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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.

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 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 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 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 ($1/\sigma^2$).

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 ± 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

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-top Height (%)		1	
Box	Density Change (%)		17	
	Vertical Turbulence (%)		2	
	Box-Top Mixing Ratio (%)		5	
	Background Mixing Ratio (%)	23		2
Screen	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

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

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

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

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, $[CH_4]_B(z)$, 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.

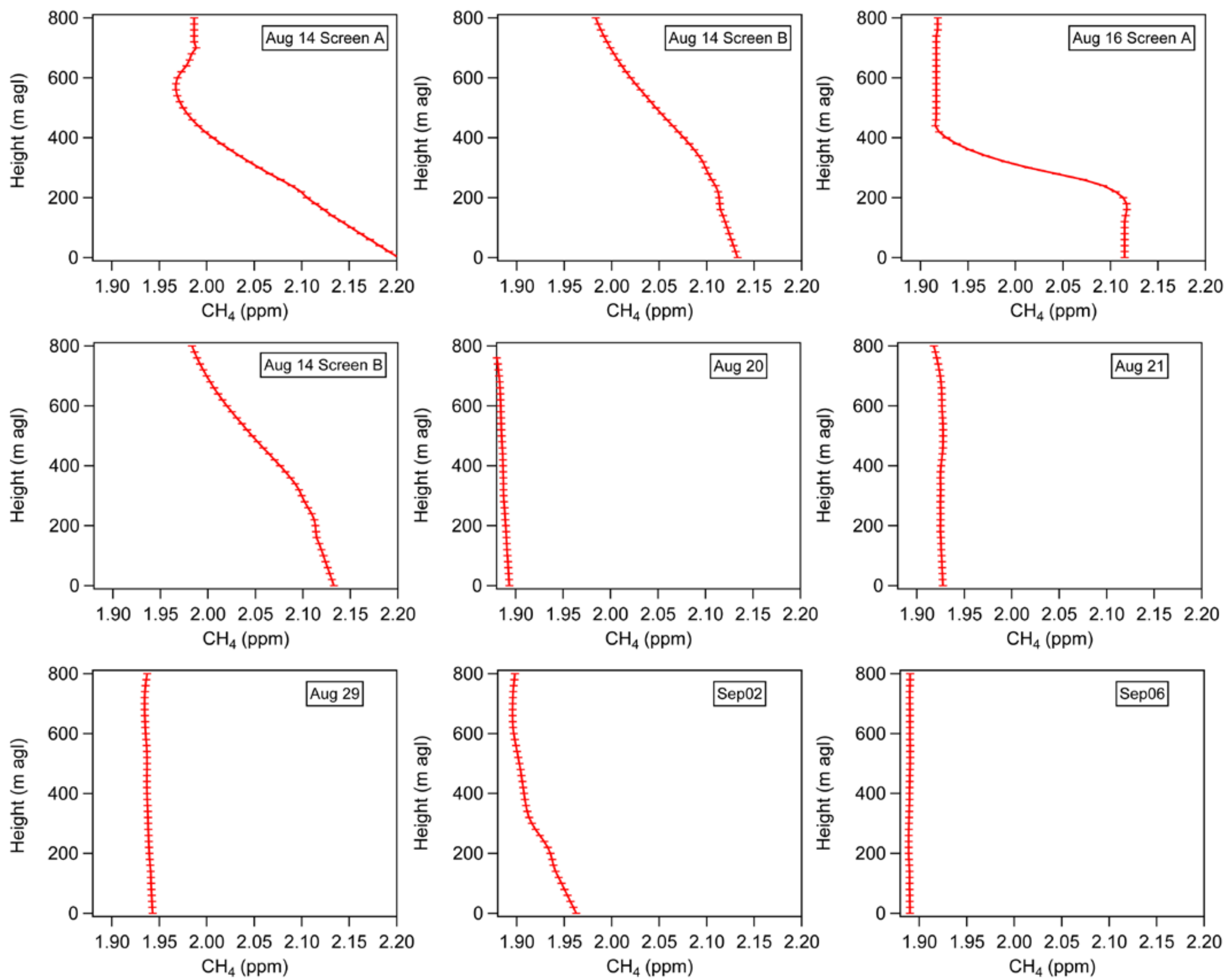

Figure S2: Correlation Plots for Plumes A-D corresponding to Figure 2 (SML Mine, SML Tailings Pond, SUN Tailings Pond, SUN Mine). CH_4 is well correlatred with tracer species NO_y, BC and BTEX for the various sources. Linear coefficients of determination (r^2) are in the range of 0.44-0.83. The lowest 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.

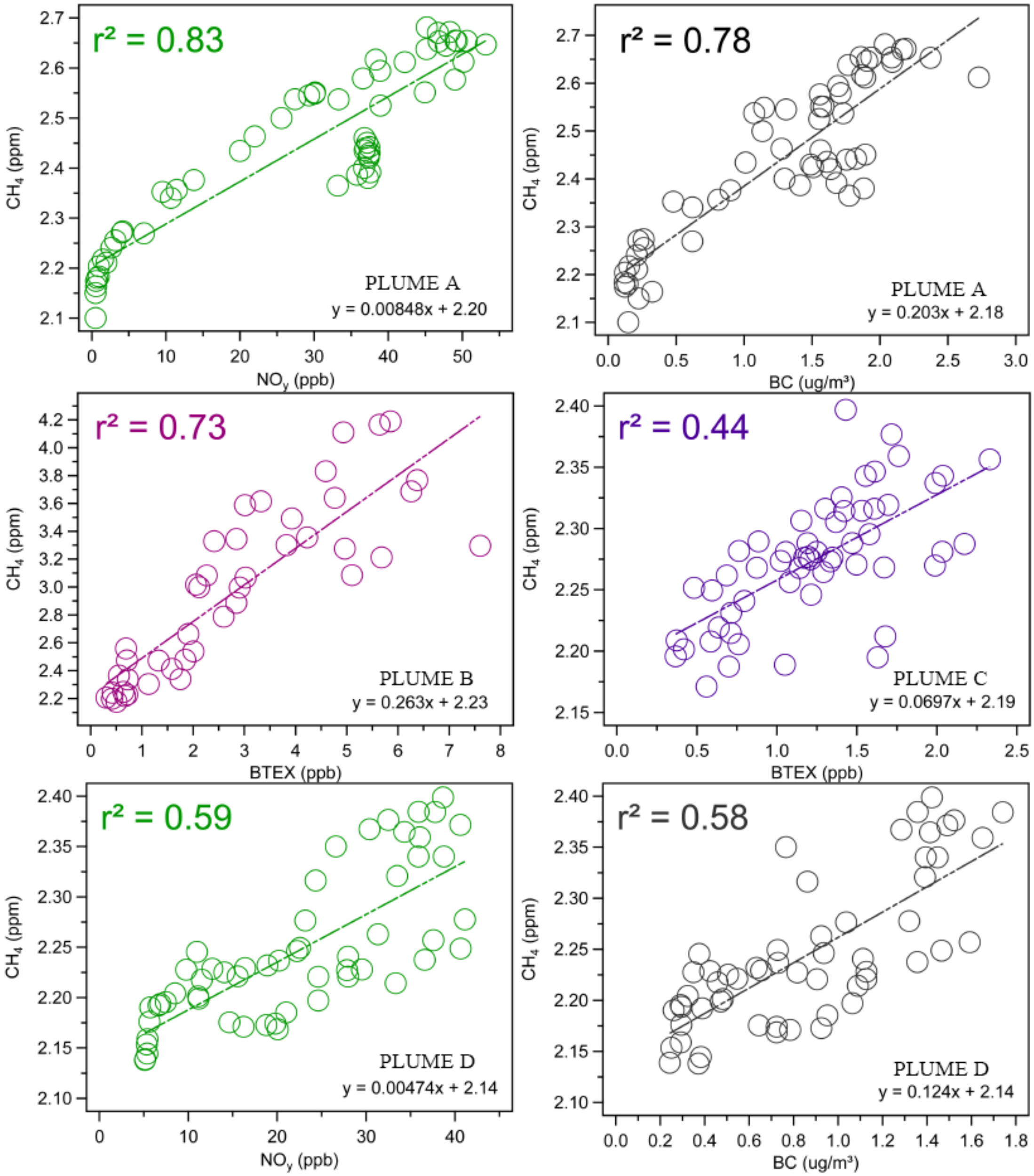

Figure S3: Time series plots of methane (red line) and discrete canisters samples analyzed for ethane (blue lines) corresponding to the same plumes used in Table 1 for the ethane/methane ratio calculations. These are a small subset of the canisters that were sampled over the aircraft campaign. These 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.