Note from authors: Reviewer comments are in black text. Our responses are in blue text. Line numbers in the reviewer comments refer to the original manuscript submission, while line numbers in our responses refer to the revised manuscript.

Response to RC1: 'Comment on acp-2023-26', Anonymous Referee #1, 21 Feb 2023

This paper uses tower and balloon observations and a 1-D chemical transport model to study ozone over a forest near an region producing oil sand. The manuscript is generally well-written and robust, but a few changes would further strengthen the paper.

The introduction needs some restructuring. The information is rich and almost complete, but poorly connected, thus does not provide the motivation of the study well enough. A paragraph explicitly talking about "Why ozone concentration and deposition over AOSR" is highly recommended.

AC1.1: We thank the reviewer for these comments and feedback. We have reorganized the paragraphs and added text to attempt to improve the connectivity of the information and to better describe the motivation for the study. The structure of the Introduction can now be summarized as the following list of paragraphs…

1) Describe the oil sands.
2) What is ozone and where does it come from.
3) Oher ozone-AOSR studies.
4) Summarize our study motivation (why ozone concentration and deposition over AOSR)
5) Describe how ozone behaves in the canopy.
6) Ozone deposition to the canopy.
7) The effects of turbulence and shading.
8) Study summary.

Text is added to paragraph 4 (lines 36 – 41) as "The motivation for this study is to a) determine how pollutant emissions associated with oil sands extraction modify ozone concentration in the surrounding forest, and b) investigate how the forest affects ozone deposition. A boreal forest site was chosen that is surrounded by oil sands processing facilities including those operated by Syncrude, Suncor, Canadian Natural Resources Limited (CNRL) as well as other facilities. Since exposure to ozone reduces photosynthesis, growth, and other plant functions (Felzer et al., 2007), we investigate what effect the elevated pollution levels of the AOSR have on the surrounding boreal forest and to determine the rate of ozone uptake to the forest."

L 38 – 40: NO does not ALWAYS dominate the in-canopy chemical sink of ozone (e.g. Wolfe et al. (2011) propose BVOC to be the dominant chemical sink in a warm pine forest)

AC1.2: We add the caveat here (Line 51) that "However, Wolfe et al. (2011) have demonstrated that chemical loss due to VOCs can also be significant.".

L 149: Need citation for the observed "shelf shape"

AC1.3: We add Raupach et al., 1996, which is the definitive study as referenced in M17.

Raupach, M.R., Finnigan, J.J. & Brunet, Y. Coherent eddies and turbulence in vegetation canopies. Boundary-Layer Meteorol. 78, 351–382, doi:10.1007/BF00120941, 1996.

L 114: The maximum height of profile measurement was 300m and most of the paper discuss about near-surface turbulent mixing and sinks. Would 1000 vertical layers be an overkill and potentially introducing unnecessary error from vertical transport? Please explain and discuss.

AC1.4: Ozone is assumed constant at the top of the model (at a height of 1 km). This is necessary in order to replace depleted ozone and to simulate downward diffusion from the stratosphere. Ozone at lower heights (near 300 m) would vary diurnally and it would be unrealistic to model it as a constant value. To further explain and discuss our choice of model height we add the following text at Line 199:

"The choice of model height (1001 m) was determined by inspecting vertical ozone profiles from ozonesonde launches at Bratt's Lake (Astitha et al., 2018), which is located approximately 500 km SSW of the oil sands region. The aggregate vertical profile shows a consistently steep gradient between the surface and a height of 1 km (approximately 20 ppb km^{-1}) and a much weather gradient between 1 km and 2 km (< 3 ppb km^{-1}). Based on this, we choose a 1 km upper boundary of the model and ozone is held constant at this height. Sensitivity to both the assumed constant value and the choice of model height (1001 m) are tested in Section 3.5."

To demonstrate that there is no error introduced by the choice of model height, we run a sensitivity test with a model height of 500 m. The results are added to Table 2 and text is added at Line 504 as "Changing the model maximum height from 1 km to 500 m results in a 30% average overestimation (due to the closer proximity of the canopy-top boundary condition to the measurement height) and a higher RMS error (15.1 ppb); however, the R^2 value is slightly improved (0.469 from 0.424)."

Astitha, M., Kioutsioukis, I., Fisseha, G. A., Bianconi, R., Bieser, J., Christensen, J. H., Cooper, O. R., Galmarini, S., Hogrefe, C., Im, U., Johnson, B., Liu, P., Nopmongcol, U., Petropavlovskikh, I., Solazzo, E., Tarasick, D. W., and Yarwood, G.:.Seasonal ozone vertical profiles over North America using the AQMEII3 group of air quality models: model inter-comparison and stratospheric intrusions, Atmos. Chem. Phys., 18, 13925–13945, https://doi.org/10.5194/acp-18-13925-2018, 2018.

L 115, 156 – 157: This approach looks weird, or underexplained at best. In the model, what height does z = 0 correspond to? Assuming z = 0 refers to soil surface, this is not most of the deposition occurs (since leaf surface is mostly the major sink over healthy forest), nor what typical big-leaf model (displacement height) takes. The choice of which layer to put the "big-leaf" foreseeably affect the modelled in-canopy ozone profile. A sensitivity run to explore how the choice of level where the big-leaf is placed, or at least argument for why choosing to put the big-leaf at soil surface is needed.

AC1.5: We acknowledge that this is a significant weakness in our model set-up. Within our model, a flux (or deposition velocity) can only be specified at the model boundary (i.e. the surface). If a deposition surface (or big-leaf) were specified at a high above the ground, there would be deposition to both the underside and the top of that surface. In a future study, we

would like to add deposition at multiple levels as a function of LAI, but this requires a rewriting of the model code that is beyond the scope of this study.

To better explain the operator splitting mechanism of the model we added the following text at Line 152: "This model version uses operator splitting in each minute. First, each species diffuses for 30 seconds using a Crank-Nicholson numerical scheme to solve the diffusion term in Eq. 1. This is followed by 1 minute of uptake or emissions (E) and chemistry (f). Then the species diffuse for another 30 seconds. This process is repeated 30 times for each 30-min time step."

At Line 192 we add "While a vertical distribution of uptake (or locating the "big leaf" at a specified height above the surface) would be more realistic, this would require placement of the ozone uptake in the emission and chemistry operator step (as opposed to the diffusion operator)."

And finally, text is added at Line 537 in the conclusions as "There is also uncertainty associated with the location of the "big leaf" at the forest floor. In future work, the model could be developed to investigate the effect of a vertical distribution of uptake throughout the canopy height."

L 230: Does GEM-MACH have enough resolution to resolve these regional details?

AC1.6: We add the following text (Line 272) to this discussion:

"The GEM-MACH resolution is 2.5 km and the mines and upgrading facilities are more than 10 km (~4 grid squares) from the tower location. Hence, GEM-MACH can resolve these different sectors within at least ± 7°."

L 310: When the wind speed is higher, there should also be more vertical turbulent mixing generated by horizontal wind shear. This factor should also be considered and discussed in comparing the ozone gradients.

AC1.7: We have added the following text at Line 357: "Higher wind speeds should also be associated with stronger turbulence, due to enhanced wind shear. The stronger turbulence and mixing could lead to a weaker gradient; however, no correlation between the gradient and the wind speed is seen here."

L 393: Does the model explicitly consider the strong diurnal variation of ozone deposition velocity? If not, explain how this might affect your result.

AC1.8: The model assumes a constant deposition velocity. To discuss this point the following text is added at Line 447: "Rannik et al. (2012) demonstrate a strong diurnal cycle of deposition velocity, averaging 0.2 cm s^{-1} at night compared to more than 0.5 cm s^{-1} during the day (in the summer months). Figure 9b demonstrates that a lower deposition velocity results in a smaller gradient (compare #6, 7, and 8). Although our model unrealistically assumes a deposition velocity that is constant with time, the results suggest that modeling a deposition velocity that is lower at night and a higher during the day would result in a weaker gradient at night and a stronger gradient during the day (relative to a constant value). This would further increase the

difference between the model results and the observations, which show stronger gradients at night."

L 408: How long did snow cover last? Since snow and the compounding low temperature during early season can also significantly reduce ozone dry deposition. This might be a worth-discussing point.

AC1.9: The gradient data are from 27 March to 23 June 2019. Although snow can persist into April in this northern region, snow depth data from the Ft. McMurray airport (Environment Canada historic data) shows that all the snow was melted by 20 March this year. Although some snow may have persisted in the forest due to canopy shading, after 9 April, temperatures were consistently above zero (expect for a few hours at night) with daily highs above 14C for more than 2 weeks.

We have added text at Line 432 as "Although the relative cold in later March and the potential presence of snow might affect the gradients, recalculating the gradients for May and June only results in an average difference ~1% relative to the complete period." While we agree that further investigation of the effects of snow could be an interesting discussion, the colder period seems to have little effect on the observed gradients.

L 464: Direct ozone (and to a lesser extent NO_2) flux measurement would also help tremendously to constrain the deposition velocity/flux.

AC1.10: This is an excellent point that we overlooked. We add the text at Line 522: "Ideally, fast ozone (and NO) analyzers could directly measure fluxes (as in Finco et al., 2018) to directly determine deposition velocity and to compare to gradient measurements and deposition parameterizations."

Response to RC2: 'Comment on acp-2023-26', Anonymous Referee #2, 09 May 2023

Ozone chemistry and transport were studied in a boreal forest in the vicinity of oil sands mining in Alberta. Observations rely on gradient measurements within a forest canopy and a few selected tethered balloon profiles. A 1-D canopy model was run with input data from the observations, yielding a comparison between the observation data and the model output. I have no doubt that this project was a challenging effort.

AC2.1: We thank the reviewer for their overview and their appreciation of the challenges of the remote field work, data collection, and modeling.

While the idea to study the influence of emission from the oil sands operations is certainly warranted, the manuscript falls short in producing significant findings that advance the understanding of the chemistry and environmental impacts, or modeling improvements.

AC2.2: We neglected to include important calibration information and statistical analysis of the results and we are grateful to the reviewer for highlighting this and helping to improve the manuscript. We have added statistical analysis to the revised manuscript to emphasize the statistical significance of the findings. This analysis is discussed in more detail below.

What is the primary objective of the study? Investigation of air pollution from oil sands mining? Determining ozone deposition within a boreal forest? Evaluation and advancement of photochemical modeling? The paper provides bits and pieces to these topics, but really only scratches the surface. I don't see a well targeted experimental approach and comprehensive outcomes of this study.

AC2.2: We have expanded on the motivation in the revised Introduction section (see also the response to Reviewer 1, AC1.1). We have added the following text at Line 36: "The motivation for this study is to **a) determine how pollutant emissions associated with oil sands extraction modify ozone concentration in the surrounding forest, and b) investigate how the forest affects ozone deposition**. A boreal forest site was chosen that is surrounded by oil sands processing facilities including those operated by Syncrude, Suncor, Canadian Natural Resources Limited (CNRL) as well as other facilities. Since exposure to ozone reduces photosynthesis, growth, and other plant functions (Felzer et al., 2007), **we investigate what effect the elevated pollution levels of the AOSR have on the surrounding boreal forest and to determine the rate of ozone uptake to the forest.**" (Bold added for emphasis).

There are some fundamental flaws in the experimental approach for determining vertical ozone gradients within the canopy. 2B ozone monitors were used. These instruments are favorable in applications where space and electrical power are limited. However, their analytical performance (precision, accuracy, signal stability (i.e. lack of a drift in the instrument response), sensitivity to water vapor interference, response to monitor temperature changes, etc.) is poorer than for standard ozone monitors. The differences that the authors report in their data for vertical ozone gradients and for ozone transported from different sectors fall well within the measurement uncertainty for these monitors. An additional source of analytical error will likely result from the steady turning on and off of the monitors. The manuscript does not appreciate these challenges and does not present an evaluation of the impact of this operation mode on the instrument performance, stability of its calibration, and gradient data quality. The manuscript contains no information on how instrument response (accuracy) and stability were tracked over time and how gradients were determined to be statistically significant (see for instance [Bocquet et al., 2011]). Statistical analysis are purely data binning and averaging. Because of these reasons most of the interpretation is not warranted and premature.

AC2.3: We thank the reviewer for drawing attention to this oversight. We neglected to provide statistical analysis relevant to the interpretation of the results. We have added a section to provide more information regarding the calibration and the performance of the 2B instruments. We have also calculated confidence intervals for all the data to demonstrate statistical significance.

The added section is as follows (Line 124):

"2.2 Ozone Instrument Uncertainty

The 49i analyzer was laboratory-calibrated prior to the study (a 7-point calibration up to 120 ppb with $R^2 = 0.997$). The standard deviation in the 5-second measurement during calibration was 1.9 ppb. All Model 205 and ozonesonde monitors were calibrated in the field against the 49i analyzer by running the instruments side-by-side for 9 consecutive days period (at a 0.5 Hz frequency) prior to the long-term averaging periods. The ozone mixing ratio varied from near 1.3 ppb to 38 ppb during this period. The root-mean-square errors (RMSE) against the calibrated 49i were less than 2 ppb (at 0.5 Hz). The 2B Ozone Monitor specifications (2B Specifications) give a drift value of < 1 ppb day^{-1} and < 3 ppb $year^{-1}$. Over the 9-day period, the RMSE (at 0.5 Hz) showed no discernable trend with time. A least-squares fit of RMSE with time give a trend of 0.004 ppb day^{-1} (which is not significantly different from zero at a 95% confidence level (C.I.)). Hence, we assume minimal drift during the 3-month measurement period. Water vapour interference is assumed to be minimal since the 2B analyzers have a built-in dryer and heater to eliminate water vapour interference and temperature effects (2B Specifications), and the inlet tubing is only 10 cm in length.

During the long-term, 2019 measurements, when the monitors were activated 4 times per day for one-hour durations, the monitors were allowed to stabilize for 45 minutes and only the last 15-minutes of measurements were used. The manufacturer specifies (2B Specification) a 20-minute warm-up period. The stabilization of the instrument is demonstrated in the supporting information (Fig. S1) from the measured data, indicating full stabilization may require approximately 35 minutes. A truncated mean is calculated from the last 15 minutes, with outliers more than 3 standard deviations from the mean removed (resulting is removal of less than 0.5% of data). The average standard deviation in this 15-minute interval is 1.8 ppb, which gives a 95% C.I. of $\pm$0.24 ppb (for each 15-minute average)."

Figure 4 is modified to show 95% confidence intervals and the text discussing the comparison (Line 323) is modified as "As discussed in Section 2.2, the 95% C.I. for each 15-mintute average is 0.24 ppb, which would imply a 95% C.I. in each gradient measurement of 0.02 ppb m^{-1}. Based on the variability in the long-term measurements, the 95% C.I. of each of the 4 mean gradients is < 0.03 ppb m^{-1}. Hence, all measured gradients are significantly different from zero and the overnight/afternoon difference is significant."

The treatise of ozone deposition is lacking understanding of important processes (e.g. deposition to surfaces, humidity effects) and omits important recent findings and literature (e.g. [Clifton et al., 2020]).

AC2.4: We have added text to the last paragraph of the Introduction (Line 71): "A recent review of ozone deposition by Clifton et al. (2020) highlights the need for both short-term field intensives and long-term deposition sites. The review synthetizes the current knowledge of deposition pathways, including stomatal, non-stomatal, and soil uptake and in-canopy chemistry. While our study is not able to distinguish these various pathways, the motivation is to investigate how oil sand extraction and processing affects ozone mixing ratios and deposition."

Discussion of the data is often speculative or depends to a large degree on comparison with other studies, rather than deriving new insight and conclusions from this data set.

AC2.5: With the addition of statistical analysis as suggested by the reviewer (see AC2.3), the conclusions are demonstrated to be significant and no longer speculative.

Understanding and presentation of ozone chemistry is at times superficial.

AC2.6: We assume that this refers to specific points raised in the annotated pdf, which we address below in points AC2.11 to 2.36.

The manuscript presents and builds on observations of nitric oxides and sulfur dioxide but lacks a description of the experiment and data quality procedures.

AC2.7: NO was not observed in this study. This is stated at Line 271: "While NO and NO_2 were not measured in this study, we can use GEM-MACH output…". The data shown in Figure 3b are GEM-MACH model data as indicated in the figure, the figure caption, and the text. We believe some poorly worded text discussing measurements made in the Finco et al. (2018) study (which we have corrected) may have caused some confusion and given the wrong impression that we measured NO and/or NO_2. The correction is shown in the response to AC2.25 below.

The collection of the SO_2 data is described in Section 2.1 at Line 97 "Ozone and SO_2 analyzers (49i and 43i, Thermo Scientific) sampled from a height of 2 m." and Line 112 "SO_2 measurements (43i, Thermo Scientific and AF22e, Envea) at ground level and a height of 30 m and size-resolved sub-micron aerosol measurements (UHSAS, DMT) helped to further identify wind sectors bringing polluted air to the site.". It is also pointed out in the text and the Fig. 3 caption that the SO_2 data presented here are reproduced from the companion paper Gordon et al. (2023). To make this clearer we also add (Line 260) "The SO_2 measurements **(reproduced from Gordon et al., 2022)** are from two time periods…" (bold is added text).

The writing/wording is at times inaccurate.

AC2.8: We assume that this refers to specific points raised in the annotated pdf, which we address below in points AC2.11 to 2.36.

I strongly recommend that the modeling work be evaluated by an expert in forest canopy chemistry and modeling.

AC2.9: This comment is for the editor as we have no control over the review process.

An annotated pdf copy with some suggested corrections and more detailed comments will be attached to these summary comments.

AC2.10: We have copied these comments and suggestions into this response and address each comment individually in points AC2.11 to AC2.36.

Annotated pdf corrections.

Line 12: Better wording would be: ...that ozone is destroyed by reaction with nitric oxide emitted from oil and gas extraction operations (as well as NO resulting from photolosis of nitrogen dioxide). emissions). AC2.11: We have changed the wording as suggested.

Line 14: Vertical gradients .... AC2.12: "Vertical" added.

Line 23: of petroleum hydrocarbon extraction from oil sands AC2.13: We change this to "…oil and gas extraction from oil sands…", as we believe this reads easier.

Line 28: , AC2.14: Comma added.

Line 35: and by non-stomatal dry deposition. AC2.15: Text added.

Line 38: AC2.16: "due to the rapid ozone removal" is removed.

Line 40: Poorly worded sentence. AC2.17: Changed to: "The dominant chemical loss process is NO reaction with O_3 below the canopy (Kaplan et al., 1988). There are also monodirectional fluxes of NO and NO_2, with NO emitted from the soil and NO_2 deposited to the ground (Finco et al., 2018)."

Line 55: Poorly worded sentence. AC2.18: We delete "no regional stagnation of air", as this is implied by vertical mixing.

Line 56: Do you mean LAI? AC2.19: We do mean shading and not LAI. The global and regional models discussed in Makar et al. (2017) did not explicitly include the shading of forest canopies in photolysis calculations.

Line 90: Not clear. AC2.20: This is changed to "which was placed 100 m from the tower in the northeast direction (at a wind direction of 40^o), since regional winds are typically not from this direction."

Line 93: Need more detailed quality control data for 2B ozone monitors. AC2.21: This is now addressed as described above in AC2.3.

Line 108: Missing quality control and calibration data. AC2.22: Text added "These instruments were factory calibrated and data were quality controlled through visual inspection of the time series, resulting in rejection of less than 0.1% of the data."

Line 181: That seems like a significant omission of an important variable? AC2.23: We are using the Makar et al. (2017) parameterization as described in that paper. We agree that the inclusion of LAI in this parameterization is a good suggestion for future improvement to the Makar et al. parameterization, but addressing this improvement in our manuscript is beyond the scope of this study.

Line 184: How realistic are the isoprene emission rates for this coniferous forest? AC2.24: As stated in the text, these rates are parameterizations for the types of trees in this boreal forest. We do not have data to confirm the Guenther et al. emission rates.

Line 210: NO measurements are not detailed in the measurement section? AC2.25: This was poorly worded as our discussion of the Finco et al. (2018) measurements gave the impression that we are discussing measurement that we made. We add text (Line 250) "While the NO between heights of 5 m and 41 m varied from 0.1 to 2.5 ppb **in the Finco et al. study**, measurements at a height of 0.15 m ranged from 5 to 20 ppb **(Finco et al., 2018)**."

Line 229: Wind sectors are not labeled in Figure 1. AC2.26: We have added the "forest", "polluted", and "other" labels to the figure and changed the figure caption text.

Line 255: Probably none of the sector differences are statistically significant, but are well within the measurement uncertainty and variability of the data. So, this whole discussion about differences should be omitted. AC2.27: We have added discussion of statistical significance (see AC2.3) and have changed the text to reflect this analysis. The final line of this discussion (Line 308) is changed to "Although the results shown here are highly variable, there **appears to be no significant increase in ozone related to increased air pollution.**" (Bold is modified text.)

Line 266: No statistical evaluation of the data. AC2.28: See AC2.3.

Line 268: For radiation measurements perfect leveling of the light sensor is critical. How was that accomplished on a moving pulley? AC2.29: We add the following text "**A table platform was used on the pulley (with ropes attached at each corner) to ensure the UV sensor remained level.** The data were collected for periods of 5-min intervals at 5-m height intervals **after ensuring the sensors were level and not moving.**" (bold text added). Radiation sensors are extremely sensitive to leveling at low light angles, but much less so in summer afternoons when the sun is higher overhead. (i.e., $\sin\theta \approx \sin(\theta + d\theta)$ when $d\theta \ll \theta$)

Line 269: Not a trend. This is a vertical profile. AC2.30: We reword this to "Ozone tended to increase with height when the UV radiation was also increasing with height…".

Line 272: Really not clear if the ozone loss is from reaction with NO or from stromatal uptake or deposition to surfaces and soil. AC2.31: We change "can be explained by" to "could be due to".

Line 273: Really not that obvious. I don't see any obvious consistent ozone profile behavior that stands out of the variability and measurement uncertainty of the data. AC2.32: We have left the sentence in (since there is a peak in many of the profiles), but we add "; however, in many cases, this peak is within the variability of the measurements."

Line 276: There is no plausible reason that ozone should be correlated with radiation as ozone production (dependent on radiation) would happen slower than the time scale of mixing. Further, it's unlikely that there is significant ozone production in this low NOx environment that occurs on time scales that are shorter than the air transport within the domain. AC2.33: This sentence is removed.

Line 300: Mostly speculation building on a rather superficial understanding of ozone chemistry and vertical mixing. AC2.34: This is a list of potential causes of positive or negative vertical gradients. We cannot infer from the reviewer's comment what specifically is wrong with the discussion. We invite the reviewer to provide further information detailing what elements of this explanation are superficial.

Line 369: NO will show very significant diurnal cycles. I can not see how any modeling assuming a constant level of NO is going to produce realistic results. AC2.35: We agree that diurnal variation in NO would be more realistic. However, the use of a constant NO produces better model agreement. Since this is already discussed in the manuscript, it is not clear from the reviewer's comment how this should be addressed further. We invite specific information outlining what corrections are required.

Line 465: The study lacks a clear analysis of the turbulent measurements within and above the canopy. Without those data there really isn't a good way for simulating the vertical transport and chemistry within the canopy AC2.36: Measured values within and above the canopy are used to drive the model. This is outlined in Section 2.2. It isn't obvious to us what the reviewer means by a lack of clear analysis of the turbulent measurements. We would invite a more detailed explanation of what exactly is lacking in the analysis.

References:

Bocquet, F., D. Helmig, B. A. Van Dam, and C. W. Fairall (2011), Evaluation of the flux gradient technique for measurement of ozone surface fluxes over snowpack at Summit, Greenland, Atmospheric Measurement Techniques, 4, 2305-2321, doi:10.5194/amt-4-2305-2011.

Clifton, O. E., A. M. Fiore, W. J. Massman, C. B. Baublitz, M. Coyle, L. Emberson, S. Fares, D. K. Farmer, P. Gentine, G. Gerosa, A. B. Guenther, D. Helmig, D. L. Lombardozzi, J. W. Munger, E. G. Patton, S. E. Pusede, D. B. Schwede, S. J. Silva, M. Sorgel, A. L. Steiner, and A. P. K. Tai (2020), Dry Deposition of Ozone Over Land: Processes, Measurement, and Modeling, Reviews of Geophysics, 58, doi:10.1029/2019rg000670.