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Atmospheric Chemistry and Physics Discussions

Interactive comment on "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" *by* I. J. Simpson et al.

Anonymous Referee #1

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General Comments

The manuscript by Simpson et al. presents a detailed chemical characterization of emissions from Alberta's oil sands and mining processes during one flight of NASA's ARCTAS campaign. Because of the increasing importance of oil sands for energy – especially in North America – along with the significant challenges and pollution associated with its processing compared to "normal" crude oil, emissions' characterization are needed. The importance of this manuscript to the scientific community is quite clear, especially because this is the first peer-reviewed study to characterize VOC

emissions from Alberta's oil sands and mining sites. While the sample size may be limited in number (17 samples collected in the boundary layer over the mining region), the results are quite impressive and provide new insight on the types and abundances of VOCs emitted from the oil sands mining process. Furthermore, I appreciate the cautiousness used in the data analysis and that the authors did not overstate the results or associated impacts from this area. In summary, the paper is well written and easy to follow and should be published in ACP after addressing a few minor issues listed below.

Specific Comments

P18509, L11: I would recommend using more precise wording and refer to "oxygenates" as either "oxygenated hydrocarbons" or "oxygenated VOCs".

P18515, L4: "double bellows pump" should be replaced by "dual head metal bellows pump" Was the pump configured in series or parallel?

P18518, L19-22: I find the increase in monoterpenes to be most interesting; however, I suspect that the emissions are likely from damaged vegetation, as discussed later in section 3.2.3. I have included a few additional references that might be useful regarding monoterpenes and other VOCs being released by vegetation in response to various sources of stress, including heat, light, drought, physical trauma, infestation, as well as from ground litter.

Räisänen, T.; Ryyppö, A.; Kellomäki, S., Impact of timber felling on the ambient monoterpene concentration of a Scots pine (Pinus sylvestris L.) forest. Atmos. Environ. 2008, 42, (28), 6759.

Niinemets, Ü., Mild versus severe stress and BVOCs: thresholds, priming and consequences. Trends Plant Sci. 2010, 15, (3), 145.

Holopainen, J. K.; Gershenzon, J., Multiple stress factors and the emission of plant VOCs. Trends Plant Sci. 2010, 15, (3), 176.

Kesselmeier, J.; Staudt, M., Biogenic Volatile Organic Compounds (VOC): An Overview on Emission, Physiology and Ecology. J. Atmos. Chem. 1999, 33, (1), 23.

Warneke, C., et al. (2010), Biogenic emission measurement and inventories determination of biogenic emissions in the eastern United States and Texas and comparison with biogenic emission inventories, J. Geophys. Res., 115, D00F18, doi:10.1029/2009JD012445.

P18519, L8-13: It would be useful to the reader to define "simple correlations", possibly in the Experimental section of the paper. Also, further details of the regression analysis (either in the manuscript or as supplementary materials) which provides the specifics on the software package used, were the regressions all linear (or nonlinear in some instances), does each data point provide equally precise information about the deterministic part of the total variation, that is, was the standard deviation of the error term constant over all values of the variables, etc. Again, while I appreciate the straightforward analysis used in the manuscript, providing certain specific details would be useful.

P18519, L19: MTBE – you introduce it on P18526, L3-4, you should introduce it here since it is the first time it's used in the body of the manuscript. Also, technically furan and MTBE are not "nonmethane hydrocarbons"; they are, in fact, oxygenated hydrocarbons – I would revise the wording to reflect this difference.

P18520, L13: In addition to the Baker et al. 2008 reference, if might prove useful to also compare levels to long-term NMHC measurements from the following manuscript:

Russo, R. S., et al. (2010), Seasonal variation of nonmethane hydrocarbons and halocarbons in New Hampshire: 2004-2008, Atmos. Chem. Phys., 10, 1-21.

P18523, L11: Monoterpenes are also "alkenes"; therefore it might be better to either say that isoprene and the monoterpenes are considered separately or refer to the alkenes as something such as "primarily anthropogenic" alkenes. However, ethene,

propene and 1-butene also have biogenic sources, so you may want to at least make note of this in the text.

P18523, L16: I would re-word this sentence, I find it reads a bit awkwardly resulting from "over" being repeated in close proximity.

P18526, L23-26: Regarding the statement made of isoprene correlating with methanol, would you expect it to? Even though they both may have biogenic sources, based on their lifetimes alone, it is not likely that you would expect them to be well correlated, especially if there has been transport, photochemical processing and/or mixing/dilution. I'm not sure what the main point you are trying to convey here because it is uncommon to observe a strong correlation of these two gases. You may also find the following manuscripts useful for comparative purposes:

Schade, G. W., and Goldstein, A. H.: Seasonal measurements of acetone and methanol: Abundances and implications for atmospheric budgets, Global Biogeochem. Cy., 20, GB1011, doi:10.1029/2005GB002566, 2006.

Jordan, C., et al. (2009), Long-term study of VOCs measured with PTR-MS at a rural site in New Hampshire with urban influences, Atmos. Chem. Phys., 9, 4677-4697.

As for the section on oxygenates overall, I do not feel that the main points/significant findings are succinctly conveyed – adding a few sentences to tie this together may be useful.

P18527, L14: "methylene chloride" should be changed to "dichloromethane"

P18528, L26: I would recommend a word change for "exceedances" – in this context it implies that regulatory standards are being broken as opposed to making the point that levels were "enhanced" by 75% over background in China.

P18529, L9-15: Regarding methyl iodide, the vertical distributions are strikingly similar to those observed from NASA DC-8 measurements during ICARTT (see Sive et al., 2007). The large-scale aircraft measurements of vertical profiles over the continental U.S. showed methyl iodide mixing ratios comparable to and greater than those observed over the North Atlantic. Moreover, the qualitative shape of the profile is remarkably similar to those during ICARTT. Also, Yokouchi et al. inferred a terrestrial source, but did not have direct evidence as in Sive et al. Because the measurements presented are consistent with the compilation of measurements presented in Sive et al., I would recommend addressing this in the methyl iodide discussion.

Sive, B. C., et al. (2007), A Large Terrestrial Sources of Methyl Iodide, Geophys. Res. Lett., 34, L17808, doi:10.1029/2007GL030528.

P18532, L4-10: regarding the "simultaneous uptake" of COS and CO2, White et al. (2010) showed that ambient CO2 levels can affect COS uptake in forested ecosystems. Furthermore, their observations revealed that substantial vegetative COS consumption occurred independently of CO2 assimilation and suggest that current estimates of the global vegetative COS sink, which assume that COS and CO2 assimilation occur simultaneously, may need to be re-evaluated. My hunch is that the higher CO2 levels observed in the boundary layer samples could be influencing COS uptake; certainly this can't be ruled out.

White, M. L., et al. (2010), Carbonyl sulfide exchange in a temperate loblolly pine forest grown under ambient and elevated CO2, Atmos. Chem. Phys., 10, 547-561.

Additionally, for the discussion regarding COS, I would also encourage the authors to look at the following papers regarding its cycling:

Sandoval-Soto, L., Stanimirov, M., von Hobe, M., Schmitt, V., Valdes, J., Wild, A., and Kesselmeier, J.: Global uptake of carbonyl sulfide (COS) by terrestrial vegetation: Estimates corrected by deposition velocities normalized to the uptake of carbon dioxide (CO2), Biogeosciences, 2, 125–132, 2005, http://www.biogeosciences.net/2/125/2005/.

Van Diest, H. and Kesselmeier, J.: Soil atmosphere exchange of carbonyl sulfide (COS)

regulated by diffusivity depending on waterfilled pore space, Biogeosciences, 5, 475–483, 2008, http://www.biogeosciences.net/5/475/2008/.

Figures 4-9: What are the "0" values that are plotted? Is "0" being plotted or are the LOD values being plotted? I understand why they are included because they provide a nice qualitative contrast, but I feel that what these values are should be stated explicitly in the text or figure captions. Also, it might be useful to extend the axis into the negative range for clarity.

Figure 10: I would recommend using ppbv for NOy.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 18507, 2010.