Atmos. Chem. Phys. Discuss., 13, C9729–C9740, 2013
www.atmos-chem-phys-discuss.net/13/C9729/2013/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Understanding atmospheric mercury speciation and mercury in snow over time at Alert, Canada" *by* A. Steffen et al.

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Received and published: 6 December 2013

Response interactive comments by Anonymous Referee #2 on "Understanding atmospheric mercury speciation and mercury in snow over time at Alert, Canada" by A. Steffen et al. Received and published: 10 October 2013

Overview Comment #1: The manuscript sums up the atmospheric Hg species concentration and Hg in snow measured at Alert over the last ten and fourteen years respectively. Unfortunately the manuscript describes this impressive data set in language that is sometimes clumsy, and sometimes rather inappropriate for a scientific article.

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Interactive Discussion

Discussion Paper

Response: The authors thank the reviewer for this comment and have cleaned up the language in the text. The responses to particular language concerns referred to in specific comments are addressed below.

Comment #2: The findings show that a combination of very cold weather and relatively atmospheric aerosol lead to higher concentrations of Hg associated with particulate matter, and that as the temperatures warm and atmospheric PM concentrations decrease the proportion of RGM increases. The Hg in snow tends to reflect the RGM concentrations. This is not altogether a surprise.

Response: The authors respectfully disagree with this statement. To us there is no a priori reason that higher temperatures should imply that atmospheric particle concentrations will decrease, nor that PHg will decrease and presumably, following the referee, will convert into RGM. This is the first data set of its kind showing that this happens each year at the same time. Furthermore, temperatures at which published laboratory tests took place, and that were used in model calculations have not gone below -10 and -17oC respectively, while our data reflect temperatures lower than -40oC.

Comment #3: I wonder whether the results presented here might have been included in a few extra paragraphs in the article recently published in ACP by Cole et al.,"Ten-year trends of atmospheric mercury in the high Arctic compared to Canadian sub-Arctic and mid-latitude site"? I am not convinced that the results presented here merit publication in their own right.

Response: The Cole et al (2013) paper, which is cited in this paper, was a trend analysis, primarily of GEM data. That paper reported the differences between the long term monthly trends from various sites in the Arctic, sub-Arctic and temperate regions. As well, that paper presented a monthly trend analysis on atmospheric mercury speciation data. The current paper is using the long term speciation data (from Alert only) is a study of processes not trends. Thus, we present the first investigation of what factors affect the transition of one mercury species to another. We also include long term mer-

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cury data from spring time snow samples (which are presented here for the first time) and couple these with the atmospheric speciation in order to investigate the processes affecting elevated levels of mercury in the snow..

Comment #4: As the authors are investigating the relative proportions of PHg to RGM as meteorological variables and time of year change, it seems very odd that in the whole of the manuscript there is not a single wind rose, no mention of wind direction, and not a single back trajectory plot. There is also no mention of total BrO columns, which as an indicator of where Hg oxidation is actually taking place can be useful. It is difficult to see how the relative concentrations of PHg and RGM can be discussed with no mention of the provenance of the air masses being sampled. This article should either be rewritten and a more in depth analysis of the results included, or withdrawn.

Response: We thank the referee for this interesting comment. This paper addresses the processes affecting the partitioning of mercury species in the air and what happens to that mercury during the springtime period as observed at Alert. How the chemical state of the air came to be as we observed it, is an interesting but impossible question to answer with any certainty, especially in the Arctic where making "upwind" measurements is nearly impossible, especially over a long period of time. But some characteristics are known and while we may have thought that they are well known we should have included a summary here. Wind direction data have been previously reported in several papers and have shown that the air masses depleted in mercury and ozone almost always originate from the North, that is to say, from the frozen Arctic Ocean. We investigated the wind roses for different months but found no significant variation in the source region of the air masses. We felt that repetition of this information and an in depth analysis including wind roses and air parcel back trajectories would yield the same information previously published and thus would add no value to this analysis. We have added the following sentences to inform the less informed reader: "In this study we investigate what can be learned from a study of the composition of the air as observed at Alert. It has to be realized that what we see is the

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result of chemico/physical processes that occurred upwind of Alert. The origin of air masses travelling to Alert have been previously studied in depth and revealed that the large majority of mercury and ozone depletion events occur when the winds are derived from over the Arctic Ocean between 315 and 90o from Alert (Cole and Steffen, 2010) and from the north pole to the Kara Sea (Bottenheim and Chan, 2006). Another study from Alert reported that the predominant wind direction in 2005 was from the south-southwest direction; yet, when depletion events occurred, the winds tended to emerge from the north (Cobbett et al., 2007).".

BrO column data from satellite imagery are often used to infer that mercury and ozone depletion events are driven by Br chemistry, and to derive some sense of time/space scale of where this chemistry might have taken place. It is common to refer to daily maps of BrO columns as can be found in open access web sites such as from the University of Bremen (http://www.doas-bremen.de/bro_from_gome.htm). However, these maps are total density and include data from the troposphere and stratosphere combined, and a large part of the BrO density resides in fact in the stratosphere. Furthermore, more recent analysis has made it clear that not only is it not straightforward to subtract the stratospheric density from the total density number, but the troposphere is often stratified with much of the BrO density not residing in the lowest boundary layer over the surface. And it is just in this boundary layer that the depletion chemistry is active. For these reasons we feel one has to be quite hesitant to use existing total BrO density data from satellite imagery to make any statements about where depletion chemistry was in fact taking place, and refrain from using such data in our analysis. Fortunately we are using the actual mercury data itself so there is no need to use other data to identify that mercury oxidation is occurring. We do not focus on regional patterns or the spatial extent of AMDEs but rather on what happens to the mercury during the depletion events; thus, the provenance from which they came does not affect our analysis.

Specific Points Abstract Comment #5: This sentence, "In May, RGM transitions to

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be significantly higher than PHg and continues into June whereas PHg sharply drops down." is not well written. It is the concentrations of the species that are changing not the species themselves. Maybe something along these lines "In May the high PHg and low RGM concentration regime of early Spring, undergoes a transition to a regime with higher RGM and much lower PHg concentrations".

Response: The text was changed as follows: "In May, the high PHg and low RGM concentration regime observed in the early spring undergoes a transition to a regime with higher RGM and much lower PHg concentrations. The higher RGM concentration continues into June. ."

Comment #6: "Firstly, the ratio of PHg to RGM is favoured by low temperatures . . .", the high PHg to RGM ratio? I don't think that ratios themselves are favoured by any particular temperature, although they may well be temperature dependent. "partitioning of oxidized mercury to produce PHg . . ..", the authors are suggesting that oxidized Hg in the gas phase condenses on to pre-existing PM, or that RGM produces PHg in a particle formation process?

Response: Yes, the authors are suggesting that oxidized mercury in the gas phase (RGM) is partitioning onto available particles in the air and the text was changed to reflect this as follows: "Firstly, a high ratio of PHg to RGM is reported at low temperatures which suggests that oxidized gaseous mercury may partition to available particles to form PHg".

Comment #7: "The highest deposition of mercury to the snow in the spring at Alert is during and after the transition of PHg to RGM in the atmosphere." Again this seems as if the authors are suggesting that PHg becomes RGM, so it desorbs from the PM? Or are he authors referring to the high PHg concentration and high RGM concentration regimes.

Response: No, we are not suggesting that the transition from PHg to RGM is a result of the RGM evaporating from the particles to the air over the springtime. We are suggest-

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ing that the highest deposition of mercury to the snow (reported as high total mercury levels in the snow) occurs when the mercury in the air shifts from PHg to RGM.

It is generally believed that the oxidation of GEM is a gas phase reaction producing RGM. If a surface is available onto which RGM can partition, it will do that under certain conditions. Throughout the spring (from March to June) AMDEs occur and produce RGM. This RGM will remain in the gas phase, partition onto a surface or deposit to the surface. This paper investigates the distribution of PHg and RGM in the air over the springtime period and tries to explain the conditions when higher levels of PHg are measured during AMDEs during March and April and higher levels of RGM are measured during AMDEs in May. We are further investigating whether this shift or transition from PHg to RGM has an impact on the levels of Hg in the snow. Each AMDE produces new Hg+2 and thus we are investigating why the repeated PHg and RGM shift occurs during the spring season.

The sentence has been rephrased for clarification as follows: "Springtime deposition of total mercury to the snow at Alert peaks in May when atmospheric conditions favour higher levels of RGM. Therefore, the conditions in the atmosphere directly impact when the highest amount of mercury will be deposited to the snow during the Arctic Spring."

Introduction Comment #8: I agree that Hg has caused quite a stir, although it probably did it in scientific/policy/local government circles rather than in the air itself.

Response: The text has been modified as follows "Attention to mercury has increased in the scientific community over the past two decades because of the interesting springtime atmospheric chemistry in the high Arctic and its potential impact on the environment."

Comment #9: p17023, 7, drive?

Response: The text has been modified as follows: "The atmospheric processes that dominate the springtime oxidation and deposition of mercury may also lead to the

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deposition of some of this long range transported mercury onto the Arctic surface.."

Comment #10: l12, unfortunately coincidental has two meanings, perhaps contemporaneously would avoid any possible confusion.

Response: The word has been changed to "concurrent".

Comment #11: p17024, l27, "Arctic Haze is due to air masses originating from anthropogenic emissions in Europe, North America and the former Soviet Union, that are transported . . .", the air masses don't originate from emissions.

Response: The text has been modified as follows: "The well known phenomenon of Arctic Haze is due to air masses originating from anthropogenic emission source regions in Eurasia and North America that are transported to and trapped in the Arctic air"

Comment #12: p17027 I think this section could be expressed differently, and the last sentence is missing a verb. "The ambient aerosol is pulled into the laboratory through a 3m long, 10cm diameter stainless steel vertical manifold at a flow rate of about 1000 L min-1. Particles are sampled out of the manifold from near the center of the flow stream, about 30 cm up from the bottom of the manifold. From there the particles are delivered to the sampling devices via stainless steel tubing. The mean total residence time of a particle from outside to its measurement point is approximately 3 s and, at this point, the particle at approximately room temperature and the relative humidity (RH) is <50%."

Response: The text has been modified as follows: "Ambient aerosol is pulled from the outside into the laboratory through a 3 m long, 10 cm diameter stainless steel vertical manifold at a flow rate of about 1000 L min-1. Particles are sampled out of the manifold from near the center of the ïňĆow stream, about 30 cm up from the bottom of the manifold. From there, the particles are delivered to the sampling devices through stainless steel tubing. The average total residence time of a particle from when it is

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collected outside to its measurement point inside is approximately 3 seconds. Once the particle reaches the analyser it is approximately at room temperature and has a relative humidity (RH) of less than 50%.

Comment #13: p17028 Really? It sounds as if someone had a long walk! “The coolers are filled with snow and hand carried from Alert to Toronto where they remain frozen until analysis.”

Response: Hand carried does not directly imply that they were walked. The text was modified as follows: “The coolers are filled with snow and hand carried/escorted on a military cargo plane and then by car from Alert to Toronto where they remain frozen until analysis.”

Comment #14: p17030 It is not clear to me why the results and conclusions were not included in the article cited below. “Few long term mercury speciation measurements have been reported around temperate regions and only one for the Arctic (Cole et al., 2013).”

Response: As outlined earlier to comment #3, the Cole et al paper was a trend analysis while the current analysis is a process study.

Results Comment #15 :p17031“This annually occurring higher level of RGM in July is variable in concentration and unexpected but is not considered to be a result from AMDE chemistry. This study focuses on the springtime chemistry from March to June inclusive. Further in depth investigations into the annual cycling of PHg and RGM at Alert must be undertaken to explain these patterns.” I think the article would have had more weight if some more in depth investigations had been presented here. I am not sure that the manuscript focusses on chemistry, most of the discussion is about meteorological parameters, aerosol loading and physisorption/condensation.

Response: The text was modified as follows: “Future investigations into the spring-summer cycling of PHg and RGM will be important to offer more detailed explanations

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of these associations.."

Comment #16: do not know much about the meteorology of Alert, but am surprised that there is no mention of prevailing wind directions (or absence of wind) in the discussion regarding the high PHg and high RGM concentration periods. Nor of whether the RGM is produced locally or whether the AMDEs observed are due to transport of already depleted air. There is no discussion, or even mention, of the BrO columns available from satellite observations. I would have thought that this would have been useful as an indicator of when Bromine chemistry 'switched on' either locally or within a region from which air was being transported to Alert. As pointed out in the overview the total lack of any mention of wind direction, air mass origin or back trajectory plot seems incredible.

Response: Please see reply to comment #4 above.

Comment #17: Still in section 3.1, p17031 1ine 12 "trails off "?

Response: The text was modified as follows "[PHg] reaches a maximum in April and then decreases in subsequent months. In May, [RGM] is highest and it decreases in June when [GEM] begins to increase again."

Comment #18: line 14 "a transition of PHg to RGM" is this really what the authors mean? Are they suggesting that RGM is desorbing from the particulate phase?

Response: At this point in the paper, this is simply a description of what Figure 2 shows. It is evident that there is a high level of PHg at the start of AMDEs and then, during the AMDE season, the predominant form of Hg measured in the air is RGM. In other words it transitions from PHg to RGM or shifts from PHg to RGM. Later in the paper, we speculate as to why we believe this is occurring.

Comment #19: Page 17032 "In Fig. 3, both RH and AWC follow the same pattern with temperature throughout the year and a similar steep increase in both parameters is shown March to May. It can be conceivable that the transition of PHg to RGM from

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April to May could be related to water absorption by aerosols. However, we suggest that other factors affect the transition of PHg to RGM more effectively and are described below." A steep increase . . ... is observed / seen?, rather than shown. Transitions again, the authors need to be precise about the nature of the transition, concentration regime, or a physical process, as I mentioned above. Transition is used a number of other times in the rest of the manuscript.

Response: The text was modified as follows: "In Figure 3, both RH and AWC follow the same pattern with temperature throughout the year and a similar significant increase in both parameters is observed from March to May."

The authors feel that the word transition is used appropriately in the text. Transition is used to describe a switch, changeover or shift in the predominant mercury species in the air. The text in this section was modified the first time the transition was mentioned to clarify what is meant by transition in this paper as follows: ". Cobbett et al. (2007) reported a transition (or shift) in the concentration of predominant species of measured mercury in the air from PHg to RGM in the spring of 2005 at Alert. We report here that this transition occurs each year around the same time (within a 2 week period) for the 10 years of measurements."

Comment #20: p17033 Hg+2 is an unusual nomenclature, Hg(II) would be more appropriate if the authors are referring to oxidation state.

Response: The nomenclature was changed in the text.

Comment #21: p17034 The following sentence is not very clear, does it mean that PHg is a function of particle volume only at certain times of the year? "These results show that PHg is associated with higher particle volume for March and April, May is a transition month to lower particle volume and June shows no association with PHg."

Response: Yes that is correct for the months where the data was analyzed because this abundance of PHg results from a combination of high levels of Hg(II) and high

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levels of particles during this time period.

Comment #22: p17034 “The higher particle volume concentrations during January to April are linked with Arctic Haze (Barrie, 1986) and we hypothesize that the presence of Arctic haze is a significant contributor to the increased levels of PHg during this period.” I think most people would agree that the Hg compounds which make up RGM are probably inorganic and really quite involatile. The fact that when it’s very cold and the available aerosol surface area is abundant, RGM will tend to condense onto PM is not a hypothesis, it’s common sense.

Response: The text was modified as follows : “The higher particle volume concentrations during January to April are linked with Arctic Haze (Barrie, 1986; Sharma et al., 2013) and we conclude that the presence of Arctic haze is a significant contributor to the increased levels of PHg during this period either by offering a surface for partitioning processes or by particles containing mercury arriving from source regions.”

Comment #23: The sentences below need rephrasing. 23a. What is ’The atmospheric transition of mercury’?

Response: The text was changed as follows” “Further study is required to identify which types of particles dominate both the change in atmospheric mercury species and deposition of mercury in the spring.”

23b. “Each year PHg at Alert begins to increase in March and then climbs to a maximum in April and are concurrent with sea salts and Arctic haze particle increases. Further study is required to identify which types of particles dominate both the atmospheric transition and deposition of mercury in the spring.”

Response: The text was modified as follows: “Each year, PHg concentration levels in the air at Alert begin to increase in March and reach a maximum in April. This pattern is consistent with increased levels of sea salts and arctic haze particles at the same time and location.”

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