

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:

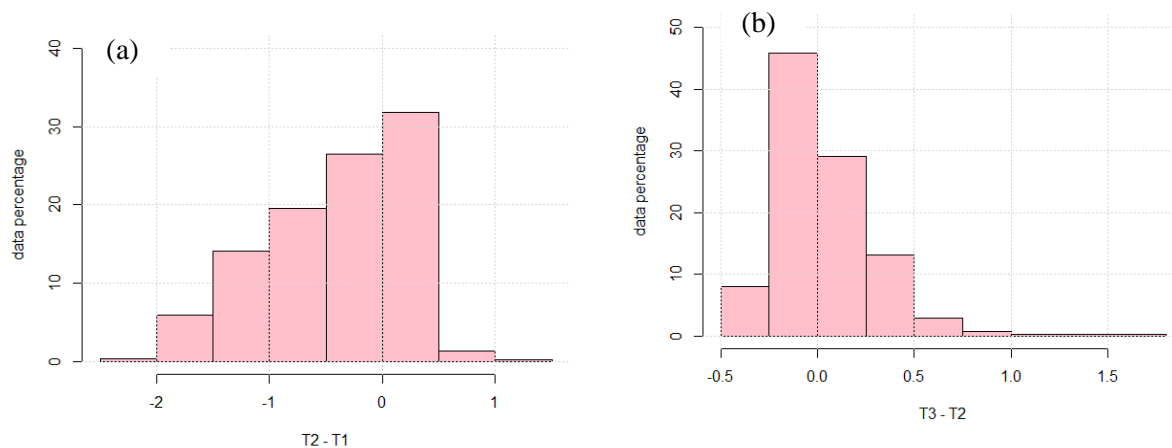


Figure: Histogram of (a) $T_{8m} - T_{1m}$ (K) and (b) $T_{18m} - T_{8m}$ (K) over the entire study period.

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.

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

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

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

Next, the H₂O mole fraction was used to calculate dry mole fractions. 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. 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 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. 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) 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
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

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 CH₃OH 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 CH₃OH in the same way as for the other pollutants, and the flux was on the order of 1 mg m⁻²day⁻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 NH₃ 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.