

Interactive
Comment

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 3 FOR ACP-2010-470

We thank the reviewer for their insightful critique of the manuscript and for taking the time to point out many technical corrections.

Page 18511, line 8: Would it be worth pointing out that the used hot water process to extract bitumen from the oil sands is very water and energy intensive? There are other methods which use less water and energy by igniting some of the bitumen un-

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derground.

Surface mining is used for deposits less than about 75 m underground, and in situ mining is used for deeper deposits (Alboudwarej et al., 2006). Each barrel of oil that is generated from surface mining requires 2 tons of oil sands, 20 m³ of natural gas and 3 barrels of water (much of which is re-used), and generates 4 barrels of waste (Holowenko et al., 2000; Siddique et al., 2006). The bitumen now appears to be extracted at a lower water temperature of 35-40°C instead of 80°C (www.syncrude.ca/users/folder.asp?FolderID=5918). In situ mining requires more natural gas/barrel (34 m³) but has the advantage that it disturbs much less land and does not require tailings ponds (www.oilsands.alberta.ca). Therefore there appear to be trade-offs. Our changes to the text include the following: “Each barrel of oil generated from surface mining requires about 2 tons of oil sands, 3 barrels of water—much of which is re-used—and 20 m³ of natural gas (<http://www.neb.gc.ca/clf-nsi/rnrgynfmrtn/nrgyrprt/lnd/pprntnsndchllngs20152006/qapprntnsndchllngs20152006-eng.html>). Deeper deposits occur in all three regions and require other in situ recovery methods such as steam injection and have higher natural gas requirements, but they have the advantage of much less land disturbance and no need for tailings ponds (www.oilsands.alberta.ca).”

Alboudwarej, H., Felix, J., Taylor, S. et al.: Highlighting heavy oil, *Oilfield Rev.*, 34–53, 2006.

Holowenko, F. M., MacKinnon, M. D., and Fedorak, P. M.: Methanogens and sulfate-reducing bacteria in oil sands fine tailings waste, *Can. J. Microbiol.*, 46 (10), 927-937, 2000.

Siddique, T., Fedorak, P. M., and Foght, J. M.: Biodegradation of short-chain n-alkanes in oil sands tailings under methanogenic conditions, *Environ. Sci. Technol.*, 40, 5459–5464, 2006.

Page 18514, lines 24ff: Are tests performed on a regular basis to exclude “rogue” tanks

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which have been activated, e.g. due to corrosion?

Every few years we recondition all of our canisters. By that we mean that the cans are baked at 200°C and then pumped-and-flushed a dozen times at White Mountain in the Sierra Nevadas. Since our cans do not sit for long with samples in them there isn't much opportunity to have water sit and cause rust.

Page 18518, lines 8-27: You present here a classification of all compounds into three groups. However, in Section 3.3 and in the Conclusion section you classify the compounds in different groups. Maybe one consistent classification could be used and added to Tables 1 and 3?

Sure. We now only use the groupings from Section 3.3 and the Conclusions, but we prefer to keep Tables 1 and 3 organized by compound class so that it's easier for the reader to find the compound they're interested in. We have changed the text as follows: "Atmospheric trace gas mixing ratios are generally higher in the Earth's BL than above in the FT. Here we seek to quantify mixing ratio increases over the oil sands that exceed the increases that may occur as the aircraft descends into the boundary layer. The 84 trace gases presented here can be classified into three groups: (1) compounds that were strongly enhanced (>10%) over the oil sands relative to levels in the local background BL air; (2) compounds that showed minimal increases over the oil sands (<10% greater than the local background average); and (3) compounds that showed no statistical enhancements over the oil sands compared to the local background."

Page 18519, line 24: Could you please explain in short the chemistry involved in the processes you think are being performed at the site, e.g. as far as I know alkanes are typically produced by hydrocracking from unsaturated compounds via addition of hydrogen, while alkenes are typically produced by steam cracking of saturated compounds.

This is a good point to clarify. Hydrocracking and hydrotreating are different in upgrading than in refining. At the operations north of Fort McMurray the purpose of upgrading

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is to produce as much liquid hydrocarbon product (i.e., synthetic crude oil) from the bitumen as possible, which can subsequently be refined in normal refining operations. The major upgrading processes north of Fort McMurray are distillation (to separate different hydrocarbons), thermal conversion/coking (to convert the bitumen into lighter, refinable hydrocarbons), catalytic conversion (an enhanced form of thermal conversion), and hydrotreating (the addition of hydrogen to unsaturated molecules to stabilize them). Dehkissia et al. (2004) describe the catalytic hydrocracking of Athabasca bitumen vacuum bottoms (ABVBs), including a characterization of the gas that is formed as a by-product. They found a predominance of C1-C7 alkanes and H₂S, with smaller fractions of alkenes. The weight per cent yield (in terms of % of gas) was found to be 23.2% H₂S, 15.0% propane, 10.5% ethane, 9.6% C₄H₁₀, 9.3% CH₄, 9.0% C₅H₁₀ and continuing down to 4.4% C₄H₈ (presumably summed butenes), 2.6% propene and 0.9% ethene. The gas formation was found to increase with hydrocracking severity (i.e., cracking temperature). Therefore both alkanes and alkenes are directly produced from the bitumen processing. We have added a summary of these comments to the text.

Dehkissia, S., F. Larachi and E. Chornet, Catalytic (Mo) upgrading of Athabasca bitumen vacuum bottoms via two-step hydrocracking and enhancement of Mo-heavy oil interaction, *Fuel*, 83, 1323–1331, 2004.

Page 18520, line 23ff: Could the presence of hydrocrackers, which typically generate ethane and heavier alkanes explain the good correlation among higher hydrocarbons and the bad correlation with methane? Similarly, the use of LPG could explain correlation among C₃ and C₄ alkanes (but not ethane).

The reviewer has brought up many good points. Following from this we have identified five potential sources of methane and/or ethane that require further discussion: (1) tailings ponds; (2) natural gas; (3) LPG; (4) fuel gas, and (5) hydrocracking.

(1) Tailings ponds. The tailings ponds are expected to release CH₄ without ethane (unlike CH₄, ethane is not known to be produced in anaerobic environments). The

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Syncrude Mildred Lake tailings pond became methanogenic in the 1990s and is currently believed to release 40 million L CH₄ day⁻¹ (Holowenko et al., 2000; Penner and Foght, 2010). Therefore tailings ponds could provide a local source of CH₄ that is independent of ethane and propane. Holowenko et al. found very high daily release rates of up to 10 g CH₄ m⁻² d⁻¹ in the most active areas. By comparison, an irrigated rice paddy field in the Philippines (also an anerobic CH₄ source) was found to release 0.5 g CH₄ m⁻² d⁻¹ (Simpson et al., 1995). The maximum methane mixing ratio over the oil sands (1983 ppbv, compared to a background value of 1843 ppbv) was measured in a different sample (sample 6) than the maximum for oil sands/diluent compounds such as n-heptane (sample 5) or industrial/upgrading compounds such as SO₂ (sample 4). Therefore it is possible that sample 6 was collected in an air mass that had a relatively higher influence from tailings ponds emissions.

(2) Natural gas. Please see our comments on natural gas in the reply to p. 18534 lines 19ff.

(3) LPG. From what we have been able to learn, we do not believe that LPG is being used as a fuel source. Having said that, the i-butane/n-butane ratio in the dominant oil sands plumes, i.e. samples 4, 5 and 6 (0.42 ± 0.03) was very close to that expected for LPG usage (0.46) (Russo et al., 2010 and references therein). By comparison, the i-butane/n-butane ratio is 0.2-0.3 for vehicles and 0.6-1 for natural gas. In the case that LPG is not used, it is possible that this signal represents manufactured fuel gas and/or hydrocracking, as outlined below.

(4) Fuel gas. Syncrude and Suncor produce refinery fuel gas as part of upgrading, which contains many compounds and also has variable composition in terms of methane, ethane, etc. We have not been able to determine the exact composition of this fuel gas, but it may explain the C₂-C₄ alkane enhancements and the i-butane/n-butane ratios.

(5) Hydrocracking. As discussed in the response to page 18519, line 24 the catalytic

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hydrocracking of Athabasca bitumen vacuum bottoms has been found to give a weight per cent yield (in terms of % of gas) of 9.3% CH₄, 10.5% ethane, 15.0% propane and 9.6% C₄H₁₀ (Dehkissia et al., 2004). When converted to a molar basis, this suggests relative yields of roughly 4:2:2:1 for CH₄:ethane:propane:butanes. In sample 6 (the sample with the highest CH₄ levels) we measured excess mixing ratios of 140 ppb CH₄, 1.1 ppb ethane, 0.3 ppb propane, 0.2 ppb n-butane and 0.08 ppbv i-butane, in other words a very large relative excess of CH₄ as well as more ethane relative to propane. Therefore, assuming the hydrocracking yields apply here and are the same as the release rates, it does not appear that hydrocracking can be responsible for the high CH₄ excesses that were observed. However, together with other sources such as fuel gas, it might be partly responsible for the excess ethane and propane levels.

We have revised the text on p. 18523 as follows: “Ethane and propane correlated well with a range of species such as other light alkanes, alkenes, NO, NO₂, NO_y and ethyne (Table 3). By contrast, even though ethane is the second most abundant component of natural gas after CH₄ (Xiao et al., 2008; McTaggart-Cowan et al., 2010), it did not correlate well with CH₄ ($r^2 = 0.52$). This relatively poor correlation is surprising given the heavy use of natural gas during bitumen extraction (Section 1), and appears to indicate low natural gas leakage levels (see Section 3.6). Because ethane and propane are primarily associated with evaporative rather than combustive fossil fuel emissions, we expect a co-located evaporative source from the industries that process the oil sands, possibly from fuel gas and/or hydrocracking.”

McTaggart-Cowan, G. P., Rogak, S. N., Munshi, S. R., Hill, P. G. and Bushe, W. K.: The influence of fuel composition on a heavy-duty, natural-gas direct-injection engine, *Fuel*, 89, 752–759, 2010.

Penner, T. J., and Foght, J. M., Mature fine tailings from oil sands processing harbour diverse methanogenic communities, *Can. J. Microbiol.*, 56(6), 459-470, 2010.

Russo, R. S., Y. Zhou, M. L. White, H. Mao, R. Talbot, and B. C. Sive, Multi-year (2004–

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2008) record of nonmethane hydrocarbons and halocarbons in New England: seasonal variations and regional sources, *Atmos. Chem. Phys.*, 10, 4909–4929, 2010.

Simpson, I. J., G. W. Thurtell, G. E. Kidd, M. Lin, T. H. Demetriades-Shah, I. D. Flitcroft, E. T. Kanemasu, D. Nie, K. F. Bronson, and H. U. Neue, Tunable diode laser measurements of methane emissions from an irrigated rice paddy field in the Philippines, *J. Geophys. Res.* 100, 7283-7290, 1995.

Xiao, Y., J. A. Logan, D. J. Jacob, R.C. Hudman, R. Yantosca, and D. R. Blake, Global budget of ethane and regional constraints on U.S. sources, *J. Geophys. Res.*, 113, D21306, doi:10.1029/2007JD009415, 2008.

Page 18521, first paragraph: Could the presence of hydrocrackers, the use or the production of LPG explain some of the observed correlations?

These are good questions. Following from the response to page 18520, line 23ff, the relative excesses of propane and the butanes appear to be reasonably consistent with what hydrocrackers may release. We do not believe that LPG is being used by the mining operations, even though the i-butane/n-butane ratio in the oil sands plumes (0.42 ± 0.03) is very close to that expected for LPG usage (0.46) (Russo et al., 2010). Instead the i-butane/n-butane ratio could also potentially represent fuel gas. We have changed the text as follows: “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 ± 0.03 pptv pptv-1) was very close to that expected for LPG. We have not been able to determine that LPG is used in the mining operations, and this signal could potentially represent emissions from hydrocrackers and/or the fuel gas that is produced and used at the major oil sands operations.”

Page 18523, line 5: Suggest to add “e.g. from the used diluent Naphtha” after “Alberta” as most listed compounds are listed as constituents of Naphtha in Siddique et al., 2007.

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We believe that these emissions are from the oil sands and/or diluents, and we have added: “e.g., from oil sands and/or diluent” to the text.

Page 18528 (18527), line 3: Is this consistent with observed isoprene levels?

Yes, it seems to be. A detailed isoprene chemistry scheme is beyond the scope of this work, but assuming MAC and MVK formation yields in the range of 0.16-0.4 from OH and O₃ reactions (Tani et al., 2010 and references therein) then the observed MAC and MVK values during Leg 7 (92 ± 63 and 141 ± 109 pptv, respectively) appear to be in the range that can be explained by isoprene chemistry. The average isoprene mixing ratio during Leg 7 was 468 ± 167 pptv. We have added these comments to the text.

Tani, A., Tobi, S. and Shimizu, S., Uptake of methacrolein and methyl vinyl ketone by tree saplings and implications for forest atmosphere, Environ. Sci. Technol., 44, 7096–7101, 2010.

Page 18534 lines 19ff: McTaggered-Cowan et al., 2010 and other sources detail that the composition of natural gas varies substantially with geographical origin, time of year, and treatment and that the content of ethane and propane can be close to zero. Do you have any information on the composition of the natural gas used at the site and whether a very low content of ethane and propane could explain the missing correlations with methane? Also, the operation of hydrocrackers could explain the emission of ethane and other alkanes without emissions of methane and thus explain the low correlations.

We thank the reviewer for these comments which prompted us to investigate possible CH₄ sources at this site more thoroughly. We are not aware of the composition of the natural gas that is typically used at the site. However, while recognizing that natural gas composition varies, a specs sheet for natural gas from western Canada suggests the following typical composition on a per mole percentage basis (http://www.naesb.org/pdf2/wgq_bps100605w2.pdf): 94.6% CH₄, 2.5% ethane, 0.2%

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propane, 0.03% i-butane, 0.03% n-butane, etc. This suggests a relative release rate of 38 moles of CH₄ to 1 mole of ethane. In our opinion this is still a relatively high ethane content. We measured a maximum CH₄ mixing ratio of 1983 ppbv over the oil sands in sample 6, or an excess of 140 ppbv over its local background value of 1843 ppbv. The ethane mixing ratio in this same air sample was 1.106 ppbv, or an excess of 0.325 ppbv over its local background. If the CH₄ enhancement were entirely due to natural gas emissions, we would expect to measure a corresponding ethane enhancement of 3.7 ppbv. Therefore the measured ethane enhancement was about 10× smaller than would be expected from natural gas emissions. That is, it does not appear that low-ethane content in natural gas explains the lack of correlation between CH₄ and ethane. We also do not believe that hydrocracking is responsible for the CH₄ enhancements (please see response to p. 18520, line 23ff). Instead we now believe that the CH₄ enhancements most likely represent tailings pond emissions. The Syncrude Mildred Lake tailings pond contains about 200 million m³ of mature fine tailings and became methanogenic in the 1990s (Holowenko et al., 2000; Siddique et al., 2008). The methanogens are believed to anaerobically degrade certain components of naphtha (C₆-C₁₀ n-alkanes and aromatics such as toluene and xylenes) into CH₄, at rates of up to 10 g CH₄ m⁻² d⁻¹ or 40 million L CH₄ d⁻¹ (Siddique et al., 2006, 2007, 2008; Holowenko et al., 2000; Penner and Foght, 2010). Ethane is not produced in anaerobic environments, and tailings ponds emissions of CH₄ would explain the relatively large CH₄ enhancements compared to ethane as well as the relatively poor correlation between CH₄ and ethane. We have added these new observations to p. 18534 and p. 18511.

Siddique, T., Fedorak, P. M., MacKinnon, M. D., and Foght, J. M.: Metabolism of BTEX and naphtha compounds to methane in oil sands tailings, *Environ. Sci. Technol.*, 41, 2350–2356, 2007.

Siddique, T., Gupta, R., Fedorak, P. M., MacKinnon, M. D., and Foght, J. M., A first approximation kinetic model to predict methane generation from an oil sands tailings

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settling basin, Chemosphere, 72, 1573–1580, 2008.

Page 18535, lines 25ff: This sentence seems somewhat strange to me. Please break it into two sentences.

We have changed this sentence to: “Carbon monoxide showed a clear (up to 48%) enhancement and strong correlations with many other compounds, but its maximum mixing ratio of the flight was not over the oil sands. By contrast the remaining 59 compounds showed greater mixing ratios over the oil sands than at any other time during the flight, and in some cases than at any other time during the entire mission.”

Page 18536, lines 17: If natural gas with low ethane and propane content is used and/or other ethane propane sources such as hydrocrackers are operated, couldn't the increased methane content by itself - without any correlations of methane with ethane and/or propane - point to natural gas leaks? Do you have knowledge on the typical natural gas content at the site or in Canada in general?

Please see response to Page 18534 lines 19ff. In short, we believe that the CH₄ emissions are inconsistent with natural gas leakage and hydrocracking emissions, and we now believe that they are primarily explained by tailings ponds emissions of CH₄. We have added the following text: “Instead, elevated CH₄ levels are consistent with methanogenic tailings pond emissions.” We have made a similar addition to the abstract.

Figure 2 A, B: The flight tracks are very hard to see. Could you use different colors, e.g. yellow? Could you add the trajectory or the prevailing wind direction somehow?

The prevailing wind direction was from the southwest quadrant but varied for each air sample. Therefore we have now added a column to Table 2 which states the wind direction for each air sample during Flight Leg 7. In addition we have added the following text to the Figure caption: “The prevailing wind direction was from the southwest quadrant, and samples 4, 5 and 6 were directly downwind of the oil sands operations (the

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grey patch just above the center of the figure).” The trajectories are shown in Figure 3 for both Flight Legs 7 and 9.

Figure 2 B: Why are not all sample locations shown?

We didn’t show all sample locations because we thought it would clutter up the map too much. Instead we have shown samples in which a maximum trace gas reading was measured.

Figure 2 lower part: The sample numbers are very hard to read.

Based on comments from Reviewer 2 we have omitted Panel C. This also avoids unintended confusion over the fact that Panel C shows Flight Legs and not sample numbers.

Figure 3: It would improve readability of the figure to zoom in much more, focusing on the trajectories, and not wasting too much space on a mostly empty map.

We have revised Figure 3 accordingly.

Figure 4: It is literally impossible to access trace gas variability from most figures. The CFC-11 and 12 figure e.g. could be modified with a y-scale from 200 to 600 ppt. The C2Cl4 data e.g. could be plotted on the altitude scale. Some of the other plots could be improved e.g. by breaking the y-scale in two scales and thus having different resolution for low and high points and/or by plotting some of data on logarithmic scales.

Reviewer 2 also requested changes to Figure 4 in order to better access the trace gas variability. In Panel A we have modified the y-scale from 200 to 600 pptv. In Panel B we have opted to change the y-scale from 20 to 16 (our concern is that it might be too confusing to have C2Cl4 on the altitude scale). For panel D we have put SO2 on a logarithmic scale. For Panels E and F we have now paired benzene with cyclohexane, and toluene with methylcyclohexane. For the remaining panels (C, G and H) broken y-scales or logarithmic scales did not apply as well because their mixing ratios were below detection limit for most of the flight and there was no low-number variability to

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present. We have made the following clarifications in the Figure 4 caption: “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.”

Figures 5-9: Many of the figures should be improved e.g. by shrinking the scales, by breaking the x-scales in two scales and thus having different resolution for low and high points and/or by plotting some of the data on logarithmic scales.

We have thought carefully about how to improve the presentation of each graph. We have shrunk the scales in Figures 5a, 8a, 8c, 8e-f and 9d-f, and we have added breaks to the x-scales in Figures 5c-f, 6a-e, 8b and 9a-b. We felt that Figures 5b, 6f, 7a-f, 8d and 9c were already sufficiently clear.

Technical corrections:

Page 18509, line 15, page 18510, line 2, line 7, etc.: Be consistent about the use of ‘commas’ in enumerations before “and”.

We have reviewed the paper paying attention to this. In general we don’t use a comma, except when there is more than one word in the penultimate clause.

Page 18509, line 18: Remove “up to”.

Done.

Page 18510, line 4: Add “x” after “383”.

Done. We also added “ppbv” after 38.7 for consistency.

Page 18510, line 12: Add “ppt” after “217”.

Done (pptv).

Page 18510, line 13: Add “ppt” after “20_7”.

Done (pptv).

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Page 18511, lines 11-12: The link does not work.

I am not sure why. It works when I click on it from the discussion manuscript on the ACPD website.

Page 18512, line 28 and similar: Rather use “45 s long integrated”.

We have changed “45-s” to “45 s” but prefer not to use “long”.

Page 18513, lines 21 and 24, etc.: Be consistent about “leg” or “Leg”.

We have changed “Flight leg 9” to “Leg 9”.

Page 18514, line 6: Replace “2002; 2006” with “2002, 2006”.

Done.

Page 18514, line 19: “liquid nitrogen cleaned” is lab jargon.

We use molecular sieve and activated charcoal traps maintained at -196°C . We have removed “liquid nitrogen cleaned” from the sentence.

Page 18515, line 5: Replace ‘1/4 in.’ with ‘1/4 “’.

Done.

Page 18515, line 20: “An instrument mass flow controller (Brooks, manufacturer place, 5850E model)”.

We have changed this to: “. . .a mass flow controller (Brooks Instrument; Hatfield, PA; model 5850E).”

Page 18514, line 21: How has the water been purified?

1 L of millipure water is added to a 2 L can and boiled.

Page 18515, lines 26: Specify manufacturer and model of each column, e.g. which PLOT column was used?

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We have changed this text to: “The sample flow is split into five streams, with each stream chromatographically separated on an individual column and sensed by a single detector, namely: (1) a DB-1 fused silica capillary column (J&W Scientific; 60 m, I.D. 0.32 mm, film 1 mm) connected to an FID; (2) a GS-Alumina PLOT column (J&W Scientific; 30 m, I.D. 0.53 mm) spliced with a DB-1 fused silica capillary column (J&W Scientific; 5 m, I.D. 0.53 mm, film 1 mm) and connected to an FID; (3) a Rtx-1701 fused silica capillary column (Restek; 60 m, I.D. 0.25 mm, film 0.50 mm) connected to an ECD; (4) a DB-5 column (J&W Scientific; 30 m, I.D. 0.25 mm, film 1 mm) spliced with a Rtx-1701 column (Restek; 5 m, I.D. 0.25 mm, film 0.5 mm) and connected to an ECD; and (5) a DB-5ms fused silica capillary column (J&W Scientific; 60 m, I.D. 0.25 mm, film 0.5 mm) connected to an MSD.” We cite J&W Scientific while recognizing that Agilent Technologies has acquired J&W.

Page 18516, line 7 (8): “: : and its integration is manually”.

Done.

Page 18516, line 8: Why do the peaks need to be manually integrated? Is the chromatography changing so much that an automatic integrator does not work?

Yes, that is the concern. On occasion the peaks can shift and co-elute, and manual integration ensures that each peak is properly captured.

Page 18516, lines 10ff: Please specify how the standards were certified.

The hydrocarbon standards are NIST-traceable. The halocarbon standards are either NIST-traceable or have been calibrated using our own in-house standards that have been compared with NOAA and AGAGE standards. We have added this to the text.

Page 18516, lines 15ff: Are there any compounds which have not been intercalibrated?

Yes. We have participated in formal intercomparison experiments including the Non-methane Hydrocarbon Intercomparison Experiment (NOMHICE) and the International HALocarbons in Air Comparison Experiment (IHALACE). Tasks 3 and 4 of NOMHICE

included 57 and 54 hydrocarbons in the master cylinder, respectively (Apel et al., 1999; 2003). Of the 50 C₂-C₁₀ hydrocarbons reported here, the 12 that were not included in NOMHICE are: 1,3-butadiene, 1,2,3-trimethylbenzene, β -pinene, furan, methanol, ethanol, acetone, acetaldehyde, MEK, MAC, MVK and MTBE. The 2005 IHALACE experiment included 15 halocarbons. Of the 26 halocarbons reported here, the 11 not included in IHALACE are: CFC-114, HFC-134a, CH₂Cl₂, C₂HCl₃, C₂Cl₄, CH₃I, CHBrCl₂, CHBr₂Cl, CHCl₃, ethyl chloride and 1,2-dichloroethene.

Page 18516, line 16: Replace “unknown” with “blindly selected”.

Done.

Page 18516, line 23: Is it “onboard” or “aboard”?

“Aboard” can mean on a ship, train, airplane or other passenger vehicle so I think it’s OK.

Page 18518, line 5: “are available at”.

Done.

Page 18518, line 16: Please list the HCFCs.

Done. We have changed this to: “...some HCFCs (HCFC-22 and HCFC-142b)...”

Page 18520, line 16: To increase readability, please use “4407 pptv ethane; 2713 pptv propane”.

Done.

Page 18522, lines 20 and 21: Please add “maximum” in the brackets.

Done (we used “maxima” for the xylenes, which are plural).

Page 18523, line 22: Please remove “,” after “ethane” to improve readability.

For consistency we have instead changed it according to your comment on p. 18520,

line 16.

Page 18523, line 27: “the summer of 2006”.

Done.

Page 18527, lines 18 and 19: Please remove brackets.

Done.

Page 18531, line 29: “the first half of the”.

Done.

Headers 2.2, 3.2.1, 3.2.2, 3.2.3, 3.5: Please add “and”.

Done.

Page 18532, last sentence and page 18533, first sentence: Please remove brackets.

Done.

Page 18533, line 23 (18): “: : : emissions lead to a titration of O₃, : : :”.

We now write: “...emissions led to a titration of O₃, a loss process which...”.

Page 18536, line 23: Add “_pinene and _pinene”.

Done.

Table 3: Please do not use compound abbreviations such as “2+3-MePentane”.

Fixed.

Table 3: How were the compounds on the y-axis selected?

Do you mean how did we choose which species we wanted to show the correlations for? We sought to show compounds from different classes as well as compounds from different sources. For each class of compounds, the representative species we

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chose was usually the one that was the most abundantly emitted. For the different sources, we chose SO₂ (coke combustion), NO (upgrader emissions), ethene (industry and combustion), propane (potentially natural gas), n-butane (mixture of evaporative sources), and n-heptane, toluene and methylcyclohexane (oil sands).

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

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