

Interactive comment on “Characterization of trace gases measured over Alberta oil sands mining operations: 76 speciated C₂–C₁₀ volatile organic compounds (VOCs), CO₂, CH₄, CO, NO, NO₂, NO_y, O₃ and SO₂” by I. J. Simpson et al.

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RESPONSE TO REVIEWER 2 FOR ACP-2010-470

We thank the reviewer for their constructive comments to improve the clarity of the manuscript, especially the Figures. Each comment is addressed below.

P18513, L17 and L20: Local times are given in the text, but all figures with timeseries are given in UTC. Please state the conversion and remove the “a.m.” on L17.

Sorry for the confusion. UTC is LT + 7 hours. We have converted the x-axis on the C9670

graphs to local time. We have also removed the “a.m.” here and in the Figure 3 caption.

P18517, L18-23: It would be very useful to the reader if the 1) location of the mine was clearly identified in Fig. 2B and 2) prevailing wind direction was included. It would be useful include the background values from Leg 9 as an additional line at the bottom of Table 2. This way the reader can more easily distinguish which of the 17 samples resembles the background air as the plane maneuvered south of the mine.

The mining operations are the grey patch below samples 4, 5 and 6 in Figure 2b, which is now stated in the Figure caption. The prevailing wind direction was from the southwest quadrant but varied for each sample, from 184-243°. Therefore we have stated the prevailing wind direction in the Figure caption, and we have also added a column in Table 2 that shows the measured wind direction for each air sample during Leg 7. We have also added an extra row of Leg 9 average background values in Table 2, to help the reader distinguish plumes from background samples during Leg 7, and we have changed “0” values to “LOD”.

P18519, L21-25: More detail should be provided on how the “simple (L12)” and “mutual (L21)” correlations were performed (e.g., linear two-sided fit, etc.). A reference to Table 3 should be included on L21.

The “simple correlations” were linear correlations using a least squares fit on Kaleida-Graph software. We have changed the text to “. . .we have instead performed linear correlations among the measured species using least squares fits to better understand their source influences”. By “mutual correlations” we just mean groups of correlating species, i.e., correlations among the various different compounds that have let us sort them into the different source groups. We have changed this to “correlations with one another”. We have also inserted a reference to Table 3 on line 21.

P18526, L 28: How well did MVK/MAC correlate with isoprene?

MVK and MAC did not correlate with isoprene ($r^2 = 0.02$). The MAC and MVK max-

ima occurred in samples 3-7, whereas the isoprene maxima were in samples 11-14. Their failure to correlate with isoprene makes sense qualitatively based on isoprene oxidation producing MAC and MVK. Based on these comments and comments from Reviewer 3 (p. 18527, line 3), the MAC/MVK section has been reworked as follows: "Methacrolein and MVK are major isoprene oxidation products (e.g., Montzka et al., 1993; Stroud et al., 2001; Karl et al., 2009b). The MAC and MVK mixing ratios were higher over the oil sands than at any other time during the flight (Figure 7e-f), with maximum respective values of 266 and 379 pptv in sample 7, or 8× and 6× the local background average (Table 1). Methacrolein and MVK correlated most strongly with each other ($r^2 = 0.87$), followed by species such as DMS and 1,2-dichloroethane ($r^2 \leq 0.69$). The highest MAC and MVK mixing ratios occurred in samples 3-7 downwind of the Syncrude Mildred Lake Facility, and enhancements associated with the oil sands industry cannot be ruled out. However because their strongest correlations were with each other, we suggest that their primary local source is likely isoprene oxidation. The average isoprene mixing ratio during Leg 7 was 468 ± 167 pptv. Assuming MAC and MVK formation yields from OH and O₃ reactions in the range of 0.16-0.4 (Tani et al., 2010 and references therein), the observed MAC and MVK values during Leg 7 (92 ± 63 and 141 ± 109 pptv, respectively) appear to be within the range that can be explained by isoprene chemistry."

P18552, Fig 2: Panel C is not very useful, especially since the flight track altitude is included in Fig. 4. The pressure level could simply be stated in section 2 when the altitude of legs 7 and 9 are discussed. Otherwise, include "C" in panel C. Add altitude to right axis. Circle markers are confusing/unnecessary. The fact that the numbers refer to the flight legs and not the sample numbers was not immediately clear.

The purpose of Panel C was just to identify Legs 7 and 9 on the flight track. It is a fair point that the numbered Flight Legs could easily be confused with sample number. We have omitted Panel C, and we now state in the Figure 4 caption that the first boundary layer run of Flight 23 is Leg 7 and the second is Leg 9.

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P18554, Fig 4: Panels C-H could have log scales for the hydrocarbon mixing ratios. This way more detail of the timeseries would be evident.

Reviewer 3 also requested more detail in the time series. For panels C-H, the log scale works very well for SO₂ (Panel D) because it ranges over several orders of magnitude and the low values are above the detection limit, and we have changed it accordingly. However for the remaining compounds the log scale seems to work less well because the majority of measurements are below detection limit (< 3 pptv), so there is no detail to zoom in on. We have explained this in the Figure 4 caption as follows: "Values below detection limit have been given a value of "0" for plotting purposes. Note that the mixing ratios of n-heptane, the cycloalkanes, the butenes and isoprene were below their detection limit for most of the flight." Instead we have tried to increase the detail by pairing benzene with cyclohexane, and toluene with methylcyclohexane.

P18560, Fig 10: Label time as UTC. It should be stated that this is data from leg 7 only.

Following from the reviewer's first comment, we have converted the time into local time (UTC – 7 hours) and labelled it accordingly. The caption now states that these are data from the first half of Flight Leg 7.

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

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