

***Interactive comment on “Characterization of trace gases measured over Alberta oil sands mining operations: 76 speciated C<sub>2</sub>–C<sub>10</sub> volatile organic compounds (VOCs), CO<sub>2</sub>, CH<sub>4</sub>, CO, NO, NO<sub>2</sub>, NO<sub>y</sub>, O<sub>3</sub> and SO<sub>2</sub>” by I. J. Simpson et al.***

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RESPONSE TO REVIEWER 1 FOR ACP-2010-470

We thank the reviewer for their positive feedback and helpful comments. Our reply to each comment is given below, and the manuscript has been revised accordingly.

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

We have replaced “oxygenates” with “oxygenated hydrocarbons” throughout the paper.  
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P18515, L4: “double bellows pump” should be replaced by “dual head metal bellows pump” – this is how Senior Aerospace refers to the MB-602. Also, I’m assuming the pump was run in series, but you should include if it was configured in series or parallel.

We have made this correction and have stated that it was configured in series.

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. Räsänen, 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.; Gershenson, 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.

We agree that the monoterpene increase is very intriguing and that monoterpenes are released in greater abundance when vegetation is damaged. However in the case of the oil sands, the pinene release is perplexing because of their excellent correlation with industrial compounds such as SO<sub>2</sub>, NO, etc. which we have attributed to the upgrader operations. That is, the maximum pinene mixing ratios occurred in the same sample as the maximum mixing ratios of SO<sub>2</sub>, NO, etc., and the pinenes are behaving as if they are being emitted industrially. The land surrounding the upgraders is already disturbed and we do not expect the industrial upgrader plumes to have had the opportunity to mix with plumes representing damaged vegetation. Also, if the elevated monoterpene levels had been caused by damaged vegetation, we might have expected maximum monoterpene values in a different air sample—for example elsewhere along

the flight track where a forest might be under stress. For these reasons it does not appear to us that the monoterpene enhancements can be easily attributed to damaged vegetation. Later on p. 18525 we have changed the text as follows: "At first glance this appears to be consistent with a number of studies that have shown increased emissions of monoterpenes and other VOCs in response to various plant stress factors (Schade and Goldstein, 2003; Räsänen et al., 2008; Niinemets, 2010; Holopainen and Gershenzon, 2010). For example, monoterpene mixing ratios and emissions from a California ponderosa pine forest showed a 10-30 fold increase during and after major forest thinning, with measured mixing ratios exceeding 3000 pptv (Schade and Goldstein, 2003). However, unlike isoprene, the pinenes were most strongly enhanced in sample 4, downwind of the Syncrude Mildred Lake Facility (Table 2; Figure 2b) and they showed strong correlations with many species that were elevated in the oil sands plumes. For example  $\alpha$ -pinene correlated best with  $\beta$ -pinene ( $r^2 = 0.92$ ) and industrial compounds such as C<sub>2</sub>Cl<sub>4</sub> ( $r^2 = 0.81$ ), SO<sub>2</sub> ( $r^2 = 0.76$ ), 1,2,3-TMB ( $r^2 = 0.74$ ), i-butene ( $r^2 = 0.73$ ) and ethyne ( $r^2 = 0.73$ ). The land surrounding the upgraders is already disturbed and we do not expect the industrial upgrader plumes to have had the opportunity to mix with plumes representing damaged vegetation. Instead these unexpected observations lead us to infer that there could be a source of pinenes associated with the oil sands mining industry, which requires further investigation."

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.

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By "simple correlations" we mean the absence of multivariate analysis such as PCA or PMF, and the simple performance of linear correlations between two species using a least squares fit. We used KaleidaGraph software version 4.0. All regressions were linear. We have changed "simple correlations" to "linear correlations among the measured compounds using least squares fits".

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.

We now introduce MTBE on p. 18519 rather than p. 18526. We have changed "non-methane hydrocarbons" to "non-methane volatile organic compounds" where appropriate throughout the paper. For furan and MTBE the text reads: "of the 48 C<sub>2</sub>-C<sub>10</sub> hydrocarbons that we measured. . .".

P18520, L13: In addition to the Baker et al. 2008 reference, it might prove useful to also compare levels to long-term NMHC measurements from the following manuscript: R.S. Russo et al. (2010), Seasonal variation of nonmethane hydrocarbons and halocarbons in New Hampshire: 2004-2006, Atmos. Chem. Phys., 10, 1-21.

We weren't able to find this paper, but we found a different 2010 paper by Russo which appears to contain the same relevant information: Russo, R. S., Zhou, Y., White, M. L., Mao, H., Talbot, R., and Sive, B. C., Multi-year (2004–2008) record of non-methane hydrocarbons and halocarbons in New England: seasonal variations and regional sources, Atmos. Chem. Phys., 10, 4909–4929, 2010. We now make reference to this paper here and elsewhere in the manuscript, for example the sections pertaining to the butanes and ethanol. We note that the Russo measurements were taken in an agricultural setting, and that the ethane and propane values measured in the oil sands plumes were larger than these rural New England values. We have changed the text as follows: "Despite minimal urbanization in northern Alberta, the oil sand plume

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values were larger than average summertime values measured in rural New England between 2004-2007 (Russo et al., 2010). Instead they were comparable to average ethane and propane levels measured in urban areas of Baltimore and New York City during a summer study of 28 U.S. cities from 1999-2005 (Baker et al., 2008)."

P18520 (18521), L7: Again, it would be useful/interesting to compare the butanes with the Russo et al. 2010, especially because of the widespread LPG leakage in the northeast.

This is a good point. We have compared the i-butane/n-butane ratio over the oil sands to that cited in the Russo paper. In fact the ratio in the dominant oil sands plumes, i.e. samples 4, 5 and 6 ( $0.42 \pm 0.03$ ) was very close to that expected for LPG usage (0.46). However from what we have learned, LPG is not used at the surface mining operations. The major companies produce fuel gas, which could potentially explain these i-butane/n-butane ratios. It is also possible that this signal represents hydrocracking (see response to Reviewer 3, p. 18521, first paragraph). We have added the following text: "[The i-butane and n-butane maxima in the oil sands plumes] were much higher than average July values measured in rural New England ( $70 \pm 39$  pptv and  $105 \pm 59$  pptv, respectively; Russo et al., 2010) despite the widespread leakage of LPG in the northeastern United States (White et al., 2008; Russo et al., 2010). The ratio of i-butane/n-butane varies according to source, for example 0.2-0.3 for vehicular exhaust, 0.46 for LPG, and 0.6-1.0 for natural gas (Russo et al., 2010 and references therein). Interestingly, the i-butane/n-butane ratio for the dominant oil sands plumes, i.e., samples 4, 5 and 6 ( $0.42 \pm 0.03$  pptv pptv<sup>-1</sup>) was very close to that expected for LPG. We have not been able to determine that LPG is used in the mining operations, but this signal could potentially represent emissions from hydrocrackers and/or the fuel gas that is produced and used at the major oil sands operations."

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

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

We have reworded this to: "Because they are primarily biogenic tracers, isoprene and the monoterpenes are considered separately below (Section 3.2.3). The 7 C2-C4 alkenes considered here are highly reactive, short-lived compounds that are primarily associated with industrial emissions and incomplete combustion (e.g., Sprengnether et al., 2002; Buzcu and Fraser, 2006; de Gouw et al., 2009)."

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

We have reworded the sentence as follows: "Whereas only ethene was detectable in the background BL during Flight 23 ( $20 \pm 2$  pptv), all of the alkenes were strongly enhanced over the oil sands by factors of up to 5-85 (Table 1; Figures 4g, 6e)."

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, just based on their lifetimes alone, it is not likely that you would expect them to be correlated, especially if there has been transport, photochemical processing or mixing/dilution. I'm not sure what the main point you are trying to convey here because it is unlikely that you find a strong correlation of these gases, even when directly in/above a forest canopy. You may also find the following manuscript useful for comparative purposes: Jordan, C., E. Fitz, T. Hagan, B. Sive, E. Frinak, K. Haase, L. Cottrell, S. Buckley, and R. Talbot (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.

This is a good point, especially considering that these are airborne measurements and that Jordan et al. point out the unique ways in which each biogenic compound can be produced and emitted. We have omitted this sentence.

As for the section on oxygenates overall, I do not feel that the main points/significant

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findings are succinctly conveyed – adding a few sentences to tie this together may be useful.

We have thoroughly reworked this section and we now present and interpret each compound more comprehensively. We also correct an omission from the original version, in that the ethanol data were not available for the first seven samples of Leg 7 and the statistics presented in Table 1 are based on samples 8-17.

P18527, L14: “methylene chloride” should be changed to “dichloromethane” – IUPAC nomenclature

We have changed this here and elsewhere in the manuscript.

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.

We have changed “exceedances” to “enhancements”.

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. (2007), I would recommend addressing this in the methyl iodide discussion. Sive, B. C., R. K. Varner, H. Mao, D. R. Blake, O. W. Wingenter and R. Talbot (2007), A Large Terrestrial Sources of Methyl Iodide, *Geophys. Res. Lett.*, 34, L17808, doi:10.1029/2007GL030528.

We agree, the profile is strikingly similar, both qualitatively and quantitatively, to that

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presented in Figure 3 of Sive et al. Also, the maximum CH<sub>3</sub>I mixing ratio during Leg 7 was measured in the final sample (#17), i.e. not in the samples directly downwind of the mining operations (#4, 5, 6), which is consistent with terrestrial emissions rather than emissions from the oil sands. The text now reads, “Methyl iodide is a very short-lived species (1-2 d) with a major oceanic source (Yokouchi et al., 2008) and minor terrestrial sources (e.g., Redeker et al., 2003; Sive et al., 2007). Its mixing ratio declined sharply with altitude, consistent with its short atmospheric lifetime (Figure 8d). In fact, the shape of the profile and the magnitude of the mixing ratios were remarkably similar to those measured elsewhere over North America during the Intercontinental Chemical Transport Experiment–North America campaign (INTEX-NA) campaign in July and August, 2004 (Sive et al., 2007). In addition, the mixing ratios of CH<sub>3</sub>I during Legs 7 and 9 (<0.45 pptv) were at the low end of global background values (0.5-2 pptv; Yokouchi et al., 2008 and references therein) and CH<sub>3</sub>I did not correlate with other species over the oil sands ( $r^2 \leq 0.37$ ). Therefore the oil sands do not appear to be a significant CH<sub>3</sub>I source. The maximum CH<sub>3</sub>I mixing ratio was measured in the final sample of Flight Leg 7 (sample #17) and the enhancements of CH<sub>3</sub>I during Leg 7 may be attributable to methyl iodide’s terrestrial source.”

Additionally, for the discussion regarding COS, I would also encourage the authors to look at the following paper regarding new insight on its cycling: White, M. L., Y. Zhou, R. S. Russo, H. Mao, R. Talbot, R. K. Varner, and B. C. Sive (2010), Carbonyl sulfide exchange in a temperate loblolly pine forest grown under ambient and elevated CO<sub>2</sub>, *Atmos. Chem. Phys.*, 10, 547-561.

White et al. document substantial nighttime uptake of COS that is independent of CO<sub>2</sub> assimilation, and show decreased nighttime uptake of COS under elevated CO<sub>2</sub> in June, but not in September. We have emphasized our daytime work as follows: “Note that even though previous work has shown similarities between OCS and CO<sub>2</sub> because of simultaneous uptake by photosynthetically active vegetation during the daytime (Montzka et al., 2007; Campbell et al., 2008; White et al., 2010). . .”.

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P18532, L4-10: regarding the “simultaneous uptake” of COS and CO<sub>2</sub>, White et al. (2010) showed that ambient CO<sub>2</sub> levels can affect COS uptake in forested ecosystems. Furthermore, their observations revealed that substantial vegetative COS consumption occurred independently of CO<sub>2</sub> assimilation and suggest that current estimates of the global vegetative COS sink, which assume that COS and CO<sub>2</sub> assimilation occur simultaneously, may need to be re-evaluated. My hunch is that the higher CO<sub>2</sub> levels observed in the boundary layer samples could be influencing COS uptake; certainly this can't be ruled out.

The maximum CO<sub>2</sub> enhancement over the oil sands was 382 ppmv, or 3% above the local background value of  $378 \pm 1$  ppmv. This occurred downwind of an industrial area that had been cleared of vegetation. Our understanding of the paper by White et al. is that the CO<sub>2</sub> enhancement was much larger (background + 200  $\mu$ L L<sup>-1</sup> CO<sub>2</sub>) and that the effect of reduced COS uptake occurred during the nighttime for a June data set but not for a September data set collected in a Loblolly pine forest. In order to clarify this discussion we have emphasized that the terrain the DC-8 flew over during Leg 7 ranged from boreal forest to cleared industrial land that included tailings ponds, tailings sand and upgrader facilities (p. 18513, line 18). In other words we seek to show that the CO<sub>2</sub> and COS enhancements occurred over land without vegetation, and therefore differences in assimilation by vegetation would not apply to the oil sands plumes that were sampled during Leg 7.

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.

The “0” values are actually “0” rather than LOD or  $\frac{1}{2}$  LOD. We now state this in the figure captions as well as on p. 18517, line 14. We have revised many of the figures according to comments by the other two reviewers, including logarithmic and broken

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scales where appropriate.

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

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