

Interactive comment on “Atmospheric bromoform at Cape Point, South Africa: a first time series on the African continent” by Brett Kuyper et al.

Anonymous Referee #2

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Comment on Kuyper et al., Atmospheric Bromoform at Cape Point, South Africa. ... This manuscript discusses measurements of bromoform at a Global Atmospheric Watch station on the coast of South Africa. Coastal zones have been identified as potentially large sources of bromoform to the global atmosphere, but measurements in these regions are limited. Thus, the month long set of measurements of bromoform along the African coast is interesting and should eventually be published. However, I find myself in full agreement with the points offered by Referee #1 that the data are either over-interpreted or misinterpreted. As the authors recognize to some degree, the correlation between anthropogenic tracers (such as CO) and bromoform in certain air masses does not necessarily indicate a common source, but more likely that the sampled air masses have been exposed to multiple and independent sources. The

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authors suggest that potential anthropogenic sources include water treatment plants, but this source might be readily identified by looking at the location of any nearby plant relative to Cape Point. Further, examination of the chromatograms might also reveal a different proportion of bromocarbons (e.g., dibromochloromethane/bromoform ratio) in anthropogenically influenced air vs. biogenic and kelp emissions. Without further information, I would suggest separating (or removing) the discussion of source attribution, and focus on the statistics of the bromoform measurements, including relationships to the standard GAW measurements of CO, CO₂, CH₄, Rn, etc. As noted by Reviewer #1, a more complete description of factors such as local and regional kelp/seaweed distributions, ocean color, tidal/diurnal factors, boundary layer height (a significant factor for surface emissions!) would be useful in the data interpretation and discussion.

Beyond this major point, I had some additional comments and questions:

1) Regarding the title: I don't know that I would advertise a one-month campaign as a "time-series". This is especially the case, since there are large gaps in the month long data set. The measurements are sufficiently novel as "first-time" data. Also, I would not refer to the other trace gas data from the month long campaign as a "climatology".

2) Not to be too picky, but the authors suggest a great advantage for single location time series over measurements from cruises or airborne surveys. All measurements contribute to understanding the various sources and transport of trace gases. One could argue that the Cape Point site is less useful for bromoform, since it appears to be dominated by local sources. Further, though I don't argue interest in the measurements, the impact of bromoform emissions near Cape Point on stratospheric bromine is likely minimal.

3) Sampling/Analytical: I would appreciate a bit more detail on the sampling and analytical methods. For example, was there some length of inlet tubing prior to the sample trap; how was water removed prior to sample trap; were aerosols removed in any way? For the GC analysis, presumably the carrier gas was operated at constant pressure?

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From the listed references, a system detection limit of 0.73 ppt bromoform is reported. This is surprisingly high for the conditions and GC system used. This DL should be included in the description since the “background” levels are only 3 x this amount. For calibration discussion, you should clarify the concentration of bromoform coming from the permeation oven. It is not 100 ul of pure bromoform. It seems more like 350 ppb of bromoform based on the flows and mixing ratios reported. Was a total of 1.5 L of air added to the trap after loading the 1 – 3 loop injections of standard? Also, I am confused by the calibration curve and, related to that, how detector drift was calculated during the study. The peak area is determined for each known standard concentration; so the uncertainty is related to the peak area not the standard concentration. Why are the error bars associated with the known standard concentrations? Given the large uncertainty associated especially with the 3-loop standard injection (Fig. 2 and also in Kuyper, 2012 and 2014), how were intermediate detector drifts determined between samples? It seems that the individual uncertainties of a standard injection could add considerable uncertainty to the estimated drift and to the final mixing ratios reported.

4) Note that Poole, 2003 not in reference list.

5) Repeat comment of Rev. #1: the polar plots are very confusing in what they are showing. Please consider alternate plots to illustrate relationships.

6) P9, Bromoform time series. It is not clear what is the meaning of the standard deviation around the maximum and minimum (also in abstract). What is being averaged?

7) P 10. Line 1 Clarify. . . “the second and third events showed higher levels of bromoform compared to the first episode.

8) P11, line 9 ; high 30s ppt? should be ppb?

9) P13, fig. 10. I think Rev #1 is correct about wrong trajectories displayed for event #2. A question I have, though, is how the “event” trajectories compare to the “background” trajectories? Or if only local wind direction or 1 day trajectories are most relevant for

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this site?

10) P14, line 18. As noted in my first comment, I disagree totally with this statement.

11) P15, line 8. I don’t understand what this sentence means.

12) P16, line 12, What is biogenic ozone?

13) P16, Table 1, Since trajectories show potential sources from Southern Ocean, it would be informative to include data from cruises in the Southern Ocean. Plus, recent measurements have been reported from Peruvian upwelling regions (see ACP)

In summary, the manuscript by Kuyper et al. offers some interesting new measurements of bromoform from a coastal region of Africa. There may be some analytical issues with the measurements, but the data quality seems reasonable. A major revision is required, though, to simplify and rethink the data interpretation.

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