Response to Referee #1, "Quantifying fugitive gas emissions from an oil sands tailings pond with open-path FTIR measurements"

We thank the referee for this thorough review. We have carefully considered all the comments, implemented many of the suggestions, and included more details on methodology to make this manuscript stronger and stand-alone. Below, we address each question in turn. Questions and suggestions are in black, and our responses are in blue.

Specific comments:

1) Questions related to FTIR measurements. I have two questions regarding the FTIR concentration retrievals and the related flux calculation.
   a.   The authors state (line 108-109) that ". . . temperature and pressure dependent reference files were used for fitting and retrieving mole fractions." It is unclear how this was done. My concern is that with vertical temperature gradients at the measurement site (as implied by Fig. 4 in the companion paper by You et al.), different temperatures should be used for retrievals for the different FTIR path heights. If not done, is there potential for "false" flux signals? The authors should comment on this.

Response: The temperature measured at 8m was used in retrieving mole fractions for the three paths. The temperature difference shown in You et al. (2020), Figure 4c, is the difference between the pond liquid surface and the temperature measured at 8m, which was usually bigger than the difference between the temperature at 8m and the actual mean temperature for each path. To address this question, we have compared the temperature at 8m to temperature at 1m, and temperature at 18m to temperature at 8m. The statistics are shown here:
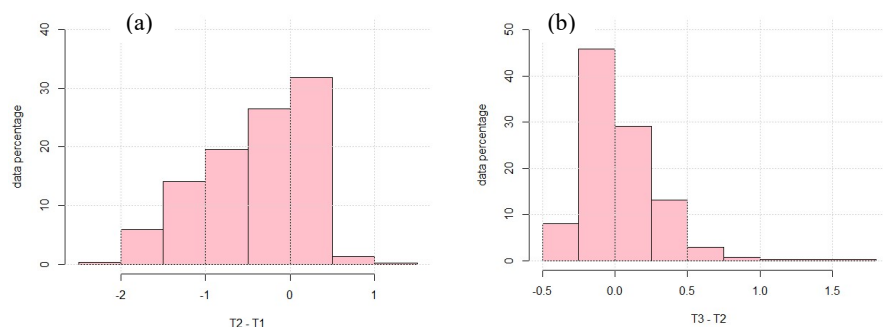

Figure: Histogram of (a) T_8m – T_1m (K) and (b) T_18m – T_8m (K) over the entire study period.

When the wind was from the pond, (T_8m – T_1m) was mainly between – 1.5 and 0.5 K, and (T_18m – T_8m) was mainly between -0.25 and 0.25 K.
To improve on the method we employed in our original manuscript, we can use T_1m for the bottom path, and an interpolation of T_8m and T_18m at 12m for the top path, to calculate mole fractions. First, the difference between the T_8m (which was used in previous retrieval for all the paths) and T_1m, as well as the difference between T_8m and T_12m, was calculated. In You et al. (2017), the sensitivity of the input temperature on the retrieved mole fractions of CH_4 and NH_3 was investigated using the same software (OPUS_RS). Over a 45-degree range (from 278 to

323K), the retrieved mole fraction time series changed by less than 4.2% for CH_4 and by less than 8.9% for NH_3. We assume that the sensitivity of temperature on retrieved mole fractions of alkanes is similar to CH_4, due to the similar absorption mechanisms. The retrieved mole fractions using T_8m (x_original) were corrected as follows:

Bottom path: x_corrected = x_original + x_original × (T_1m – T_8m)/45 × 4.2%

Top path: x_corrected = x_original + x_original × (T_12m – T_8m)/45 × 4.2%

For NH_3, the 4.2% is replaced by 8.9%.

Next, the H_2O mole fraction was used to calculate dry mole fractions. Finally, the same gradient flux calculations were performed (using the original Kc-FTIR) with these new temperature corrected dry mole fractions for CH_4, NH_3 and total alkanes. Results are shown in the Table 1 below. The relative changes in the final fluxes are 8%, 0%, and -25%, for CH_4, NH_3 and total alkanes respectively. While these changes do not affect the main results and conclusions in this paper, they are significant enough that we included them in our flux calculations in the revised manuscript. Note that the numbers in Table 1 below are different from those presented in the revised manuscript, since the latter incorporate other modifications in response to question 3) below.

Table 1: Statistics of gradient fluxes from FTIR with different processes.

	Flux (g m^{-2} d^{-1})	q_25%	median	q_75%	mean
CH$_4$	Original	1.9	3.4	5.5	3.7
	Dry correction	2.1	3.3	5.6	3.9
	T correction + Dry correction	2.1	3.3	5.6	4.0
NH$_3$	Original	0.01	0.04	0.08	0.05
	Dry correction	0.02	0.04	0.08	0.05
	T correction + Dry correction	0.02	0.04	0.08	0.05
Total alkanes	Original	0.25	0.95	1.97	1.33
	Dry correction	0.23	0.66	1.55	1.00
	T correction + Dry correction	0.23	0.67	1.55	1.00

b.   The second question regards the concentration measurement used to calculate flux in Eq. 1. Following the classic WPL flux corrections for flux-gradient formulae (Webb, et al. 1980. Quart. J. R. Meteorol. Soc. 106, 85–100), should the concentrations be the mole fraction with respect to dry air (mixing ratio)? This should be clarified.

Response: We appreciate the reviewer pointing out this. Yes, the concentration used for flux calculations should properly be the mole fraction with respect to dry air. To investigate how much of a difference this makes to the final gradient fluxes, we recalculated the fluxes using dry mole fractions. The temperature and relative humidity at 1m, 8m and 18m were used to calculate H_2O mole fractions at these heights, respectively. The calculated H_2O mole fraction at 1m was used to calculate dry mole faction of gases for the bottom path. The average of the calculated H_2O mole fractions at 8m and 18m was used to calculate dry mole fraction of gases for the top path (with an average height of 12m). The calculated dry mole fraction of CH_4 for the bottom path was calibrated with the CRDS CH_4 dry mole fraction at 4m, with the exactly same process as illustrated in Figure S1. After calculating the temperature corrections discussed in point 1 (a)

2

above, the last steps were calculating dry mole fractions and new gradient fluxes, as described in point 1 (a) above.

2) The exact procedure for calculating the FTIR fluxes is unclear. In one section the authors indicate the critical tracer diffusivity (Kc) for the FTIR calculations was extrapolated from Kc measured from point concentrations (Eq. 2), and at another point they state that Kc is determined from the measured eddy diffusivity Km (Line 314). Looking over this paper, the companion paper, and the supplemental material, I am uncertain as to what was done. The methodology needs to be better explained.

Response: We thank both reviewers for pointing out that more text was needed in this manuscript to make it stand on its own. We have added substantial material to Section 2 on the measurement details and calculation methodology.

3) I am concerned about how tracer diffusivity (Kc) is calculated in Eq (2). The calculation assumes a linear change in Kc with height, but the general view is that diffusivities (heat, momentum, moisture) are non-linear except in neutral stratification. This may have an impact on the calculated fluxes. Consider the standard definition of Km:
$Km = k_v * ustar * z / PHI\_m$,
where PHI_m is the non-dimensional wind shear. A commonly used PHI_m relationship is given by Hogstrom (1996) for unstable conditions:
$PHI\_m = (1 – 19*z/L)\ \hat{}\ -0.25$
If we redo the calculation outlined in the manuscript Eq. (2) to determine Km for the FTIR gradient ($z = 1, 12$ m) using the Km calculated from the point measurements ($z = 8, 32$ m), with the above expressions and assuming $L = - 20$ m, then $Km\_FTIR/Km = 0.25$. This is 25% lower than the 0.325 value the authors calculated assuming a linear relationship. This implies the fluxes calculated by the authors may overestimate the fluxes in unstable conditions. While this example is for the case of Km, one would expect a similar non-linear relationship for Kc.

Response: We thank the reviewer for pointing this out. We have recalculated the fluxes using a stability-dependent ratio of Km_FTIR/Km. Details are provided in the revised manuscript. The new mole fraction gradients are the results after temperature effect and dry mole fraction calculations, as discussed in responses for the first two comments above. The new gradient fluxes, incorporating the temperature and density effects discussed under question 1) as well as the new eddy diffusivity scaling factors, are less than the original fluxes, by 8%, 20%, and 37% for CH_4, NH_3 and total alkanes respectively.

4) a. How much are the flux-gradient (FG) measurements constrained to match the eddy covariance (EC) measurements? It strikes me that calculating the tracer diffusivity (Kc) from the concentration gradient and the EC flux, and then using that Kc in the FG calculation will act to force the FG and EC fluxes to be equivalent. Yet in several places (lines 180-210) the authors discuss how the FG and EC fluxes are different. How do we reconcile those two things?

Response: Yes, Kc for 8m and 32m was indeed derived from combining the CH_4 EC flux and CH_4 gas vertical gradients as measured on the EC tower, as described in detail in You et al. (2020). The difference between that paper and this manuscript is that here the gradient fluxes

3

were from the FTIR top and bottom path as opposed to from the tower measurements. Differences and uncertainties arise from the vertical profile of Kc as discussed under question 3 above), as well as from the vertical profile of the CH_4 mole fraction, investigated in detail in the Supplement.

b. As mentioned before, it is unclear how the FTIR fluxes were calculated in this study. Based on the companion paper, I suspect the turbulent Schmidt number (Sc) was used to estimate Kc from the eddy diffusivity Km (in the companion paper the authors give an interesting evaluation of Sc and conclude that over a broad stability range Sc = 0.923). A conclusion of this manuscript is that the FG fluxes from the pond are 40% lower than the EC fluxes (Line 192). This difference between FG and EC could be erased with a smaller Sc (for which there is good evidence in the literature). In looking at the CH4 fluxes from the three different measurement techniques (Table 2), could the average from all three be statistically identical if Sc = 0.6 is used in the FG calculations?

Response: Using Sc = 0.6, the mean gradient flux from the tower (8m, 32m) would be 7.4 $gm^{-2}d^{-1}$, statistically not different from the mean EC flux. Assuming Sc = 0.6 and the original Kc vertical scales, the mean gradient flux from FTIR top-bottom paths would be 4.8 $gm^{-2}d^{-1}$, which is also statistically equivalent to the mean EC flux.
However, based on our literature search on atmospheric Schmidt numbers, we felt that there is no strong consensus on their value. Flesch (2002) presented Sc results that covered a broad range from 0.17 to 1.34. Gualtieri et al.(2017) showed Sc values from previous experimental and numerical simulations from 0.1 to 1.3. Based on our own tower flux gradient measurements, described in You et al (2020), we found that Sc varied from 0.04 to 3.26 as a function of stability. In order to make the tower EC and gradient fluxes mutually consistent, the calculated Sc=0.923 (neutral) needs to be used. Since these two measurements were collocated on the same tower, it is reasonable to assume that they should result in the same flux. The comparison to the FTIR gradient fluxes is not as direct due to differing measurement geometries and slight lateral displacement, which may explain some of the differences in the calculated fluxes.

c. The authors discuss the difference in fluxes from the FG and the EC techniques in terms of their different measurement footprints. I am not convinced the difference is large. The authors state that the mole fraction footprint (FG) is larger than the flux (EC) footprint (Line 206). It is true that a concentration footprint is much larger than the corresponding flux footprint, but an FG footprint is given by a difference in two concentration footprints (two heights), which is not so different from the flux footprint (if the two FG heights are not too far apart). In other words, a distant source contributes almost exactly the same concentration at both the top and the bottom measurement heights, so the footprint difference for distant sources is zero. I think the difference between the FG and EC measurements may have another explanation.

Response: We completely agree with the reviewer that for locations with very large homogeneous fetches, EC footprints and gradient footprints with equivalent geometric mean heights are indeed equivalent. In our case, however, the median footprint in northern sectors was under most stability conditions just slightly smaller than the pond, which means that the upper gradient level was more likely to see non-pond influences. Another potential reason for differences is that as seen in Fig. 1, the FTIR path was offset by an average of about 100m to the

4

east relative to the EC tower, and integrated over a path with some horizontal extent (200m). If the pond had less homogeneous in terms of fugitive emissions than generally assumed, there may be a difference in fluxes even over such a small distance.

d) The authors compare the fluxes calculated using their FG formula with those using the slant-path FG formula from Flesch et al. (2016), and found the slant-path calculations give fluxes that are 27 to 56% lower. This result is difficult to understand, given that both calculations start with the same underlying FG calculation approach and use the same concentration gradients. The difference could be due to the assumed Sc, or how the path integration of the FTIR concentration and Kc is handled. There is a difference in Sc between the two calculations. But because the Sc used in the slant-path formula (0.64) is smaller than used in this study (0.923), the slant path flux magnitudes should be higher, not lower. I suspect the difference is related to the diffusivity calculation discussed in comment 3 above. The authors should explain how these two different FG formula can lead to such different results. This is important for confidence in their FG methodology, as the slant-path formula is a more rigorous expression of the FG relationship for path-integrated measurements than their working formula.

Response: We thank the reviewer for this thoughtful question. Yes, the slant-path and our calculations both start with the same gradient flux equation containing Kc = Km/Sc. The two calculations become different when calculating Km. In this study, Km was calculated from the measured momentum flux and measured wind speed vertical gradient $\Delta u/\Delta z$ between 8m and 32m. This detail has now been inserted into the manuscript. In Flesch et al. (2016), Δu was calculated in terms of the stability corrected log-wind profile in their Eq (5) and (6), as explained in Section 3.6. There was no other difference in the two approaches. We stated in the Supplement, Section 5, that "In this study, calculated S_c is allowed to vary with dynamic stability (You et al. (2020) Fig. 3), while in Flesch et al. (2016) S_c was a constant 0.64." To evaluate this, in the current version of the manuscript we used equation (9) from Flesch et al. (2016) in comparison with our gradient approach using a variable Sc in equation (9). So in the two approaches presented in this study, the exactly same time series of Sc were used.
In addition, this Table S2 was also revised. The flux calculation was the same as the original fluxes. The difference is the input mole fraction gradient changed after correction temperature and dry mole fractions. The recalculated results show reasonable agreement between the slant-path and our gradient fluxes (differences are within 30% in Section 3.6).

Technical Corrections
Line 75: it is unclear what is meant by "turbulent fluxes" in this context. Gas fluxes?

Response: We meant sensible heat fluxes and momentum fluxes. "Turbulent fluxes" are now changed to "sensible heat fluxes and momentum fluxes".

Line 85: "Other experimental details of the project can be found in You et al. (2020)". This is one of several places in the manuscript where critical pieces of information are missing and should be included: e.g., a figure showing the equipment locations with respect to the tailings pond. I noted that Lines 128, 150, and 160 refer the reader to critical details in You et al. (2020). I would like to see some of that other-source material moved into this manuscript.

Response: We appreciate this comment. The revised manuscript includes substantially more details on measurements and calculation methods in order for it to be able to stand on its own. Section 2.1, the site and measurement setup, is included this time. In line 80, we have included details of CRDS measurements at different levels on the tower and EC flux measurements. In the Method section, a new subsection is included to describe the details of calculating Kc. In the section on the method of IDMs, more details were also included.

Line 117. "For these trace gases at this site, the detection limits of this open path system were insufficient . . .". This is very interesting.

Response: We have revised this to "Given the mixture of interfering gas signatures at this site, the detection limits of this open path system were insufficient …"

Line 122. Does the flux calculation really fit the usual description of a modified bowen ratio (MBR) method? It's difficult to know because of uncertainty as to how the fluxes are calculated. Usually an MBR measurement means the unknown flux of the gas of interest is related to the known flux of another tracer gas, plus the gradient of that tracer gas, and the gradient of the gas of interest . No theoretical flux gradient relationships are needed. In this study, it is likely that the tracer diffusivity Kc is estimated from a stability corrected Km measured with a sonic anemometer, I would say the technique is better described as an aerodynamic flux-gradient approach.

Response: We have inserted more details on how the Kc and gradient fluxes were calculated. By using the EC flux of CH_4 at 18m, and CH_4 gradient measurements on the tower between 8m and 32m, we calculated Kc for CH_4. Since the directly calculated Kc time series had many gaps, we took the approach of relating Kc to the more continuously available Km, in order to use the resulting Sc(t) to establish a continuous Kc' time series through Kc' = Km/Sc. This Kc' was then applied to the NH_3 and total alkanes gradients. Therefore, our method is closer to MBR than to an aerodynamic flux-gradient approach, although it is true that it is not MBR in the strictest sense. We have replaced all references to the MBR with a more generic "gradient flux method" or similar phrasing.

Line 160: ". . . the warm pond surface . . . resulting in continuing transport of pollutants . . . without significant diurnal variation." When the pond is warm relative to the air, does this mean there are no diurnal changes in atmospheric stability over the pond? I doubt it. This statement also implies that aerodynamic resistance is the limiting factor controlling pond emissions.

Response: Half-hour periods surface turbulence statistics in this study show that the surface layer was unstable (z/L < - 0.0625) 98% of the time when the wind was from the pond. In addition, our measurements in this study only show results during that 5-week period in the summer. Emissions in other seasons remain an unresolved question.

Line 314: "In our modified Bowen ratio approach, Kc is derived from a measured and stability corrected Km . . .". This sentence highlights the confusing description of the methods used in this paper: I do not think Km has been defined to this point in this manuscript; and Eq. (2) suggests that Kc for the FTIR is calculated from Kc taken from point measurements (and not from Km).

Response: We thank the reviewer for pointing this out. As what mentioned in the previous response, we have inserted more details on the methods of calculation fluxes in Section 2.3. Km is now explained. Yes, Kc for the FTIR measurement is calculated from Kc for CH_4 from the gradient measurements on the tower.

References:

You, Y., Staebler, R. M., Moussa, S. G., Beck, J., and Mittermeier, R. L.: Methane emissions from an oil sands tailings pond: A quantitative comparison of fluxes derived by different methods, Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2020-116, in review, 2020.

You, Y., Staebler, R. M., Moussa, S. G., Su, Y., Munoz, T., Stroud, C., Zhang, J., and Moran, M. D.: Long-path measurements of pollutants and micrometeorology over Highway 401 in Toronto, Atmos. Chem. Phys., 17, 14119–14143, https://doi.org/10.5194/acp-17-14119-2017, 2017.

Flesch, T. K., Prueger, J. H., and Hatfield, J. L.: Turbulent Schmidt number from a tracer experiment, Agric. For. Meterol., 111, 299-307, https://doi.org/10.1016/S0168-1923(02)00025-4, 2002.

Gualtieri, C., Angeloudis, A., Bombardelli, F., Jha, S., and Stoesser, T.: On the Values for the Turbulent Schmidt Number in Environmental Flows, Fluids, 2, http://doi.org/10.3390/fluids2020017, 2017.

Response to Referee #2, "Quantifying fugitive gas emissions from an oil sands tailings pond with open-path FTIR measurements"

We thank the referee for the comments and questions. In response, we have added substantial material in order for the manuscript to stand on its own. Below, we address each specific comment in turn. Questions and suggestions are in black, and our responses are in blue.

For this reason, I recommend that the authors undertake a complete rewrite, with the aim of producing a stand-alone, coherent paper.

Response: We thank the reviewer for the suggestion. We have added substantial material to sections 2.1, 2.2, and 2.3, and have moved Figure S1 in the supplement to the main text, to ensure that this paper can stand on its own in a coherent manner. We have carefully considered all the comments and implemented many of the changes.

The open-path FTIR is subject to density effects due to vertical temperature and humidity gradients. Because they are stronger for gases of lower concentration, ratio-ing the uncorrected molar concentration gradients will not eliminate these effects. I am not sure that I trust their flux values without correcting for these effects.

Response: The temperature measured at 8m was used in retrieving mole fractions for the three paths. The temperature difference shown in You et al. (2020), Figure 4c, is the difference between the pond liquid surface and the temperature measured at 8m, which was usually bigger than the difference between the temperature at 8m and the actual mean temperature for each path. To address this question, we have compared the temperature at 8m to temperature at 1m, and temperature at 18m to temperature at 8m. The statistics are shown here:
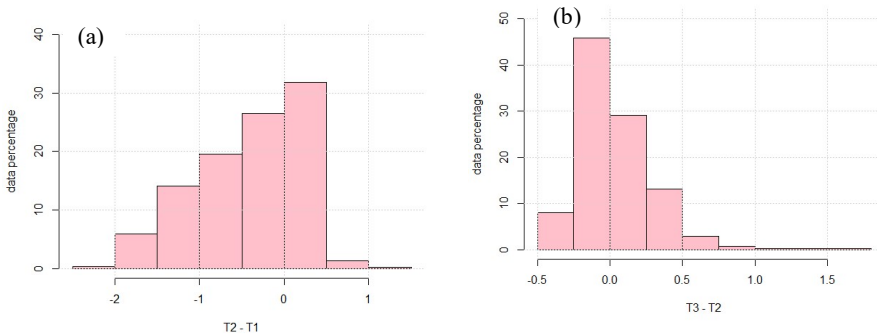

Figure: Histogram of (a) $T\_8m - T\_1m$ (K) and (b) $T\_18m - T\_8m$ (K) over the entire study period.

When the wind was from the pond, $(T\_8m - T\_1m)$ was mainly between -1.5 and 0.5 K, and $(T\_18m - T\_8m)$ was mainly between -0.25 and 0.25 K.

8

To improve on the method we employed in our original manuscript, we can use T_1m for the bottom path, and an interpolation of T_8m and T_18m at 12m for the top path, to calculate mole fractions. First, the difference between the T_8m (which was used in previous retrieval for all the paths) and T_1m, as well as the difference between T_8m and T_12m, was calculated. In You et al. (2017), the sensitivity of the input temperature on the retrieved mole fractions of CH_4 and NH_3 was investigated using the same software (OPUS_RS). Over a 45-degree range (from 278 to 323K), the retrieved mole fraction time series changed by less than 4.2% for CH_4 and by less than 8.9% for NH_3. We assume that the sensitivity of temperature on retrieved mole fractions of alkanes is similar to CH_4, due to the similar absorption mechanisms. The retrieved mole fractions using T_8m (x_original) were corrected as follows:

Bottom path: x_corrected = x_original + x_original × (T_1m – T_8m)/45 × 4.2%

Top path: x_corrected = x_original + x_original × (T_12m – T_8m)/45 × 4.2%

For NH_3, the 4.2% is replaced by 8.9%.

Next, the H_2O mole fraction was used to calculate dry mole fractions. The temperature and relative humidity at 1m, 8m and 18m were used to calculate H_2O mole fractions at these heights, respectively. The calculated H_2O mole fraction at 1m was used to calculate dry mole faction of gases for the bottom path. The average of the calculated H_2O mole fractions at 8m and 18m was used to calculate dry mole fraction of gases for the top path (with an average height of 12m). The calculated dry mole fraction of CH_4 for the bottom path was calibrated with the CRDS CH_4 dry mole fraction at 4m, with the exactly same process as illustrated in Figure S1. The calculated mole fractions for top and bottom paths were applied to temperature correction mole fractions to get dry mole fractions. The calculated dry mole fraction of CH_4 for the bottom path was calibrated with the CRDS CH_4 dry mole fraction at 4m, with the exactly same process as illustrated in Figure S1. Finally, the same gradient flux calculations were performed (using the original Kc-FTIR) with these new temperature corrected dry mole fractions for CH_4, NH_3 and total alkanes. Results are shown in the Table 1 below. The relative changes in the final fluxes are 8%, 0%, and -25%, for CH_4, NH_3 and total alkanes respectively. While these changes do not affect the main results and conclusions in this paper, they are significant enough that we included them in our flux calculations in the revised manuscript. Note that the numbers in Table 1 below are different from those presented in the revised manuscript, since the latter incorporate other modifications in response to question 3) of Referee#1.

Table 1: Statistics of gradient fluxes from FTIR with different processes.

	Flux (g m^{-2} d^{-1})	q_25%	median	q_75%	mean
CH4	original	1.9	3.4	5.5	3.7
	Dry correction	2.1	3.3	5.6	3.9
	T correction + Dry correction	2.1	3.3	5.6	4.0
NH3	original	0.01	0.04	0.08	0.05
	Dry correction	0.02	0.04	0.08	0.05
	T correction + Dry correction	0.02	0.04	0.08	0.05
Total alkanes	original	0.25	0.95	1.97	1.33
	Dry correction	0.23	0.66	1.55	1.00
	T correction + Dry correction	0.23	0.67	1.55	1.00

You seem to rely on eddy-covariance methane flux and concurrent measurement of methane concentration gradient to obtain fluxes of other trace gases from the modified Bowen ratio method. How did you get the gradient CH4 flux then? The gradient CH4 flux was biased low in comparison with the eddy-covariance flux. Were other fluxes similarly biased (due to a limited fetch). Can you estimate the "true" emission fluxes of the tailings pond via footprint modeling?

Response: Although no single method exists that can provide a "true" emission flux, eddy covariance is considered the most direct measure of turbulent fluxes between the atmosphere and an underlying surface, since it requires no parameterizations of exchange coefficients / eddy diffusivities, transport modeling or other empirical relationships. Regarding footprint modeling, the Inverse Dispersion Model applied is essentially a footprint model, in that it starts with a defined surface source area and then calculates the emission rate from this source based on a parameterization of the transport mechanisms and the resulting concentration increase observed downwind.

The section on methanol CH3OH should be enhanced. What was the average flux? Did the flux vary with environmental conditions?

Response: we did not discuss CH_3OH much because its mole fraction showed no increase when the wind was from the pond compared to other directions, as shown in Figure S16 (was Figure S17). We attempted to calculate gradient flux of CH_3OH in the same way as for the other pollutants, and the flux was on the order of 1 mg m^{-2}day^{-1}, but with an uncertainty that made it not statistically different from zero.

The section on comparison with published fluxes is a bit superficial. The reader is interested in knowing if your emission numbers are representative of a typical tailings pond. Also a solid comparison will require footprint correction to your gradient fluxes.

Response: Unfortunately, there is very little published research on quantifying emissions from an oil sands tailings pond. For instance, this study is the first to our knowledge on NH_3 emissions. In addition, there is no such thing as a typical tailings pond, in that they serve a large range of purposes, with different chemical and physical characteristics. Tailings ponds also change over the time; previous research has shown that as ponds age, methane emission can start increasing at some point due to the change of microbial activities in the tailings pond (cf. Small et al., 2015). Regarding the footprint, as long as the footprint of the measurement falls within the boundaries of the pond, no correction is required (see Figure 1 (was Figure S1)).

References:

You, Y., Staebler, R. M., Moussa, S. G., Su, Y., Munoz, T., Stroud, C., Zhang, J., and Moran, M. D.: Long-path measurements of pollutants and micrometeorology over Highway 401 in Toronto, Atmos. Chem. Phys., 17, 14119-14143, https://doi.org/10.5194/acp-17-14119-2017, 2017.

Small, C. C., Cho, S., Hashisho, Z., and Ulrich, A. C.: Emissions from oil sands tailings ponds: Review of tailings pond parameters and emission estimates, Journal of Petroleum Science and Engineering, 127, 490-501, https://doi.org/10.1016/j.petrol.2014.11.020, 2015.

385

Quantifying fugitive gas emissions from an oil sands tailings pond with open-path FTIR measurements

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Abstract. Fugitive emissions from tailings ponds contribute significantly to facility emissions in the Alberta Oil Sands, but details on chemical emission profiles and the temporal and spatial variability of emissions to the atmosphere are sparse, since flux measurement techniques applied for compliance monitoring have their limitations. In this study, open-path Fourier transform infrared spectroscopy was evaluated as a potential alternative method for quantifying spatially representative fluxes for various pollutants (methane, ammonia, and alkanes) from a particular pond, using vertical flux gradient and inverse dispersion methods. Gradient fluxes of methane averaged 3.4 g m^{-2}d^{-1} but were 44% lower than nearby eddy covariance measurements, while inverse dispersion fluxes agreed to within 11%. Significant NH$_3$ emission fluxes were observed (0.04 g m^{-2}d^{-1} (34 tonnes y^{-1})), and total alkane fluxes were estimated to be 0.84 g m^{-2}d^{-1} (705 tonnes y^{-1}), representing 8% of the facility emissions.

1 Introduction

Tailings from the oil sands industrial processes in Alberta's Athabasca Oil Sands consist of a mixture of water, sand, non-recovered bitumen, and additives from the bitumen extraction processes (Small et al., 2015). These tailings are deposited into large engineered tailings ponds on site. Separation of processed water from remaining tailings occurs continuously in the tailings pond, and the processed water is recycled (Canada's Oil sands. Tailings Ponds: https://www.canadasoilsands.ca/en/explore-topics/tailings-ponds). The total liquid surface area covered by tailings ponds in the Athabasca Oil Sands was 103 km^2 in 2016 and continues to grow (Alberta Environment and Parks, 2016). Emissions to the atmosphere from tailings ponds include methane (CH$_4$), carbon dioxide (CO$_2$), reduced sulfur compounds, volatile organic compounds (VOCs), and polycyclic aromatic hydrocarbons (PAHs) (Siddique et al., 2007; Simpson et al., 2010; Yeh et al., 2010; Siddique et al., 2011; Siddique et al., 2012; Galarneau et al., 2014; Small et al., 2015; Bari and Kindzierski, 2018; Zhang et al., 2019). Emissions from tailings ponds vary with pond conditions, such as pond age and solvents additives in the ponds, and can contribute significantly to total facility emissions (Small et al., 2015).

Very few studies focusing on emissions of air pollutants from tailings ponds have been published (Galarneau et al., 2014; Small et al., 2015; Zhang et al., 2019). Compounds of particular interest include alkanes and ammonia (NH$_3$). Alkanes are part of the solvents used in the extraction process (Small et al., 2015), and can dominate VOCs emissions from oil sands facilities (Li et al., 2017). Previously reported VOCs emissions by facilities had large uncertainties,

12

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430 especially from fugitive sources, due to limitations of the methods used to estimate emissions for compliance monitoring purposes (Li et al., 2017). VOCs in the atmosphere are important because of their effects on ambient ozone and secondary aerosol formation (Field et al., 2015; Kroll and Seinfeld, 2008). Emissions of NH_3 from tailings ponds to the atmosphere have not been published, although NH_3 has been observed in the oil sands region (Bytnerowicz, et al., 2012; Whaley et al., 2018). NH_3 emissions have important environmental implications, such as forming

435 atmospheric aerosols with sulfuric acid (Kürten, et al., 2016) and affecting nitrogen deposition in the ecosystem (Makar, et al., 2018). This information is important for model simulations of critical loads of acidifying deposition in the ecosystem (Makar, et al., 2018). This field measurement project provided a great opportunity to continuously measure and to quantify tailings pond emissions over more than a month, especially for NH_3 and total alkanes.

Open-path Fourier transform infrared (OP-FTIR) spectroscopy has been considered a good candidate for an alternative

440 method to monitor fugitive emissions from industrial or hazardous waste area sources, since the method is non-intrusive, integrates over long path-lengths, and has the ability to quantify several different gases of interest simultaneously and continuously (Marshall et al., 1994), without sample line issues . It has previously been used to quantify mole fractions of various air pollutants from different sources such as forest fires (Griffith et al., 1991; Yokelson et al., 1996; Yokelson et al., 1997; Goode et al., 1999; Yokelson, 1999; Yokelson et al., 2007; Burling et

445 al., 2010; Johnson et al., 2010; Akagi et al., 2013; Yokelson et al., 2013; Akagi et al., 2014; Paton-Walsh et al., 2014; Smith et al., 2014), volcanoes (Horrocks et al., 1999; Oppenheimer and Kyle, 2008), industrial sites (Wu et al., 1995), harbours (Wiacek et al., 2018), and road vehicles (Bradley et al., 2000; Grutter et al., 2003; You et al., 2017). OP-FTIR measurements with vertically separated paths have previously been conducted to derive emission rate of air pollutants. Schäfer et al. (2012) deployed two OP-FTIR spectrometers with parallel paths 2.2 meter vertically apart at

450 a grassland at Fuhrberg Germany, to measure nitrous oxide (N_2O) emissions with a flux-gradient method, and showed the calculated flux is comparable to the chamber measurements at the same grassland. Flesch et al. (2016) deployed OP-FTIR measurement with one spectrometer and two paths vertically separated by about 1 m on average ("slant path" configuration) at a cattle field in Alberta, Canada. They derived emission rates of N_2O and NH_3 by flux-gradient and inverse-dispersion methods, demonstrating the capability of OP-FTIR systems to measure emission rates of N_2O

455 and NH_3. Following the flux-gradient method in Flesch et al. (2016), Bai et al. (2018) measured the flux of N_2O, NH_3, CH_4, and CO_2 from a vegetable farm in Australia by an OP-FTIR system with two paths vertically separated by 0.5 m on average. At the same vegetable farm, Bai et al. (2019) measured emission rates of N_2O by flux chambers and OP-FTIR "slant path" configuration with flux-gradient methods, and showed a large variation of the ratio of N_2O fluxes with these two measurements. Inverse dispersion models have also been applied to OP-FTIR measurements to quantify

460 emission rates in previous studies (Flesch et al., 2004; Flesch et al., 2005; Bai et al., 2014; Hu et al., 2016; Shonkwiler and Ham, 2018).

Longer continuous coverage with a greater height difference between paths is one distinguishing feature of this study compared to previous research. The motivation of this work is to quantify emission rates of pollutants from one specific tailings pond by combining OP-FTIR measurements with micrometeorological methods. Emissions of CH_4,

465 NH_3, and total alkanes as well as a comparison of gradient and inverse dispersion methods are presented in this study.

13

2 Open-path FTIR field measurements and methods for deriving fluxes

2.1 Site and measurement set up

The main site of this study was on the south shore of Suncor Pond 2/3 (Fig. 1; 56°59'0.90"N, 111°30'30.30"W, 305m ASL). Sensible heat and momentum fluxes were measured on a mobile tower with sonic anemometers (model CSAT-3, Campbell Scientific, USA) at 8m, 18m, and 32m above ground. Vertical gradients of gaseous pollutant mole fractions were measured by drawing air from 8m, 18m, and 32m on the tower to instrumentation housed in a trailer on the ground. A fourth sample inlet at 4m was on the roof of the main trailer beside the mobile tower. CH_4 and H_2O mole fractions at these 4 levels were measured sequentially by cavity ring-down spectroscopy (CRDS) (model G2204, Picarro, USA). CH_4 mole fractions at 4m were used to calibrate the mole fraction from OP-FTIR retrievals. At 18m, CH_4 mole fractions were also measured by another CRDS (model G2311-f, Picarro, USA) at 10Hz, to be combined with sonic anemometer measurements to calculate the eddy covariance (EC) flux. Meteorological parameters including temperature and relative humidity (RH) were measured at the same three levels on the tower, and 1m above ground. A propeller anemometer (Model 05103-10, Campbell Scientific, USA) on the roof of the main trailer at 4m above ground provided an additional measurement of wind speed and direction. Measurements were conducted from July 28 to September 5, 2017. The FTIR spectrometer was located 10m to the east of the flux tower and the paths were along the south shore of the pond. This manuscript focuses on derived fluxes from the measurement of OP-FTIR. Other experimental details of the project can be found in You et al. (2020).

2.2 Open-path Fourier transform infrared spectrometer (OP-FTIR) system

The FTIR measurements were taken with a commercial Open Path FTIR Spectrometer (Open Path Air Monitoring System (OPS), Bruker, Germany), which was setup at 1.7m above the ground in a trailer. The infrared source is an air-cooled Globar. The emitted radiation is directed through the interferometer where it is modulated, travels along the measurement path (200m horizontal distance) to a retroreflector array that reflects the radiation, travels back to the spectrometer, and enters a Stirling-cooled mercury cadmium telluride (MCT) detector (monostatic configuration). Three retroreflectors were employed in this study: one near ground level (1m) on a tripod, and two at higher elevations on basket lifts, resulting in heights of reflectors of approximately 1m, 11m and 23m above ground. Three paths with these three retro-reflectors are referred as bottom, middle and top paths. The bottom retro-reflector was approximately twice the size of the upper two (59 vs. 30 reflector cubes). All retro-reflectors were cleaned with an alcohol solution once during the study, and the bottom mirror were rinsed with de-ionized water three times. Return signal strength decreased by around 65% during the 5-week study due to reflector deterioration, presumably mostly due to impaction by particulate matter. This reflector deterioration also decreased the signal-to-noise by around 67%, based on spectral retrievals for CH_4, but did not affect the mean mole fractions measured.

In this study, spectra were measured at a resolution of 0.5 cm^{-1} with 250 scans co-added to increase signal-to-noise ratio, resulting in roughly a one-minute temporal resolution. Stray light spectra were recorded regularly by pointing the spectrometer away from the retroreflectors. This stray light spectrum accounts for radiation back to the detector

14

from internal reflections inside the spectrometer, i.e. not from the retroreflector array, and was subtracted from all the measurement spectra before performing further analysis.

Spectral fitting was performed with OPUS_RS (Bruker), which uses a non-linear curve fitting algorithm (You et al., 2017). Spectral windows and interference gases for each gas (Table 1) were determined by optimizing capture of the absorption features while minimizing interferences. To further improve fittings, baselines were optimized through either linear or Gaussian fits under given spectral windows and interfering gases. For CH_4 and CO_2, temperature-dependent reference files were used for fitting and retrieving mole fractions. For other pollutants, reference spectra at 296K were used and retrieved mole fractions were corrected for air density using measured ambient temperature and pressure. For the bottom path, the retrieved mole fractions were corrected for the temperature effect given the difference between the temperatures at 8m (used as the input temperature) and 1m. For the top path, the retrieved mole fractions were corrected for the temperature effect given the difference between the temperature at 8m and the temperature at12m (linearly estimated using the temperatures at 8m and 18m). The corrected mole fractions from the three paths were then converted to dry mole fractions using the RH, temperature and pressure measured at 1m, 8m, and 18m. The dry CH_4 mole fractions from FTIR were then calibrated against CH_4 mole fractions from point cavity ring-down spectrometer (CRDS) measurements (Picarro G2204) at 4 m (Supplemental Material 1.1. Fig. S1). These calibrated CH_4 mole fractions from the FTIR were then used in flux calculations.

We also attempted to retrieve several other pollutants from measured FTIR spectra, but encountered insufficient signal-to-noise ratios, given the existing mole fractions at this location, variability in ambient H_2O vapor, etc. These pollutants include toluene, benzene, xylenes, sulfur dioxide, dimethyl sulfide, carbonyl sulfide, formic acid, and hydrogen cyanide. Given the complex mixture of interfering gas signatures at this site, the detection limits of this open path system were insufficient for flux calculations.

2.3 Method of deriving the gradient flux

2.3.1 Method of deriving the eddy diffusivity (K_c)

Gradient flux estimates are derived from the vertical gradient of mole fractions and the associated turbulence, given by

$$F_c = -K_c \frac{\partial c}{\partial z} \qquad (1)$$

where F_c is the flux for a pollutant gas c, and $\frac{\partial c}{\partial z}$ is the vertical gradient of mole fractions of gas c. K_c is the eddy diffusivity of the gas c, a transfer coefficient characterizing turbulent transport (Monin and Obukhov, 1954) and relating the vertical gradient of gas c to its flux. In this study, K_c is calculated using a variation on the "modified Bowen ratio" method (Meyers et al., 1996; Bolinius et al., 2016), which was described in detail in You et al. (2020). The key steps are repeated here. With the EC flux of CH_4 measured at 18m and mole fraction gradient measured at 8m and 32m by CRDS, K_c was calculated using Eq.(1). The limitation of using this K_c is that when the vertical gradient $\frac{\partial c}{\partial z}$ is close to zero, both F_c and K_c are poorly defined. A much better behaved eddy diffusivity is that for momentum,

15

calculated by combining the wind profile with the momentum flux (Eq.(2)). To construct a continuous time series of K_c for CH_4, we used K_m and the relationship between K_m and K_c in Eq.(3).

$$F_m = -K_m \frac{\partial u}{\partial z} \tag{2}$$

$$S_c = \frac{K_m}{K_c} \tag{3}$$

K_c can thus be calculated from K_m if the Schmidt Number S_c is known. You et al. (2020) showed the details of two approaches to calculate S_c. In this manuscript, we employed the stability corrected variable S_c from the second approach in You et al. (2020).

2.3.2 Gradient flux based on OP-FTIR measurements

K_c is a function of height above the surface (Monin and Obukhov, 1954). The K_c calculated above applies to a height of 18m, and needs to be adjusted to the OP-FTIR path heights. In this study, the vertical profiles of the CH_4 mole fractions varied over time and mostly showed linear vertical profiles when the wind was from the pond (Supplemental Material Section 2.2). In the following calculation, the vertical profiles of CH_4 and other gases are considered linear over the entire project. Therefore, the representative average height of the FTIR top path is taken as the height of the middle point (at 12 m). K_{c_FTIR} for gradient flux calculated from the top and bottom FTIR paths has been adjusted linearly based on the $K_{c\ (8m,32m)}$ calculated from point measurements at 8m and 32m on the tower:

$$\frac{K_{c\_FTIR}}{K_{c(8m,32m)}} = \frac{\frac{K_{m\_FTIR}}{S_c}}{\frac{K_{m(8m,32m)}}{S_c}} = \frac{K_{m\_FTIR}}{K_{m(8m,32m)}} \tag{4}$$

K_m is a function of φ_m, which in turn is a function of stability (z/L), where z is the height above ground and L the Obukhov length (Dyer and Hicks, 1970; Businger et al., 1971):

$$K_m = \frac{ku_*z}{\varphi_m} \tag{5}$$

$$\varphi_m = \begin{cases} 1 + \frac{4.7\,z}{L} & for\ \frac{z}{L} > 0 \quad (stable) \\ 1 & for\ \frac{z}{L} = 0\ (neutral) \\ \left[1 - \frac{15z}{L}\right]^{-1/4} & for\ \frac{z}{L} < 0\ (unstable) \end{cases} \tag{6}$$

Here u_* is the friction velocity. From Equations (4)-(6), $K_{m\_FTIR}/K_{m(8m32m)}$ is calculated for each half-hour period. The FTIR gradient flux is then calculated by multiplying this K_{c_FTIR} by the mole fraction gradient between top and bottom path of the FTIR in Eq (1). The difference between assuming linear and logarithmic vertical profiles of the mole fractions is discussed in the Supplemental Material Section 1.2. The logarithmic vertical profile assumption resulted in average flux, which is 19% greater than the average gradient flux calculated with linear vertical profiles.

16

In addition to calculating gradient fluxes by using CH_4 mole fractions gradient between top and bottom paths, gradient fluxes of CH_4 were also calculated by using mole fractions gradient between middle and bottom paths. Results show that the average gradient fluxes with the middle-to-bottom path gradient are 29% less than that with top-to-bottom path gradient (Supplemental Material Section 1.2, Table S1). These results suggest the gradient fluxes in this study may include uncertainties from the vertical profile of Kc. Lastly, the approach developed by Flesch et al. (2016) was applied and compared to the approach shown above. Fluxes were within 25%. K_c for NH_3 and total alkanes are assumed to be the same as K_c for CH_4.

2.3.3 Inverse dispersion fluxes

Inverse dispersion models (IDMs) are a useful method for deriving emission rates estimates based on line-integrated or point mole fraction measurements downwind of a defined source. IDMs require inputs including the mole fraction measurements, the surface turbulence statistics between the measurements and the source, and the background mole fraction (mole fraction upwind of the source) of the pollutant. In this study, we used WindTrax 2.0 (Thunder Beach Scientific, http://www.thunderbeachscientific.com; Flesch et al., 1995; Flesch et al., 2004), which is based on a backward Lagrangian Stochastic (bLS) model. Details on IDM calculations and resulting CH_4 fluxes were presented in You et al. (2020). Key information is repeated here. The emission rate is derived through:

$$Q = \frac{(c - c_b)}{(\frac{C}{Q})_{sim}} \qquad (7)$$

where C is the mole fraction of the pollutant measured at a given location, C_b is the background mole fraction, $(C/Q)_{sim}$ is the simulated ratio (calculated by the bLS model) of the pollutant mole fraction at the site to the emission rate at the specified source. In this study, the inputs of surface turbulence statistics are u_* and L calculated from the ultrasonic anemometer measurements at 8m, as well as ambient temperature and wind direction. All surface turbulence statistics inputs were half-hour averages. Half-hour periods when $u_*<0.15$ ms^{-1} were excluded (Flesch et al., 2004). IDM fluxes of NH_3 and total alkane are shown in this work for the first time for comparison with gradient fluxes. Meteorological inputs for calculating inverse dispersion fluxes of NH_3 and total alkanes are the same as for CH_4 fluxes. CH_4, NH_3, and total alkanes mole fraction inputs were obtained from the bottom path of OP-FTIR.

3 Results and discussion

3.1 Meteorological conditions

The measurement site including the OP-FTIR was at the south shore of the pond (Fig. 1), therefore the north wind (wind direction (WD) $\geq 286°$ or WD $\leq 76°$) was defined as the wind coming from the pond (You et al., 2020). The wind came from the north for about 22% of the entire measurement period (You et al. (2020), Fig. S1). There was no significant diurnal variation in wind direction during the study period. Detailed ambient temperature, water surface temperature, wind speed, and other meteorological parameters can be found in You et al. (2020). As discussed in You

17

et al. (2020), the warm pond surface resulted in continuing convective turbulence at night, resulting in continuing transport of pollutants from the pond into the atmosphere without significant diurnal variation.

Gradient and IDM fluxes for NH_3 and total alkanes are averages for half hour periods when the wind came from the pond. The half-hour fluxes were binned into 16 wind direction sectors, and the area-weighted averages of fluxes from the pond were calculated as described in You et al. (2020).

3.2 Methane

Path-integrated mole fractions and associated gradient fluxes of CH_4 from OP-FTIR are presented here to test if the gradient fluxes derived from the mole fractions with OP-FTIR are comparable to CH_4 fluxes from eddy covariance and IDM methods (You et al. (2020)). The area-weighted flux statistics from different methods are summarized in Table 2. The path-integrated measurement from the FTIR bottom path clearly indicates that the CH_4 mole fraction was elevated when the wind was from the pond direction, while it was steady near 2 ppm when the wind was from other directions (Fig. S2 and S3). In addition, a clear vertical gradient (Fig. S3), with mole fractions along the bottom path on the order of 0.5 ppm to 1ppm higher than mole fractions from the top path, identified the pond as the CH_4 source. The fact that the CH_4 mole fraction increased when the wind was from the pond direction, and decreased with height, clearly points to the pond as the dominant local source.

For comparison, vertical profiles of the CH_4 mole fraction by point measurements on the nearby tower are given in Supplemental Material Section 1.2. A linear vertical extrapolation of the profiles to the point where the mole fraction reaches 2.0 ppm (background levels) indicated a median plume height of 64m (Fig. S4 and Fig. S5).

The gradient flux derived from the OP-FTIR shows that the flux was minimal when the wind was from other directions, except for the sector centered at 270° (Fig. 2), which represented a mix of pond and shoreline influences). The average and interquartile ranges of fluxes in wind direction sectors centered at 315°, 337.5° and 0° are comparable. This gradient flux result is consistent with the eddy covariance fluxes measured on the adjacent flux tower (You et al. 2020), and these results also suggest that the pond is the main source of measured CH_4 fluxes. However, the sector centered at 292.5° shows average flux 22% and 73% greater than sectors centered at 315° and 337.5°. This is different from the EC fluxes which showed closer agreement between the 292.5°, 315°, 337.5° and 0° sectors (You et al., 2020, Fig. 7). The footprint of the eddy covariance fluxes measured on the adjacent flux tower at 18m was calculated by using the Flux Footprint Prediction (FFP) model in Kljun et al. (2015), and results showed the 80% contribution distance was typically within 1km which is closer to the main site than the north edge of pond liquid surface (Fig. 1; You et al. (2020)). The outfall was about 1.4 km from the main site. The discrepancy suggests that the footprint of the gradient method incorporated emissions from the outfall more clearly than the smaller footprint of the eddy covariance method.

FTIR CH_4 gradient fluxes and eddy covariance (EC) fluxes showed a linear correlation, but on average, the gradient fluxes were lower than the EC fluxes by 44% (r^2=0.63) (Fig. S7). In agreement with EC, the gradient flux showed no significant diurnal variations when the wind was from the pond (Fig. S8, with a relative standard deviation of 38%). To investigate the difference between CH_4 gradient fluxes derived from FTIR and EC fluxes, the latter were examined in relation to meteorological conditions, similar to the analysis presented in You et al. (2020). The analysis in You et

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al. (2020) showed no correlation between EC flux and friction velocity (u_*) or wind speed, while a weak correlation between gradient flux and wind speed is observed (You et al. (2020) Fig. S9). As described in Supplemental Material Section 1.2 (Fig. S4, S5, and S6), CH_4 vertical profiles were closer to linear when the wind speed was less than 6 m/s, and were more logarithmic with wind speed greater than 6 m/s. The sector centered at 292.5° was often associated with wind speeds greater than 6 m/s (21% of the time). The approximation of linear vertical profiles may underestimate the CH_4 flux with periods of high winds by 19%. This dependence of the gradient flux on wind speed contribute to the uncertainty in the vertical profile of K_c.

Model calculations by Horst (1999) showed that the estimated footprint of a gradient flux measurement at the geometric mean height of the gradient is similar to the footprint of EC flux at that same height, for homogeneous upwind area sources. However, mole fraction footprints are significantly larger than perturbation (flux) footprints (Schmid, 1994), and some CH_4 sources on the far shore (e.g. the outfall) may have contributed to the upper path CH_4 mole fraction. This decreased the vertical gradient difference and thus the derived flux relative to the eddy covariance flux with its smaller footprint, since the latter is more likely to represent water surface emissions only. As an approximate estimation, the footprint of the path-integrated mole fraction of the top path is about 2.3 km (23m × 100, Flesch et al. (2016)), and this covers the whole pond including the north edge (Fig. 1).

Background mole fractions, upwind of the source under investigation, must be provided for the bLS calculations of CH_4 fluxes. We quantified these using two methods. First, the background mole fraction was determined with the FTIR measurements at the south of the pond, as follows: for most of the days, it was taken as the minimum CH_4 mole fraction from the FTIR bottom path on each day while the wind direction was between 180° and 240°. On Aug 7th and 30th, there was no half-hour period when the wind was from this sector, and the background mole fraction was chosen as the minimum mole fraction for the day. For Aug 1st, there was also no half-hour period for this sector, and the minimum of the day was 2.40 ppm, significantly greater than the minimum mole fraction of other days. Therefore, the background mole fraction of the previous day, 1.92 ppm was used for Aug 1st.

Alberta Environment and Parks (AEP) conducted OP- FTIR measurements (RAM2000 G2; KASSAY FSI, ITT Corp., Mohrsville, PA, USA) at the north side of the pond (Fig. 1), quantifying CH_4 to be used as the second estimate of background mole fractions. For most of the days, the half-hour averaged mole fractions were directly used as the background mole fractions. From Aug 3rd 22:00 to Aug 4th 13:30, Aug 6th 08:00 to 17:00, Aug 23rd 1:30 to 2:00, there were no data from AEP, so background mole fractions for these periods were picked as the interpolation of mole fractions before and after this period. In this approach, the bLS flux results can be negative when the AEP mole fraction is greater than the mole fraction from the measurements at the south shore, possibly due to influences by other emission sources in the surrounding area, gas diffusion under low wind speeds, plume inertia when wind directions changes suddenly, or instrument mismatch differences.

CH_4 IDM fluxes with background determined from the first approach (using measurements at the south of the pond) agreed with IDM fluxes with background determined from the second approach (using measurements at the north of the pond), with a linear regression r^2 of 0.92, and a slope of 0.90; there was a 20% difference between average fluxes from the two approaches (Fig. S10; Table S1). These results confirm that the CH_4 flux estimate from this inverse

dispersion approach is consistent and that the first approach to determining backgrounds is appropriate. In the following results and discussion, IDM fluxes with background mole fractions from the first method are used.

780 IDM and EC flux showed good comparison (slope=0.93, r^2=0.46, You et al., (2020), Fig. 8(b)). The interquartile range of the fluxes from these two methods overlap, and the mean IDM fluxes are 11% smaller than EC flux.

3.3 NH$_3$

The mole fraction of NH$_3$ was elevated when the wind was from the pond, but was mainly below 5 ppb when the wind was from the south (Fig. 3(a)). NH$_3$ gradient fluxes were significant when the wind came from the pond direction (Fig.

785 4(a)).

The time series of mole fraction vertical gradient of NH$_3$ and CH$_4$ were similar (Fig. S3). The NH$_3$ gradient flux and CH$_4$ gradient flux showed good correlation (r^2=0.7, Fig. 5(a)). The diurnal variation in NH$_3$ gradient flux (relative standard deviation =72%) was stronger than for the CH$_4$ gradient flux (relative standard deviation =36%), with greater fluxes from 13:00 to 18:00 MDT (Mountain Daylight savings Time) (Fig. S11 (a)). Previous studies showed tailings

790 pond waters contained elevated NH$_3$ concentrations, which makes them potential sources of NH$_3$ to the atmosphere (Allen, 2008; Risacher et al., 2018). NH$_3$ in the pond is mainly produced through nitrate and/or nitrite reduction during microbial activities (Barton and Fauque, 2009; Collins et al., 2016). In addition, some of these nitrate and/or nitrite reduction microbes may also produce reduced sulfur (Barton and Fauque, 2009). The water sample collected from Pond 2/3 on August 2017 during this study was alkaline (pH = 8.0 ± 0.5), which also supports the emission of NH$_3$.

795 The average flux in the sector centered at 292.5° was 33% and 57% more than the average flux in the sectors centered at 315° and 337.5°, but the median fluxes in these three sectors are within 14%. These suggest the high average flux in 281-304° is skewed by big spikes which are associated with the outfall (with wind directions in 281-304°), but the majority of NH$_3$ fluxes in the 281-304° wind sector correlated well with CH$_4$ fluxes which were less affected by the outfall. Although hydrotreating processes in upgraders remove most of the sulfur and nitrogen from the bitumen

800 residue, a small amount of NH$_3$ might still be carried with the processed water and tailings (Bytnerowicz et al., 2010), and transported with the outfall liquid into the pond. The negative fluxes observed for the 67.5° sector may be due to elevated NH$_3$ plumes originating from the upgrader facility 3 km upwind in this direction, resulting in a negative gradient and thus deposition to the pond under some circumstances.

IDM fluxes of NH$_3$ were calculated the same way as CH$_4$, and show a weak correlation with CH$_4$ IDM fluxes (Fig.

805 5(b)). The NH$_3$ background mole fraction was based on the mean daily minimum, approximately 1ppb (Fig. 3). Vertical profiles of NH$_3$ mole fraction (Fig. S12) with northerly wind also show roughly linear profiles similar to CH$_4$. Profiles of sectors centered at 292.5° and 315° are linear. Therefore, the outfall on average did not significantly contribute to the NH$_3$ profile, i.e. the pond surface was the main source of NH$_3$. NH$_3$ fluxes from the gradient method were significantly less than from the IDM method. This difference is mostly due to the input background NH$_3$ mole

810 fraction. The background NH$_3$ mole fraction was not measured, and could be greater than 1 ppb if there was any source to the north of the pond. Assuming the NH$_3$ gradient flux as a reference, different backgrounds were tested in IDM to match the mean gradient flux. A background of 7 ppb of NH$_3$ was required to close the gap between gradient and IDM fluxes. This seems large but cannot be verified, since there was no ground level measurement of NH$_3$ near the north

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of the pond. This illustrates the advantage of using either eddy covariance or gradient flux measurements, which are based on mole fraction fluctuations or gradients at a single location and are therefore independent of upwind background mole fraction.

3.4 Total alkane

Total alkane derived from FTIR spectra used butane and octane as two surrogates in this study, following the method in EPA OTM10 (Thoma et al., 2010). Results only reflect alkanes which have similar absorption features as butane and octane, and cannot accurately represent other VOCs. Total alkane fluxes from the pond were evident (Fig. 4(b)). A comparison to CH_4 fluxes showed only a weak correlation (r^2=0.3, Fig. S13), unlike the correlation between NH_3 and CH_4 (Fig. 5(a)). This difference can be explained by sources of alkane and CH_4 at this site. Figure 4(b) shows the average flux from the sector centered at 292.5° is 1.9 g m^{-2} d^{-1}, which is 2.1 and 2.3 times of the average fluxes from the sectors centered at 315° and 337.5°. Figure 2 shows that the average fluxes of CH_4 from the sector centered at 292.5° is 1.2 and 1.7 times of the average fluxes from sectors centered at 315° and 337.5°. These results indicate that there was an enhanced contribution (27%) from around 281° to 304° to total alkane flux measured at the site, but not to the observed CH_4 flux. This enhancement of alkane flux is likely due to the outfall, which was at the edge of the pond, 1.9 km from the site at 295°. The liquid mixture flowing into the pond contained naphthenic solvent which include a mixture of alkanes, alkenes, and aromatic hydrocarbons, and since the outfall is at a temperature of approximately 33℃, enhanced evaporation of volatile components can be expected from this area. The outfall also introduces some mechanical mixing in the upper layers of the pond water, which may contribute to elevated emission rates. The diurnal variation of total alkane gradient flux when the wind came from the pond direction was also weak (the standard deviation of average fluxes at each hour is comparable to the interquartile ranges, Fig. S14). The vertical profiles of total alkane mole fraction with northeastern winds were vertically invariant (Fig. S15). With northwestern winds, profiles showed a decrease mole fraction from bottom to middle path and minimal decrease or even increase from middle to the top path. These total alkane vertical profiles with northern wind, which are different from CH_4 or NH_3 profiles, suggesting there were additional sources other than the pond surface to measured total alkane flux, such as the outfall, and industrial activities upwind.

3.5 Methanol (CH_3OH)

Unlike pollutants studied above, the CH_3OH mole fraction did not show significant enhancement when wind was from the pond (Fig. S16), suggesting the pond was not significantly contributing to CH_3OH compared to potential sources surrounding the pond. The lifetime of CH_3OH is around 10 days (Simpson et al., 2011; Shephard et al., 2015), and the main source is vegetation (Millet et al., 2008). The mole fractions observed at the site were consistent with satellite measurements representative of the general oil sand region (Shephard et al., 2015), and with an airborne study of VOCs (Simpson et al., 2010). In addition to emissions from vegetation, CH_3OH observed in the oil sands region could be due to transport from biomass burning (Simpson et al., 2011; Bari and Kindzierski, 2018), and local traffic (Rogers et al., 2006; You et al., 2017).

3.6 Comparison of calculated fluxes to reported emissions and approaches

As a test of the robustness of these results, fluxes of CH_4, NH_3 and total alkane are also calculated from the "slant path" method described by Flesch et al. (2016). Calculation inputs and results are summarized in the Supplemental Material Section 5. Compared to results from our flux gradient approach, CH_4, NH_3, and total alkane fluxes with the "slant path" flux-gradient method were comparable (24%, 25%, and 30% lower, respectively (Table S1)). The difference in fluxes from the two approaches could be due to differences in assumptions regarding the vertical profiles. In our gradient flux approach, we used linear vertical mole fraction profiles of pollutants to calculate the difference of mean heights between the two paths. In Flesch et al. (2016) the gradient flux for pairs of points along the two paths was integrated along the entire path length assuming the flux was uniform horizontally. In that approach, the dependence of K_c on height is incorporated explicitly, assuming a logarithmic wind profile including a stability correction. In our gradient flux approach, K_c is derived from a measured and stability corrected K_m, and therefore did not require a wind profile shape assumption.

To facilitate a transparent comparison of the emission results from this study to reported facility wide emissions of Suncor, we present emission rates based on simple extrapolation of the measured August emissions to the whole year. Other possible seasonal emission profiles have been reported (Small et al., 2015); using these to convert from August emissions to annual average values would for example result in a scale factor of 0.92 (mass transfer model), 0.64 (mass transfer model adjusted for ice cover), or 0.42 (thawing degree-day model) (Cumulative Environmental Management Association, 2011). The seasonally invariant total emission estimate for NH_3 and total alkanes from Pond 2/3 to the air were 34 and 705 tonnes y^{-1} in 2017. However, NH_3 emissions from Pond 2/3 have not been reported in the past, because NH_3 was not being measured as part of compliance flux chamber monitoring. Therefore, the facility wide NH_3 emissions reported to the Government of Canada National Pollutant Release Inventory (NPRI) (0.82 tonnes y^{-1}) in 2017 did not include fugitive emissions from tailings ponds. The solvents entering this tailings pond are naphtha additives with octane, nonane and heptane as the biggest contributors. Li et al. (2017) quantified alkane emissions (including n-alkanes, branched-alkanes, and cycloalkanes) as 36.2 tonnes d^{-1} from the whole facility using airborne measurements in 2013, which is 73.9% of 49 tonnes d^{-1} total VOC emission. Alkanes account for 54% of total VOC emitted from Pond 2/3 in 2017 (Moussa et al., 2019). If we use reported facility wide VOC annual emissions in 2017 (17242 tonnes y^{-1}, NPRI) to estimate facility wide total alkane annual emission, we obtain 17242 × 53% = 9138 tonnes y^{-1}, and total alkane emissions from Pond 2/3 contribute 8% to facility wide emissions for 2017. The fugitive NH_3 emissions from Pond 2/3 in this study were 34 tonnes y^{-1}, a number that is 41 times the process related emission number reported for the facility to NPRI. Negligible volumes of ammonia may be carried over to the pond through the naphtha recovery unit and FTT line, and it is believed that the ammonia is mainly generated from the biogenic activities in the MFT layer of the pond. The majority of H_2S, NH_3 and CH_4 emissions are related to microbiological activities as evidenced in this study.

22

4 Conclusions and Implications

We have shown that OP-FTIR is an effective method to quantify mole fractions and vertical gradients of CH_4, NH_3, and total alkanes continuously and simultaneously for an area source such as a tailings pond. Benefits are the integration of mole fractions over long path lengths, thus providing a spatially representative average, and the avoidance of sample line issues that can be serious problems for sticky gases such as NH_3. Results from the gradient flux method and IDM calculations suggest OP-FTIR is a useful tool for deriving emission rates of CH_4, NH_3 and total alkane from this type of fugitive area source. For the two approaches of determining background mole fractions of CH_4 with the IDM method, i.e., upwind background measurement vs. local background estimation, the area weight-averaged fluxes of CH_4 were within 20%. FTIR CH_4 gradient fluxes and EC fluxes showed a linear correlation, but on average, the gradient fluxes were lower than the EC fluxes by 44%. IDM and EC flux showed good comparison, and the mean IDM fluxes are 11% smaller than EC flux. NH_3 gradient flux and IDM flux showed a difference of more than 50%, which suggests that there may have been sources of NH_3 upwind (north) of the pond that were not captured by assuming that southern and northern background NH_3 were similar, thus illustrating a limitation of the IDM method. CH_4, NH_3, and total alkane fluxes were also calculated using the "slant path" flux-gradient method (Flesch et al. 2016), to compare to the our flux gradient approach, and results from the slant path method were comparable (24%, 25%, and 30% lower, respectively).

The NH_3 emissions results in this study are the first to quantify NH_3 fugitive fluxes from a tailings pond and clearly showed that Pond 2/3 is a significant source of NH_3, most likely through microbial activities in the pond. This suggests that at least some tailings ponds in the oil sands could be significant sources of NH_3, compared to process-related facility emissions. Further measurements of NH_3 emissions from tailings ponds are recommended to elucidate our understanding of the mechanisms behind NH_3 emissions and to improve the total facility emission estimates reported to NPRI.

Total alkane gradient fluxes from OP-FTIR measurements clearly showed that the pond is a significant source of total alkane. Annual alkane emissions extrapolated from these measurements represented 12% of facility emissions. The outfall area contributed significantly (27%) to pond alkane emissions, showing spatial variability of alkane emissions from the pond. Observed CH_3OH mole fractions show that the pond was unlikely a significant source of CH_3OH. This study demonstrated the applicability of OP-FTIR combined with gradient flux or inverse dispersion methods for determining emission fluxes of multiple gases simultaneously, with high temporal resolution and comprehensive spatial coverage.

Data availability.

All data are publicly available at http://data.ec.gc.ca/data/air/monitor/source-emissions-monitoring-oil-sands-region/emissions-from-tailings-ponds-to-the-atmosphere-oil-sands-region/.

Author contributions.

YY and RS wrote the manuscript; SM, LZ, LF and JB contributed data and comments.

Competing interests.

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1245 **Tables**

Table 1 Spectral windows of OP- FTIR spectra for retrieving mole fractions of pollutants in this study.

Pollutant name	Chemical formula	Spectral Window (cm^{-1})	Interference gases	Threshold correlation coefficient[a]	Detection limit[c]	Paths
Methane	CH_4	3006-3021	H_2O	0.95	1.1 ppb	All three
Ammonia	NH_3	957-973	H_2O, CO_2	0.3	1.1 ppb	All three
Methanol	CH_3OH	1020-1040	H_2O, NH_3, O_3, C_2H_5OH, C_6H_6	0.3	1.1 ppb	All three
Butane[b]	n-C_4H_{10}	2804-3001	H_2O, CH_4, CH_3OH, HCHO, n-C_7H_{16}, n-C_6H_{14}, n-C_8H_{18}, $CH_3CH(CH_3)C_3H_7$	0.1	1.1 ppb	All three
Octane[b]	n-C_8H_{18}	2804-3001	H_2O, CH_4, CH_3OH, HCHO, n-C_7H_{16}, n-C_6H_{14}, $CH_3CH(CH_3)C_3H_7$, $C_2H_5CH(CH_3)C_2H_5$	0.1	0.9 ppb	All three
Formaldehyde	HCHO	2730-2800	H_2O, CO_2, CH_4	0.2	2.3 ppb	Bottom only
Carbon dioxide	CO_2	2030-2133	H_2O, CO	0.8	-	Bottom only

[a] Threshold correlation coefficient is a input for OPUS_RS when performing fitting analysis of FTIR spectra. When
1250 the correlation coefficient between measured spectrum and reference spectrum with the defined spectral window is below this threshold, that pollutant is not "identified" and the mole fraction is reported as zero in OPUS_RS (You et al., 2017).

[b] Butane and octane mixing ratio are quantified as two surrogates to quantify a "total alkane" mixing ratio = Butane + Octane (Thoma et al., 2010).

1255 [c] Detection limit is calculated by converting 3σ of the noise of the measurements with a retroreflector distance of 225m by Bruker to 3σ of the noise with 200m in this study.
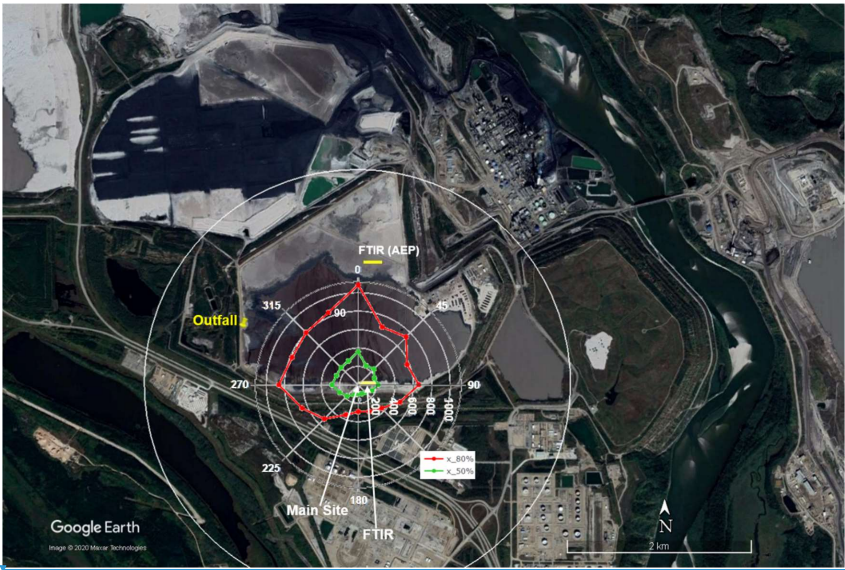
Table 2 Summary of fluxes from OP-FTIR measurements. Results are area weight-averaged fluxes from the pond.

All fluxes in g m^{-2}d^{-1}	Flux method	Q_25%	Median	Q_75%	Mean[a]
CH$_4$	Tower EC	4.2	5.9	7.9	6.1± 0.5
	FTIR gradient	1.8	3.0	4.8	3.4 ± 0.7
	IDM	3.6	5.2	6.6	5.4± 0.4
NH$_3$	gradient	0.02	0.03	0.07	0.04 ± 0.01
	IDM	0.06	0.09	0.15	0.11 ± 0.01
Total alkane	gradient	0.20	0.56	1.28	0.84 ± 0.22
	IDM	0.57	0.94	1.56	1.33 ± 0.10

1260   [a] Errors with the mean fluxes are calculated with a "top-down" approach: the average of standard deviations of fluxes from five periods when the fluxes displayed high stationarity.

Figures

Figure 1 Map of the site: FTIR paths are shown as yellow lines (main FTIR on the south shore, AEP FTIR on the north shore), and the outfall is shown as a yellow pin on the west shore. The colored rose plot shows 50% and 80% contribution distances for eddy covariance fluxes at 18m using the Flux Footprint Prediction (FFP) model (Kljun et al. (2015)). Distances are in meters. The large white circle labels the 2.3 km distance from the main site, equivalent to 100 times the height of the highest point of the top FTIR path. This figure is adapted from You et al., (2020), Figure 1.

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Figure 2 **Gradient flux of CH$_4$ from FTIR binned by wind direction in 22.5-degree bins. Lower and upper bounds of the box plot are 25th and 75th percentile; the line in the box marks the median and the black square labels the mean; the whiskers label the 10th and 90th percentile.**
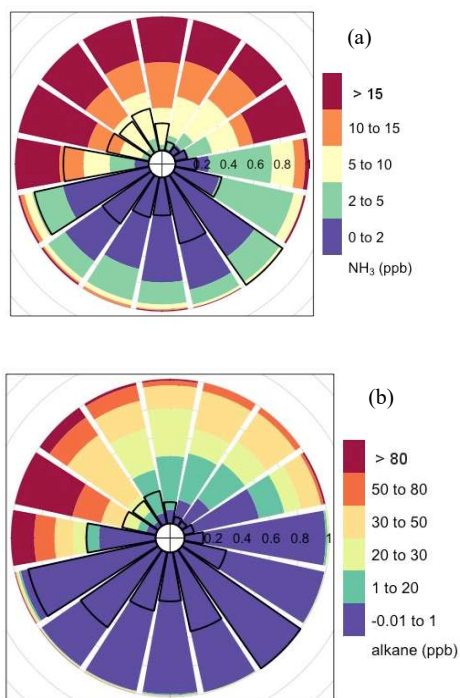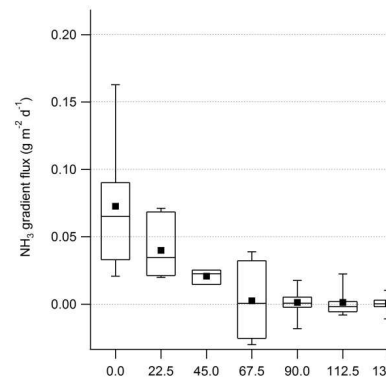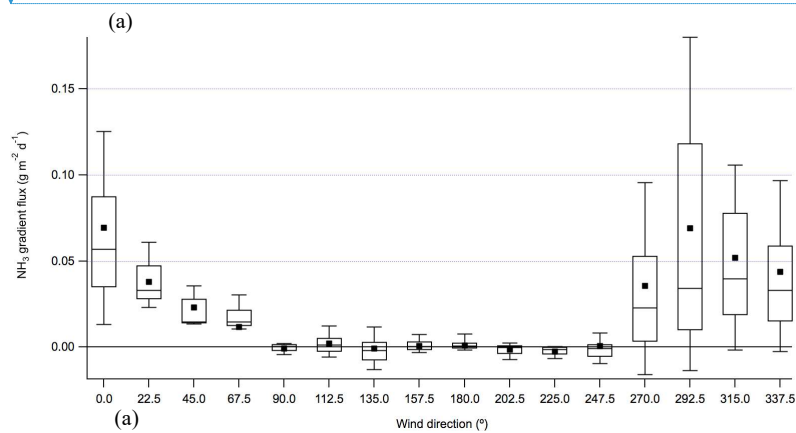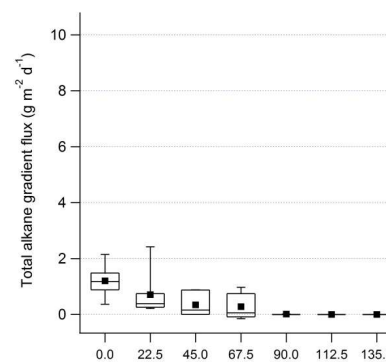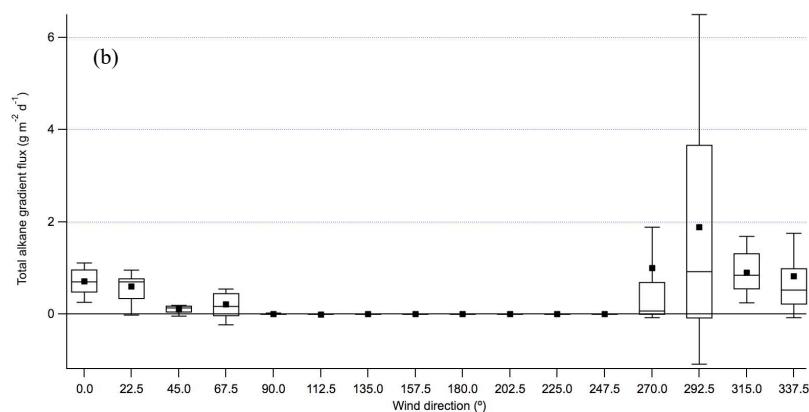
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Figure 3Normalized rose plot of NH$_3$ (a) and total alkane (b) mole fractions from FTIR bottom path. Colors represent mole fraction in ppb. The length of each colored segment presents the time fractions of that mole fraction range in each direction bin. The radius of the black open sectors indicates the frequency of wind in each direction bin; angle represents wind direction, straight up is north, and straight left is west.

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(a)

(a)

(b)

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Figure 4 Gradient flux of NH₃ (a) and total alkane (b) from FTIR top-bottom path binned by wind direction in 22.5-degree bins. Lower and upper bounds of the box plot are 25th and 75th percentile; the line in the box marks the median and the black square labels the mean; the whiskers label the 10th and 90th percentile.
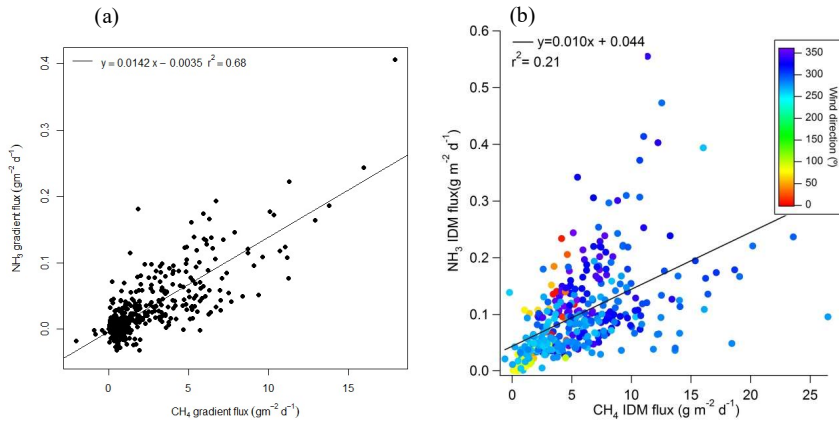
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(a)

NH_3 gradient flux $(gm^{-2}\ d^{-1})$

CH_4 gradient flux $(gm^{-2}\ d^{-1})$

$y = 0.0142\ x - 0.0035\ r^2 = 0.68$

(b)

NH_3 IDM flux$(g\ m^{-2}\ d^{-1})$

CH_4 IDM flux $(g\ m^{-2}\ d^{-1})$

$y=0.010x + 0.044$
$r^2= 0.21$

Wind direction (°)

Figure 5 (a): NH$_3$ gradient flux compared to CH$_4$ gradient flux; (b): NH$_3$ IDM flux compared to CH$_4$ IDM flux

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open-path FTIR on the south shore marked in red, open-path FTIR of AEP on the north shore marked in yellow, and the outfall on the west side. The colored rose plot shows 50% and 80% contribution distances for eddy covariance fluxes at 18m using the Flux Footprint Prediction (FFP) model (Kljun et al. (2015)). The unit of contribution distances is in meters. The