

Thank-you to both referees for their comments. We respond to both sets of comments here.

**Anonymous Referee #1 Received and published: 5 January 2018**

Summary/General comments: Baray et al. present aircraft measurements made around the Athabasca Oil Sands region and employ multiple mass balance approaches to quantify methane emissions from the entire region as well as individual facilities/components to the region. They also use multiple trace gases to attribute to specific processes, and compare results with reported inventories emissions. This paper is well placed in ACP. This paper contributes to our understanding of methane emissions from a unique but potentially high impact source region. Overall this is a well-written paper, a very nice/sound analysis, and I enthusiastically recommend publishing with only a few minor suggestions.

**Response:** Thank-you for your efforts. Your comments are appreciated.

Minor comments: Page 4, lines 1-20: this introduction portion is long and dedicated to the recent confusion about global methane and global methane trends. While accurately written, I don't think it is helpful for this paper. Addressing methane emissions from the oil sands is not going to help with these large questions, and motivating the oil sands emissions does not need invoking some of the global decadal confusion, but instead could be better motivated focusing on the work in the last 10 years attempting to address methane emissions from the oil and gas production sector, where large discrepancies have been found and this work contributed nicely.

**Response:** Yes, both reviewers agree on this point. We have now shortened the introduction significantly, while retaining the important points that motivate the current study.

Throughout: Please change the units for methane from ppm to ppb. It is standard to work with methane in ppb, and as the signals observed and discussed make more sense to see in ppb than ppm, this change should be made throughout.

**Response:** With respect, we would prefer to leave the units presented in many figures and throughout as ppm, rather than ppb. Standardization is not always the best way. At times it is more convenient to use ppm, while sometimes (i.e., when we discuss enhancements) it is more convenient to use ppb. It depends on the size of the numbers. For example, the scale in Fig 2a goes from 2.0 to 4.5 ppm with two significant figures. If converted to ppb, the scale in this figure (and many others) would need to be have four significant figures for every tick, from 2000 to 4500ppm, an unnecessary use of excess figures, in our opinion. At other times when discussing an enhancement of say 1.1 ppm, because of a lack of precision in the number we would be forced to present the enhancement as  $1.1 \times 10^3$  ppb if using ppb, so as not to use excessive significant figures. It would be better to discuss such an enhancement as 1.1 ppm. Scientific readers should not have trouble interpreting both ppb and ppm in the same publication we think. We have seen many publications that publish CH<sub>4</sub> using ppm, as well as ppb.

Figure 1: Would help a lot to have spatial scale on these figures. Also would be useful to have some wind arrows indicating what winds look like on each of these flight days.

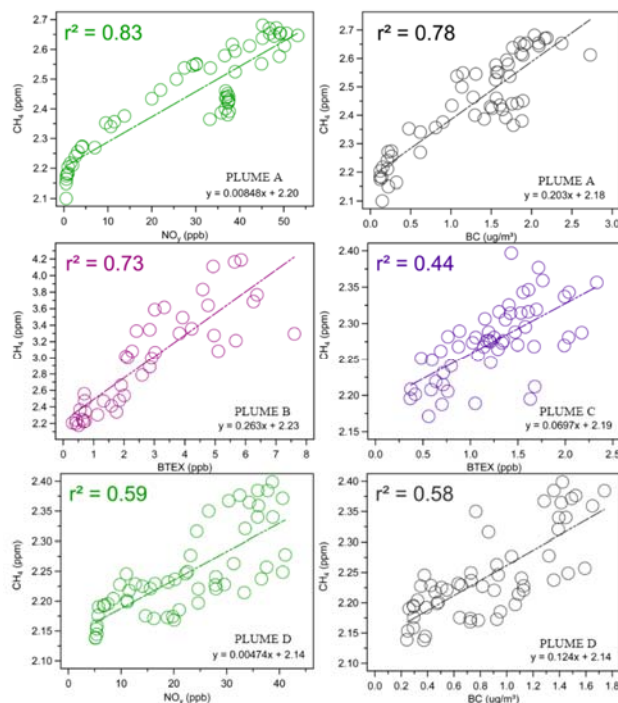
Response: Agreed. We have now added both a spatial scale and the average wind direction vector for each plot in Figure 1.

Figure 3 (and applies to other plumes): I would like to see what the correlation looks like between different gases within each designated plume. Some tracer-tracer plots with the different plumes shown would be helpful to show/establish how robust the correlations are for each of these tracer-tracer relations.

Response: We have now included a Figure in Supplemental (see below) that demonstrates the correlation of CH<sub>4</sub> (vs NO<sub>y</sub>, rBC, and BTEX), in the major plumes seen in Figure 2. Text has been added to the main paper alerting the reader to the Supplemental Figure.

*“The in-plume correlations of CH<sub>4</sub> with the associated tracers (NO<sub>y</sub>, rBC and BTEX) for each of the Plumes identified in Figure 2 are shown in Figure S2 (Supplemental Information).”*

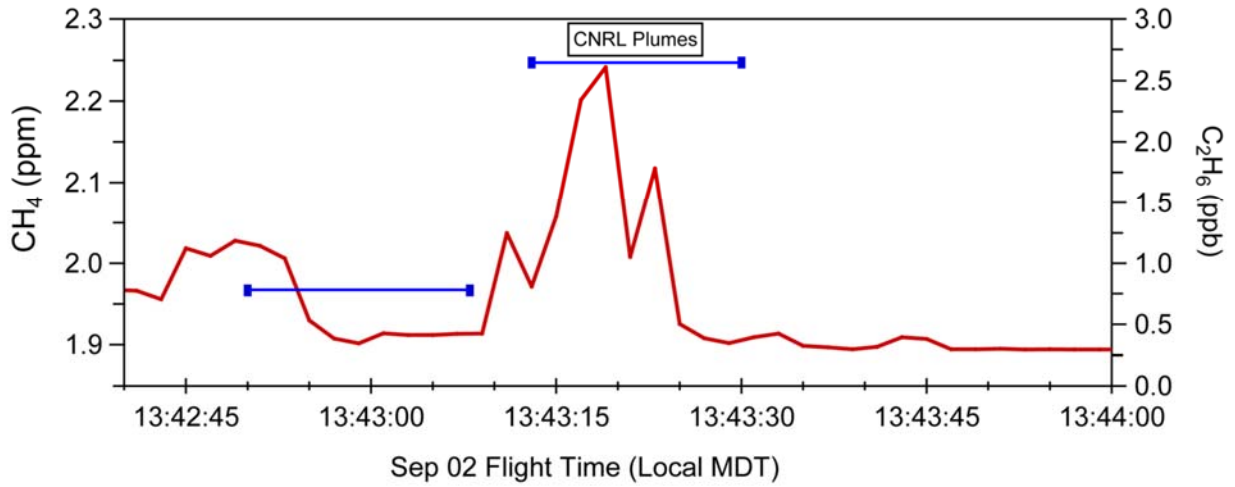
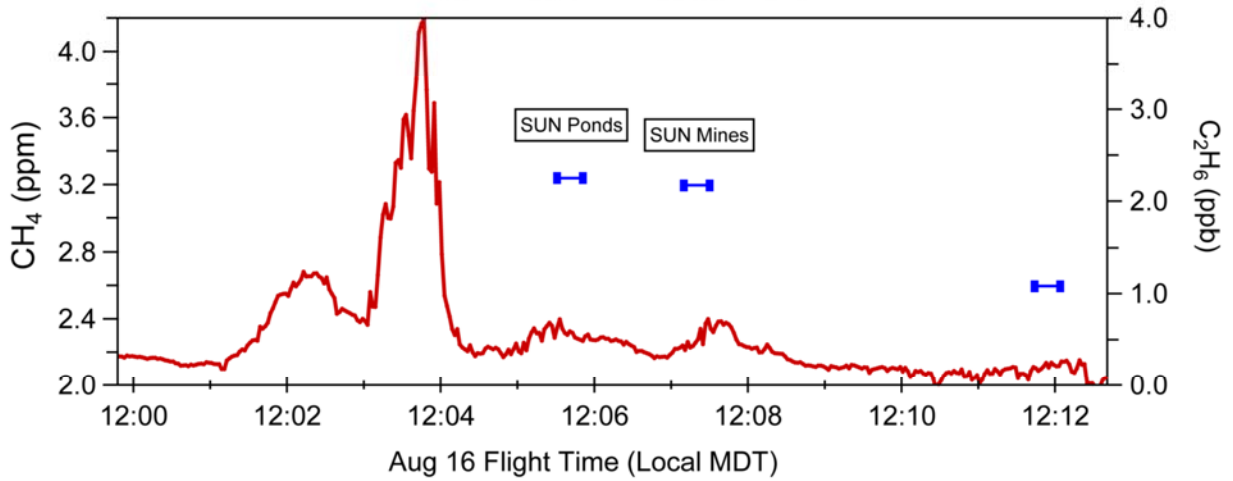
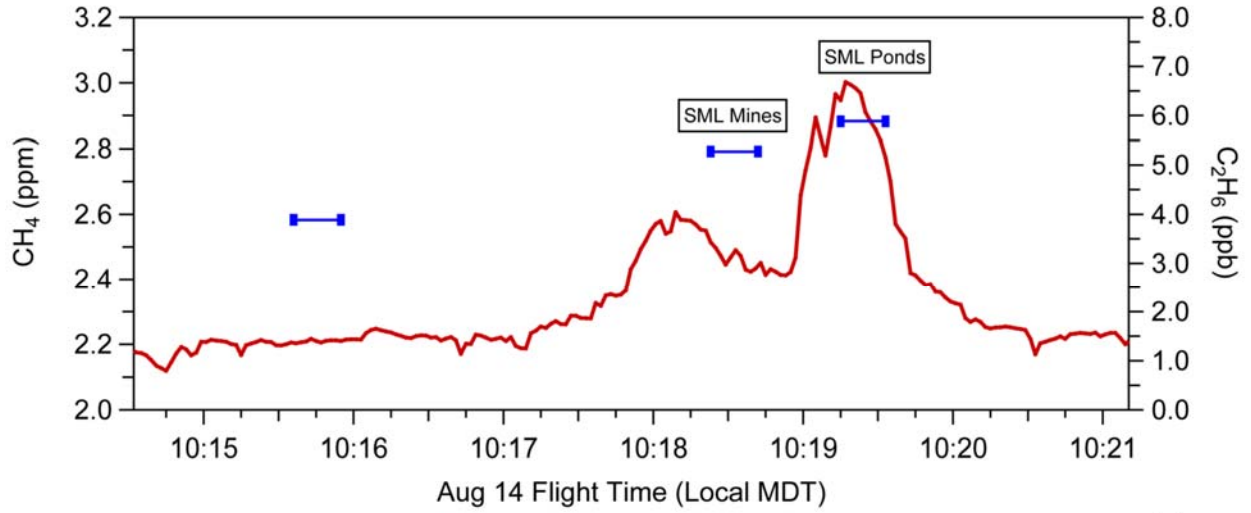
*Fig S2: Correlation Plots for Plumes A-D corresponding to Figure 2 (SML Mine, SML Tailings Pond, SUN Tailings Pond, SUN Mine). CH<sub>4</sub> is well correlated with tracer species NO<sub>y</sub>, BC and BTEX for the various sources. Linear coefficients of determination ( $r^2$ ) are in the range of 0.44-0.83. The lowest  $r^2$  values are from the CH<sub>4</sub> vs BTEX plot for Plume C and the CH<sub>4</sub> vs NO<sub>y</sub> and CH<sub>4</sub> vs BC plots for Plume D. These two sources correspond to lower emissions and mixing ratios of both CH<sub>4</sub> and the associated species. In the context of our results, this analysis confirms the correlation of CH<sub>4</sub> with various species as shown in Figure 2 which are used to spatially define plume boundaries.*



Page 16, Lines 1-18 as well as Table 1: I'm a little worried about the ethane:methane analysis and would like more supporting information. Smith, Kort, Karion et al., 2015 ES&T used continuous ethane:methane measurements over the Barnett Shale and showed that using limited, discrete flask samples could lead to erroneous ethane:methane ratios. It would help if the authors showed on the time series plot illustrating the plume where in the plume(s) the flasks were collected to help illustrate what the flask ethane may be representative of. The limited discrete samples may have been sufficient, or there may be important gaps causing an uncertainty in how much ethane in fact was emitted – at this point I cannot assess this and this should be improved.

Response: Good point. We have now added a figure in supplemental that shows where the discrete canisters were taken in relation to the CH<sub>4</sub> plumes. The key result is that none of the sources mentioned in the paper appear to be significant sources of ethane, and overall there was low ethane observed in the AOSR, consistent with Simpson et al., 2010. We agree that limited discrete sampling can be misleading, and the uncertainty of the ethane/methane ratios will be much higher than would be available if continuous ethane and methane measurements were available. However, our purpose was to demonstrate the low ethane/methane ratios of the sources in the region, in contrast to methane sources in other conventional oil and gas regions. The following text has been added to the paper...in addition we will add a reference to the Smith et al. paper and add a line acknowledging the potential for problems with EMR's when combining discrete and continuous samples.

*Figure S3: Time series plots of methane (red line) and discrete canisters samples analyzed for ethane (blue lines) corresponding to the same plumes used in Table 1 for the ethane/methane ratio calculations. These are a small subset of the canisters that were sampled over the aircraft campaign. These example plumes attempt to isolate known sources from the three facilities and support the conclusion that there were not any significant sources of ethane in the AOSR, in agreement with Simpson et al., 2010.*

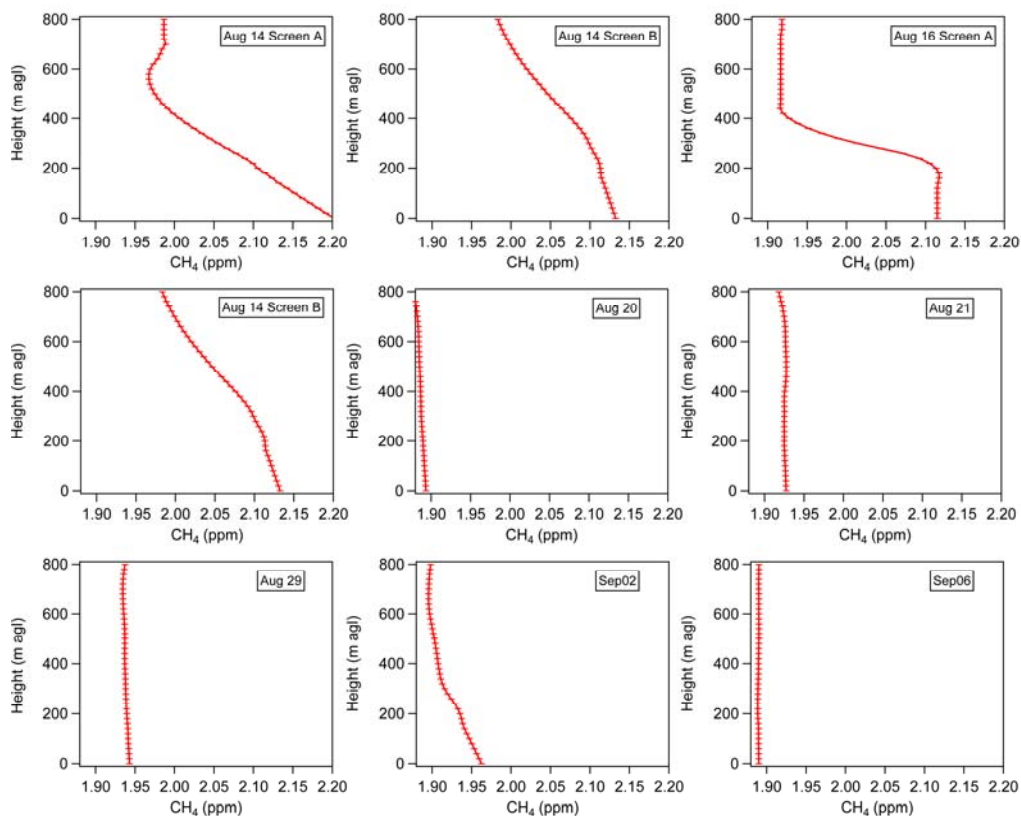


Page 18 Line 6: The vertically varying background can be troublesome/worrisome. It would be helpful to see the profile that is used here and understand how variable the background is.

Response: We have now included the vertical profiles  $[CH_4]_B(z)$ , for each screen determination, in Figure S1 (Supplemental Information). The use of vertically variant profiles is an improvement over the use of a single invariant background number at all heights, since on some days, a regional buildup of  $CH_4$  from other surface sources upwind of the source in question can occur. This is an established method in the literature, as stated in Section 2. We have added the following text in section 2:

*“Example vertical profiles of  $[CH_4]_B(z)$  for each day are included in Figure S1 (Supplemental Information)”*

*Figure S1: Background profiles,  $[CH_4]_B(z)$ , were selected from regions of the interpolated screens away from plume sources, corresponding to 2-20km spatial lengths depending on the flight paths. Error bars are the  $1\sigma$  variability within the 2-20km spatial regions of background air. Background  $CH_4$  for the vertical regions 150-200m above ground to the surface are estimated based on extrapolations (constant or linear) from the lowest transects to the surface and included in the uncertainty analysis. The lowest aircraft transects usually converged to a constant value (Box 3,5,6,7,9 left to right) or showed a small linear enhancement (Box 2,4,8) which provided best fits to the surface.*



Page26,lines1-2: Should specify the seasonality of fugitive emissions from this unique oil sands source are unknown, not fugitive emissions in general.

Response: Yes. Wording was changed to:

*"...however, we consider this assumption to be highly uncertain as the seasonality of fugitive emissions rates of CH<sub>4</sub> in the Athabasca Oil Sands region is still a major uncertainty."*

**Anonymous Referee #2 Received and published: 12 January 2018**

This paper presents a thorough study of emissions from oil sands facilities. While methane is the focus of these aircraft measurements, a number of complimentary species help to characterize emissions and separate individual sub-sources at each site. The authors do a nice job of contrasting the emissions from the different facilities visited, and bring in previous measurement and inventory work for context. The paper is well-written and organized. The curtain and box methodologies are accurately and simply described. I believe this paper is appropriate for publication in ACP, with only a few minor edits:

Response: Thank-you for your efforts. Your comments are appreciated.

The first two and a half pages of introductory material discuss methane and its climate and ozone formation impacts. I think that this background material should be condensed, with more of a focus on the oil sands region.

Response: Yes, both reviewers agree on this point. We have now shortened the introduction significantly, while retaining the important points.

The introductory material starting on page 5, line 11 is of utmost interest to this study. I recommend this section be supplemented with a sentence or two about anaerobic methane formation in tailings ponds, which is mentioned briefly later (p. 14 line 5).

Response: Yes, we will do this, after more careful study of the Small et al paper. Final text will be decided upon in the revised paper.

Related to the above comment, on p. 20 line 24, the authors note that younger ponds should produce less methane. The subject of tailing pond methane emissions warrants a paragraph of discussion in the text, explaining why the high emissions from P23 and WIP might be expected (age, any other process differences), and why emissions of methane were low/undetected from other ponds.

Response: Perhaps instead of WIP, you meant MLB? In any case, a few lines will be added, yes. A paragraph of discussion on this topic might be beyond the scope of this paper though. Final text will be decided upon in the revised paper.

p.14, line 19: "we did not detect methane": Were any canisters taken showing light hydrocarbon enhancements?

Response: No and yes. A few canisters were taken on these flights, but unfortunately they were too sparse and uncertain as to isolate the tailings ponds emissions. Canister samples were opportunistic, usually taken downwind of facilities within major plumes identified by the major pollutants (NO<sub>x</sub>, SO<sub>x</sub>, CH<sub>4</sub>, CO<sub>2</sub>). Perhaps future studies could address this.

p. 20 line 12: Is there a reference or previous study that looks at this degassing rate?

Response: We are not aware of such a study. However, the stated assumption is scientifically reasonable. The only analogy we can draw is to the difference in vapor composition of a spilled gasoline sample vs gasoline vapor in equilibrium with liquid gasoline. In the former case, due to the time allowed for complete evaporation (minutes to hours depending on the size of the spilled gasoline sample), the vapor composition is identical to the spilled sample composition...quantitatively, due to mass balance (This is what we expect for methane). For the equilibrated vapor sample, the vapor composition reflects the distilled vapor composition which can be predicted using the saturated vapor pressure of the individual components, their mole ratios, and Raoult's Law. Methane is more volatile than any individual component of a gasoline sample. We have reworded the sentence to say...

*"This is reasonable considering that it would be expected that degassing of an extremely volatile gas such as CH<sub>4</sub> from the oil sands material would be quantitative in a short period of time after the ore is exposed or crushed."*

p. 22 line 19, and elsewhere: When discussing seasonality of emissions, it would be useful to remind the reader that these measurements were taken in August-September

Response: We agree such a reminder would be useful here. For most effect, we add the reminder in the very last sentence, before moving to Section 3.5 on comparison to emission inventories...

*"The two values are combined here using an error-weighted uncertainty resulting in a final AOSR facility emissions estimate of  $19.6 \pm 1.1$  tonnes CH<sub>4</sub> hr<sup>-1</sup>, measured during a summertime period."*

p. 23, line 25: The wording "rightly or wrongly" suggests a contested issue, and I would suggest re-wording. Is there more background material on tailings ponds and their anaerobic activity that could supplement this discussion?

Response: " rightly or wrongly" has been removed with a slight rewording of the sentence to ....

*"The argument used to justify the use of a constant seasonal temporal factor in the GOA report is that temperatures at depth in a tailings pond are said to remain relatively constant throughout the year and thus, biogenic gas formation continues in the winter (GOA, 2014)."*

p. 24 line 28: Describe this methodology, e.g. by changing to "recent core sampling methodology".

Response: Yes. As suggested this has been changed to "...recent core sampling methodology..."

Figure 1: Include wind barbs or a wind direction arrow on each map

Response: We have now added both a spatial scale and the average wind direction vector for each plot.

Figures 2 and 3: The colored markers appear to be wind direction arrows, which is an important parameter in these graphs. However, the arrows are very difficult to see. I recommend mentioning them in the figure captions, and making the markers more obvious (sparser, outlined, or some other format).

Response: We have now mentioned them in the figure caption, making them sparser would mean removing data points as well. We feel it may be too sparse. The large red arrows in the figure are a backwards extension of the small wind barbs, which give a good idea of wind direction.

Text has been added to each Figure caption in Fig 2 and Fig 3...

*"Each data point is color coded for CH<sub>4</sub> mixing ratio as well as instantaneous wind vector measured on the aircraft at that location."*

Figure 8: remove "date" from bottom axis

Response Yes, the label (including date) has now been removed from the Figure.

### **Typos/typesetting**

p. 4, line 19: CH<sub>4</sub> subscript

Response: fixed.

p.9 line 17: double-check notation/formatting of U-square. subscripts on sn, s1

Response: fixed.

p. 12 lines 24-25: degree symbol

Response: fixed.

p. 24: I suggest more emphasis on Figure 8 in this section (e.g. reference it on line 8)

Response: Our reference to Fig 8 in the text is somewhat later, yes. We have now added the reference sooner in the section...

*"The annual emission rates of CH<sub>4</sub> extracted from the inventory were downscaled to hourly emissions rates for comparison with our measurements with an assumption of equal seasonal*



*and diurnal profiles 365 days a year, 24 hours per day; for consistency with upscaling factors used to generate annual emissions (see Figure 8).*”

Most of the section before this is a discussion of how we get the last column in Fig 8...Inventory.

We then have a full paragraph discussing Fig 8, which we feel is perhaps adequate.