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Atmospheric Chemistry and Physics Discussions

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 #1

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Review of MS No.: acp-2017-244, Kuyper et al.

Atmospheric bromoform at Cape Point, South Africa: a first time series on the African continent

General comments

This paper presents some in-situ atmospheric measurements (~130 samples) of bromoform (CHBr3) from Cape Point, South Africa over a 2 month period in 2011. These are the first reported measurement of this important halocarbon from the southern African continent (although some of the data has already been discussed in Kuyper et al. 2012) so do provide a useful, if limited, new dataset. The concentrations observed are, on occasion, at the higher end of those previously reported.

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Discussion paper

I have a number of serious reservations about the measurements, the interpretation of the data and the conclusions which prevent me from recommending the paper for acceptance in its present form. I fully understand that sometimes it is difficult to draw firm conclusions from a limited set of measurements, but in this case I believe the authors are rather over-interpreting their data.

My major concerns are identified below, followed by some specific comments and suggestions.

1. The instrumental methods are not described particularly well. The authors refer to a previous publication which does have a lot more detail, but there are some outstanding questions related to the identification of bromoform (CHBr3) and the exclusion of possible co-eluting species. The electron capture detector (ECD) is not particularly specific so is subject to potential interferences in different types of air mass, particularly when trapping such large volumes of air or when sampling in more polluted environments. Have potential co-elutions been thoroughly tested for and ruled out?

2. Much of the discussion is highly speculative and potentially wrong. For example the conclusions on (a) anthropogenic sources of CHBr3, (b) ozone stimulation of CHBr3 release from seaweeds, and (c) a CHBr3 source from the upwelling region, are all highly dubious. The authors present very little firm evidence to support these theories and, to some extent, they overlook a more likely, or simpler, explanation for the high levels of CHBr3 at the site. They state that Cape Point and the surrounding coastlines for many kilometres to the north and west (and south?) support large, extensive seaweed beds. If this is true then surely the most likely origin of the high CHBr3 they observed is simply local (and regional) seaweed? The flux to the atmosphere would then be highly dependent on local tidal patterns, with large concentrations to be expected when the kelp becomes exposed to the air. Although this is mentioned briefly in one case study, which suggests that this process may be occurring further to the north, can the authors confirm that the same phenomena is not occurring closer to the site on a daily basis? Here a detailed description of the local /regional seaweed populations

would be very helpful, ideally identified on a map of the area (Figure 1?). The authors need to convince the reader that the high levels of CHBr3 are not simply from very local sources.

There needs to be a wider discussion of the tidal phenomenon as it is very likely to be the reason for the high concentrations and some, if not all, of the spatial/temporal variation. Similar, and more extensive, studies have been carried out over different seaweed areas such as Mace Head and NW France so references to these should also be provided.

3. Results section The order seems wrong. Why not start the results section by discussing the CHBr3 time series before going into the chemical climatologies? I would further suggest that you show the radon and wind direction data on the same plot as Figure 7 as this would make it much easier to spot patterns, etc. Similarly, when discussing the 3 individual episodes it would be helpful to see the same Figure expanded for the periods of interest.

I found some of the diagrams rather difficult to interpret. In particular the various polar plots (Figs 5, 6, 8). These types of diagram can sometimes be a little over-complicated. A better explanation, if not a full rethink, is required. For example, in the case of Figure 5, what do the individual circles represent? Are they individual samples or averages in a particular sector? Why is the red circle to the NE not represented somewhere in Figure 6. I would expect to see a red circle, albeit closer to the origin, in Figure 6. Perhaps this is because the colour scaling in the 2 Figures is different?

Why not show Figure 8 before Figs 5 and 6, perhaps after discussing the time series (see earlier comment).

However, before using these polar plots the authors need to explain why they would be expecting to see correlations of CHBr3 with tracers like CO and ozone. Furthermore, the argument that ozone increasing from, say, 25 to 35 ppb represents a significant enhancement of ozone is contentious. Can you really label this as “enhanced ozone”

and would you really expect such a small enhancement to have any significant effect on CHBr3 release from seaweeds? Please provide a reference to support this. Surely any ozone effect will be much smaller than the local tidal effect (which has not been discussed)?

There is no discussion of any diurnal pattern in the data. Were there measurements at night? Can boundary layer height or temperature have an impact on the observed concentrations?

4. The references to previous measurements (e.g. in Table 1) are not up-to-date. There have been a number of new studies in recent years that should be included (including a possible reference to the HALOCAT database).

Specific comments

P1, L2: why is the location “unique”?

P1, L13-14: the “sweet odour similar to chloroform” is irrelevant

P1, L14: what are these anthropogenic sources of bromoform? Please list with references. What fraction of global emissions are likely to be anthropogenic?

P1, L16: “Outgassing to the atmosphere” sounds better than “Atmospheric outgassing”

P2, L20: replace “within this region” with “in the tropics”

P2, L22: same as above

P2, L22: What is meant by “discrete shipboard measurements”?

P2, L23-24: “No time series .... Like Cape Point.”. The authors need to be careful with this sentence. Do they mean there are no time series in Africa, the tropics or globally? The latter 2 would both be wrong. Cape Point of course is also not in the tropics.

P2, L27-28: please explain why these gases might play a significant role in climate change.

P2, L31: delete “to”, i.e. “a unique location from which to measure. . ..”

P2, L33: what is meant by an “intermediate air sample”?

P3, L1: Why might the subtropical location of CP make the region be an important source bromoform? Do you mean that if the region were a strong source of bromoform then this would be significant globally? I assume this is because it is relatively close to the tropics where convection could potentially transport it to the stratosphere? Please explain this sentence more clearly.

P3, L5: “biologically active” or similar is possibly better than “highly productive”. Is the southern ocean active everywhere or just in certain regions? I assume the authors are referring to phytoplankton rather than macroalgae?

P3, L11: The location of the local and regional kelp beds is highly relevant to the arguments used later in the paper. Is it possible to indicate on Figure 1 where the main kelp beds are?

P4, L5: define the term “GC-ECD”

P4 L7: insert “the”, i.e. “as per the method”

P4, L12: What is meant by a “quasi-discrete sampling pattern”? “Quasi-continuous would be more appropriate, although you could simply say that 131 samples were collected during the period xxx to yyy.

P4, L18: Please explain what the relevance of the sentence about gas viscosity is.

P4, L20: a ramp rate of 65 degrees per minute is very fast. Why was this necessary as it surely doesn’t help with peak separation?

P4, section 2.3: there are a few details missing in this section which should be included. Was the air stream dried before pre-concentration? How did you measure the volume of air trapped? Did the system trap CO2 and, if so, how did this affect the chromatography? An example chromatogram would also be helpful as well as some

discussion on possible co-elutions (see earlier comment).

P5, calibration section: this section needs some further clarification as it is not clear how the calibration was done. How does 100-300 μl of pure bromoform equate to a concentration? Was it diluted prior to trapping? What is meant by a calibration loop? How were the 99% accuracy and 12% precision estimates derived?

P5, Figure 2: Normally the fixed entity (mixing ratio) would be on the x-axis and the variable entity (peak area) would be on the y axis? What do the error bars represent (how many samples)? Why is the uncertainty given in the mixing ratio rather than the peak area?

P6, L6: “flow path” not “flow pass”.

P6, L31: What is meant by “rapid shifts” on the 19th, 29th and 30th?

P6-7: what is the significance of wind speed?

P8, L7: “Measurements of bromoform at all ranges were recorded at CO levels below 100ppb”. If this is the case why are there no red or orange circles in this CO range?

P8, L11: I fail to see the 2 periods of elevated ozone referred to.

P9, Fig.6: What is the impact of boundary layer height on the measurements? This might also explain some of the variability. I am not convinced that the observed variation in ozone is sufficient to be able to get any real meaning from the analysis in Fig. 6.

P9, L9: What are the stated uncertainties in the reported maximum and minimum measurements and how do these differ from the somewhat lower uncertainties in the mean?

P10, Fig.7: It would help if the 3 periods of interest were highlighted (shaded?) on the Figure. Can the authors say something about the very low values of bromoform on the Figure? There are a number of points very close to zero. Where does the air

come from at these times? Can the authors be sure that this is not a measurement problem – it seems unlikely that values would drop to zero in a region where bromoform is generally rather high?

P10, L4-5 and Fig.8: The wind speed associated with the higher concentrations to the NE and West seem very similar to me (one is described as “high” and the other as “intermediate to low”). I cannot really see any difference.

P10, L6: This sentence needs rephrasing. I assume the authors mean that at low wind speeds the average concentration was 30 ppt and they are speculating that this is maintained by some “low level” local sources? What does low level actually mean and perhaps showing wind speed in Fig. 7 would help the reader to see this more clearly.

P10, L12: “a background of low mixing ratios were observed from all wind directions”. How does this relate to what was said in my previous comment? Was the “background” signal 10 ppt or 30 ppt? There are no data less than 10 ppt in the N, NE and SE sectors.

P11, episodic events: it would help to have a repeat time series for these events so the reader can see the patterns/correlations more clearly. Alternatively please put all data in one Figure (Fig 7) and perhaps some more axis markers to help distinguish between days.

P11, L11 – P12, L1: The authors state that the concentration of bromoform decreased slowly between the maximum on the 18th until the 23rd. The only problem here is that there is a large gap (several days?) in the data when we have no idea what is happening. To describe this period as a single “event” is therefore a little odd.

P12-13, Event 2: The winds are predominantly from the west-north-west but the back trajectories suggest that the air is coming from the south and east. This apparent contradiction needs to be explained. In fact the trajectories in Figure 10 for Event (b) are dated November 2011, not October. Have the authors used the correct trajectories?

P13, Event 3: again it is very difficult to follow the ups and downs in the various pa-

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rameters. I find it hard to pick out 2 events in elevated ozone (line 11). Again there is a large gap with no data which makes linking the period more difficult. The authors cannot say that "bromoform rose to a maximum of 70.2 ppt" because there is a gap. P14, Section 4.1: this section is highly speculative using such terms as "circumstantial evidence" and "tentatively appear"

P14, L14-15: If air is flowing from the southern ocean in a "north-westerly direction" over Cape Town, how is it possible for this air to then pass over Cape Point which is due south of Cape Town?

P14, L18-20: there is really very little concrete evidence for this anthropogenic source and its impact on the measurements at Cape Point. There is more coast directly to the north of Cape Town so even if the air was coming from this direction and picking up anthropogenic emissions, what is to say that the bromoform and CO/radon are not coming from completely different sources?

P14, L21-22: how well do CO and Radon correlate for the entire period. It is hard to tell when they are on separate graphs using different axis ranges. It seems there are periods of high radon and low CO, but what about low radon and high CO? I assume this is unlikely if you assume a continental source for both, but it is very difficult to tell from separate figures.

P14, L30: why have you not investigated the impact of tides at the local site? (see major comment above and the next comment below).

P15, L4-5: "The extensive kelp beds at CP may contribute bromoform to both the consistent baseline and extreme events observed". If this is the case, can the presence of local kelp beds not explain the entire set of measurements? Without ruling this out, the majority of the preceding discussion is surely obsolete? Where are the local kelp beds? Are they underwater or exposed at low tide? If the latter, do you see an impact of local tide time with bromoform concentration?

P15, L6: what is meant by “other typical meteorological conditions”?

P15, L8: “quasi-continuous” is better than “quasi-discrete”.

P15, L21-22, and Table 1: Why not report some median values as well as means?

P15, L25-26: the evidence for an anthropogenic source of bromoform is not really apparent (see earlier comments).

P15, L26-27: radon CO and ozone were not all elevated throughout Event 1. CO and radon were elevated at times during the period, and it is hard to say whether ozone was elevated or not. Higher ozone wouldn’t necessarily be an indicator of recent anthropogenic influence. Were there no other tracers in the GC output that might help?

P16, L1-7: this section is highly speculative and rather confirms that no conclusions can be drawn as to the importance of any anthropogenic source. It would be helpful if some measurements could be made near to the water processing plants to confirm the levels of bromoform.

P16, L11: I cannot easily identify a period of “moderately elevated ozone”

P16, L12: How was the ozone “biogenic in origin”?

P16, L15: “from the west” - see point earlier about the discrepancy between measured wind direction and the back trajectories.

P16, L16: there is no clear evidence in this analysis that supports the theory of ozone-induced bromoform release.

P17, L6: the Benguela current is far to the north of CP according to Figure 1. How will this affect the concentrations at CP during Event 2? I do however agree that a study of the local kelp would be a sensible thing to do.

P17, L19: It has not been proven that the anthropogenic source of bromoform was strong during Events 1 and 2. This statement is inaccurate. In fact the whole of this

final paragraph is highly speculative.

P17, conclusions: The whole section will need to be rewritten once the various issues above have been addressed. I do also note that the extremely high values reported from Gran Canaria were measured many years before the majority of data in Table 1, so, with due respect to the original authors, I would perhaps treat these data carefully. There have been substantial improvements in analytical technology and calibration since these measurements were obtained.

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