Response to anonymous reviewer #2

Steven Howell

January 2, 2014

I'd like to thank the reviewer for his or her careful attention. There were some mistakes and some weak arguments identified. I'll go through the reviewer's comments in order. They (or condensed versions) are in **bold**.

There is only one flight across the oil sands at one level. How can the authors be convinced that this one flight represents the average emissions of the industry in the region. There may be considerable day to day and week to week variability. How is the data representative? The discussion of the emissions from oil sands and boreal forest fires on page 21315 seems fraught with ambiguity.

Of course it would be absurd to claim that 2 flybys can possibly represent an average condition, so we didn't make any such statement. We did mention that it was a questionable assumption that our measured fluxes could be compared to the annual emissions at all.

That said, the decent agreement between the annual emissions database and the measured fluxes of SO_2+SO_4 and NO_x is not entirely fortuitous. The big upgrading facilities tend to run around the clock and dominate local emissions of those species, so unless we happened to go by during a maintenance period or something such, odds are high that emissions would be about average. We have had no communications with the operators of any of the plants, so we do not know whether they were doing anything atypical.

Since both reviewers complained about this, I guess it needs to be emphasized that there is no particular reason to expect our flybys to represent average conditions. I'll add it to the abstract and discuss it more fully in the discussion.

The comparison between oils sands emissions and biomass burning was the source of some controversy while writing the paper. It is not possible to do the like to like comparison as the reviewer hopes for; arbitrary choices for time and space scales of the comparison must be made. Limiting forest fire emissions to a smaller region would make the oil sands more important, while reducing the time to the summer fire season when we were there would weight the biomass-burning aerosols more. There is simply no right choice to make.

Given that, the only real role for such a comparison is to give a sense of perspective: are the oil sands aerosol emissions important compared to a large natural aerosol source. Because of the inherent ambiguity, it makes sense to do something straightforward, and annual Canada-wide fires seem as appropriate as anything.

Page 21316: there is a discussion of aerosol ageing based on two different days of sampling. How can the authors be sure that the differences are not simply due to changes in emissions or advection from one day to the next rather than, as they have done, conclude that the differences are due to ageing?

It is of course possible that emissions were different between days, but as mentioned above, the industrial facilities usually operate continuously. We do try to make it clear that the assumption that SO_2 production is the same is just that: an assumption.

It is unlikely that the types of emissions would have changed; the industrial processes and mining were presumably the same. Therefore the exhaust from the upgraders would still be nucleating vast numbers of tiny sulphate particles in the presence of organic vapors. As on 10 July, there were sparse cumulus clouds on 28 June, though a thin higher-altitude overcast probably slowed photochemistry. Nevertheless, the processes important for aerosol aging–condensation, coagulation, photochemical reactions, and (lack of) effective scavenging would be occurring on both days, though perhaps not at the same rates.

Page 21302 line 12: SO4= is used. If these are AMS measurements you cannot assume that this is the sulphate ion.

That's true. Sulphur-containing organic compounds can break up in the AMS election beam and masquerade as sulphates. I will change all instances of $SO_4^=$ to SO_4 and add a note that the AMS does not clearly distinguish between inorganic and organic S.

That said, sulphate has been measured previously in the plume by ion chromatography of filter samples, so we know not all of the SO_4 is organic.

Page 21302 Line 19: were clouds present?

Sparse clouds were present over the oil sands region, but were not a factor since the mixed layer where we did the flux measurement was well below cloud level. I suppose this argument belongs in the body of the paper, but I'm not sure it's important enough for the abstract.

Page 21302 Line 21-22: over what spatial scale is this true?

The flip answer is that it depends on the distance to the nearest fire.

I'll add that the comparison is on a nationwide, annual basis.

Page 21304 line 3: cite the web address in the text

Ah right. I had the text as an active link in the PDFs I generated, but that didn't survive the Copernicus typesetting. I'll put it in plain text.

Page 21 line23-24: what were these sources?

(Assuming you're referring to page 21304.) Simpson et al. [2010] did not identify any particular sources. The DC-8 did not fly close enough to do so.

Page 21305 line 7 figure 8 is confusing suggest writing as eight

Good point that it's potentially confusing. I hadn't thought of that. The character "8" seems appropriate though, as it is a graphic representation of the route. How about "figure 8 pattern"?

Page 21305 line 26: concentration not plural

Oops. Good find.

Page 21306: were the SMPS measurements made by continuously sampling ambient air or by grab sampling? The P3-B SMPSs used grab samplers. I'll add that to the text. The DC-8 apparently did not, though no DC-8 SMPS data are presented.

Page 21307 line 5: why is ion strength supposed from the AMS measurements? Ion strength? I expect this is related to the $SO_4^=$ versus organic sulphur question above. I will note that these AMS measurements are not definitive as to whether these are ions or part of something else.

Page 21309 line 8: indicates Page 21309: why is this likely other than there are large concentrations of sulphate observed? Further you should explain clearly what it is you propose that is reacting with H2SO4 in this sentence.

This is a bit garbled; I'm not sure exactly what is being asked. line 8 refers to our observation that when SO_4 rose downwind from the oil sands facilities, so did OM, suggesting a common source, unlike the situation with BC, which was also clearly emitted from the oil sands region, but was not well correlated with SO_4. That suggests a common source, which is a bit strange since at the industrial facilities, the little OM present was not at all correlated with SO_4.

I'm not sure how to respond to the request that the species reacting with H_2SO_4 be mentioned in that sentence. (Presuming line 19 is being referred to). The rest of the paragraph is speculation about that. Sulphuric acid is not fussy–we learn in intro organic chemistry that it will attack almost any organic with oxygen in it. We mention a few organic vapors that are both present and have been reported to react.

Fluxes section. It would be good to reference previous work using this approach such as Ryerson et al., 2012 and earlier references.

Fair enough. The idea of measuring fluxes from an aircraft isn't anything like original. I'll add a quick discussion of those earlier sources.

Page 21313 cm3 Line 16? Another good catch. Thanks.

Page 21313 line 16-17: I would like to see a discussion of the potential oxidation pathways of SO2 to sulphate that explain this deficit?

The simple answer is that we don't know. Cloud processing can oxidize SO_2 rapidly, but the clouds were separated from the mixed layer in this case.

Page 21315 lines 4-13: If the CO emission is so different to the inventory I would not like to see it used as the denominator in the emission ratio calculations without comment or discussion seems.

The ideal denominator would be measured on both aircraft, present in both sources, and stable on the time scales of the sampling. Nothing really fits, especially since CO and O_3 were the only gases measured on the P-3B. CO does have the advantage that it is commonly used as a standard in biomass burning plumes.

I'll add a note that CO isn't ideal for the reason you mention, but is the best option available.

Page 21317: DMA distributions, better to write SMPS as this describes the type of scanning

Okay.

The comments end here rather abruptly. I fear that the reviewer had more comments that got cut off. That would be unfortunate.

References

I. J. Simpson, N. J. Blake, B. Barletta, G. S. Diskin, H. E. Fuelberg, K. Gorham, L. G. Huey, S. Meinardi, F. S. Rowland, S. A. Vay, A. J. Weinheimer, M. Yang, and D. R. Blake. Characterization of trace gases measured over Alberta oil sands mining operations: 76 speciated C_2–C_{10} volatile organic compounds (VOCs), CO_2, CH_4, CO, NO, NO_2, NO_y, O_3 and SO_2. *Atmospheric Chemistry and Physics*, 10(23):11931–11954, 2010. doi: 10.5194/acp-10-11931-2010. URL `http://www.atmos-chem-phys.net/10/11931/2010/`.