

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:

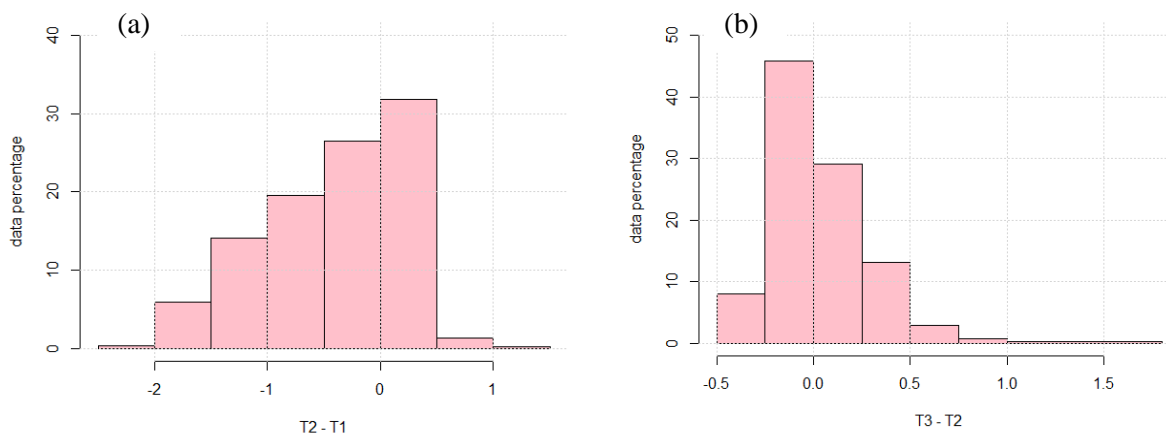


Figure: Histogram of (a) $T_{8m} - T_{1m}$ (K) and (b) $T_{18m} - T_{8m}$ (K) over the entire study period.

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 CH₄ and by less than 8.9% for NH₃. We assume that the sensitivity of temperature on retrieved mole fractions of alkanes is similar to CH₄, due to the similar absorption mechanisms. The retrieved mole fractions using T_{8m} (x_{original}) were corrected as follows:

Bottom path: $x_{corrected} = x_{original} + x_{original} \times (T_{1m} - T_{8m})/45 \times 4.2\%$

Top path: $x_{corrected} = x_{original} + x_{original} \times (T_{12m} - T_{8m})/45 \times 4.2\%$

For NH₃, the 4.2% is replaced by 8.9%.

Next, the H₂O 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 CH₄, NH₃ and total alkanes. Results are shown in the Table 1 below. The relative changes in the final fluxes are 8%, 0%, and -25%, for CH₄, NH₃ 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 H₂O mole fractions at these heights, respectively. The calculated H₂O mole fraction at 1m was used to calculate dry mole fraction of gases for the bottom path. The average of the calculated H₂O 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 CH₄ for the bottom path was calibrated with the CRDS CH₄ 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) 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 (K_c) for the FTIR calculations was extrapolated from K_c measured from point concentrations (Eq. 2), and at another point they state that K_c is determined from the measured eddy diffusivity K_m (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 (K_c) is calculated in Eq (2). The calculation assumes a linear change in K_c 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 K_m:

$$K_m = k_v * u_* * z / \text{PHI}_m,$$

where PHI_m is the non-dimensional wind shear. A commonly used PHI_m relationship is given by Hogstrom (1996) for unstable conditions:

$$\text{PHI}_m = (1 - 19*z/L)^{-0.25}$$

If we redo the calculation outlined in the manuscript Eq. (2) to determine K_m for the FTIR gradient (z = 1, 12 m) using the K_m calculated from the point measurements (z = 8, 32 m), with the above expressions and assuming L = - 20 m, then K_{m,FTIR}/K_m = 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 K_m, one would expect a similar non-linear relationship for K_c.

Response: We thank the reviewer for pointing this out. We have recalculated the fluxes using a stability-dependent ratio of K_{m,FTIR}/K_m. 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 CH₄, NH₃ 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 (K_c) from the concentration gradient and the EC flux, and then using that K_c 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, K_c for 8m and 32m was indeed derived from combining the CH₄ EC flux and CH₄ 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 were from the FTIR top and bottom path as opposed to from the tower measurements. Differences and uncertainties arise from the vertical profile of K_c as discussed under question 3 above), as well as from the vertical profile of the CH₄ 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 K_c from the eddy diffusivity K_m (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 CH_4 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 $7.4 \text{ gm}^{-2}\text{d}^{-1}$, statistically not different from the mean EC flux. Assuming $Sc = 0.6$ and the original K_c vertical scales, the mean gradient flux from FTIR top-bottom paths would be $4.8 \text{ gm}^{-2}\text{d}^{-1}$, 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 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 S_c , or how the path integration of the FTIR concentration and K_c is handled. There is a difference in S_c between the two calculations. But because the S_c 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 $K_c = K_m/S_c$. The two calculations become different when calculating K_m . In this study, K_m 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 S_c in equation (9). So in the two approaches presented in this study, the exactly same time series of S_c 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 K_c . 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 K_c is estimated from a stability corrected K_m 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 K_c 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 K_c for CH_4 . Since the directly calculated K_c time series had many gaps, we took the approach of relating K_c to the more continuously available K_m , in order to use the resulting $Sc(t)$ to establish a continuous K_c' time series through $K_c' = K_m/Sc$. This K_c' 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, K_c is derived from a measured and stability corrected K_m . . .”. This sentence highlights the confusing description of the methods used in this paper: I do not think K_m has been defined to this point in this manuscript; and Eq. (2) suggests that K_c for the FTIR is calculated from K_c taken from point measurements (and not from K_m).

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. K_m is now explained. Yes, K_c for the FTIR measurement is calculated from K_c for CH_4 from the gradient measurements on the tower.

References:

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