

Response to anonymous reviewer #1

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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.

1: How can we claim that primary OM was not produced at the upgraders when the AMS cannot detect particles <50 nm?

It is true that Liu et al. [2007] found poor transmission efficiency at small particle diameters. However, when they tested transmission efficiency at lower inlet pressure (585 torr), detection efficiencies rose considerably, from 11% to 27% for 50 nm particles. We mentioned a pressure regulated inlet to the AMS, but neglected to include the pressure: 600 hPa, or 450 torr. Therefore, the inlet size 50% cut is probably similar to the ~ 55 nm from Liu et al. [2007].

So the question is whether we can have a significant mass of OM below 50 nm. We cannot utterly rule it out, but there are reasons to consider it unlikely:

We do in fact see sharp jumps in SO_4 , even though we know those particles are freshly nucleated. We may be missing a large fraction of the SO_4 mass, but condensation and coagulation were sufficient to generate particles big enough for the AMS to detect. It is difficult to figure out why organic-containing particles would not grow as well; H_2SO_4 is notoriously sticky, rapidly condensing on any surface available. (Note that even if sub $50 \mu\text{m}$ OM grew solely by addition of sulfates, it would be detectable.)

It's really hard to get much mass on very small particles. For example, the DC-8 saw about $3 \mu\text{g m}^{-3}$ of OM. If that was on particles 25 nm in diameter, the concentration would be about $3.7 \times 10^5 \text{ cm}^{-3}$. We have some weak evidence that that was not the case: at about an order of magnitude fewer particles, the TSI 3010 CN counters we used run into an ambiguity problem, where there is a particle in the sensing volume more than 50% of the time. Above that, and the reported count actually goes down, as more and more particles get included in longer and longer spikes. Given enough particles, there should be very few spikes. We haven't actually tested our 3010s with concentrations like that, so there may be something limiting that process.

Of course we do mention the possibility that the OM may be primary, but is condensing slowly as the plume cools.

2: Dust particles smaller than 1 μm diameter have been observed. The statement that the 1 μm mode is too small for mechanical generation needs either more qualification.

It is certainly true that dust particles smaller than 1 μm exist (e.g. Clarke et al. [2004]). What one essentially never sees is a mass (or volume) mode peaking below 1 μm . Desert dust [Mahowald et al., 2013; Maring et al., 2003] and road dust [Singh et al., 2002] are larger. Fly ash size distributions are variable, depending on the conditions in the flames and stacks.

The 0.6 μm mode caught our attention because it is very unusual in our experience. As mentioned in the text, attributing the to fly ash is just a guess; confirmation would require chemical composition, which we do not have. There are previous reports of fly ash from a petroleum coke fired power plant, so it seems a likely candidate. Of course we cannot exclude some other industrial process that happens to create particles like that.

I will make it clearer in the text that the attribution to fly ash is merely a hypothesis for which we lack confirmation.

3: If the BC particles are initially small, then light absorption will be reduced. As the plume ages, coagulation will enhance the absorption by the BC mass by increasing the effective size of the BC. Coatings may also play a role, but there is ambiguity in that process. This needs a better discussion.

There are 4 factors at play here that complicate things:

1. For small particles, mass absorption efficiency is constant with diameter. It rises only modestly to a peak as particle sizes reach ~ 200 nm then drops [Fuller et al., 1999; Seinfeld and Pandis, 2006, p.1132–1133].
2. There is no secondary source of BC. No condensation occurs.
3. The SP2 (used for BC mass) loses sensitivity to particles < 100 nm and misses those below 80 nm. Their incandescence is too faint for the detectors. In contrast, the PSAP is sensitive to absorption from all sizes of particles.
4. Particles large enough to be detected by the SP2 do not coagulate quickly.

If the BC particles started out very small, then the SP2 would have missed most of the mass and the apparent absorption efficiency would have been very large near the source. In contrast, we know that particles are growing by adding SO_4 and OM (whether through coagulation or condensation), and numerous theoretical and experimental studies have

shown that coating BC increases BC absorption efficiency (e.g. [Bond and Bergstrom, 2006; Fuller et al., 1999]).

Your question did get me thinking about whether absorption could have risen due to production of brown carbon (BrC). That turns out not to be the case: BC has an absorption Ångstrom exponent ($a_{\text{Å}}$) of about 1, while $a_{\text{Å}}$ for BrC is higher [Andreae and Gelencser, 2006; Yang et al., 2009]. During the 6/29 flyby, $a_{\text{Å}}$ of sub- μm particles was approximately 1. Dust also tends to have a high $a_{\text{Å}}$ and sure enough, $a_{\text{Å}}$ for all particles did rise to about 2.5, indicating that coarse particles had a considerably higher $a_{\text{Å}}$.

I will insert text reflecting these points.

4: Meteorological profile

Thin lines were during the descent to the sampling loop; thick lines were during the ascent afterwards. That should have been mentioned (and will be).

Perhaps “obvious convections” was a poor choice of words. There was certainly some convection; it shows up in figure 7 (the LIDAR curtain) as a plume of aerosol reaching from the mixed layer to cloud base, and we noted in section 3.1 that cloud outflow clearly had signs of the plume.

I will note that z_m in the figure is 1200 m.

5: Too high a venting rate to cloud

The calculation was meant to be an upper bound. I assumed 1 m/s updrafts under cloud in the absence of any data, and that clouds covered 25% of the region, yielding an overall venting rate of 0.25 m/s. My experience with weak convection over land is quite limited; I chose 1 m/s from experience with trade wind Cu because I actually had some data. I’m happy to reduce the venting rate to 0.1 m/s. That would lower the calculated error a bit.

6: Convection in the LIDAR image

Yes, things get more complicated whenever clouds are involved. Perhaps some of the confusion here is due to the definition of the mixed layer. I was referring to 1200 m, the approximate height to which the oil sands plume appears to be well-mixed. The convection from the mixed layer is from 18:04 to 18:06, where a plume of aerosol certainly appears connected to the mixed layer at the bottom and a cloud at the top. Why the cloud is not directly over the plume is unknown, but clouds are very dynamic, growing and deteriorating rapidly. Perhaps wind shear stripped the top of the cloud away; maybe the enhanced backscatter at 3 km directly above the plume is the remnants of a dying cloud that was responsible for the convection. Why there is no similar plume under the cloud from 18:06 to 18:09 is equally unknown but plausibly explainable. It’s clearly a weak cloud—the LIDAR penetrates much of it. Perhaps it was dying, and had no convective connection

to the surface since before reaching the oil sands area. Or it could be just forming and had no chance to pull air from low altitude.

Without a more extensive survey of the conditions, about all we can say is that a: the lidar detected elevated aerosol returns downwind of the oil sands facilities and Ft McMurray; b: that the aerosol plume was fairly well mixed from the surface to 1.2 km altitude downwind of the upgrades and 1 km downwind of Ft McMurray; and c: between 18:04 and 18:06, low-altitude aerosol was mixed up to cloud base altitudes. I don't believe we claimed any more than that, and it pointless to spend time speculating about details we can't really resolve.

I think some of the confusion can be avoided if I add another dashed line with Z_m so the meaning of "mixed layer" is clearer and include a bit of discussion of it in the caption.

7: Indicate the altitude of the aircraft in the image or caption of Fig 7a.

I'm not sure why the aircraft altitude is relevant. The DC-8 was at 5.5 km (GPS altitude) until 18:10, when it started descending. At 18:15 it was at 4 km.

8: Page 21315 "7 July" ? do you mean 10 July? If not, please explain

Whoops! Yes, I meant 10 July. Well spotted.

9: Sulphate scavenging by dust reducing measured SO_4

Sulphate can in theory wind up on dust in several ways:

- H_2SO_4 created photochemically in the vapor phase can deposit to dust particles. That won't be important here since sulfuric acid has a very low vapor pressure and a high accommodation coefficient. Basically, it deposits on the first surface it diffuses to and large dust particles have a very small fraction of the available surface area.
- Metal-catalyzed reactions oxidizing SO_2 on the dust. I'm not sure this counts as scavenging, though it could reduce the OM to SO_4 ratio. In any case, it happens in cloud (an aqueous environment is required) and reaction rates with Fe are suppressed at low pH [Seinfeld and Pandis, 2006]. We do not know enough about dust composition, solubility of the metals, or conditions in the clouds to quantify this. In cloud other oxidation processes will also be important, including reaction with O_3 and the acid-independent reaction with H_2O_2 , but are not limited to dust-containing particles.
- Coagulation of dust particles with sulfate particles. I suppose I could do a model of coagulation rates given our size distributions. I hadn't bothered because those rates are normally too small to matter. Here's a dramatically simplified version: assume all particles sensed by the APS are $1 \mu\text{m}$ (they are actually 0.6 to about $5 \mu\text{m}$, given inlet losses), and all particles seen by the UHSAS are $0.1 \mu\text{m}$ (actually 0.05 to

1 μm). At the peak of the plume, the UHSAS saw about 3×10^4 particles $\cdot\text{cm}^{-3}$. The APS measured only 20 particles $\cdot\text{cm}^{-3}$. From Seinfeld and Pandis [2006], the rate coefficient for coagulation between 0.1 and 1 μm particles is 2.4×10^{-9} , giving a coagulation rate in this case of 0.001 particle $\cdot\text{cm}^{-3}\text{ s}^{-1}$ or 5 particles $\cdot\text{cm}^{-3}\text{ hour}^{-1}$. That's not an effective way to transfer SO_4 to large particles.

- Coagulation can also happen in cloud, but since most of the CCN are accumulation mode SO_4 and OM particles, they will dominate, unless the dust particles grow much larger than the others and fall, collecting smaller droplets. That seems far-fetched given the weak convection noted by the reviewer and the low solubility of dust, making it an indifferent CCN source.

None of these mechanisms are likely to be effective for scavenging SO_4 . Perhaps they could be at much higher dust concentrations, but in this case there aren't enough dust particles present.

10: What does “minimal plume period” mean? Did your PSAP filter transmission drop about 1930 on June 28?

I should have been clearer. It is not immediately obvious what criteria should be used to define the plume for flux calculations. The AMS SO_4 is elevated for a relatively short span of time, and is used to define the “minimum plume period”. In contrast, the BC and APS data are elevated for almost 3 times as long. Using the longer time gives dramatically different fluxes for some species.

Perhaps the SO_4 period is the plume directly from the industrial facilities while the extended plume is a product of other activities.

I am not sure what the question about dropping PSAP transmission refers to. The PSAP detects absorption by measuring the rate of transmission change with time. There was a peak in absorption near 19:30, so yes there was a drop in transmission.

11: Page 21319, line 19 change “appear to” to “may also”.

Sure.

12: For reasons of cloud venting discussed above, your flux estimates need to be recalculated. It is also important to indicate that these are only one daytime estimate.

I guess it wasn't clear enough. The cloud venting calculation is not in fact part of the flux estimates. Instead it is considered a likely source of error, with a range of -0% to +50%.

There were actually two daytime estimates: 28 June and 10 July. Of course it would be absurd to pretend that these can possibly represent long-term emissions from the oil sands.

We have no measurements at night, in bad weather, or in other seasons. We don't even know whether the plants were operating normally. The conclusions open with

While 2 flybys and 3 incidental plume penetrations can only provide short-term estimates of the aerosol output of the Alberta oil sands mining and upgrading operations

and section 3.3 admits that it is a

... questionable assumption that SO₂ production on 10 July were representative of annual emissions

I gather you'd like this point brought up more forcefully. Okay. I'll put it in the abstract as well.

For the SO₂ and NO_x, the agreement between measured fluxes and the Environment Canada database is probably not fortuitous; the upgraders run essentially continuously, are by far the dominant reported sources in the area, and are likely to dwarf undocumented emissions (only large stationary sources are in the database). Those conditions may not be true for OM, CO, CO₂, and BC.

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