Thank-you to both referees for their comments. We respond to both sets of comments here. Black are comments. Our responses are in blue, normal font, with text additions *"also in blue with quotes, italicized and sometimes underlined."* Following is the paper with track changes.

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 inventorie 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 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 x10^3 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_4 in 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 demonstates the correlation of CH_4 (vs NOy, 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_4 with the associated tracers (NOy, 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_4 is well correlated with tracer species NOy, 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_4 vs BTEX plot for Plume C and the CH_4 vs NOy and CH_4 vs BC plots for Plume D. These two sources correspond to lower emissions and mixing ratios of both CH_4 and the associated species. In the context of our results, this analysis confirms the correlation of CH4 with various species as shown in Figure 2 which are used to spatially define plume boundaries."
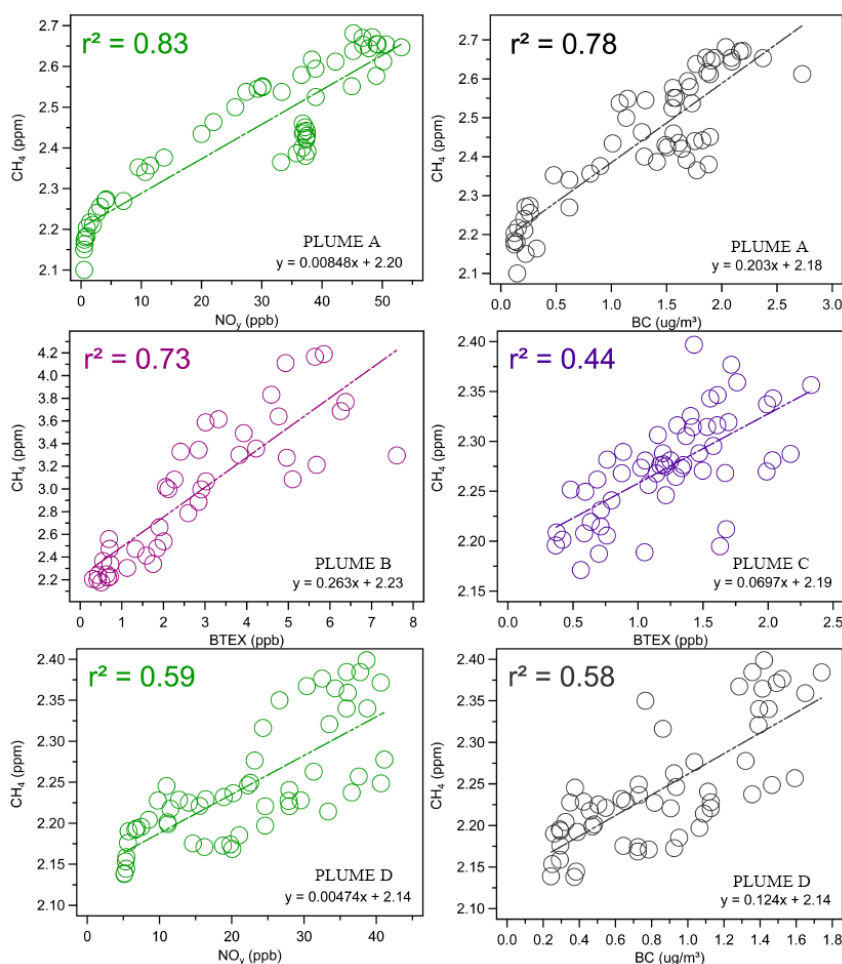
Page 16, Lines 1-18 as well as Table 1: I'm a little worried about the ethane:methane analysis and would like more supporting information. Smith, Kort, Karion et al., 2015 ES&T used continuous ethane:methane measurements over the Barnett Shale and showed that using limited, discrete flask samples could 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_4 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 this section, including references to Smith et al., 2015. Thanks for pointing out this reference,

"Source profiles of CH_4 are further compared to measurements of ethane (C_2H_6). Source-attribution studies for CH_4 commonly use higher ethane-to-methane ratios (EMRs) as a signature for oil and gas emissions, on both a regional (Peischl et al., 2016) and global (Hausmann et al., 2016) scale, while low EMR ratios can be indicative of microbial sources of methane that do not emit ethane (agriculture, landfills, wetlands, etc.) (Smith et al., 2015)."

and

"The problems associated with determining EMR ratios from a combination of continuous CH_4 measurements and discrete canister sampling of ethane from aircraft have been highlighted recently, where it was shown that actual EMR ratios determined in this way can be off by up to a factor of two (Smith et al., 2015). Thus the limited EMR data shown in the Table 1 are not intended to be a comprehensive measure of EMR in the AOSR but simply to support the conclusion that the major sources of methane from the facilities in the AOSR are microbial in nature without a significant co-emission of ethane."

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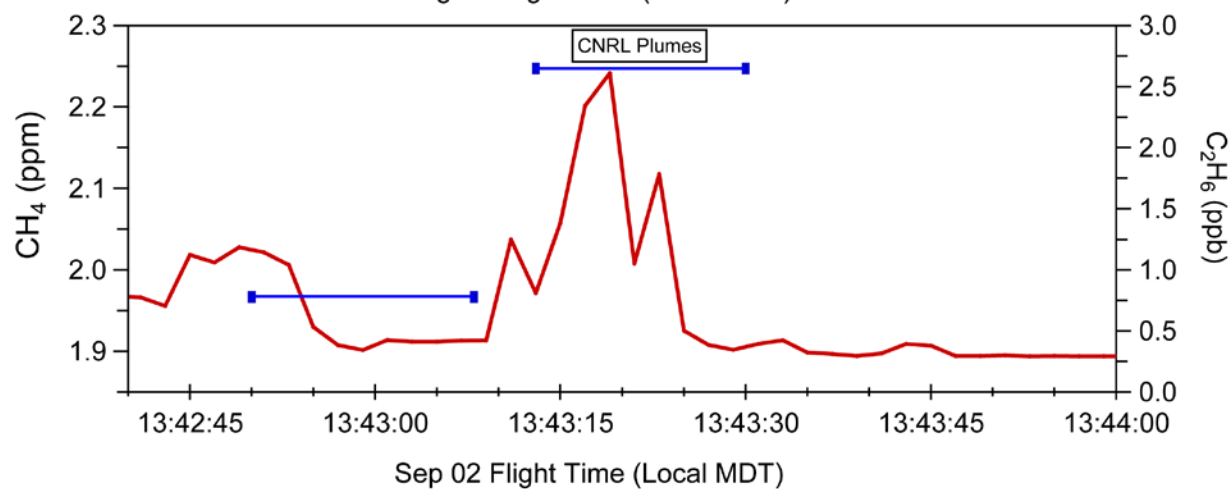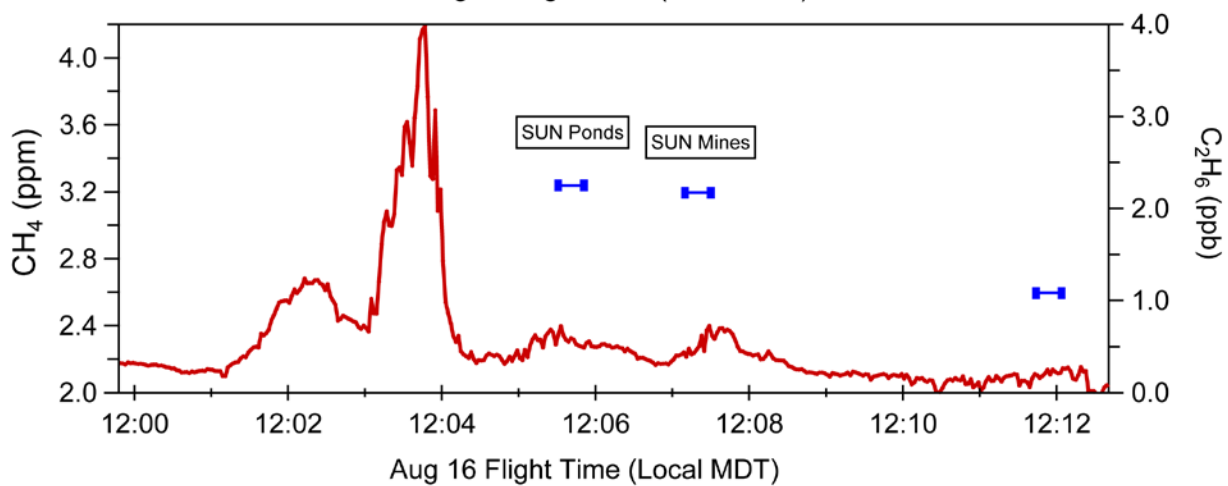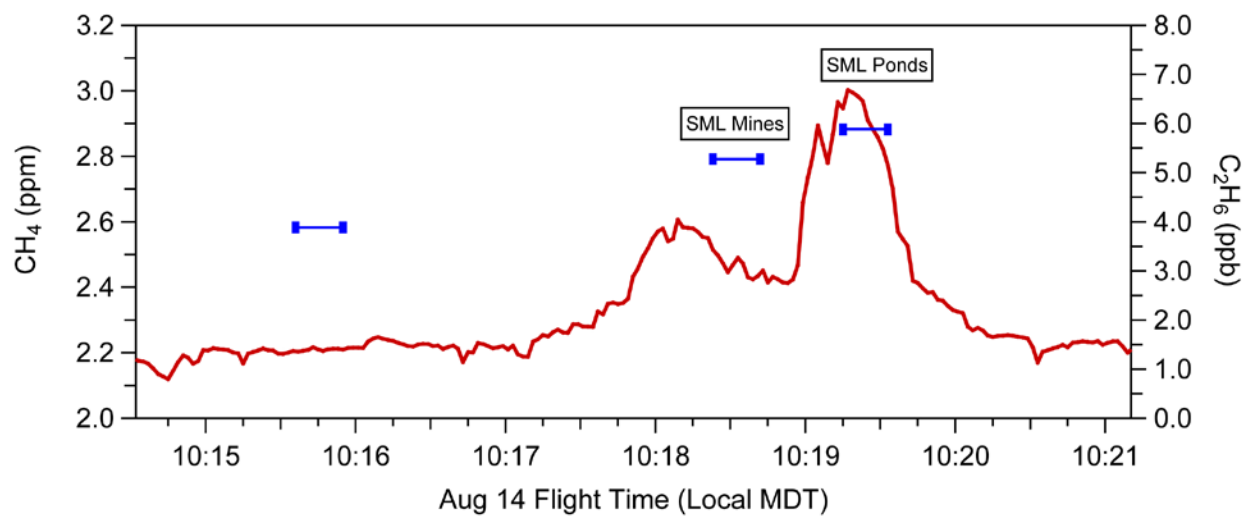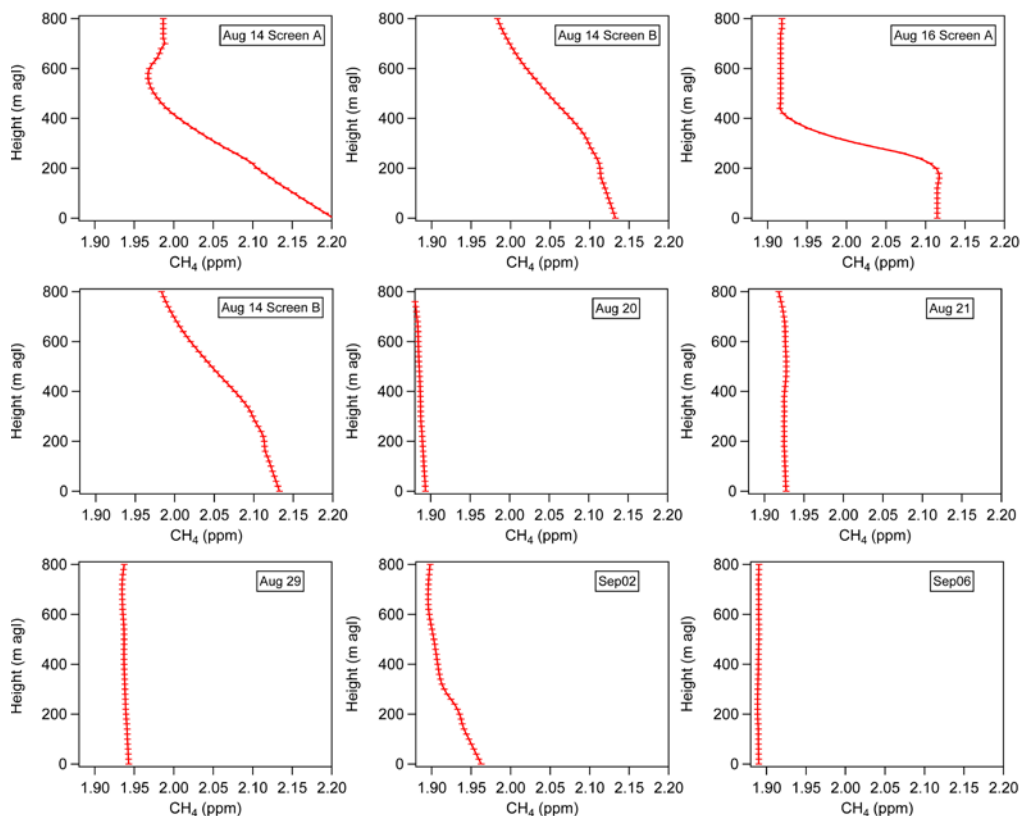
Page 18 Line 6: The vertically varying background can be troublesome/worrisome. It would be helpful to see the profile that is used here and understand how variable the background is.

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 1σ 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$_4$ 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 have added the following text.

In particular, a significant fraction of the CH$_4$ is not associated with fossil fuel reserves, but is emitted from the tailings ponds (Small et al., 2015). The factors giving rise to the release of CH$_4$ from these ponds are complex but include the organic and inorganic chemical composition of the ponds, the diversity and types of microbial communities, especially methanogens, as well as the age of the ponds. It is reported that it took 20 years and 15 years for the largest ponds at Syncrude and Suncor respectively, to show evidence of methane bubbling from the surface (Small et al., 2015).

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 and we want to avoid being speculative, going beyond the scope of the paper. A few lines were added as such…

"Our method requires CH_4 plumes to be clearly enhanced above background, so trace amounts of CH_4 from ponds in the other three facilities were not detected. This could be related to differences in the chemical composition of the process streams being released into these ponds, or it could simply be due to these ponds being younger in age, with insufficient time for the anaerobic methanogenic communities to be established (Small et al., 2015)."

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 (NOx, SOx, CH_4, CO_2). 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_4 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 ± 1.1 tonnes CH_4 hr^{-1}, <u>measured during a summertime period."</u>

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_4 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: CH4 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_4 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.

Quantification of Methane Sources in the Athabasca Oil Sands Region of Alberta by Aircraft Mass-Balance

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Abstract. Aircraft-based measurements of methane (CH_4) and other air pollutants in the Athabasca Oil Sands Region (AOSR) were made during a summer intensive field campaign between August 13 and September 7 2013, in support of the Joint Canada–Alberta Implementation Plan for Oil Sands Monitoring. Chemical signatures were used to identify CH_4 sources from tailings ponds (BTEX VOC's), open-pit surface mines (NO_y and rBC) and elevated plumes from bitumen upgrading facilities (SO_2 and NO_y). Emission rates of CH_4 were determined for the five primary surface mining facilities in the region using two mass balance methods. Emission rates from source categories within each facility were estimated when plumes from the sources were spatially separable. Tailings ponds accounted for 45% of total CH_4 emissions measured from the major surface mining facilities in the region while emissions from operations in the open pit mines accounted for ~50%. The average open pit surface mining emission rates ranged from 1.2 to 2.8 tonnes of CH_4 hr^{-1} for different facilities in the AOSR. Amongst the 19 tailings ponds, Mildred Lake Settling Basin, the oldest pond in the region, was found to be responsible for the majority of tailings ponds emissions of CH_4 (>70%). The sum of measured emission rates of CH_4 from the five major facilities, 19.2 ± 1.1 tonnes CH_4 hr^{-1}, was similar to a single mass balance determination of CH_4 from all major sources in the AOSR determined from a single flight downwind of the facilities, 23.7 ± 3.7 tonnes CH_4 hr^{-1}. The measured hourly CH_4 emission rate from all facilities in the AOSR is $48 \pm 8\%$ higher than that extracted for 2013 from the Canadian Green House Gas Reporting Program, a legislated facility-reported Emissions Inventory, converted to hourly units. The measured emissions correspond to an emissions rate of 0.17 ± 0.01 Tg CH_4 yr^{-1}, if the emissions are

assumed temporally constant, an uncertain assumption. The emission rates reported here are relevant for the summer season. In future, effort should be devoted to measurements in different seasons to further our understanding of seasonal parameters impacting fugitive emissions of CH_4 and to allow better estimates of annual emissions and year to year variability.

Introduction

Methane (CH_4) is a significant greenhouse gas (GHG), second in rank to carbon dioxide (CO_2) in terms of its direct radiative forcing (Montzka et al., 2011;IPCC, 2013). Controlling emissions of CH_4 is an attractive climate control strategy because of its shorter atmospheric lifetime ($\tau \sim 9$ years) and larger global warming potential (GWP) compared to CO_2 (IPCC, 2013). ~~Sources~~ Emissions of CH_4 ~~to the atmosphere fall into three broad categories:~~ include biogenic (animal husbandry, ~~waste/~~landfills, wetlands, agriculture), pyrogenic (biomass burning) and thermogenic sources (~~coal bed methane,~~ fossil fuel reservoirs~~, etc~~). The most important ~~In order of importance, the~~ sinks of CH_4 ~~include~~ is reaction with the hydroxyl radical (OH) in the troposphere (Vaghjiani and Ravishankara, 1991) .~~, destruction in the stratosphere, soil uptake processes (IPCC, 2013) and reaction with Cl atoms in the upper troposphere-lower stratosphere. With an atmospheric lifetime of about 9 years, CH_4 is first oxidized to~~ which produces formaldehyde (HCHO)~~,which~~ that is subsequently photolyzed or oxidized to yield CO and eventually CO_2. ~~Controlling emissions of CH_4 is an attractive climate control strategy because of its short lifetime and its larger global warming potential (GWP) and global temperature change potential (GTP) compared to CO_2 (IPCC, 2013).~~

In addition to climate implications, CH_4 ~~can~~ also ~~have~~ has air quality implications through its role in NO_x catalysed ozone formation in the troposphere, especially in areas with large sources of CH_4. ~~on global and regional scales. Of r~~Recent interest~~ly are,~~ wintertime rapid ozone formation events (OFEs) seen in regions of intense oil and gas extraction ~~with advanced directional drilling and hydraulic fracturing, boundary layer O_3 greater than 140 ppb has been observed frequently in wintertime~~ (Pinto, 2009;Schnell et al., 2009). ~~These high O_3 levels are associated with enhanced VOC levels (including CH_4) and moderate NO_x levels that result from the oil and gas extraction activities. These rapid ozone formation events (OFEs) in winter are interesting not only because~~ that are associated with snow coverage ~~is a necessary ingredient~~ (Edwards et al., 2013)~~(Edwards et al., 2014),~~. ~~but also due to their contrast to both summertime smog events (Finlayson-Pitts and Pitts, 1997) and ozone depletion events (ODE's) over snow in arctic regions (Barrie et al., 1988). Further study has shown that the winter OFE's are driven by stagnation in~~ shallow boundary layers (Schnell et al., 2016), ~~enhanced photolysis rates over snow,~~ high levels of ozone precursors and enhanced photolysis of HCHO and other carbonyls

under radical limited conditions ~~during these events~~ (Edwards et al., 2014). ~~The budget of HCHO during OFE's is still uncertain; however, oxidation of CH4 at levels up to 10 times background likely plays a role in the budget that is not insignificant.~~

~~Following an increase in T~~the growth of the atmospheric burden of CH_4 increased in the post industrial revolution, ~~growth of CH4~~ slowed in the 1980's and 90's~~, simultaneous with the economic collapse of the Soviet Union and a reduction of emissions from fossil fuel exploration in Eurasia~~ (Worthy et al., 2009)~~,~~. ~~The~~ paused ~~in the growth of global methane observed from~~between ~1990-2007 ~~was only~~but temporary ~~as evidenced by the recent increase seen~~has increased again ~~since~~ starting in 2007, with a~~n~~ ~~current~~ atmospheric growth rate of ~0.4% yr^{-1} from 2007-2014 in the northern hemisphere (Hausmann et al., 2016). ~~Presuming that the lifetime of methane was constant during this period, the imbalance suggests an additional net methane source of ~24-45 Tg CH4 per year. Increased tropical precipitation and anomalously higher temperatures in the Arctic were first suggested as drivers for the increase in atmospheric CH4 (Dlugokencky et al., 2009). More recently total increases in tropospheric columns of ethane and methane have been used to deduce minimum contributions, C, of the global oil and gas sector to the post 2007 methane increase of C >39%, using realistic ethane to methane emission ratios (Hausmann et al., 2016).~~ Satellite observations have ~~been used to~~ suggest~~ed~~ a 30%~~n~~ increase in CH_4 emissions in the USA ~~of 30% over the~~during 2002-2014 ~~period~~ (Turner et al., 2016)~~;~~, while a~~the~~ ~~similar~~ 2009-2014 trend in ~~global~~ CH_4 mixing ratios and tropospheric columns of ethane ~~is~~was ~~also~~ attributed to oil/gas production in the USA (Helmig et al., 2016) and recent increases in tropospheric columns of ethane and methane have suggested the global oil and gas sector to be partially responsible (Hausmann et al., 2016). ~~On the other hand~~Contrasting this, a recent study suggests that North American CH_4 emissions have been flat ~~over the years~~from 2000–2012 (Bruhwiler et al., 2017) and there is still ambiguity in the source versus sink role ~~in~~ for the recent increase in atmospheric CH_4 (Turner et al., 2017). ~~Clearly there are still~~The above uncertainties underline a need ~~in the~~ ~~contribution~~for better quantification of anthropogenic emissions of CH_4 to the atmosphere and motivate the current study ~~and emissions of CH4 need further quantification~~.

Emission inventories ~~help~~ can quantify ~~determine~~ the contributions of specific sources to ~~trace gas~~ ~~levels in~~ the atmosphere. However, bottom-up ~~emission~~ inventories benefit from top-down

measurements and validation (Fujita et al., 1992), due to the difficulty in identifying all possible points of emission and ~~accurately calculating~~quantifying all emissions ~~from all those points~~ in a large complex source (e.g., a city or a facility). Top-down measurements of various types have long been used in the validation of emission inventories and emission ~~factor~~ models including comparison of surface based

5 pollutant profiles and ratios (Fujita et al., 1992;Jiang et al., 1997;Fujita et al., 1995), source-receptor methods (Scheff and Wadden, 1993;Fujita et al., 1995;McLaren et al., 1996), aircraft based flux measurements (Mays et al., 2009), measurement/modelling hybrid methods (Allen et al., 2004;Shephard et al., 2015) and satellite measurements (McLinden et al., 2012;McLinden et al., 2014;Turner et al., 2016;Kort et al., 2014;Jacob et al., 2016). Multiple studies have suggested underestimation of CH_4

10 emissions from natural gas infrastructure (Brandt et al., 2014;Hendrick et al., 2016). Several recent aircraft studies using mass balance approaches have quantified CH_4 emissions in oil and gas regions and compared these to ~~emissions~~ inventory emission rates and/or leakage rates (Karion et al., 2013;Peischl et al., 2013;Karion et al., 2015;Peischl et al., 2015;Peischl et al., 2016;Lavoie et al., 2015). Other studies have used top-down satellite measurements to quantify emission of CH_4 in oil and gas regions

15 (Schneising et al., 2014;Kort et al., 2014). As such, top down measurement of methane emissions and comparison with bottom up inventories can make a significant contribution to our understanding of the ~~global budget~~sources of CH_4.

In this study we quantify total emission rates of CH_4 from facilities in the Athabasca Oil Sands Region (AOSR) of Alberta in the summer of 2013. Alberta has large deposits of oil sands, an unconventional

20 viscous mixture of bitumen, sand, silt, clay, water and trapped gases (Stringham, 2012). Canada has proven reserves of 1.69×10^{11} barrels of oil (2.7×10^{13} litres), third largest in the world, 97% of which are located in the oil sands [Orbach, 2012]. Approximately 82% of the oil sands are located in the AOSR north of Fort McMurray with 20% located in near surface deposits (depth < 100m) that can be mined using open pit techniques and the remainder located in deeper deposits requiring underground in-situ

25 extraction. In both cases the oil must be separated from sand requiring the use of hot water or steam froth treatment, and organic solvent diluents (naphtha or paraffin) are used to help separate water and solids and/or to decrease the bitumen viscosity. For surface mining processes, once the bitumen is separated, process water containing unrecovered organic diluents is recycled but some is discharged in

large tailings ponds open to the atmosphere for further remediation. Oil extraction in the AOSR is unique in that unlike other oil and gas regions, CH_4 is not the primary economic commodity being extracted, but is an unintended by-product. In particular, a significant fraction of the CH_4 is not associated with fossil fuel reserves, but is emitted from the tailings ponds (Small et al., 2015). The

5 factors giving rise to the release of CH_4 from these ponds are complex but include the organic and inorganic chemical composition of the ponds, the diversity and types of microbial communities, especially methanogens, as well as the age of the ponds. It is reported that it took 20 years and 15 years for the largest ponds at Syncrude and Suncor respectively, to show evidence of methane bubbling from the surface (Small et al., 2015). Additional fugitive CH_4 is associated with the gaseous component of

10 the oil sand along with other gases (Strausz, 2003;Johnson et al., 2016) that are released during overburden removal, open pit mining and/or subsequent processing.

In the summer of 2013, an intensive ambient air measurement campaign took place in the AOSR with both ground and airborne components in support of the Joint Oil Sands Monitoring (JOSM) Plan (JOSM, 2012). The airborne measurements were conducted to address four objectives: i) to measure

15 and quantify air emissions from the oil sands mining facilities, ii) to study the downwind physical and chemical transformation of pollutants emitted, iii) to provide spatio-temporal measurement of pollutants suitable for intercomparison with simultaneous satellite nadir overpasses in the region, and iv) to support air quality model prediction capabilities. In this paper, we report CH_4 emissions from industrial facilities in the AOSR based on the airborne campaign. We applied the Top-down Emissions Rate

20 Retrieval Algorithm (TERRA) mass-balance approach (Gordon et al., 2015) to determine total CH_4 emissions rates from each of the major industrial facilities, as well as a second mass-balance approach using downwind flight tracks to spatially separate CH_4 emissions from different sources in each facility. Emissions rates of CH_4 are determined for the five major facilities in the region: Syncrude Mildred Lake (SML), Suncor Energy OSG (SUN), Canadian Natural Resources Limited Horizon (CNRL), Shell

25 Albian Muskeg River and Jackpine (SAJ) and Syncrude Aurora (SAU). These results are the first source-attributed emissions estimates for the facilities in the AOSR, obtained by identifying and characterizing plume origins according to signatures of chemical tracer species.

Experimental

2.1 Instrumentation

An array of instruments for the measurement of trace gases, aerosols, meteorological and aircraft state parameters were installed aboard the National Research Council of Canada Convair 580 research

5 aircraft. Measurements of CH_4, CO_2, CO and H_2O were made using a cavity ring-down spectrometer (Picarro G2401-m) at an interpolated rate of approximately 0.5 Hz with a flow rate of ~435 sccm min^{-1}. The precision of the CH_4 measurement was 2 ppb, and the uncertainty of the measurement at background (~ 1.9 ppm) was 3.3 ppb (@2 sec). The instrument was calibrated six times before, during and after the project using two standard reference gases traceable to NOAA GMD standards. Methane

10 mixing ratios are reported throughout as dry mole fractions in the paper. Necessary parameters for emissions estimation included Temperature (T), measured using Rosemount probe, Dewpoint temperature (T_d), measured with an Edgetech hygrometer, and pressure (P), measured with a DigiQuartz sensor. The three-component wind speed (Ux, Uy, Uz) was derived from a Rosemount 858 probe, GPS and Honeywell HG1700 inertial measurement unit. The uncertainty of horizontal and

15 vertical winds on the aircraft are 0.6 and 0.4 m/s respectively (Williams and Marcotte, 2000). Geospatial information (latitude, longitude, ellipsoid height altitude) was measured by GPS.

Nitrogen oxides (NO, NO_2 and NO_y) were measured with a modified trace level chemiluminescent analyser (Thermo Scientific Model 42i-TL). A molybdenum converter (325 °C) was used to convert NO_y species to NO and an NO_2 specific converter (Droplet Measurement Technologies) was used to

20 convert NO_2 to NO. Detection limits for NO, NO_2, and NO_y were determined to be 0.08 ppb (1 sec), 0.20 ppb (2 sec), 0.09 ppb (1 sec) respectively. Sulfur dioxide (SO_2) was measured with a pulsed UV fluorescence analyser (Thermo Scientific: Model 43i-TLE) with a detection limit of 0.7 ppb (1 sec). Ambient air was drawn in through filtered 6.35 mm (1/4") diameter PFA tubing taken from a rear-facing inlet located on the roof toward the rear of the aircraft. Measurements of NO, NO_2, NO_y and SO_2

25 were made downstream of a constant pressure inlet system maintained at 770 mmHg with a total flow rate of 5 Lpm. In flight zero and background determinations were made several times throughout each

flight and the analysers were calibrated multiple times during the study against National Institute and Standards Technology (NIST) certified reference gases.

Refractory black carbon mass (rBC), was measured with a Droplet Measurement Technologies (DMT) Single Particle Soot Photometer (SP2). Ambient air was subsampled from the main aerosol flow that

5   was brought into the main cabin with a forward-facing shrouded diffuser isokinetic aerosol inlet (Cheng et al., 2017). Benzene, toluene, ethylbenzene and xylenes (BTEX) were measured by a Proton Transfer Reaction time-of-flight Mass Spectrometer (PTRMS) from the main gas inlet. Further technical details are provided elsewhere (Li et al., 2017). The delay time of each instrument was determined experimentally and through calculations based on sample flow rates and inlet volumes. Total delays are

10   contributed to by the response time of the instruments (1–3 sec) as well as the volume of sampling tubing. Data were adjusted to account for the total delay times of 2-6 sec to spatially and temporally synchronize the different measurements (Picarro delay time = 6 sec). The average speed of the aircraft was 90 ms^{-1} during the research flights, thus providing a spatial resolution of 90-270 m based upon the internal response time of each measurement.

15   **2.2 Aircraft Flights**

In total, there were 22 flights with 84 hours of measurements in the AOSR between August 13 and September 7, 2013. The flights were designed for three purposes; measurement of pollutant emissions from facilities (Gordon et al., 2015;Li et al., 2017), measurement of pollutant transformation downwind of the AOSR (Liggio et al., 2016) and comparison with satellite overpasses (Shephard et al., 2015).

20   Thirteen flights were dedicated to quantifying facility emissions with a minimum of two flights for each of the SML, SUN, CNRL, SAJ and SAU facilities. CH_4 above background was not detected during the 2013 flights targeting the Imperial Kearl Lake (IKL) facility, which was not in full production mode at the time (but has since expanded significantly), nor from the Suncor Firebag in-situ operation. We did detect CH_4 above background suspected to originate from the Suncor MacKay River operation (west of

25   SML). We were not able to quantify this source separately, however emissions from this source are included in one measurement of the total emissions from all mining facilities in the AOSR using a wide downwind screen (see section 3.4 and Fig. 7). Several other flights are not included in the analysis due

to unfavourable meteorological conditions including wind shear problems or insufficient numbers of transects. In total, seven flights were found to be suitable for identifying and quantifying emissions of CH_4 from the facilities. Figure 1 displays several of the flight tracks over and downwind of the target facilities north of the Fort McMurray airport.

5   The flight patterns designed for the quantification of emissions rates were of two types: i) screen flights, wherein the aircraft flew transects perpendicular to the plume downwind of one or more facilities, and ii) box flights, wherein the aircraft flew transects at multiple heights around a single target facility in a box-type pattern (Gordon et al., 2015;Li et al., 2017). The transects were performed at heights from 150 to 1370 m above ground level (agl), complemented by vertical profiles designed to determine the height
10   of the planetary boundary layer (PBL) and to compare with ground based measurements.

2.3 Mass Balance Approaches for Determining CH_4 Emissions

Following the TERRA methodology (Gordon et al., 2015), the time resolved measurements were interpolated using covariance kriging to produce a 40 m (horizontal, s) by 20 m (vertical, z) contiguous screen of CH_4 mixing ratios. Within TERRA, the CH_4 mixing ratios are extrapolated from the lowest
15   transect (~150 m agl) to the surface using a constant, linear or half-gaussian extrapolation, depending on the type of source and the boundary layer conditions at the time. Uncertainty estimates (see section in Supplemental) are included according to the various types of surface extrapolation applied. Interpolated matrices were constructed for measurements of air pressure (P_{air}) and temperature (T_{air}) in order to determine the air mass balance within the box and to convert mixing ratios to mass densities. Spatially
20   equivalent interpolations of wind velocity perpendicular to aircraft motion ($U_\square$) were created from the vector components of wind speed and direction measurements.

Emissions rates were determined according to the two different mass-balance approaches for screen and/or box flight patterns. Horizontal tracks at multiple altitudes flown perpendicular to the general wind direction produce a virtual screen downwind of the target that is intercepted by emission plumes
25   from the facilities. Fluxes of CH_4 moving through each 40 x 20 m (s × z) pixel can be determined from the interpolated matrices and integrated for a dimensional s by z target area according to Equation 1.

$$E_{Screen} = \int\int_{S_{s1,z_b}}^{S_{sn,z_t}} ([CH_4] - [CH_4]_B) \times U_{T\boxminus} \, ds \, dz$$

────────────(Eq. 1)

where $([CH_4] - [CH_4]_B)$ is the enhanced mixing ratio of CH_4 above background, $U_{T\boxminus}$ is the horizontal

wind velocity perpendicular to the screen (e.g. $U \times \sin \theta$, θ = angle between wind vector and airplane

vector), s_1 and s_n are the horizontal integration limits along the screen transect, z_b and z_t are the bottom

and top vertical integration limits. Background mixing ratios of CH_4 were determined from the outside

edges of the screens away from plume sources. Because $[CH_4]_B$ varies with height, a vertically variant

background profile was subtracted from each vertical measurement column, an approach used in other

mass balance determinations (Cambaliza et al., 2014;Karion et al., 2013). <u>Example vertical profiles of</u>

<u>$[CH_4]_B$ (z) for each day are included in Figure S1 (Supplemental Information.I.).</u> The simple mass

balance approach represented by Eq.1 can be applied to individual downwind screens from other flight

paths (i.e. box flights) to determine CH_4 emissions from specific sources within a facility.

The second mass balance method used in this paper is to apply the full box-model TERRA algorithm

(Gordon et al., 2015), to compute total emissions from all sources within a box, where the box is made

up of multiple (4-6) screens forming a polygon encompassing a facility. This more rigorous mass

balance approach used for calculating total emissions from a facility is represented by Equation 2

$$E_{Box} = E_{CH} + E_{CHT} + E_{CV} + E_{CVT} + E_{CM} \qquad \text{(Eq. 2)}$$

where E_{Box}, the total emissions rate from all sources within a box, is the sum of the horizontal advective

and turbulent fluxes (E_{CH} and E_{CHT}), vertical advective and turbulent fluxes (E_{CV} and E_{CVT}), and the

change in CH_4 mass within the box volume (E_{CM}). Because the box includes screens that are downwind,

upwind and lateral to sources, incoming (background) and outgoing (background + source) fluxes are

determined as a part of the horizontal flux terms (E_{CH} and E_{CHT}). Vertical fluxes through the box top,

normally ignored in the conventional mass balance approaches (Eq. 1), are estimated according to the conservation of air mass within the box volume and the mixing ratio at the top edge of the box. E_{CM} is estimated according to the time derivative of the ideal gas law, based on measured changes in pressure and temperature over the flight time (see Gordon et al., 2015 for a full discussion).

5

The advantage of the box approach (Eq. 2) over the screen approach is a more precise estimate of total emissions by accounting for incoming and outgoing fluxes and meteorological effects within a volume. However this flight pattern takes more time to completely surround a target facility. The advantage of the screen approach (Eq. 1) is the computation of CH_4 fluxes per pixel, which can thus be used to

10   spatially integrate individual emission plumes of arbitrary shapes when the sources can be spatially resolved. Studies applying aircraft mass-balance methods have used each of single-height transect (Karion et al., 2013;Peischl et al., 2016), single screens (Cambaliza et al., 2014;Walter et al., 2012), spiral (Wratt et al., 2001;Gatti et al., 2014), and full box flight paths (Gordon et al., 2015) for the purpose of determining emissions rates and characterizing meteorological conditions. The aircraft

15   flights presented contained various segments of tracks that allowed applications of all the above methods. In this work we apply a systematic approach deriving information from each of these techniques for a comprehensive top-down characterization of CH_4 sources and emissions in the region. Single-height transects are used to determine source chemical signatures by identifying CH_4 enhancements and their associations with other trace-gas species. Vertical profiles are used to determine

20   the PBL height throughout flights. Single screens are used to determine CH_4 emissions rates (Eq. 1) for facilities and their individual sources when plumes are spatially resolved. Box flights are used to determine total CH_4 emissions from facilities at a lower uncertainty (Eq. 2) and source-specific emissions are determined where possible (Eq. 1).

25   The summer time emission rates measured in this study are reported in units of metric tonnes CH_4 per hour, an appropriate unit given the duration of the flights (i.e., a few hours). We do not attempt to derive annual emissions as the assumptions needed to do so are highly uncertain without measurements in other seasons for a volatile species such as CH_4. However, we do make a first order comparison to

emission inventories and other studies that report emissions on an annual basis by downscaling the annual emissions to hourly emission rates using an assumption of a constant temporal factor throughout the entire year. This is appropriate for emission inventories that are based upon measurement of emissions or emission factors in summer, that then upscale their emission rates of CH_4 to annual emissions using a constant temporal factor assumption (e.g., GOA, 2014). However the assumption of a constant temporal factor is far from being validated and further measurements in different months are needed to understand the potential for seasonal variability of fugitive emissions of CH_4.

Previous work shows the box approach has a demonstrated uncertainty of 25-27% for total emissions of CH_4 from a facility in the AOSR (Gordon et al., 2015). Uncertainty due to extrapolation of CH_4 mixing ratios from the lowest height measurements to the surface was estimated to be 15% and 26% in that study. In contrast, screen approaches used in other studies have estimated uncertainty in the range of 30-50% (Cambaliza et al., 2014) with the main sources of error attributed to the reliability of plume characterization and the stability of meteorological conditions. In this study, uncertainties in both the box and screen estimates are reduced through i) a high number of transects over a wide vertical range to accurately characterize vertical structure in the PBL, ii) reliable measurements of background CH_4 (or incoming fluxes for boxes), iii) measurements of the PBL height to account for meteorological variance, and iv) measurements within time periods of minimal PBL change. In addition, the enhancement of CH_4 in the plumes downwind of the facilities and high precision of the Picarro instrument minimize uncertainties in plume characterization and background CH_4. The overall uncertainty for computed CH_4 emission rates for an individual determination was estimated to be less than 30% (see Supplemental for a complete evaluation and discussion of uncertainties).

3. Results and Discussion

3.1 Identification of Sources of CH_4

Two example flights from three different facilities (SML, SUN and CNRL) are presented to demonstrate CH_4 emissions in the AOSR are mainly from three source types: open pit mining, tailings

ponds, and facility activities. Emissions from the remaining two facilities (SAJ and SAU) were shown to be primarily open pit mining. Source categories were identified by measurements of CH_4, NO_y, BTEX, and rBC. Figure 2 shows measurements from one low-level transect of a screen flight on Aug 16, 2013 (9 transects in total). This transect was flown at a height of approximately 150 m agl

5   downwind of the SML and SUN facilities, showing clear separation of emission sources from the two facilities. Four distinct plumes are visible, labelled A-D, with linear air parcel back-trajectories indicated in red arrows. Back trajectories were determined using the wind speeds and wind directions measured on the aircraft at flight level from the positions of maximum CH_4, back extrapolated as a general indicator of plume origin. This methodology creates a western bias in our plume origins. A

10   more careful analysis of surface winds at several meteorological stations in the local vicinity at the time of the aircraft transect shows that surface wind directions were from $\sim$ 140-180° (SE) compared to the flight level winds, $\sim$220° (SW). The low level surface winds are likely channelled by the river valley, which runs in a SE to NW direction. Thus the trajectories of air masses originating at the surface and mixing upwards have a clockwise rotation, a very local effect, placing the actual plume sources further

15   east than the linear tracks show in Figure 2. Plume A shows a maximum mixing ratio of 2.68 ppm CH_4, an enhancement of $\sim$ 0.58 ppm above a background of $\sim$2.1 ppm on this day in this region. This enhanced CH_4 is associated with values of 2.3 $\mu g/m^3$ rBC and 47 ppb NO_y. The simple linear wind back-trajectory places the origin of the air mass near the western edge of open pit surface mining activity $\sim$100-min earlier, although as mentioned the actual source is likely slightly east of that location

20   due to the clockwise rotation of the plumes. The combination of rBC and NO_y is indicative of exhaust of heavy hauler diesel trucks that operate in open pit mines. However, significant CH_4 emissions are not expected from the truck exhaust, as emissions factors of CH_4 from off-road gasoline and diesel combustion indicate that the CH_4/CO_2 emission ratio would be 1 to 2 orders of magnitude lower (Environment Canada, 2015) than the $\Delta CH_4/\Delta CO_2$ observed in this plume (0.58 ppm CH_4 / 16.1 ppm

25   CO_2). Disturbance of the oil sands at the mine faces by the trucks is a well-known source of CH_4 with minor emissions of CO_2 and other VOC's (Strausz, 2003) as well as intermediate volatility organic compounds (Tokarek, 2017). Thus, Plume A is interpreted to be a combination of heavy truck exhaust, indicated by the presence of rBC and NO_y, that spatially overlaps with the mine face source of CH_4.

Plume D shows a similar chemical profile with a maximum CH_4 of 2.40 ppm, ~ 0.30 ppm above background, associated with elevated levels of NO_y (40ppb) and rBC (1.5 µg/m^3). The back-trajectory for Plume D is in agreement with an origin at one of two locations of open pit mining activity at SUN. The two plumes show a similar $\Delta NO_y/\Delta rBC$ ratio within the range of 15-30 ppb per ug/m^3. We consistently measure this profile of NO_y and rBC enhancements from active mines across all five facilities.

Plume B (Fig. 2) shows the highest CH_4 mixing ratio at 4.19 ppm, an enhancement of ~2.09 ppm above background. The back-trajectory from the position of the maximum CH_4 places the air mass over the western edge of Mildred Lake Settling Basin (MLSB) tailings pond ~ 20 minutes earlier. The CH_4 enhancement occurs simultaneously with a decrease in NO_y and rBC and an enhancement of total BTEX from ~0 ppb to a maximum of 7.6 ppb. Tailings ponds are known to contain significant quantities of BTEX compounds due to waste streams of mature fine tailings containing naphtha diluent flowing into the pond (Small et al., 2015). This is similar to the chemical profile observed in Plume C, with a back-trajectory placing the air mass over one of several possible SUN facility tailings ponds shown in Figure 2 (Ponds 6, Pond 5 and Pond 2/3 in figure Small et al, 2015). This indicates the presence of CH_4 emissions from multiple tailings ponds. Anaerobic digestion of organic matter in the tailings pond is the primary mechanism for the production of this biogenic CH_4 (Siddique et al., 2012). For Plume C the measured mixing ratio enhancements are 0.25 ppm CH_4 and 2.3 ppb of BTEX. The lower CH_4 enhancement compared to Plume B suggests less CH_4 is emitted from this pond, in agreement with Small et al (2015). The peak-to-peak CH_4/BTEX ratios from Plume B and Plume C are ~300 ppb ppb^{-1}, and ~100 ppb ppb^{-1} respectively. The difference in measured inter-facility CH_4/BTEX ratios could arise from a number of factors including different pond ages, history, depth, methanogenic behaviour, or use of different diluents in each facility. The in-plume correlations of CH_4 with the associated tracers (NO_y, rBC and BTEX) for each of the Plumes identified in Figure 2 are shown in Figure S2 (Supplemental Information).

Our observations are qualitatively consistent with pond-specific industry reported CH_4 emission factors, which present SML and SUN Ponds 2/3 (Small et al., 2015) as the highest CH_4 emitting tailings ponds in the region. We consistently measured relative enhancements from plumes downwind of SML and SUN according to the pattern of Plumes B and C in Figure 2, demonstrating the feasibility of using

5 BTEX compounds as tracers for CH_4 being emitted from tailings ponds. We expect that BTEX would be greatly reduced from the tailings ponds of those facilities using paraffinic froth treatment (e.g., SAJ) instead of naphtha. In such cases, light hydrocarbons could in principle be used as tracers for the tailings ponds emissions of CH_4. However, we did not detect methane plumes above detection limit that were distinct from the open pit mining plumes of CH_4 associated with rBC and NOx for any

10 facilities other than SML and SUN.

Elevated plumes from facility stacks are the primary sources of SO_2 in the AOSR due to the bitumen upgrading process. Hence, a significant enhancement of SO_2 can be used as a tracer for plant or stack CH_4 sources. However, this is not measured at the height shown in Figure 2, which shows a maximum

15 SO_2 of only 5 ppb for this transect between Plumes C and D at 150 m agl. For the same flight (Figure 2), maximum SO_2 was 131 ppb for a transect ~350 m above ground, with an associated narrow peak of CH_4 with maximum mixing ratio of 2.11 ppm. While higher-altitude SO_2 plumes were frequently measured downwind of various facilities over the course of the aircraft campaign, in most cases no significant CH_4 enhancements were observed in these plumes. A similar case is discussed in Section **3.2**

20 where we show the full range of vertical measurements and a lack of enhanced CH_4 in the SO_2 plume. Ground-level CH_4 from tailings ponds and open pit mine faces therefore dominate the CH_4 emissions in the region, with minor contributions from industrial plants.

We next compare the profiles from SML and SUN to a third facility, CNRL Horizon. Figure 3 shows a

25 similar transect at ~150 m agl from the Sep 02 flight in the vicinity of CNRL. The bottom panel of Figure 3 shows that there was considerable wind divergence at this time (see back trajectory arrows for A, B, C). This wind divergence was also present in the next pass of the aircraft on the south side of CNRL at a height of 300m (not shown). While this divergence aids in the visualization of source

separation, they invoke uncertainty in the mass balance determinations. The emission rates on Sept 02 were determined using ten transects from a flight much earlier in time than that shown in Fig 3., when the winds were more consistent in direction (NNW).

5   While Plume A shows a small enhancement of ~1 ppb BTEX downwind of the tailings pond, in contrast to SML and SUN no significant CH_4 was associated with it. This is consistent with the pond-specific emission factors presented in Small et al. (2015) that do not list the CNRL tailings pond as a significant source of CH_4. The primary Plume B included a CH_4 mixing ratio up to 2.24 ppm (enhancement of ~0.34 ppm above background) associated with 12 ppb NO_y and 0.7 ug/m^3 rBC downwind of the CNRL

10 mine. Consistent with the previously described open pit profile and the back trajectory, we identify Plume B as an open pit mining source of CH_4. A secondary Plume C was measured with maximum CH_4 of 2.02 ppm (enhancement of ~0.12 ppm) east of the open pit mine. The lack of associated species does not relate the origin of Plume C to either a tailings pond nor an open pit mine source of CH_4. The plume is downwind of the main CNRL plant and closer in horizontal proximity to SO_2 plumes measured

15 during higher altitude transects. This suggests a CH_4 source near the main plant that could originate from venting or flaring activity, electricity cogeneration using natural gas or natural gas leakage. Thus the primary source of CH_4 from the CNRL facility is open pit surface mining activity with a secondary undetermined source from the main plant.

20 Source profiles of CH_4 are further compared to measurements of ethane (C_2H_6). Source-attribution studies for CH_4 commonly use higher ethane-to-methane ratios (EMRs) as a signature for oil and gas emissions, on both a regional (Peischl et al., 2016) and global (Hausmann et al., 2016) scale, while low EMR ratios can be indicative of microbial sources of methane that do not emit ethane (agriculture, landfills, wetlands, etc.) (Smith et al., 2015). C_2H_6, along with other VOC's, was measured from 20-

25 second grab samples collected in 3-L Summa canisters. The VOC's were analysed offline using GC-MS and GC-FID methods described elsewhere [Li et al., 2017]. Table 1 shows C_2H_6 measurements from three different flights (Aug 14, Aug 16 and Sep 02) when canister sampling overlapped with the plume descriptions listed previously. In all cases shown, enhancements of C_2H_6 above background (0.8

– 1.5ppb) were in the range of only 1-2 ppb, normally the highest enhancements for each flight (within 1 ppb of 95th percentile). The small emissions rates of ethane (EMRs <1.4%) across flights contrasts with the high EMRs (i.e. 40-50%) seen for conventional oil and gas fields in other regions of North America (Peischl et al., 2016;Smith et al., 2015) and is lower than all the possible EMR source

5   scenarios tested in Hausmann et al. (2016). The problems associated with determining EMR ratios from a combination of continuous CH_4 measurements and discrete canister sampling of ethane from aircraft have been highlighted recently, where it was shown that actual EMR ratios determined in this way can be off by up to a factor of two (Smith et al., 2015). Thus the limited EMR data shown in the Table 1 are not intended to be a comprehensive measure of EMR in the AOSR but simply to support the conclusion

10   that the major sources of methane from the facilities in the AOSR are microbial in nature without a significant co-emission of ethane. The low EMRs are consistent with previous measurements in the region (Simpson et al., 2010) and are an indication of the unique character of unconventional bitumen sources. As such, global estimates of the relative contributions of oil and gas emissions to decadal increases in atmospheric CH_4 that are based on C_2H_6 and CH_4 measurements in the free troposphere

15   (Hausmann et al., 2016) would not capture AOSR emissions due to the low C_2H_6 emissions in this region.

3.2 Quantification of CH_4 Emission Rates from Sources

The source chemical profiles in section 3.1 can be used in combination with the screen mass-balance method (Eq. 1) to isolate and quantify categories of AOSR emissions. As an example, we show the Aug

20   14 flight surrounding the SML facility, which consisted of a box and screen path flown in rapid succession. Figure 4 shows an image of the interpolated aircraft measurements from the box path creating a contiguous mesh superimposed on a map of the region. Winds were from the south at 186 ± 48 degrees over the course of the day. Three distinct ground-based plumes of CH_4 are visible, a primary plume (Plume N) on the northern screen (~6500 m wide) exiting the box, a secondary plume (Plume

25   NW) at the northwest corner (~7000 m wide) exiting the box and a smaller plume (Plume E) on the eastern screen (~3000 m in width) entering the box from outside the SML facility boundary. The lowest aircraft transect was at a height of ~150 m agl, with maximum CH_4 mixing ratios of 3.00 ppm, 2.60

ppm and 2.63 ppm respectively for the three plumes. Mixing ratios of CH_4 below 150 m agl, are based on a linear extrapolation of interpolated pixels to the surface, corresponding to maximum surface mixing ratios of 3.48, 3.17 and 3.06 ppm for the primary (N), secondary (NW) and tertiary (E) plumes respectively. Extrapolation to the surface is the primary source of uncertainty for surface sources in this method, however the uncertainty can vary between flights depending on the meteorological conditions (Gordon et al., 2015). As a part of our uncertainty analysis in the Supplemental material, we have included an uncertainty associated with the differences in emission rates that arise from the use of linear, constant and half-Gaussian extrapolations in the calculations.

Unwrapped curtain plots of CH_4, BTEX, NO_y, rBC and SO_2 from the Aug 14 box flight (Fig 4) are shown individually in Figure 5, projecting the 3-D virtual box onto a 2-D grid. The same three plumes from Fig 4 are highlighted by dotted boxes in red (N screen), yellow (NW corner), and black (E screen). The red and yellow boxes show sources originating from within the SML facility and the black boxes show a source originating outside of the SML boundaries and entering the box from the east. The largest SML CH_4 plume is associated with > 10 ppb BTEX and the absence of rBC and SO_2, with some NO_y (~20 ppb). This is consistent with the chemical signature associated with tailings pond emissions discussed previously. The NW plume is associated with >60 ppb of NO_y and up to 5 $\mu g/m^3$ of rBC, with minimal BTEX and SO_2, consistent with the expected chemical signature from open pit surface mining. The smaller plume on the E screen is associated with elevated BTEX and CH_4 and is likely a plume from one of the SUN tailings ponds as the winds indicate the plume is entering the box. The elevated plume in Fig 5 (orange circles) with ~100 ppb SO_2 and ~30 ppb of NO_y is traced to the SML upgrader activities, but with no enhancement of CH_4 above background on this day. A second NO_y plume is visible at the north-eastern corner of the box, not associated with any of the identified CH_4 source types. This NO_y plume likely originates from traffic on the main highway that passes between the SML and SUN facilities and/or trucks and other vehicles operating in and around the main SML facility.

Boundaries of the plumes from separate sources are estimated using the tracer species listed in Fig. 5 by evaluating where the chemical signatures reached background levels. However, the SML tailings pond

and open pit mine plumes were not completely resolved from one another, overlapping within a range of ~800 m. The uncertainties in the emission rates due to plume overlap were estimated by contracting and expanding the horizontal integration boundaries (s) by 800 m on each side (a total of ±1600 m) as part of the sensitivity analysis. A vertically varying background profile ($[CH_4]_B(z)$) is determined using data from the upwind southern screen, as mentioned previously. Using a spatially identical screen of perpendicular wind $U_{\square,}(z)$, the fluxes are determined through each pixel and the total source emission is calculated by integrating the pixels within the plume boundaries (Eq. 1). CH_4 emissions rates are computed to be 6.4 ± 1.2 metric tonnes per hour (tonnes hr^{-1}) for the SML main tailings pond and 2.7 ± 0.6 tonnes hr^{-1} for the SML open pit mine source. It is possible that the CH_4 plume from the SML tailings pond includes CH_4 emissions from the main SML plant facility (flaring, venting, natural gas leakage, etc.) that cannot be spatially separated from one another due to their proximity, however we anticipate the magnitude of these emissions are minor and captured within the error intervals listed.

This screen-based mass-balance approach for determining specific source emission rates (Eq. 1) is applied to flights with appropriate conditions for plume separation. Mean emissions rates of CH_4 from specific sources within the facilities SML, SUN, CNRL, SAU and SAJ are shown in Figure 6. SML emissions rates are the average of three mass-balance flights over two days (two on Aug 14 and one on Aug 16). Two flights on separate days were used for each of the SUN (Aug 16 and Aug 29), SAJ (Aug 21 and Sep 06) and SAU (Aug 29, Sep 06) facilities. One CNRL flight (Sep 02) had northerly wind conditions showing plume separation on a southern screen. No significant daily variability is observed as the emissions rates for the same source agree within error. Duplicate and triplicate estimates for the same source are combined using an error-weighted uncertainty (Supplemental). SML and SUN had significant open-pit mining emissions of CH_4, 2.8 ± 0.4 tonnes hr^{-1} and 1.8 ± 0.2 tonnes hr^{-1} respectively, and were the only facilities with tailings ponds emissions above detection limit, 6.4 ± 0.8 tonnes hr^{-1} and 2.4 ± 0.3 tonnes hr^{-1}. CNRL had open-pit mining emissions (2.6 ± 0.7 t/hr) and significant emissions originating from the main plant facility (1.0 ± 0.3 t/hr). Plumes of CH_4 from SAJ and SAU were only attributed to open-pit emissions, 1.2 ± 0.2 t/hr and 1.4 ± 0.2 t/hr respectively.

The plume-targeting screen mass balance method described here is unable to resolve emissions of CH_4 from multiple sources not characterized by the chemical profiles described in Section 3.1 if they cannot also be spatially separated. Because spatial s and z constraints are manually chosen by plume boundaries from chemical profiles, minor emissions may contribute to overestimation of the emissions from an individual source when highly coincidental in space such that the sources are not separable. For example, the emissions from the main plant were identifiable in the case of CNRL due to the separation and orientation of the plant, the open pit and the tailings ponds with respect to the winds. This was not the case for the other major facilities in the AOSR where many of the sources were highly coincidental in space. It is possible, and even likely, that other major facilities in this study also have CH_4 emissions from their main plants (venting, cogeneration, natural gas leakage, etc.) that are identified as tailings pond emissions or open pit emissions due to close proximity and our inability to deconvolute the sources spatially or chemically. However, we expect that the total emission rates of CH_4 from each facility are still accurate.

Emissions rates from each flight and individual sources (where possible) using the screen mass balance method are tabulated in the supplemental (Tables S1-S5). We did not measure a detectable tailings pond source of CH_4 from CNRL, SAJ and SAU. Associated enhancements of rBC and NO_y with CH_4 suggest that the CH_4 source from SAJ and SAU is also predominantly open pit mining. The results using the screen mass balance approach (Eq. 1) are further verified in Section 3.3 using emissions rates for each facility determined from the box approach (Eq. 2).

3.2.1 Comparison to Fugitive Emissions Literature

Average open pit surface mining emissions from the five facilities are within a range of 1.2-2.8 tonnes hr^{-1} (Fig 6 and Table S1-S5). This shows some consistency in the nature of CH_4 release from open pit mining activity in the region, with differences that may possibly be attributed to the size of the surface disturbance taking place and the intensity of the mining activity. Methane emissions from open pit mines were recently estimated using a bottom-up emissions factor approach by analysing the gaseous composition in the overburden and oil sand component of drill core samples (Johnson et al., 2016).

Emissions factors of CH_4 were then scaled up according to the total mass of material mined or the total bitumen produced. For 2013, Johnson et al. estimate total fugitive mining emissions in the region to be 21.4-46.0 ktonnes of CH_4 using total mined material, and 33.1-85.0 ktonnes of CH_4 using total mined bitumen. Our top-down approach estimates total fugitive emissions from open pit mining to be 9.7 ± 0.9

5 tonnes hr^{-1}, corresponding to 84.9 ± 7.9 ktonnes yr^{-1} CH_4 if constant temporal emissions are assumed. Agreement with the upper estimates in Johnson (2016), despite the uncertainty associated with extrapolation to annual emissions, suggests that their bottom-up emissions factors from gases in core samples may reliably predict real-world emissions provided there is accurate characterization of CH_4 in the core samples over the entire disturbed area. This is reasonable considering <u>that it would be expected</u>

10 <u>that</u> ~~oil sands~~ degassing <u>of an extremely volatile gas such as</u> ~~tends to release~~ CH_4 <u>from the oil sands</u> <u>material would be</u> quantitative~~ly~~ <u>in a</u> <u>short period of time after the ore is exposed or crushed.</u>~~predictable~~ ~~way.~~

From our 2013 measurements, only two facilities, SML and SUN, had significant emissions of CH_4

15 from tailings ponds. Tailings ponds emissions accounted for ~70% and ~58% of total CH_4 from SML and SUN respectively. This accounted for ~45% of total emissions in the AOSR. Recently, bottom-up area-weighted emissions factors of CH_4 from 19 major tailings ponds in the AOSR were provided for the year 2012 (Small et al., 2015). The top three emitting ponds reported were 'Mildred Lake Settling Basin' (MLSB) and the 'West In-Pit' (WIP) pond within SML, and 'Pond 2/3' (P23) within SUN.

20 These tailings ponds account for >96% of tailings ponds CH_4 in the region according to that study. This is qualitatively consistent with our measurements of CH_4 mainly from SML and SUN. Our method requires CH_4 plumes to be clearly enhanced above background, so trace amounts of CH_4 from ~~less~~ ~~active younger~~ ponds in the other three facilities were not detected. <u>This could be related to differences</u> <u>in the chemical composition of the process streams being released into these ponds, or it could simply</u>

25 <u>be due to these ponds being younger in age, with insufficient time for the anaerobic methanogenic</u> <u>communities to be established</u> (Small et al., 2015)<u>.</u> We are unable to differentiate emissions from ponds within the same facility due to overlapping chemical profiles from ponds within close proximity. However, using the ratios of relative pond emissions rates within the same facility presented in Small et

al. (2015), (i.e. MLSB contributes 92% to SML emissions, Ponds 2/3 contribute 85% to SUN), we can infer individual pond emissions from our measurements assuming the relative contributions are accurate. The resulting emissions rates are 5.8 ± 0.8 tonnes hr^{-1} for MLSB and 2.0 ± 0.3 for Ponds 2/3. This ranks the MLSB tailings pond as the highest area source of CH_4 in the AOSR, followed by the

5   open-pit mines in SML and CNRL, and fourth Ponds 2/3 in SUN. Total CH_4 from tailings ponds in Small et al. (2015) are estimated to be 30.3 ktonnes of CH_4 per year, with 29.7 ktonnes of CH_4 from the SML and SUN facilities (~98%). Our total CH_4 emission rate determined for tailings ponds is 8.8 ± 0.9 tonnes hr^1, which corresponds to 77.1 ± 7.9 ktonnes yr^{-1} if a constant temporal factor is assumed. This is 2.3-2.9 times larger than the emissions inferred from the data in Small et al (2015), despite the

10   uncertainty of extrapolation to an annual emissions rate. Our measurements suggest more work is needed to reconcile top-down and bottom-up CH_4 emissions.

3.3 Emission Rates of CH_4 from AOSR Facilities

Total emissions rates of CH_4 from each facility determined using the box mass balance method (TERRA) are tabulated in the supplemental (Tables S1-S5) along with the determinations using the

15   screen approach. Where multiple screen estimates or multiple box estimates were available, uncertainty weighted ($1/\sigma^2$) averages were determined for each method for each facility and are summarized in Table 2.   While the box method is in some cases based on the same downwind measurements as the screen approach, the two methods have several key differences (described in **2.3**) and are treated as independent estimates. In particular, the box method does not resolve specifically targeted, individual

20   plumes and instead determines the net outgoing flux from the closed volume surrounding the facility. Thus, consistency between the two estimates is evidence that the primary sources of CH_4 from facilities in the AOSR are tailings ponds, open pit mines and facility emissions captured by the source characterization in sections 3.1 and 3.2. In general, the total emissions from each facility using the screen and box methods are in agreement within uncertainty, which adds confidence to the measured

25   emission rates reported here. In the final row of Table 2, we calculate a weighted average emission rate for each facility using all screen and box measurements. The CH_4 emission rates from the facilities are

8.6 ± 0.9, 4.2 ± 0.4, 3.6 ± 0.5, 1.3 ± 0.2, and 1.5 ± 0.2 tonnes CH_4 hr^{-1} from the SML, SUN, CNRL, SAJ and SAU facilities, respectively.

3.4 Total Emissions of CH_4 from the AOSR

The total CH_4 emissions from the five mining facilities in the AOSR, obtained by summing the best estimates (i.e., uncertainty weighted average of multiple measurements, bottom row, Table 2) of the individual facility emission rates is given in the final row and column of Table 2. The 5-facility total emission rate of CH_4 is 19.2 ± 1.1 tonnes CH_4 hr^{-1}. A final independent estimate of total AOSR emissions was obtained from a flight on Aug 16, utilizing an independent transect screen ~75 km wide (Aug 16 Screen B) downwind of all major mining facilities in the AOSR (excluding Imperial Kearl Lake and Suncor Firebag operations; but also inclusive of any emissions from Suncor MacKay River in-situ facility). The details of this flight are given in Supplemental Table S6. The interpolated screen from the Aug 16 flight (Total OS) is shown in Figure 7. The screen was constructed from 10 aircraft horizontal transects from 250-900 m agl. Enhancements of CH_4 were measured over a wide horizontal subrange of ~60 km of the entire ~75 km screen. Winds were perpendicular to the plane from the southwest (225°), showing a large flux of CH_4 through the screen from upwind sources. The highest measured mixing ratios of CH_4 were 2.67 ppm at the ~250 m (agl) transect. Background CH_4 in the region was ~2.00 ppm taken as a vertical profile from the wings of the screen. Using the screen method (Eq. 1), the emissions rate was determined to be 23.0 ± 3.7 tonnes CH_4 hr^{-1}, which represents the emissions from all major facilities within the AOSR domain. This AOSR total is only slightly larger than the previous 5-facility total emission rate of 19.2 ± 1.1 tonnes hr^{-1}, but not statistically so, demonstrating the reproducibility of our measured estimates. It is entirely possible that there are other minor sources of CH_4 included in this larger number from smaller industrial operators in the region, trucks and vehicles on the main highway, and wetland emissions. In fact, the Canadian GHGRP inventory (see section 3.5) indicates that there is an additional 0.13 tonnes CH_4 hr^{-1} emitted upwind and 0.17 tonnes CH_4 hr^{-1} emitted downwind of the aircraft screen (Fig 7) from minor industrial facilities within the AOSR (both numbers downscaled from the facility reported annual emissions). The amount of CH_4 emitted from vehicles on the highway though is expected to be smaller. The fact that the two

numbers are not statistically different supports the determination that the majority of the CH4 in the AOSR is emitted from the 5 major industrial facilities in the region. The two values are combined here using an error-weighted uncertainty resulting in a final AOSR facility emissions estimate of 19.6 ± 1.1 tonnes CH4 hr^{-1}, measured during a summertime period.~~.~~

5 **3.5 Comparison to Emission Inventories**

Emissions of anthropogenic greenhouse gases are estimated by ECCC in Canada's GHG Inventory, which forms the basis for Canada's annual report to the United Nations Framework Convention on Climate Change , UNFCCC (ECCC, 2016). Currently, industrial facilities that emit more than 50 ktonnes CO_2eq yr^{-1}are required to report their emissions annually to ECCC using the Greenhouse Gas
10 Reporting Program (GHGRP), which is Canada's legislated, publicly accessible inventory of facility-reported greenhouse gas (GHG) data (ECCC, 2017b). Although the GHGRP inventory data is not necessarily used in Canada's GHG Inventory, changes are being proposed to expand monitoring requirements in the GHGRP, including lowering the reporting threshold to 10 ktonnes CO_2eq yr^{-1} in order to enable direct use of the reported data in Canada's GHG Inventory (ECCC, 2017a). Emissions
15 of CH4 from all five major oil sands facilities discussed in this paper are present in the GHGRP Emissions Inventory on an annual basis. The annual emission rates of CH4 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).   While this may be questioned, it should be
20 noted that fugitive emissions of CH4 from mine faces and tailings ponds in the inventories are estimated based upon emission factors measured at oil sands facilities during summer months (June- Sept), which are then up scaled from hourly emissions to annual emissions using the same assumption that we used to downscale (365 x24), as per recommendation by the Government of Alberta (GOA, 2014). Specifically it is noted from the GOA report that emissions of gaseous species such as CH4 (and CO2)
25 are not temperature dependent, (unlike VOC's that have temperature dependent vapour pressures (Li et al., 2017)). ~~One~~ The argument ~~for the~~ used to justify ~~of the~~the use of a constant seasonal temporal factor in the GOA report is that temperatures at depth in a tailings pond~~, rightly or wrongly,~~ are said to remain

relatively constant throughout the year ~~(GOA, 2014)~~ and thus, biogenic gas formation continues in the winter (GOA, 2014). For mine faces, the GHG component of the oil sand does not change with temperature and is likely released completely in a short period of time after being mined. Thus the government recommendation to oil sand facilities in preparing annual emission estimates of fugitive

5 GHG's is that reduction factors should not to be used in extrapolating summertime emissions over the rest of the year (GOA, 2014). Figure 8 shows a comparison of the total measured emission rates of CH_4 from the five industrial facilities (2013), the total measured CH_4 emission rate in the AOSR from the single downwind screen on Aug 16, 2013 and the sum of the facility emission rates from the Canadian GHGRP Emissions Inventory for 2013, expressed in hourly units. The combined facility emissions rate

10 of 19.6 ± 1.1 tonnes hr^{-1} is approximately 48 ± 8 % higher than the 5-facility total of 13.2 tonnes hr^{-1} extracted from the inventory for 2013. Facility-to-facility comparisons show higher measured than reported emission rates for three out of the four facilities (SML and SAU facilities are combined as one in the inventory). In contrast, for CNRL our measured emission rate is 1.2 tonnes hr^{-1} lower than the inventory. Since we have determined the composition of SML, SUN and SAJ emissions to be primarily

15 from tailings ponds and open pit mining, there appears to be underestimation in the inventory of those particular area sources within these sites.

These discrepancies indicate a need for inventory reconciliation between the bottom up and top-down estimates. It has been shown possible to reconcile divergent bottom-up and top-down CH_4 estimates for the Barnett Shale by using more comprehensive activity factors and better characterization of emissions

20 from high emitter sites (Lyon et al., 2015) and continuous monitoring to identify these super emitters (Zavala-Araiza et al., 2015). Currently, bottom-up estimates in the AOSR are accomplished by systematic surface flux chamber measurements of area sources (surface mines, tailings ponds) to derive area-based emissions factors (GOA, 2014). While surface flux chamber measurements (Klenbusch, 1986;Conen and Smith, 1998) are estimated to be 50-124% of the true emissions rate for a homogenous

25 source (Klenbusch, 1986), it is unclear how the uncertainty propagates when the emissions factors are scaled to the full surface area of the heterogeneous AOSR emissions sources. The official survey protocol for open pit sources attempts to minimize the possibility of underestimating emissions by explicitly requiring fugitive surveys to include sampling at a range of locations within the open pit

mine, where safe to do so, including high priority zones (disturbed in the last week), normal priority zones (disturbed from 1 week to 6 months ago) and low priority zones (disturbed > 6 months ago) (GOA, 2014). However, it seems that the recent core sampling methodology outlined by Johnson et al. (2016) has great promise and reduced uncertainty (Johnson et al., 2016) for estimating fugitive

5   emissions from open pit mining.

Conclusions

We present a detailed approach to identifying and quantifying CH_4 emission sources from the surface mining facilities in the Athabasca Oil Sands Region of Alberta in the year 2013. Emissions of CH_4 are attributed to three major fugitive source types: tailings ponds, open pit mining activity, and emissions

10   from plant facilities. Our method demonstrates the use of BTEX/VOCs as tracers for tailings ponds CH_4 plumes due to the use of diluent, and NO_y/rBC as tracers for surface mining due to heavy hauler diesel trucks operating co-spatially at mine faces in the open pit mines. The combination of SO_2/NO_y is used as a tracer for stack facility plumes which are observed to contain minor but detectable quantities of CH_4, although infrequently. We use the chemical signatures of sources and the screen mass-balance

15   approach for 7 flights to determine total emissions rates of 8.8 ± 0.9 tonnes hr^{-1} from tailings ponds, 45% of total CH_4 emissions in AOSR, 9.8 ± 0.9 tonnes hr^{-1} from open pit surface mining (50%), and 1.0 $\pm$ 0.3 tonnes hr^{-1} primary facility-associated and other sources (5%). Open pit mining emissions are measured from all five facilities in the range of 1.2-2.8 tonnes hr^{-1}. In contrast amongst the 19 tailings ponds in the region, CH_4 emissions above determinable levels were only measured from two facilities,

20   SML and SUN. These emissions are likely due to two tailings ponds, MLSB (5.8 ± 0.8 tonnes hr^{-1}) and Ponds 2/3 (2.0 ± 0.3), which are ranked amongst the highest area sources of CH_4 in the region. These results demonstrate the large contributions (~45%) of a few tailings ponds sources to total fugitive CH_4 emissions in the AOSR and highlight opportunities for strategic GHG mitigation. Our individual-plume sum is consistent with estimates derived using the TERRA box approach to determine total emissions

25   within facility boundaries. The agreement between these two methods demonstrates that the three source types listed are representative of the major emissions of CH_4 in the AOSR. Further results from a ~75km flight screen that captured almost all AOSR emissions are able to reproduce total emissions

derived from the sum of the five major facilities. Our final top-down estimate of the 2013 summer time emission rate in the region is 19.6 ± 1.1 tonnes CH_4 hr^{-1} or 0.17 ± 0.1 Tg CH_4 yr^{-1}. We note that the annual emissions rate is only a first order approximation of what annual emissions might be if the temporal emissions are constant throughout the year; however, we consider this assumption to be highly

5 uncertain as the seasonality of fugitive emissions rates of CH_4 in the Athabaska Oil Sands region is still a major uncertainty. Further effort should be devoted to measurements of these emission rates in different seasons, and to understand if ambient temperature and ice coverage on tailings ponds are important parameters or not. Our limited measurements of ethane and methane downwind of the AOSR facilities suggest that the EMR's are quite low, $< 1.4\%$, likely because the fundamental source of the

10 majority of the methane emissions are methanogenic, not thermogenic, in nature. Thus global estimates of the relative contributions of oil and gas emissions to increases in atmospheric CH_4 based on EMR measurements in the free troposphere would not capture AOSR emissions due to the low C_2H_6 emissions in the region.

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Table 1: Enhancements of ΔC_2H_6 from canister measurements overlapping with CH_4 plumes across three flights (Aug 14, Aug 16 and Sep 024). Mean enhanced ΔCH_4 is shown over the course of ~20s canister sampling times with ethane-to-methane ratios (EMRs) computed.

Scenario	ΔC_2H_6 (ppb)	ΔCH_4 (ppb)	EMR (%)
SML Ponds (Aug 14)	3.2	814	0.40
SML Mines (Aug 14)	2.6	365	0.72
SUN Ponds (Aug 16)	1.2	215	0.56
SUN Mines (Aug 16)	1.1	185	0.59
CNRL (Sep 0402)	1.9	137	1.39

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Table 2: Comparison of emissions rates (in tonnes CH_4 hr^{-1}) determined from the screen approach (n estimates per facility), the box-approach (n estimates per facility), and the uncertainty weighted average for each method and facility. The 5-facility AOSR total is show in the final column and row.

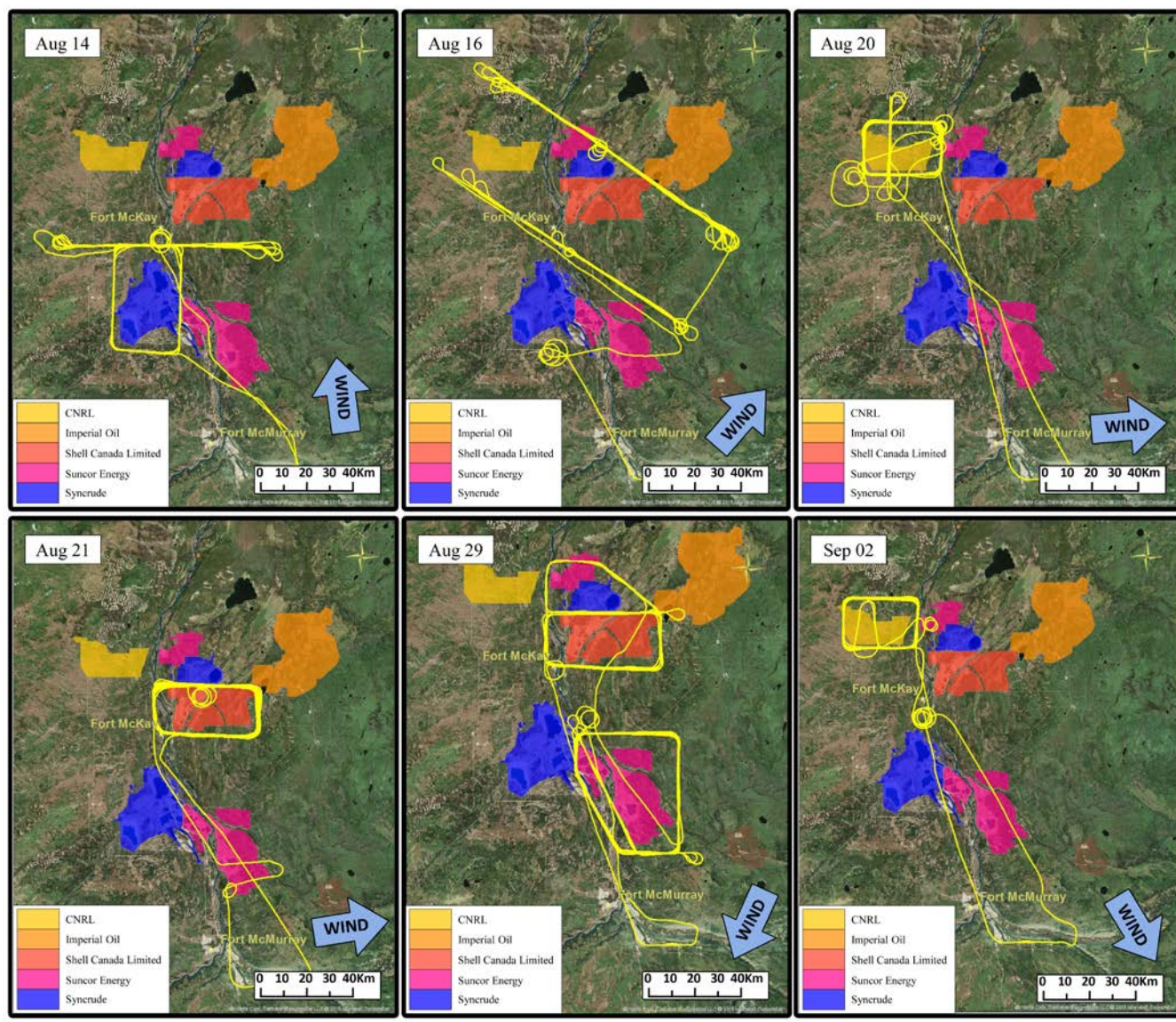| Method	SML (n)	SUN (n)	CNRL (n)	SAJ (n)	SAU (n)	Total AOSR
Screen	9.1±0.9 (3)	4.2±0.4 (2)	3.6±0.8 (2)	1.2±0.2 (2)	1.4±0.2 (2)	
Box	7.7±1.5 (1)	3.9±0.9 (1)	3.6±0.6 (2)	1.4±0.2 (2)	1.7±0.3 (1)	
Average	8.6±0.9 (4)	4.2±0.4 (3)	3.6±0.5 (4)	1.3±0.2 (4)	1.5±0.2 (3)	**19.2 ± 1.1**

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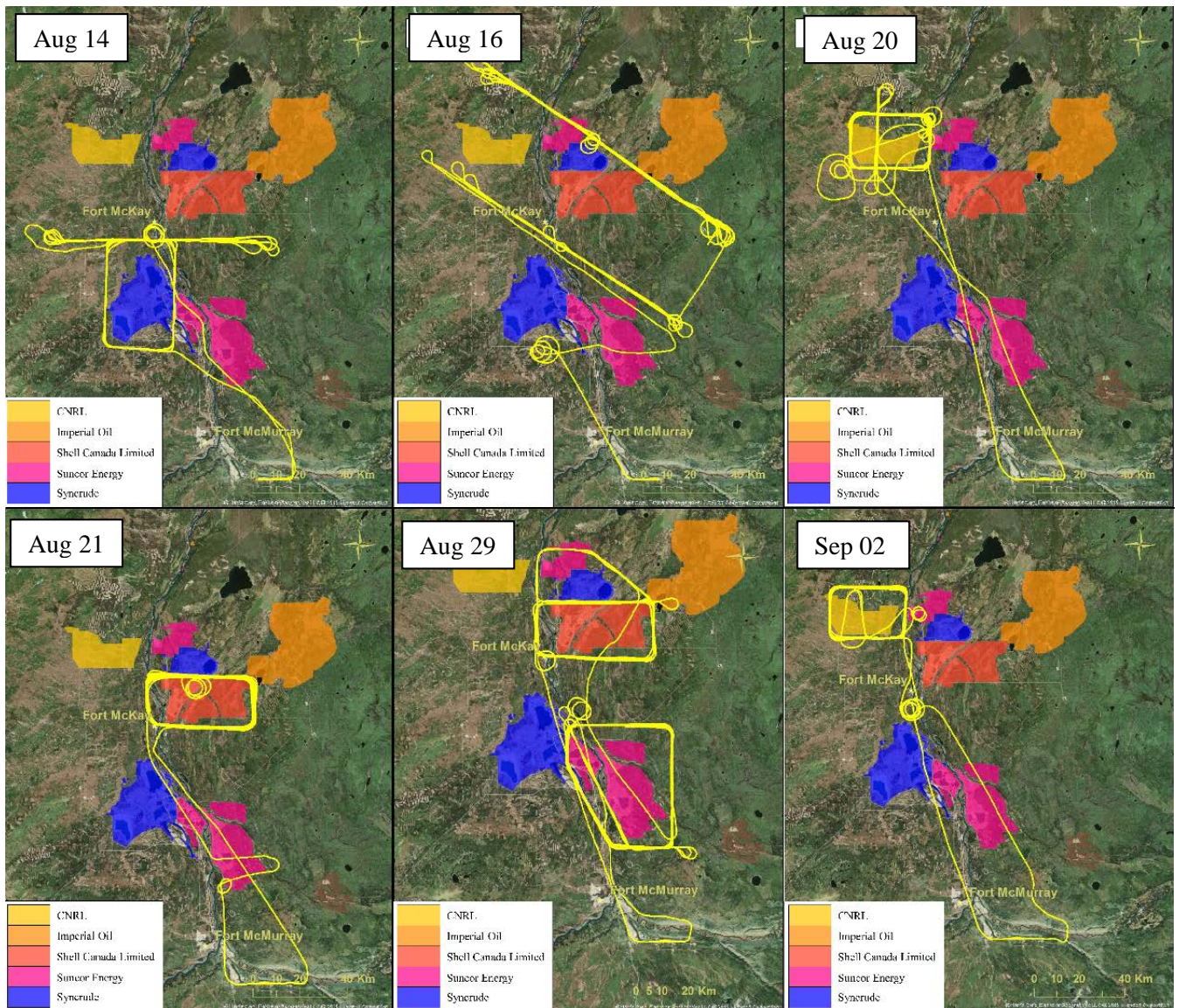
Figure 1: Flight tracks from flights capturing emissions from SML (Aug 14, Aug 16), SUN (Aug 16, Aug 29), CNRL (Aug 20, Sep 02), SAJ (Aug 21, Sep 06 not shown), and SAU (Aug 29, Sep 06 not shown). SML and SAU are shown in blue, SUN in pink, CNRL in yellow and SAJ in dark orange.
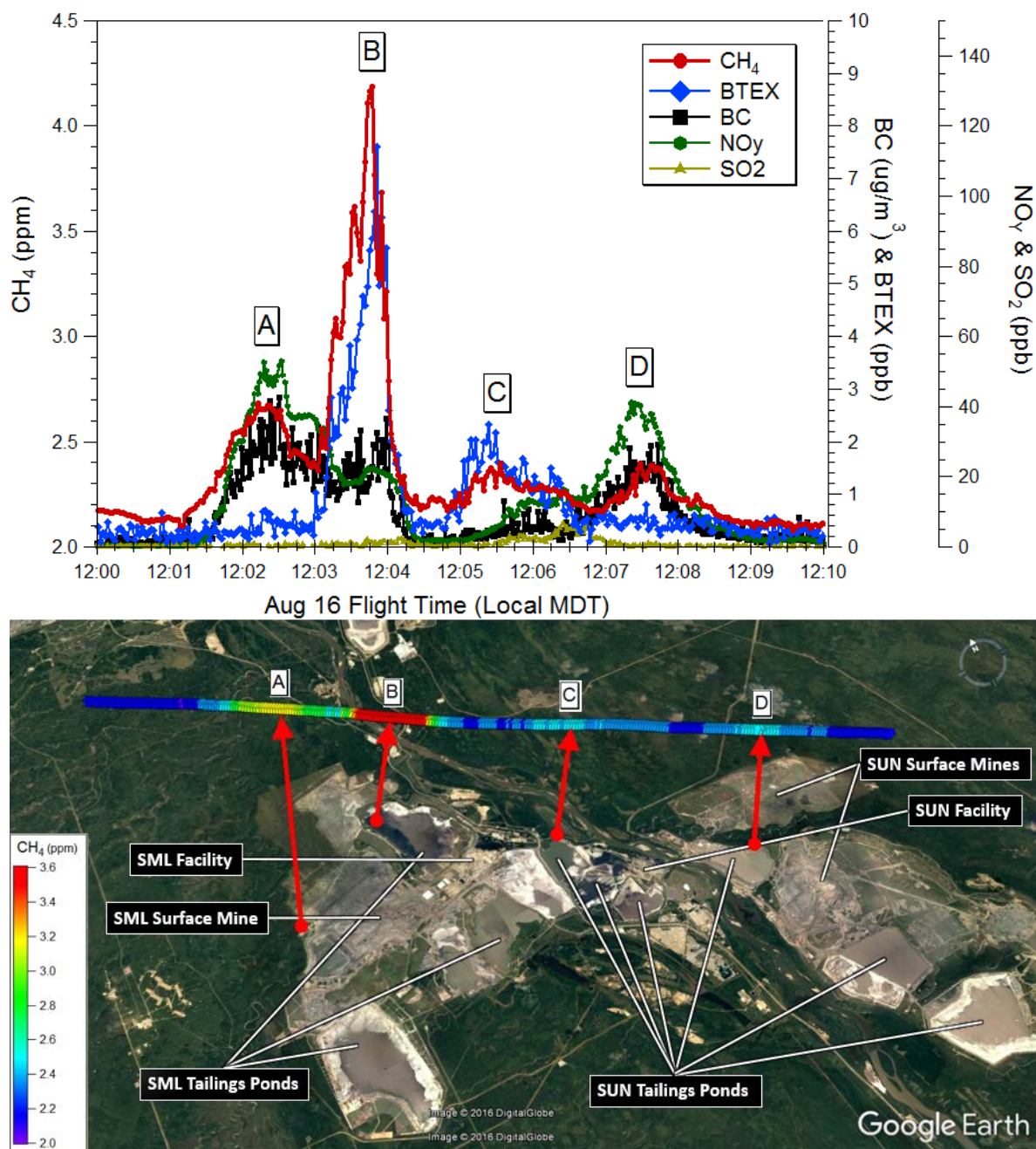
Figure 2: Top: Aircraft measurements of CH4 (red), BTEX (blue) and rBC (black) from a single transect at 150 m agl downwind of SML and SUN on Aug 16. Four plumes are labelled A (SML Mine), B (SML Tailings), C (SUN Tailings), D (SUN Mine). Bottom: CH4 mixing ratios along the 150 m agl transect for the above time series. Each data point is color coded for CH4 mixing ratio as well as instantaneous wind vector measured on the aircraft at that location. Red arrows indicate air parcel back-

trajectories based on linear back extrapolation of ~~flight level measured~~the aircraft measured wind vectors at plume centres, with end points at 100 min (A), and 20 min (B-D).

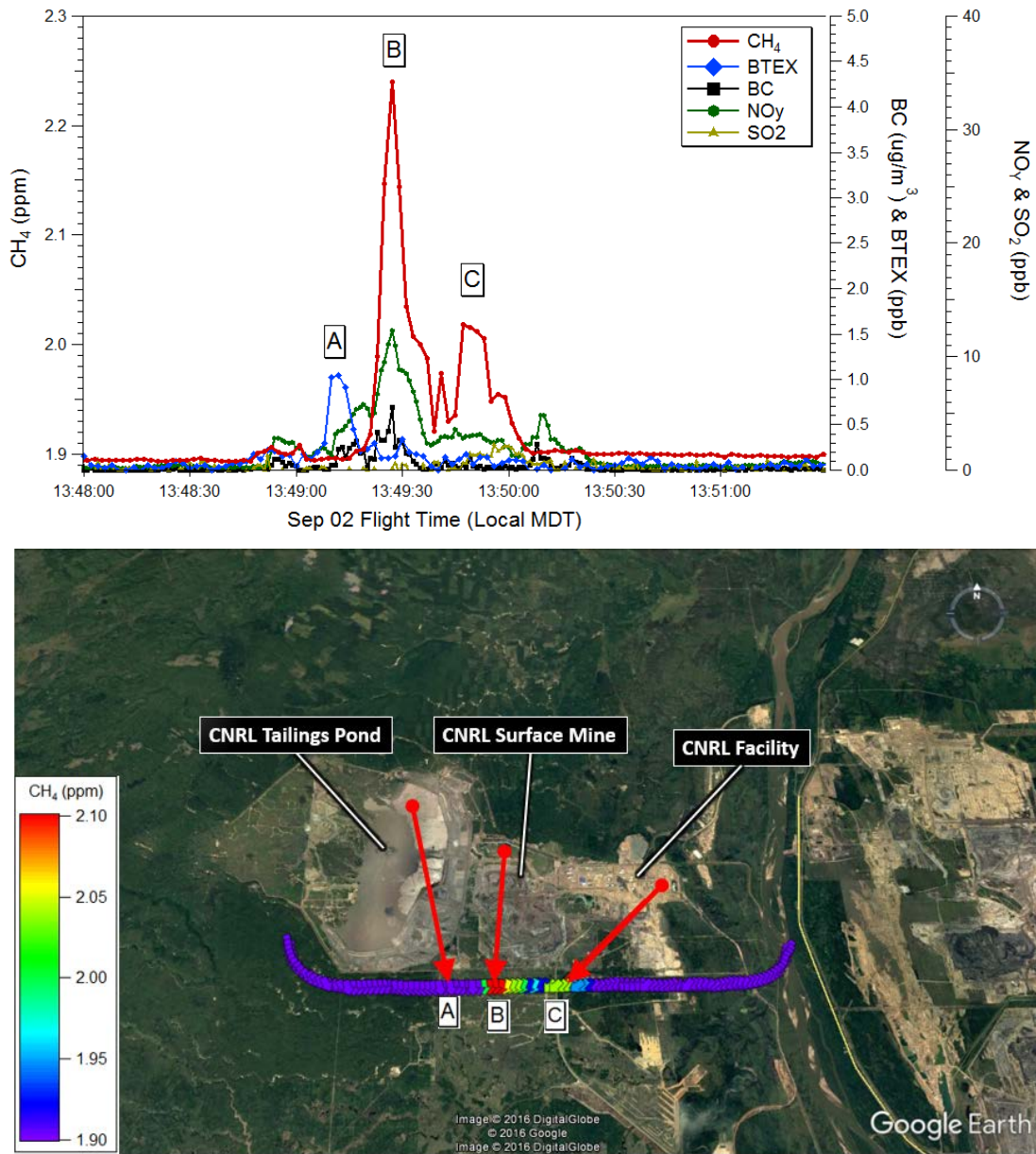**Figure 3:** Top: Aircraft measurements of CH_4 (red), BTEX (blue) and rBC (black) from single transect ~150 m agl downwind of CNRL. Plume A (CNRL Tailings Pond), Plume B (CNRL Mine) Plume C CNRL Facility. Bottom: CH_4 mixing ratios along 150 m agl transect for above time series. Each data point is color coded for CH_4 mixing ratio as well as instantaneous wind vector measured on the aircraft

Red arrows show back-trajectories based on linear extrapolation of measured wind speed and direction.
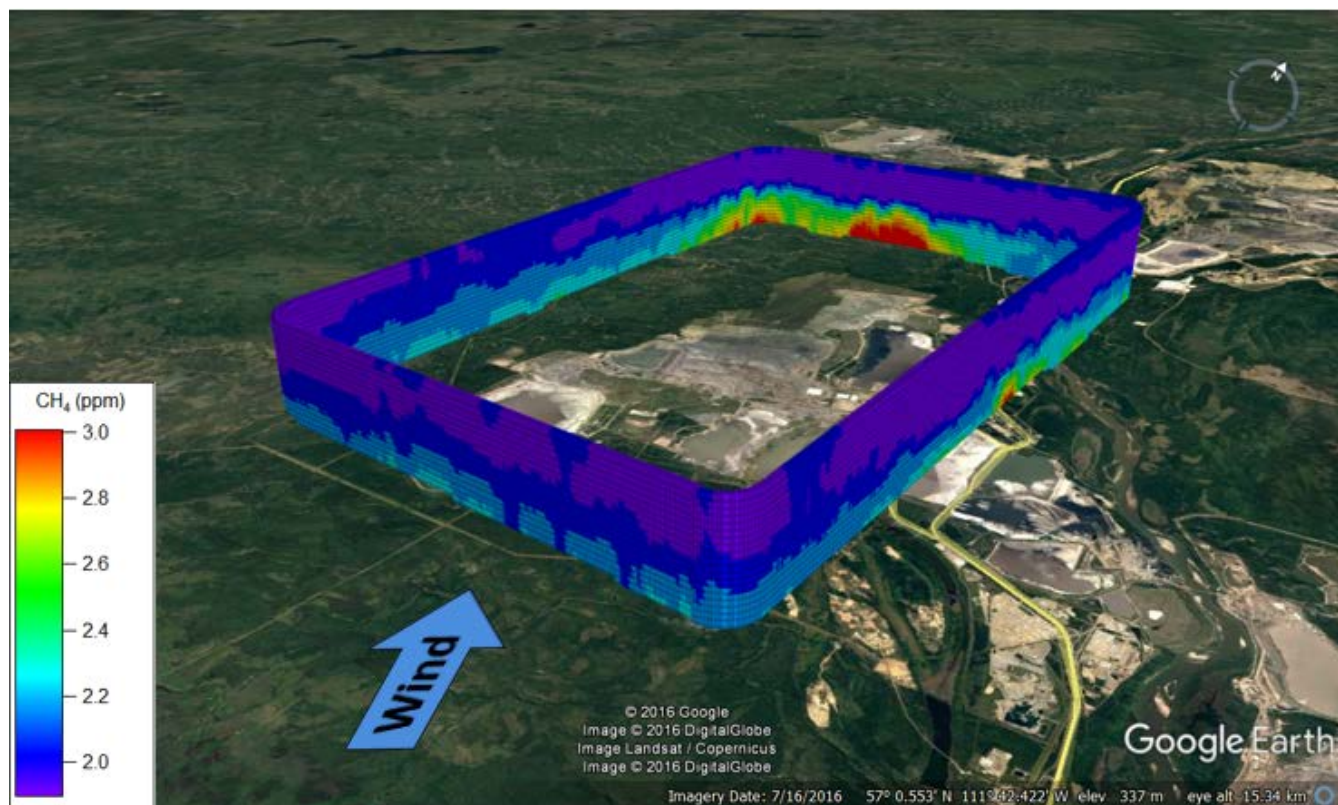
5 **Figure 4:** Interpolated CH$_4$ mixing ratios for the Aug 14 box flight surrounding SML.

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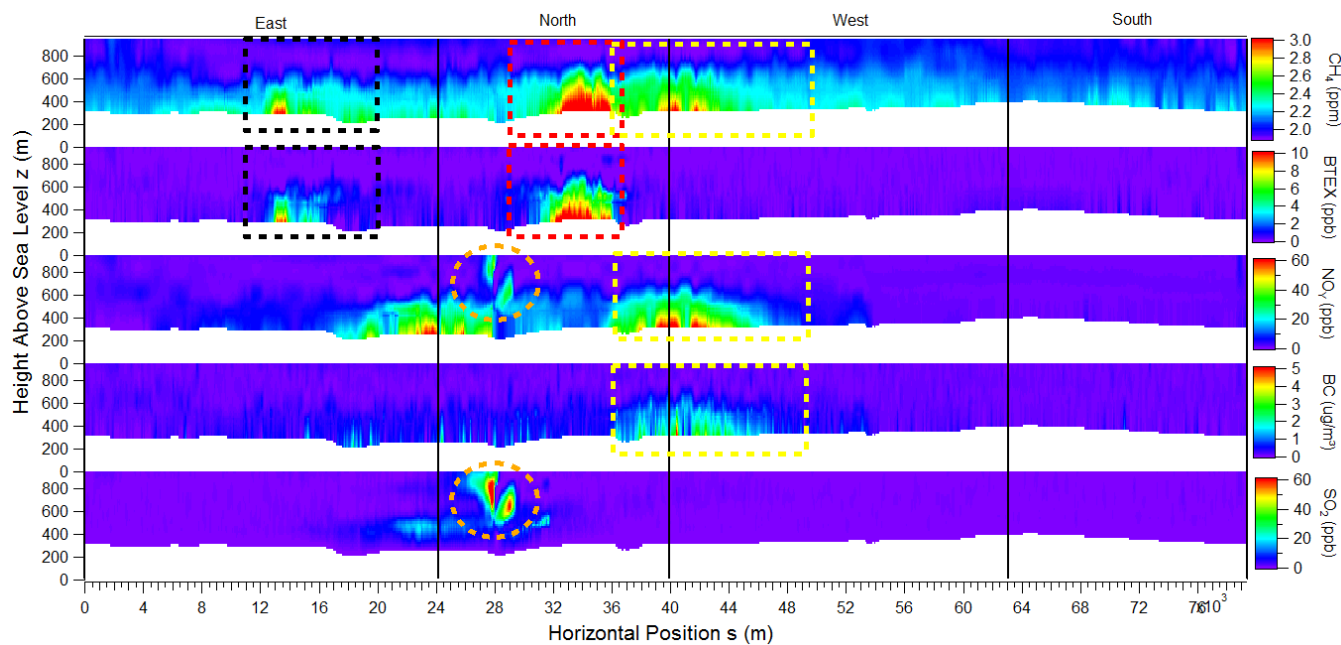
Figure 5: Curtain plots showing interpolated CH_4, BTEX, NO_y, rBC and SO_2 mixing ratios for the Aug 14 box flight around SML. Red-dashed box indicates the primary plume on the North screen, yellow-dashed box indicates the secondary plume on the West screen, and black-dashed box indicates the tertiary incoming plume on the East screen. Orange dashed-circle shows the upgrader plume on the North screen.
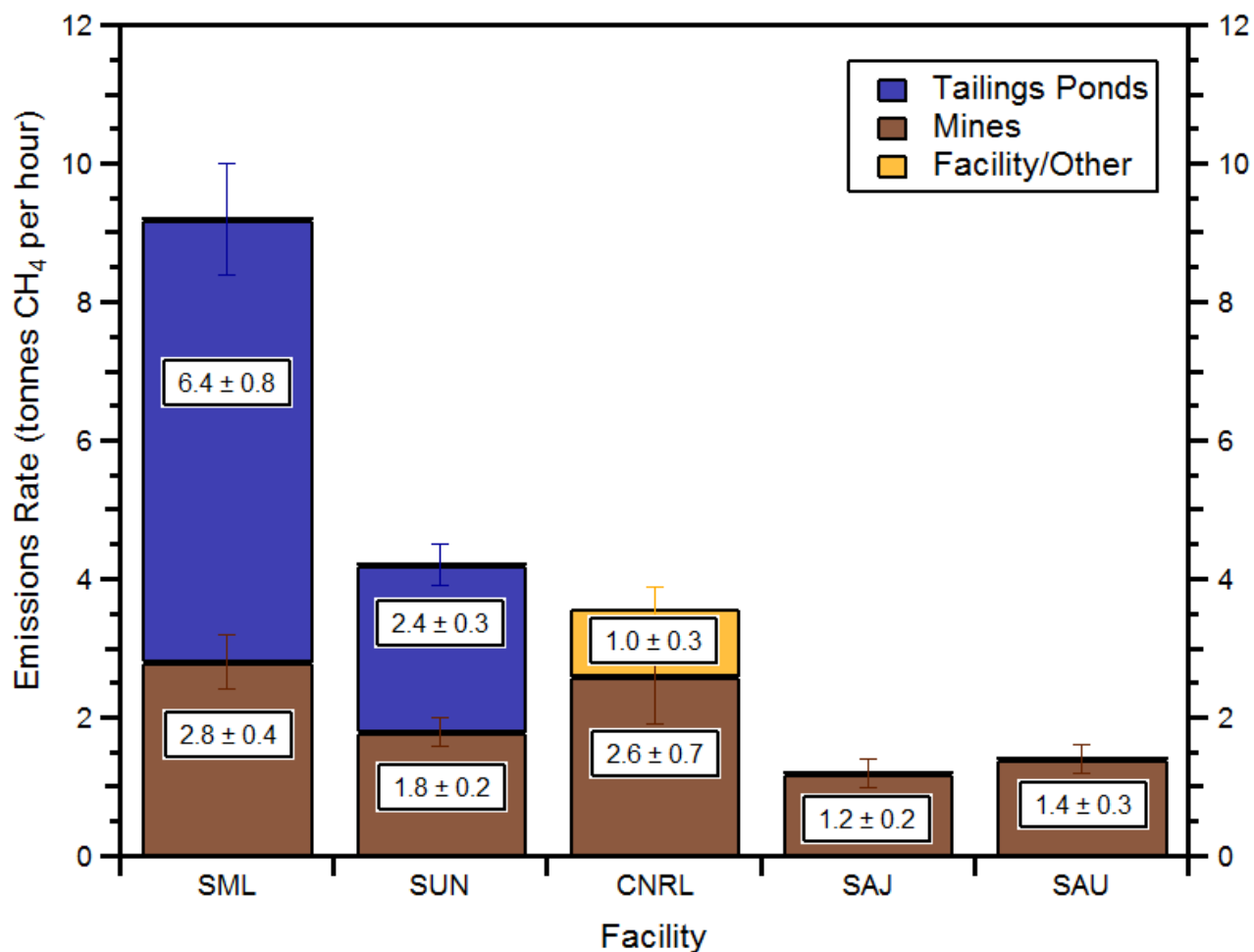
Figure 6: Source-apportioned emissions rates of CH_4 determined by the screen mass-balance method (Eq. 1) for the SML, SUN, CNRL, SAJ and SAU facilities. Emissions rates are the average of three mass-balance flights for SML over two days, two flights each for SUN, SAJ and SAU on separate days, and one flight for CNRL.
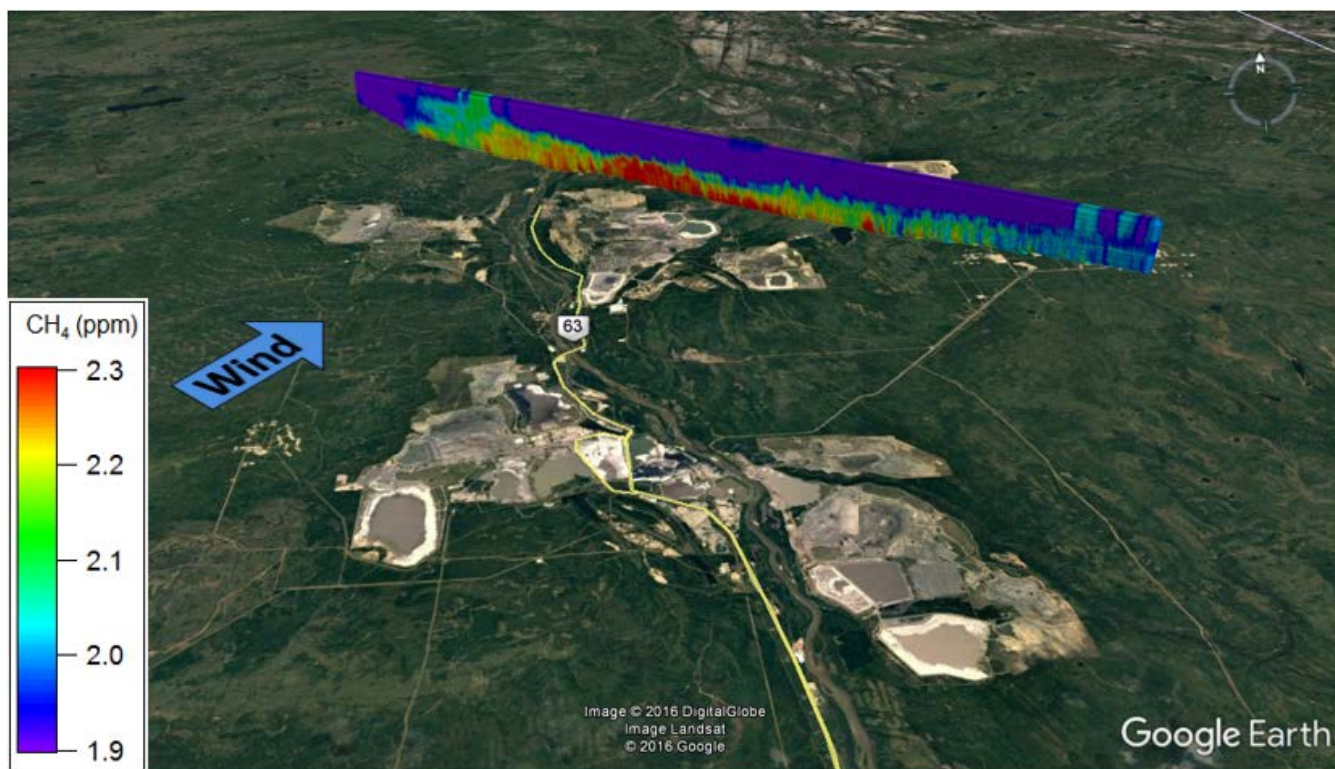
Figure 7: Map image showing interpolated CH$_4$ mixing ratios for the Aug 16 Total Oil Sands screen.

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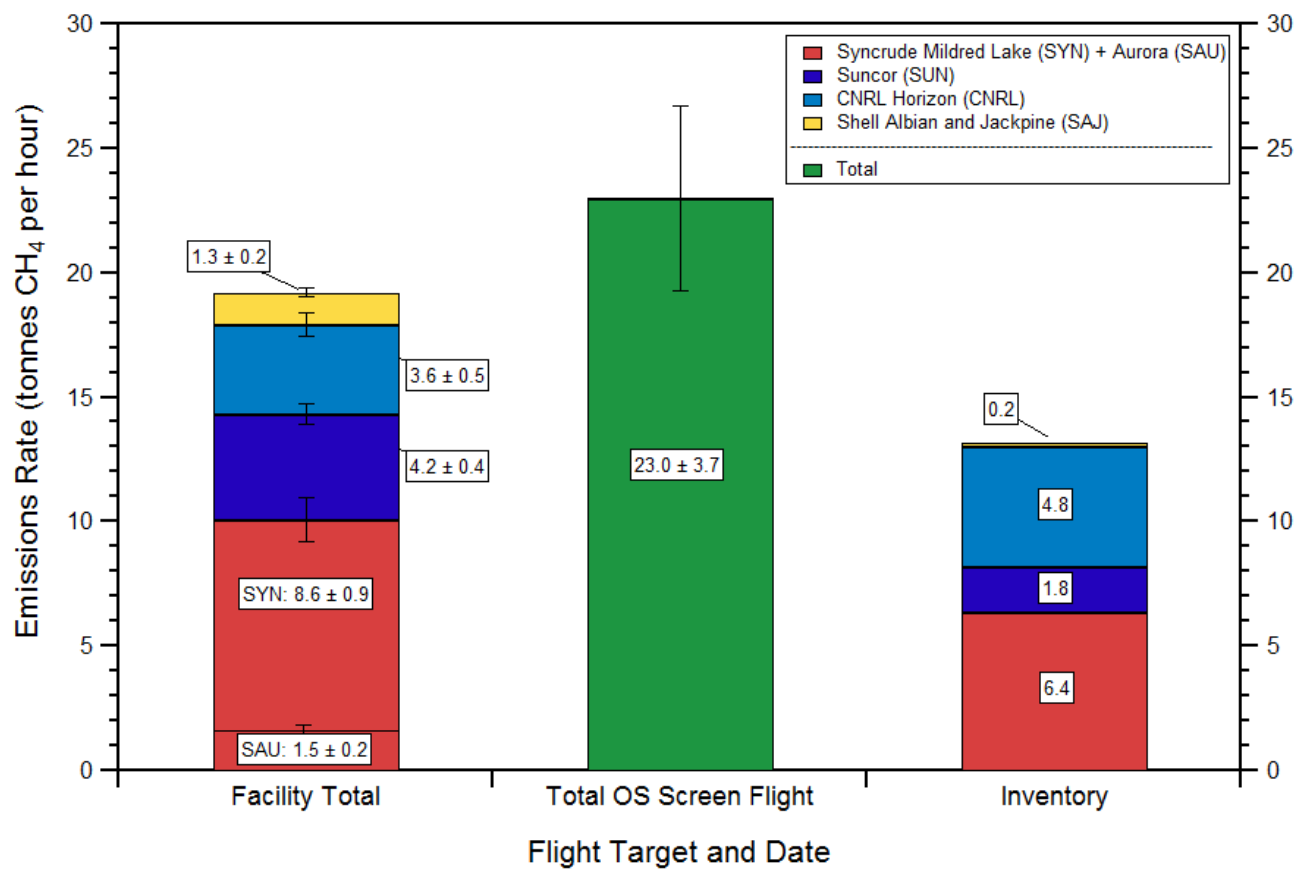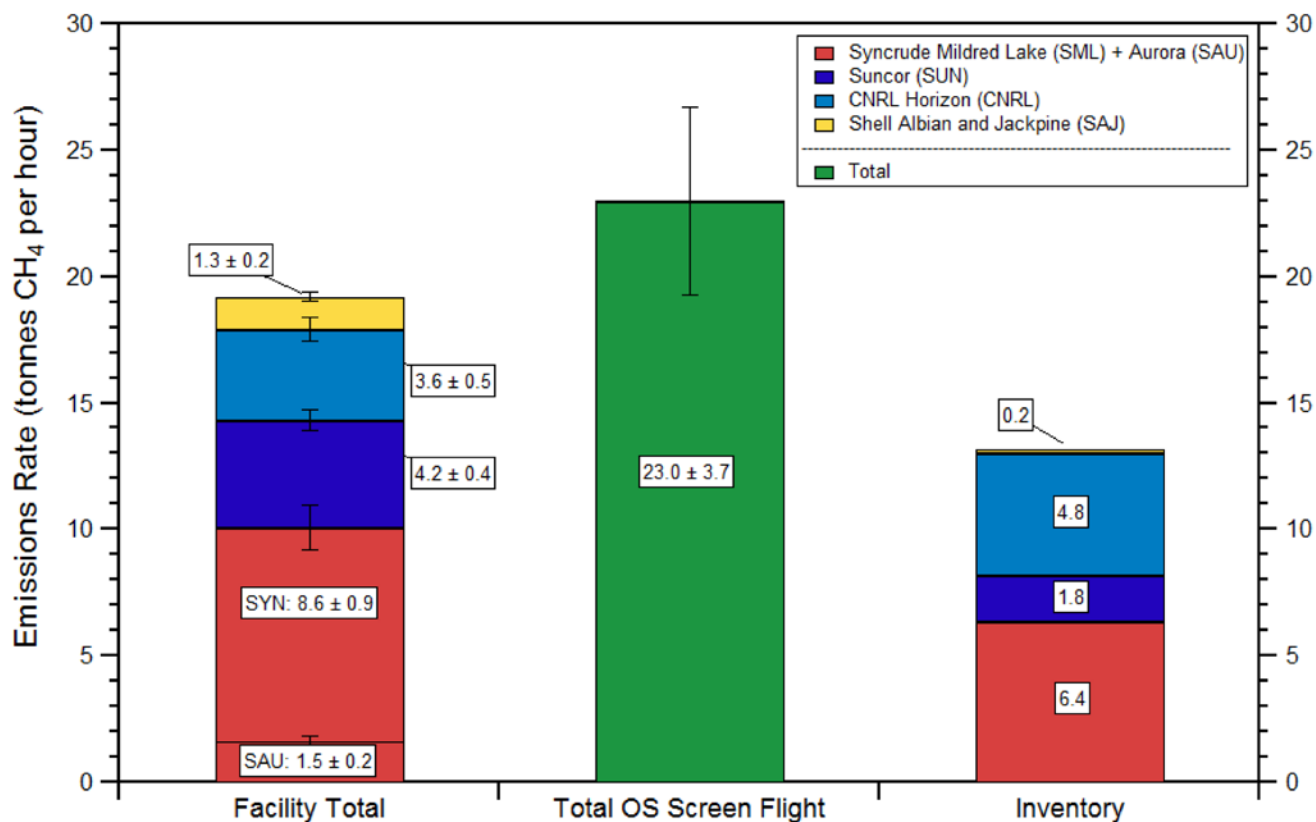
Figure 8: Comparison of emissions rates determined for the five major facilities (SML, SAU, SUN, CNRL, SAJ, SAU) with the Total OS Screen Flight (see Fig. 7 for the flight track). Also shown is the CH4 emissions taken from the Canadian GHGRP Emissions Inventory for the year 2013, scaled down from annual to hourly emissions assuming constant temporal emissions. Note that in the inventory, SML and SAU emissions are reported as a single facility, while our estimates are derived separately.

Supplementary Information for:

Quantification of Methane Sources in the Athabasca Oil Sands Region of Alberta by Aircraft Mass-Balance

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Assessment of Uncertainties

Tables S1-6 show the results of the sensitivity analysis to estimate contributions to total uncertainty. Parameters contributing to uncertainties depend on the mass balance method used and the screen-based (Eq. 1) or the box-approach (Eq. 2). Minor uncertainties that contribute to both methods are errors in the CH_4 mixing ratio measurement and wind measurements. CH_4 measurement errors from the instrument are <1%. Measurements of trace species from other instruments were used qualitatively to deduce plume origins, thus they do not contribute to total uncertainties. In a previous study, a Monte Carlo simulation was used to demonstrate the wind measurements contribute <1% to the change in uncertainties (Gordon et al., 2016). A significant source of uncertainty for both mass balance methods is the extrapolation of CH_4 mixing ratios to the surface for ground-level plumes. Surface extrapolation uncertainties are highly variable with flight, consistent with the literature. Cambaliza et al. (2014) found surface extrapolation uncertainties to be 4, 9 and 16% for three different mass balance flights downwind of Indianapolis to determine CH_4 fluxes, and Gordon et al., 2016 found this to be 15% and 26% for two Oil Sands flights for the CNRL facility. The uncertainty depends on the range of surface mixing ratios resulting from fitting varying extrapolation methods. We derive a range of possible emissions rates by comparing results from constant, linear and half-Gaussian extrapolations to the surface. CH_4 measurements at Fort McKay are used as constraints on surface mixing ratios when flight paths are

directly overhead (Aug 16 Flight 4A, SML and SUN). Half-guassian extrapolations are used where fits are above constraints ($r^2 > 0.40$). Future studies can further minimize these uncertainties with simultaneous ground-level mixing ratio measurements.

5   Additional uncertainties specific to the box-approach (Eq. 2) are assessed according to the methodology described in Gordon et al., 2016. Contributing factors are: (1) the uncertainty in the box-top height (affecting the E_{CH} and E_{CV} terms), estimated by reducing the box height by 100 m, (2) changes in air mass density within the volume of the box (affecting E_{CM}), estimated using the minimum and maximum of pressure and temperature ratios derived from surrounding meteorological stations, (3) inclusion of

10   the estimated vertical turbulence term (E_{CVT}), and (4) uncertainty in the mean CH_4 mixing ratio at the box-top (affecting E_{CV}) determined from the 95% confidence interval ($2\sigma/\sqrt{n}$) of interpolated measurements. These terms are recalculated according to the range of possible input parameters in order to derive resulting uncertainties in the emissions rates. Screen-approach specific uncertainties (Eq. 1) are mostly due to the variability in the background mixing ratio $[CH_4]_B$, determined using the outer

15   edges of the screen away from plume sources (screen flights) and upwind measurements (box flights). For each flight measurements from multiple background regions (>1km) occurring closely in time are used as possible inputs, which are identified clearly due to the high CH_4 mixing ratios observed from plumes. Other sources of uncertainty are the vertical extent of the screen (upper bound, z) and the horizontal boundaries (s_1-s_2) of individually characterized plumes. These plume boundaries are

20   expanded and contracted to derive a range of possible integrals.

Uncertainties for each mass balance flight are added in quadrature to derive a range of possible emissions rates. Estimates for the same source category within a facility, as well as total estimates for the same facility, are treated as independent estimates and combined using an error-weighted mean

25   ($1/\sigma^2$).

Meteorological Conditions

Tables S1-6 (bottom) present various flight details and meteorology. Flights used are those with a high number of aircraft transects (≥6) that show full characterization of plume vertical extent. Boundary layer heights are determined using visual inspection of dew point temperature alongside LIDAR backscatter reports from ground-site AMS13 during flight times. Ground temperature and wind direction measurements are based on ground-site data at AMS13 over the course of the day. Wind speeds shown are from interpolated screens $\pm$ 1σ.

Table S1-6: **Top: Sensitivity analysis displaying uncertainty contributions (1σ) shown in percent change from the best-estimate emissions rate, added in quadrature for totals. Uncertainties in individual plumes are noted with superscripts for tailings ponds (t), mines (m) and facility/other (f). Screen estimates using an overlapping subset of downwind measurements from a box flight of the same day are shown with an asterisk (*). Middle: List of emissions rates for source categories and facility totals in tonnes CH$_4$ per hour (tonnes hr^{-1}). Bottom: Various aircraft flight details and meteorological parameters.**

Table S1: Syncrude Mildred Lake (SML)

		Aug 14 Box	Aug 14 Screen A*	Aug 14 Screen B	Aug 16 Screen A
	Measurement Error (%)	1	1	1	1
	Wind Error (%)	1	1	1	1
	Surface Extrapolation (%)	4	11	3	28
Box	Box-top Height (%)	15			
	Density Change (%)	11			
	Vertical Turbulence (%)	2			
	Box-Top Mixing Ratio (%)	**4**			
Screen	Background Mixing Ratio (%)		13	19	8
	Screen-Top Height (%)		6	6	1
	Plume Separation (%)		6^t, 11^m	5^t, 12^m	5^t, 8^m
	Total Uncertainty Facility (%)	20	19	21	30
	Total Uncertainty Plumes (%)		20^t, 22^m	21^t, 24^m	30^t, 31^m
	Emissions Rate Ponds (tonnes hr^{-1})		6.38 ± 1.23	5.83 ± 1.22	8.63 ± 2.59
	Emissions Rate Mines (tonnes hr^{-1})		2.71 ± 0.60	2.67 ± 0.64	3.07 ± 0.95
	Emissions Rate Facility/Other (tonnes hr^{-1})				
	Emissions Rate Total (tonnes hr^{-1})	**7.68 ± 1.54**	**9.10 ± 1.73**	**8.50 ± 1.79**	**11.82 ± 3.55**
	Aircraft Transect Count	6	6	8	9
	Boundary Layer Height (m agl)	360-400	360-400	400-600	350-400
	Temperature (°C)	20.8 ± 6.0	20.8 ± 6.0	20.8 ± 6.0	19.5 ± 3.8
	Wind Speed (m/s)	3.1 ± 2.5	3.1 ± 2.5	5.1 ± 1.6	2.8 ± 0.8
	Daily Mean Wind Direction (°)	220 ± 37	220 ± 37	220 ± 37	225 ± 57

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Table S2: Suncor Energy OSG (SUN)

		Aug 16 Screen A	Aug 29 Box	Aug 29 Screen*
	Measurement Error (%)	1	1	1
	Wind Error (%)	1	1	1
	Surface Extrapolation (%)	4	14	4
Box	Box-top Height (%)		1	
	Density Change (%)		17	
	Vertical Turbulence (%)		2	
	Box-Top Mixing Ratio (%)		5	
Screen	Background Mixing Ratio (%)	23		2
	Screen-Top Height (%)	1		9
	Plume Separation (%)	12[t], 1[m]		9[t], 9[m]
	Total Uncertainty Facility (%)	24	23	11
	Total Uncertainty Plumes (%)	27[t], 24[m]		14[t], 14[m]
	Emissions Rate Ponds (tonnes hr^{-1})	3.16 ± 0.85		2.30 ± 0.32
	Emissions Rate Mines (tonnes hr^{-1})	1.53 ± 0.37		1.88 ± 0.26
	Emissions Rate Facility/Other (tonnes hr^{-1})			
	Emissions Rate Total (tonnes hr^{-1})	**4.69 ± 1.13**	**3.96 ± 0.91**	**4.18 ± 0.42**
	Aircraft Transect Count	9	7	7
	Boundary Layer Height (m agl)	350-400	400-500	400-500
	Temperature (°C)	19.5 ± 3.8	15.2 ± 2.4	15.2 ± 2.4
	Wind Speed (m/s)	2.8 ± 0.8	1.8 ± 1.3	1.8 ± 1.3
	Daily Mean Wind Direction (°)	225 ± 57	26 ± 40	26 ± 40

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Table S3: Canadian National Resources Limited Horizon (CNRL)

		Aug 20 Box	Aug 20 Screen*	Sep 02 Box	Sep 02 Screen*
	Measurement Error (%)	1	1	1	1
	Wind Error (%)	1	1	1	1
	Surface Extrapolation (%)	22	26	12	11
Box	Box-top Height (%)	1		18	
	Density Change (%)	5		6	
	Vertical Turbulence (%)	2		7	
	Box-Top Mixing Ratio (%)	3		8	
Screen	Background Mixing Ratio (%)		16		25
	Screen-Top Height (%)		5		2
	Plume Separation (%)				6^m, 12^f
	Total Uncertainty Facility (%)	23	31	25	28
	Total Uncertainty Plumes (%)				29^m, 30^f
	Emissions Rate Ponds (tonnes hr^{-1})				
	Emissions Rate Mines (tonnes hr^{-1})				2.56 ± 0.74
	Emissions Rate Facility/Other (tonnes hr^{-1})				0.98 ± 0.29
	Emissions Rate Total (tonnes hr^{-1})	**3.65 ± 0.84**	**3.67 ± 1.14**	**3.53 ± 0.88**	**3.54 ± 1.00**
	Aircraft Transect Count	12	12	10	10
	Boundary Layer Height (m agl)	700-900	700-900	600-1000	600-1000
	Temperature (°C)	16.3 ± 4.3	16.3 ± 4.3	12.7 ± 5.1	12.7 ± 5.1
	Wind Speed (m/s)	2.4 ± 1.9	2.4 ± 1.9	5.9 ± 2.8	5.9 ± 2.8
	Daily Mean Wind Direction (°)	262 ± 35	262 ± 35	338 ± 59	338 ± 59

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Table S4: Shell Albian and Jackpine (SAJ)

		Aug 21 Box	Aug 21 Screen*	Sep 06 Box	Sep 06 Screen*
	Measurement Error (%)	1	1	1	1
	Wind Error (%)	1	1	1	1
	Surface Extrapolation (%)	5	7	12	7
Box	Box-top Height (%)	8		5	
	Density Change (%)	10		16	
	Vertical Turbulence (%)	5		2	
	Box-Top Mixing Ratio (%)	9		7	
Screen	Background Mixing Ratio (%)		27		17
	Screen-Top Height (%)		10		5
	Plume Separation (%)				
	Total Uncertainty Facility (%)	18	30	22	20
	Total Uncertainty Plumes (%)				
	Emissions Rate Ponds (tonnes hr^{-1})				
	Emissions Rate Mines (tonnes hr^{-1})		1.44 ± 0.43		1.18 ± 0.24
	Emissions Rate Facility/Other (tonnes hr^{-1})				
	Emissions Rate Total (tonnes hr^{-1})	**1.60 ± 0.29**	**1.44 ± 0.43**	**1.25 ± 0.28**	**1.18 ± 0.24**
	Aircraft Transect Count	10	10	10	10
	Boundary Layer Height (m agl)	1200-1500	1200-1500	900-1200	900-1200
	Temperature (°C)	16.5 ± 3.6	16.5 ± 3.6	14.8 ± 6.2	14.8 ± 6.2
	Wind Speed (m/s)	1.3 ± 0.8	1.3 ± 0.8	4.3 ± 0.9	4.3 ± 0.9
	Daily Mean Wind Direction (°)	258 ± 50	258 ± 50	7 ± 50	7 ± 50

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Table S5: Syncrude Aurora (SAU)

		Aug 29 Box	Aug 29 Screen*	Sep 06 Screen*
	Measurement Error (%)	1	1	1
	Wind Error (%)	1	1	1
	Surface Extrapolation (%)	10	14	6
Box	Box-top Height (%)	4		
	Density Change (%)	9		
	Vertical Turbulence (%)	2		
	Box-Top Mixing Ratio (%)	3		
Screen	Background Mixing Ratio (%)		11	13
	Screen-Top Height (%)		4	13
	Plume Separation (%)			
	Total Uncertainty Facility (%)	15	19	20
	Total Uncertainty Plumes (%)			
	Emissions Rate Ponds (tonnes hr^{-1})			
	Emissions Rate Mines (tonnes hr^{-1})		1.29 ± 0.25	1.56 ± 0.31
	Emissions Rate Facility/Other (tonnes hr^{-1})			
	Emissions Rate Total (tonnes hr^{-1})	**1.70 ± 0.26**	**1.29 ± 0.25**	**1.56 ± 0.31**
	Aircraft Transect Count	3	3	10
	Boundary Layer Height (m agl)	400-500	400-500	900-1200
	Temperature (°C)	15.2 ± 2.4	15.2 ± 2.4	14.8 ± 6.2
	Wind Speed (m/s)	2.3 ± 0.7	2.3 ± 0.7	4.3 ± 0.9
	Daily Mean Wind Direction (°)	26 ± 40	26 ± 40	7 ± 50

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Table S6: Total Oil Sands Screen

		Aug 16 Screen B
	Measurement Error (%)	1
	Wind Error (%)	1
	Surface Extrapolation (%)	3
Box	Box-top Height (%)	
	Density Change (%)	
	Vertical Turbulence (%)	
	Box-Top Mixing Ratio (%)	
Screen	Background Mixing Ratio (%)	14
	Screen-Top Height (%)	5
	Plume Separation (%)	
	Total Uncertainty Facility (%)	16
	Total Uncertainty Plumes (%)	
	Emissions Rate Ponds (tonnes hr^{-1})	
	Emissions Rate Mines (tonnes hr^{-1})	
	Emissions Rate Facility/Other (tonnes hr^{-1})	
	Emissions Rate Total (tonnes hr^{-1})	**23.6± 3.8**
	Aircraft Transect Count	10
	Boundary Layer Height (m agl)	400-450
	Temperature (°C)	19.5 ± 3.8
	Wind Speed (m/s)	2.8 ± 1.0
	Daily Mean Wind Direction (°)	225 ± 57

Figure S1: Background profiles, [CH4]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 1σ variability within the 2-20km spatial regions of background air. Background CH4 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.

Figure S2: Correlation Plots for Plumes A-D corresponding to Figure 2 (SML Mine, SML Tailings Pond, SUN Tailings Pond, SUN Mine). CH_4 is well correlatred with tracer species NO_y, 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_4 vs BTEX plot for Plume C and the CH_4 vs NO_y and CH_4 vs BC plots for Plume D. These two sources correspond to lower emissions and mixing ratios of both CH_4 and the associated species. In the context of our results, this analysis confirms the correlation of CH_4 with various species as shown in Figure 2 which are used to spatially define plume boundaries.

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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.