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## ***Interactive comment on “Statistical exploration of gaseous elemental mercury (GEM) measured at Cape Point from 2007 to 2011” by A. D. Venter et al.***

### **Anonymous Referee #2**

Received and published: 4 May 2015

Review of Venter et al. – Statistical exploration of gaseous elemental mercury (GEM) measured at Cape Point from 2007 to 2011 –

#### General comments

Venter and co-authors present a statistical exploration of a 4-year record (2007–2011) of gaseous elemental mercury (GEM) concentrations measured at Cape Point, South Africa. Firstly, this paper aims at identifying the origin of high and low mercury concentrations events using a dataset already presented and discussed elsewhere (e.g., Slemr et al., 2013; Slemr et al., 2015) and based on back-trajectories and cluster analysis. Secondly, multi-linear regression analysis was used to predict GEM concentrations from other atmospheric parameters measured at the station. The paper is clearly or-

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ganized, easy to follow and well written but overall lacks robust statistics. I recommend major revisions.

## Major comments

### 1.Cluster analysis

I generally agree with the comments of B. Denzler and will avoid duplication. Briefly, I would focus the analysis on the extreme data points. Indeed using only two clusters, most of the points lie very close to the 0.904 ng/m<sup>3</sup> threshold and results from the two clusters are very close (Fig.4).

2.Trend sign at Cape Point The authors report a decline in GEM concentrations at Cape Point over the 2007-2011 period. In contrast, Slemr et al. (2015) reported a change in the trend sign at the same station from decreasing mercury concentrations in 1996-2004 to increasing concentrations over the 2007-2013 period. How do the authors explain these contrary conclusions? 3.Back-trajectories as an alternative tool to distinguish continental/marine GEM contributions Several studies (e.g., Slemr et al. (2013) and Brunke et al. (2004)) used 222Rn measurements to determine the continental/maritime origin of air masses reaching the Cape Point station. In this paper, the authors used back-trajectories as an alternative tool in order to distinguish continental and marine GEM contributions. The hourly arriving back trajectories were divided into groups according to the time that these air masses had spent over the continent. This work needs to include a more critical discussion of results obtained by both methods and associated uncertainties. According to the authors, the errors accompanying a single trajectory are 15-30% of the trajectory distance travelled. How does it compare with 222Rn measurements uncertainties? Could 222Rn concentrations also be a tool to determine the time spent by a trajectory over the continent? Lacking any of the above, it is not clear to me what new results this paper brings to the topic.

Minor comments p. 4026 l. 8: please define SA l. 17-19: "Both measured and MLR calculated data confirm a decline in GEM concentrations at CPT GAW over the period

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evaluated”. See major comment #2. p.4028 l. 3-5: Angot et al. (2014) and Slemr et al. (2015) should be included as references in addition to Ebinghaus et al. (2002). p. 4031 l. 24-28: “Eight-day back trajectories with hourly arrival times at an arrival height of 100m (...). An arrival height of 100m was chosen since the orography in HYSPLIT is not very well defined, and therefore lower arrival heights could result in increased error margins”. I wonder why the authors used an arrival height of 100m given that measurements were carried out higher, on the top of a cliff at 230m a.s.l. p. 4033 l.21-23: “However, significant differences between these two overlay trajectory maps (...) are not that evident”. I agree, see major comment #1. p. 4035 l. 12-13: “An evident trend is observed in Fig. 6, i.e. an increase of GEM concentrations for air masses that spent more time over the continent”. Air masses spending less than 10 hours over the continent are associated with highly variable GEM concentrations. Is the mean statistically different from one group to another? This should be tested statistically. p. 4036 l. 1-3: “The average marine background GEM concentration for the entire sampling period according to the 222Rn level classification (<350 mBq/m<sup>3</sup> – as proposed by Slemr et al. (2013) and Brunke et al. (2004)) was  $0.92 \pm 0.275$  ng/m<sup>3</sup>.” I believe they rather used a 100-250 mBq/m<sup>3</sup> threshold. Does it affect the calculated mean marine background GEM concentration? l. 17-20: “When GEM concentrations were classified according to 222Rn levels, i.e. 222Rn levels > 1200 mBq/m<sup>3</sup> indicating continentally influenced air masses ((Slemr et al., 2013) and (Brunke et al., 2004)), 50% of the data was greater than 0.99 ng/m<sup>3</sup>”. Same as above, Slemr et al. (2013) used a threshold of > 1000 mBq/m<sup>3</sup> rather than > 1200 mBq/m<sup>3</sup>. Does it affect the calculated mean GEM concentration of continentally influenced air masses? p. 4037 l. 7-9: “Minimization of the RSME was attained when the number of independent variables included in the optimum solution of the equation was increased to eight, and had a RMSE of 0.1205”. Values of RMSE are very close to each other. How do you know if the small difference is statistically significant? p.4039 l.14: “a slight decrease of GEM concentrations at CPT GAW over the evaluated period”. Please see major comment #2. p.4040 l.2-3: “such analyses could be used as an alternative tool to

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distinguish between continental and marine GEM contributions". Please see major comment #3.

Figure 1: It is hard to see anthropogenic point sources. Please consider using different colors. Table 1: What about the eight-, nine- and ten-cluster solutions? Table 2: Please define WGS.

References Angot, H., Barret, M., Magand, O., Ramonet, M., and Dommergue, A.: A 2-year record of atmospheric mercury species at a background Southern Hemisphere station on Amsterdam Island, *Atmospheric Chemistry and Physics* 14, 11461-11473, 2014.

Brunke, E.-G., Labuschagne, C., Parker, B., Scheel, H. E., and Whittlestone, S.: Base-line air mass selection at Cape Point, South Africa: application of  $^{222}\text{Rn}$  and other filter criteria to  $\text{CO}_2$ , *Atmospheric Environment*, 38, 5693-5702, 2004.

Ebinghaus, R., Kock, H. H., Temme, C., Einax, J. W., Löwe, A. G., Richter, A., Burrows, J. P., and Schroeder, W. H.: Antarctic springtime depletion of atmospheric mercury, *Environmental Science and Technology*, 36, 1238-1244, 2002.

Slemr, F., Brunke, E.-G., Whittlestone, S., Zahorowski, W., Ebinghaus, R., Kock, H. H., and Labuschagne, C.:  $^{222}\text{Rn}$ -calibrated mercury fluxes from terrestrial surface of southern Africa, *Atmospheric Chemistry and Physics*, 13, 6421-6428, doi:10.5194/acp-13-6421-2013, 2013.

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Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/15/C2211/2015/acpd-15-C2211-2015->

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