about RGM formed in situ in the dry upper troposphere/lower stratosphere where wet scavenging is infrequent?

The distance RGM can be transported depends on meteorological conditions. Our aim was to emphasize the fact that, due to its physico-chemical properties, RGM is quickly deposited compared to Hg⁰.

We already mention that RGM can originate from entrainment from the free troposphere.

Page 14452:

Line 3-12: Please connect this paragraph more to RGM. Its relevance is not obvious. Also, please conclude with the take home message for RGM. It's not entirely clear what the bottom line is for RGM and what are the most important controlling variables at Amsterdam Island.

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 (characterized 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).*

While enhanced photochemistry and biological activity in summer might explain more frequent RGM events at Amsterdam Island between December and March, further field studies are needed to fully understand divalent mercury formation pathways”.

Line 14: Why would GEM adsorb to particles? Does that make sense based on its vapor pressure?

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)”.*

Line 16: Rutter and Schauer (2007) and Amos et al. (2012) should be included as references in addition to Steffen et al. (2014).

Done.

Section 3.3.2: Are RGM and PBM decoupled at Amsterdam Island? Is there any influence from marine sea salt?

Yes RGM and PBM are decoupled at Amsterdam Island.

According to Feddersen et al. (2012), Holmes et al. (2009) and Talbot et al. (2011), most of divalent mercury in the marine boundary layer is present in coarse sea salt aerosols rather than gas-phase. Marine sea salts influence the marine boundary layer chemistry by scavenging soluble gases or outgassing compounds such as Cl₂ and BrCl (Hedgecock et al., 2003).

Page 14453:

Lines 22-23: Please be more specific about how your work “opens the way for new avenues in future modeling studies”.

We provide new measurement constraints on the mercury cycle.

Why are future efforts at Amsterdam Island focused on lower detection limits? Huang et al. (2013) suggest RGM is biased low by 1.3-3.7x. The detection limit issue is moot if what Huang et al. (2013) found is true at Amsterdam Island. Why go after the detection limit and not aim improve oxidized Hg measurements by addressing the biases, interferences, and lack of calibration.

We fully agree. This sentence has been changed in the revised manuscript: *“Further studies involving wet deposition, simultaneous measurements of other trace gases, and interference and calibration tests of the Tekran speciation unit are needed to improve our understanding of deposition processes and oxidation mechanisms.”*

Figure 3: Consider adding the month to the x-axis to help orient the reader.

Done.

Figure 4: The asterisk (*) to denote statistical significance looks like an outlier.

Corrected.

Figure 6: Please put dGEM under Rn 222 and align the x-axis. Then the reader can track the temporal evolution of the two together.

Done.

Figure 8: You might consider merging this with Figure 5. It would be easier to see the relationship between fire counts and PBM. Also please define “events” in the caption.

Done.

Figure 9: Please provide a bit more of a description in the figure caption, so that the figure can stand alone from the text. Right now, if I was a reader scanning the figures I wouldn't know why Figure 9 was important without digging into the main text.

Done.

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
<i>GEM parameters</i>			
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

“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/m³ [range: <detection limit-4.07 pg/m³] and mean: 0.67pg/m³ [range: <detection limit-12.67 pg/m³]*”.

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 ^{222}Rn is differentiated from $^{220}\text{Rn}/^{212}\text{Pb}$.

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 intercomparison 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/m³ (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 ($r = -0.27$, $p\text{-value} = 0.295$).

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

I. 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.

I. 5: omit “primary” and “an”

Done.

I. 6: “Due to its short lifetime...”

Corrected.

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

Done.

I. 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 of solution. If 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.

I. 18: remove “at stake”

Done.

I. 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

I. 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 (characterized 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).*”

I. 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)*”.

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

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

I. 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

I. 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*”.

I. 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 Amsterdam 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 ^{222}Rn , ^{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 ^{222}Rn , ^{220}Rn 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 quantification 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
<i>GEM parameters</i>			
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
<i>Speciation parameters</i>			
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