Response to RC3: 'Comment on acp-2022-668', Anonymous Referee #3, 31 Mar 2023

AC3.1: We wish to thank the reviewer for their feedback and for bringing the Meredith et al. (2016) study to our attention. We agree that we neglected to fully investigate and discuss the effect of the canopy on the use of the flux/gradient technique. We have modified the manuscript text including changes to Figure 1 and Table 1. We have added new information which we hope addresses these concerns and removed text with incorrect implications. Primarily, we have added deposition velocity calculation using the concentration gradient derived from the two highest (above-canopy) measurement heights. The average deposition velocity calculated with this 2-point, above-canopy gradient is higher than the deposition velocity calculated using all 5 measurement heights throughout and above the canopy, but it also shows much greater variation across the 9 profiles and the two averages are not statistically different (i.e. they are within < 1 standard error). Hence, we believe that our main conclusions are still supported by this modified analysis.

Herein any modified text within quotes is underlined (unless the entire quote is new). Line numbers refer to the newly revised manuscript.

General comments:

This study presents a detailed analysis of SO2 deposition velocity over a coniferous forest in Western Canada. This region is influenced by emissions from O&G and mining activities. The authors find that the removal rate is much faster than implied by a resistance-based model.

This study supports the findings of a recent study in the same region that used airplane and tower measurements (in an urban setting) to infer SO2 deposition rate.

AC3.2: We wish to clear up some confusion about the tower site from the Hayden et al. (2021) study, which is not an urban setting. We have added the text to the manuscript at line 42 as "Although the tower site was within the small town of Fort McKay (population 750), it was surrounded by wooded and grassy areas and can be considered a residential/rural site."

I have questions regarding some of the assumptions used to estimate the deposition velocity that need to be addressed before I can recommend publication.

Major comments

1. As pointed out by reviewer 2, the flux/gradient method generally requires that there be no source or sink within the region over which the gradient is estimated. As a result, the gradient is generally measured well above the canopy (see for instance Meredith, et al. (10.5194/amt-7-2787-2014) and references therein). In this study, the gradients are calculated using observations collected above and below the canopy (Fig. 2). This implications of this setup on the derivation of vd(SO2) need to be addressed very carefully given the body of literature that argues against it.

AC3.3: We have revised the paper to address this important issue. Text is added to Sections 2.2, 2.4, 3.3, 4.1, and the Conclusions. The LAI density profile is added to Figure 1 to demonstrate the vertical distribution of the leaves at this site. A column is added to Table 1 in which the deposition velocity is calculated with the 2 above-canopy measurement heights. The figure below (not included in the revised manuscript) compares the LAI profile for our study with the LAI profile of the Harvard Forest where the Meredith et al. (2014) study was done. Although we define the canopy height in our study as 19 m based on the highest vertical extent of the trees, Meredith et al. (2014) define the canopy height based on the mean leaf-foliage value (giving a height of 18 m for that forest). Defining the canopy height in this way for the boreal forest in our study would give a height of ~11 m, demonstrating that our 2 highest measurements can also be considered well above the canopy.

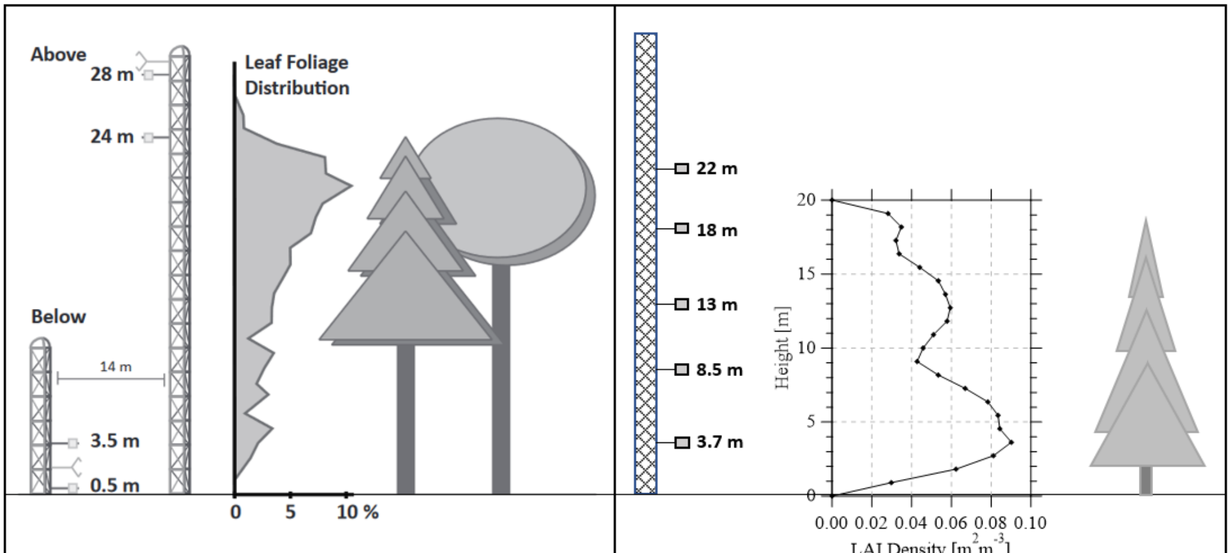

Fig. 2 From Meredith et al., 2014

Measurement heights and LAI profile at the YAJP and 1004 towers from this study

This figure (not included in the revised manuscript) compares the above-canopy measurement locations and LAI from Meredith et al. (2014) with the measurement heights and LAI from this study, demonstrating that the two highest measurement heights can be considered "above-canopy" relative to the forest leaf distribution.

Here we list a summary of the additional text:

Lines 146-157: "This approach has been demonstrated to reproduce deposition velocities by Wu et al. (2016) using gradients at heights of 16.5 m and 33 m in a 22-m high mixed-deciduous canopy. This mixed-deciduous forest had an LAI of 4.6, compared to the LAI of 1.17 at our boreal forest site, suggesting that the denser foliage would have a greater effect on the in-canopy gradient at the mixed-deciduous site relative to our boreal site. The approach was also demonstrated by Meredith et al. (2014) using gradients measured at heights of 24 m and 28 m in a nearly 24-m high temperate forest with an LAI of approximately 4. Here we determine the concentration gradient using a least-squares fit to the measured 5-point profile within and above the canopy. Although some profiles had 6 points, the lowest measurement is not used in these cases for consistency in the analysis. We also compare this to a 2-point concentration gradient determined using the two highest measurement heights. As the LAI density distribution in Figure

1d demonstrates, the two upper measurement heights (18 m and 23 m at YAJP or 17.5 m and 22 m at 1004) can be considered above-canopy relative to the canopy height of 19 m. Results from both gradient calculation techniques are compared in Section 3.3."

Lines 212-221: "As discussed in Section 2.2, the gradient (dC/dz) is determined using either a least-squares fit to 5 measurement heights (the 5-point gradient), or only using the two above-canopy measurement heights (the 2-point gradient). Using the 2-point gradient means that all uptake resistance ($r_{t,23\mathrm{m}}$) is below the gradient. However, due to uncertainty in the measured value of C using the passive samplers, there is higher uncertainty associated with a 2-point gradient measurement. This uncertainty can be reduced by calculating the gradient as a least-squares fit to the five values of C at all measurement heights. However, there are likely sinks in the region over which the 5-point gradient is estimated. As Figure 1d demonstrates, most of the leaf area is closer to the surface and the mean canopy height (50% total LAI) is 11.5 m. Hence, the deposition velocity is calculated with the 5-point gradient assuming that the error in the calculated gradient due to sinks throughout the canopy is small compared to the uncertainty in a 2-point gradient measurement. Both approaches are compared in Section 3.3."

Lines 291-300: "The gradients (dC/dz) are determined either as a 2-point gradient above the canopy (to give $v^{+}_{d,23\mathrm{m}}$) or from a least-squares fit to the 5-point gradient (to give $v_{d,23\mathrm{m}}$). The mixing ratio (C) is determined from the highest sampler location. Using the 2-point, above-canopy gradients, the deposition velocities calculated with Eq. 8 range from 1.4 to 28.0 cm s^{-1}, with an average of 9.5 cm s^{-1}. Using the 5-point gradients, the deposition velocities calculated with Eq. 8 range from 2.9 to 9.4 cm s^{-1}, with an average of 6.9 cm s^{-1}. The R^2 values for the least-squares fits are given in Table 1. Although the above-canopy, 2-point gradient results in a higher average deposition velocity, there is much higher variation across the 9 profile measurements, and the average values from each method (9.5 cm s^{-1} and 6.9 cm s^{-1}) are not statistically different at a 55% confidence level (i.e. $\overline{v_d} \pm 0.75\ \sigma/\sqrt{n}$). Hence, we conservatively focus on the lower deposition velocities calculated with the 5-point gradient determined by least-squares fit ($v_{d,23\mathrm{m}}$), but note the high uncertainty associated with these measurements."

Lines 331-337: "As discussed above, the use of the 5-point gradient effectively moves the total resistance (including aerodynamic, quasi-laminar sublayer, and bulk surface resistances) to the ground level, following the "big-leaf" assumption typically used by regional and global-scale models, as opposed to a vertical distribution of uptake throughout the canopy. While there is uncertainty associated with this assumption which is difficult to quantify, the average deposition velocity calculated with the 2-point, above-canopy gradient is greater than the average deposition velocity calculated with the 5-point gradient, suggesting that the deposition velocity calculated with the 5-point gradient may be a conservative estimate (although the averages are within $\pm$0.75 standard errors and hence not significantly different)."

Lines 449-459: "The flux/gradient method does not account for flux divergence through the canopy and is equivalent to assuming that the total deposition occurs near the ground level only. Although the uncertainty associated with that assumption is difficult to quantify, calculating the gradient using above-canopy measurements results in a higher average deposition velocity and a greater disparity between our measurements and those determined by Hayden et al. (2021). However, using the above-canopy measurements, there is high variability between the deposition velocities calculated from the different profiles, suggesting high uncertainty in the average measured value. We note that the deposition velocities calculated with the 5-point measurement (throughout and above the canopy) show good agreement with the Hayden et al. (2021) tower measurements located in a relatively clear and residential/rural area in Fort McKay, suggesting that the error associated with the vertical positioning of the uptake elements may be small. To quantify this uncertainty, the use of a high-resolution, one-dimensional canopy model (such as the model used in the Zhang et al., 2023) which can correctly model the vertical distribution of uptake is recommended for future studies."

The authors suggest that the lack of curvature in the SO2 profile implies that SO2 removal by needles is minimal. This would be quite surprising.

AC3.4: This text was confusing and has been removed. There is no longer any reference to the lack of curvature in the profiles.

This could also mean that some of the assumption used are not correct. For instance, I am surprised that du/dz is assumed to be constant throughout the canopy (see for instance, https://rmets.onlinelibrary.wiley.com/doi/epdf/10.1002/qj.49709741414).

AC3.5: We have changed the wording here (at line 161) as "…the wind speed gradient (du/dz') is approximated as $\Delta u/\Delta z$ from the wind velocity difference between heights of 29 m and 5.5 m. The uncertainty due to this approximation is investigated below." This is followed (at line 172) by "A least-squares fit to all the 30-min values of $K_{M,P}$ as a function of $K_{M,G}$ over the ~10-month period gave a slope of 2.6 with $R^2 = 0.83$ (Fig. 3), which supports the use of the $\Delta u/\Delta z$ approximation."

Although the wind profile within a canopy is unlikely to be linear, this direct comparison of the diffusion coefficients derived using either u_*($K_{M,P}$) or the linear gradient ($K_{M,G}$) demonstrates that the two values compare well (See Fig. 3).

2. The authors assumptions for flux/gradient require that R_needle >>1

If I am not mistaken, the GEM-MACH model would imply that the maximum deposition velocity = 1/Rcan (Table S3, Makar (2018)) which for evergreen yields vd_max ~1 cm/s or 2-5x slower than observed.

This would suggest that significant removal of SO2 needs to happen within the canopy to explain the observed vd(SO2). Such removal would contradict the assumption made to estimate vd(SO2).

This discrepancy needs to be addressed.

AC3.6: As stated in our responses above, we did not mean to imply that the removal by needles in minimal. As quoted above (line 332) "…the use of the 5-point gradient effectively moves the total resistance (including aerodynamic, quasi-laminar sublayer, and bulk surface resistances) to the ground level, following the “big-leaf” assumption typically used by regional and global-scale models, as opposed to a vertical distribution of uptake throughout the canopy.”

Now that the deposition velocity is verified using the above-canopy, 2-point gradient, the assumption of R_needle >> 1 is not required and there is no contradiction.

Minor comments

Line 12. Human exposure to what? (SO4?)

AC3.7: For clarity, we have removed “and human exposure” from this sentence.

Line 15. "predict". I would suggest to rephrase to clarify that vd(SO2) is not directly observed

AC3.8: We change “predict” to “infer”.

Line 19. The statement that the estimated vd(SO2) is close to aircraft observations is a bit confusing. The numbers quoted on line 16 are ~2x greater than the aircraft estimates (line 19). This also holds for line 274.

AC3.9: We agree this is a better way to present the comparison. We were thinking of it as two ranges (1.2-3.4 and 2.7-7.7) which overlap in the 2.7-3.4 range (and are hence “near” or “similar”). As noted by the reviewer, the minimum (and maximum) of each range differs by a factor of 2 so that is indeed a better comparison method.

We have modified the text in the Abstract as “Accounting for these uncertainties, the range of measurements is approximately double the previous aircraft-based measurements (1.2–3.4 cm s^{-1}) and are more than 10 times higher than model estimates for the same measurement periods (0.1–0.6 cm s^{-1}).”

The text at line 301 (formerly line 274) is modified as “The values measured here are <u>approximately double</u> those of Hayden et al…”.

Line 21. Please specify that this conclusion only applies to the type of environments investigated here.

AC3.10: The text at line 20 is modified to “…suggesting that SO_2 <u>in the AOSR region</u> has a much shorter lifetime in the atmosphere than is currently predicted by models.” We also modified the conclusions (at line 460) from “… to the environment” to “… to the type of environment studied here”.

AC3.11: As a further note (not a response to a specific reviewer comment), because of the added discussion comparing the “2-point” above-canopy gradient to the 5-point gradient, we have modified the description of the SO_2 gradient measurements made by gas analyzers above and below the canopy (at 2 heights). While these were referred to as “2-point” measurement in the previous version (primarily in the Conclusions), we now refer to them as “continuous” measurements to distinguish them from the passive samples while avoiding confusion with the 2-point, above-canopy passive sampler measurements.