Quantifying the decay rate of volcanic sulfur dioxide in the stratosphere

Response to reviewer in red

Note: An additional figure and section were added, and figure and section numbers in our responses refer to those in the updated manuscript.

Reviewer #1

l.22: '…is produced naturally in seawater':

This is only one of the several sources of OCS. It is even not clear if the major source is direct emission from sea-water, or if OCS is mainly produced by oxidation of CS2 and DMS (which originate in sea-water) (e.g. Kremser et al., 2016). Please be either more specific (or more general) here.

We have updated the language to be more specific as follows (see lines 22-25 in the revised manuscript):

> "An important source of stratospheric SO_2 in non-volcanic conditions is the photolysis of carbonyl sulfide (COS), which is the most abundant sulfur-containing gas in the atmosphere (Kremser et al., 2016). Important sources of COS include its direct flux from the ocean, oxidation of marine-originating dimethyl sulfide and carbon disulfide, and direct and indirect anthropogenic emissions, among others (Kremser et al., 2016)."

l.81: '…they potentially provide greater sensitivity to volcanic SO2'; l.86: 'the greater sensitivity of limb sounders may be advantageous'; l.332: 'This is likely to be a bias in the OMI data, perhaps due to the limited sensitivity of nadir instruments as the plume disperses…'; l.399: 'This may be a bias…'

I acknowledge the scientific caution when attributing biases in stratospheric SO_2 decay timescales to nadir-viewing instruments. However, the evidence presented in this study, as well as in previous works, strongly supports the existence of such a bias. This bias arises from the limited sensitivity of nadir-viewing instruments to diluted stratospheric SO_2 amounts compared to limb-viewing instruments, which benefit from significantly longer optical path lengths (several hundred times greater) through the dispersed plume. Given the robustness of this evidence, I recommend adopting clearer

language to describe this phenomenon. Such clarity is important to avoid potential misinterpretation of nadir-viewing data, particularly in the future, when a substantial volume of nadir-derived data remains available while limb-measurements might no longer be conducted.

This is a great point, and we have adjusted the language throughout the manuscript for increased clarity. For example, the text:

"This is likely to be a bias in the OMI data, perhaps due to the limited sensitivity of nadir instruments as the plume disperses"

has been changed to:

> "Additionally, there is a known bias in the OMI data due to the limited sensitivity of nadir instruments as the plume disperses" (see lines 401-402 in the revised manuscript).

l.98: 'high spectral resolution'

Should this not read 'high spatial resolution'?

When downloading the data from https://imk-asf-mipas.imk.kit.edu/mipas/, we had to select either "V5 high spectral resolution" or "V5 low spectral resolution". We used the V5 high spectral resolution data.

l.106: 'are reported on pressure levels with an approximate spacing of…'

The reported retrieval-grid of remote sensing data is generally not equal to its spatial resolution. Therefore, I would suggest to add the information on resolution from here: https://mls.jpl.nasa.gov/data/v5-0_data_quality_document.pdf, p. 157

Thank you for the suggestion. We updated the resolution numbers and added a citation for the data quality document. See lines 134-136 in the revised manuscript.

l.146: 'to the pressure coordinate of the MIPAS data'

Shouldn't this read 'to the altitude coordinate…'?

Yes it should! Thank you for the catch. We changed the text as suggested.

l.236: 'The reason for this remains unclear, and no explanation or documentation for this difference was found in the literature.'

You might try to contact the MLS-team for a possible explanation(?)

We have had personal correspondence with Hugh Pumphrey, one of the leading scientists working with MLS. He was also perplexed by the difference, and we did not get a resolution talking with him.

Chapter 3.2: 'Background seasonal cycle in the MLS data'

Is there any possibility to infer the disturbing seasonal cycle from comparing different years with less volcanic influence?

Thank you for the question and suggestion. At each day of the year, there is a spread of around 100-200 Gg in the SO2 seasonal cycle during non-volcanic times. Supposing we take the mean of the background years as the reference seasonal cycle, the actual disturbing seasonal cycle could be $\pm$50-100 Gg offset from the reference. This would impart a large bias on the calculated decay rate, thus limiting our ability to constrain the uncertainty.

The interfering background seasonal cycle is interesting in its own right, and to our knowledge under-explored in the literature. Given that it is likely due to O_3 and HNO_3, perhaps one might be able to calibrate the seasonal cycle based on observed values of these trace gases. However, we feel this would be beyond the scope of the current study. Nonetheless, we have added further discussion on this point (lines 305-312) in Section 4.2 as well as a supplementary figure (S2).

> "The approach outlined above samples possible seasonal cycles using the observed time series in a given year of an eruption. One could also potentially infer the interfering seasonal cycle from years without large volcanic eruptions; however, this presents its own challenges. There is a 100 to 200 Gg spread in SO_2 mass on any given day of the year in non-volcanic conditions (Fig. S2). Using the mean across years for the background seasonal cycle could result in an offset of $\pm$50 to 100 Gg from actual disturbing seasonal cycle. This difference is large enough to impart a significant bias in the estimated decay rate, thus limiting our ability to constrain the uncertainty. The seasonal cycle and inter-seasonal variability in MLS SO_2 is interesting in its own right: it warrants further investigation and could potentially be calibrated based on the observed amounts of O_3 and HNO_3 but this is beyond the scope of the current paper."

l.290, Table 1:

I strongly recommend consolidating all the information from Table 1 and Table B1 into a single comprehensive table. Additionally, I suggest including the uncertainties reported in Höpfner et al. (2015) and the results from the WACCM simulations, including those for the 18–22 km layer if available. This enhancement would greatly improve the readability of the discussion in Chapter 3.3, allowing readers to follow the analysis more easily without needing to consult multiple tables.

Thank you for the suggestion. We agree this improves readability, and Table 1 and the surrounding discussion in section 4.3 has been updated accordingly

l.290: 'Their values show a clear increase of e-folding time with height, which is not as apparent in our results.'

However, the decay timescales provided here also show increasing values (with one exception of MLS in case of Kasatochi). Further, I suggest also to try to provide best-estimates from your analysis of the decay-timescales at 18-22 km for MIPAS in case of Kasatochi and Sarychev – when looking at Fig. 2 and Fig. A1, there seems to be a clear signal.

We adjusted the text following Table 1 to read:

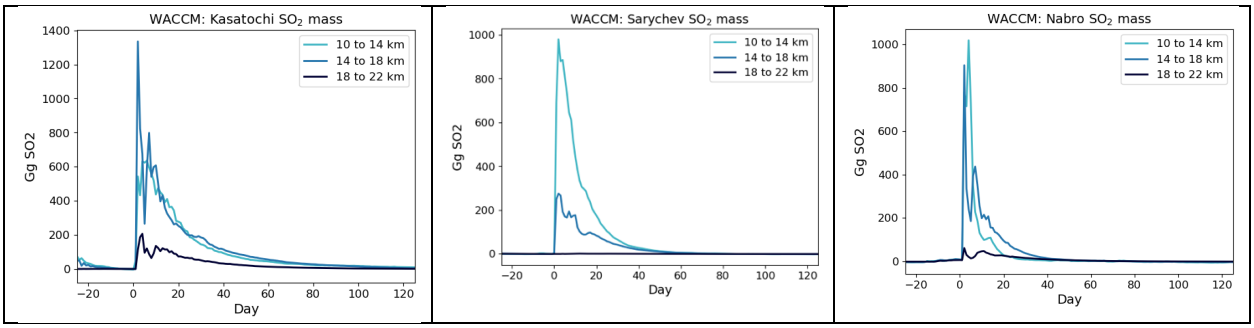
> "Their values show a clear increase of decay rate with height, which is generally also seen in our results (with the exception of some of the values for Kasatochi)" (lines 349 to 351 in the revised manuscript).

We also added MIPAS estimates for Kasatochi and Sarychev in the 18-22 km height bin in Fig. 3, Fig. 5. Fig. A1, and Table 1.

l.295-314: comparison to WACCM

The discussion may give the impression that the uncertainties in the decay timescales derived from the measurements are too large to allow for meaningful comparisons with the model. However, upon examining Figures 5, C1, and C2, it appears that for the Sarychev and Nabro eruptions, the model significantly underestimates the decay timescales compared to the limb-sounding datasets, whereas this discrepancy is less pronounced for the Kasatochi eruption. Could you provide possible explanations for this observed difference?

One possible explanation for the observed difference could be the fact that the model puts most of the SO_2 from the Kasatochi eruption into the 14-18 km height bin, whereas most of the SO_2 for the Sarychev eruption is in the 10-14 km height bin. The model also puts a substantial amount of SO_2 in the 10-14 km height bin for the Nabro eruption. As OH decreases with height in the model, SO_2 is going to get oxidized and removed more slowly the higher up it is. This could account for the slower decay timescales (and thus closer to MIPAS) reported for Kasatochi (as compared to Sarychev and Nabro) when looking at the larger vertical column. We added a figure (S2) to the supplement showing this and a brief discussion in lines 405-409 in the revised manuscript.



l.355: 'our main focus here is on the decay times of the stratospheric inputs of the indicated eruptions and not the total stratospheric mass.'

The entire chapter 5 of the manuscript (as well as section 2.5 'Calculation of total stratospheric SO2 burden') is dedicated to the 'Estimating the stratospheric SO2 burden'. Therefore, I don't understand this statement. I would suggest to delete this sentence and extend chapter 5 a bit by extending Table 2 to include the estimations of stratospheric SO2 mass by the extrapolation methods used by Pumphrey et al. (2015) and Höpfner et al. (2015). I would also suggest to add the results (M(t0)) from the fits

performed in the present work. It should be made clear that the method described here in section 2.5 is not adequate to calculate the total stratospheric SO2 burden in case of MIPAS and, to a less extend, also for MLS.

We have adjusted the sentence you highlighted to read (lines 465 to 466 in the revised manuscript):

> "The main focus of the paper is on the decay times of the stratospheric inputs from the indicated eruptions, and Table 2 explores the implications of such information for estimating the total stratospheric mass burden."

Your comment about presenting the inadequacy of method presented in Section 2.5 is well taken, and we have adjusted the text in Section 6 to emphasize this more clearly. For example, see lines 428-430 in the revised manuscript. Note we have removed Section 2.5 and included its content in Section 6.

> "As discussed in more detail below, this method proves inadequate for accurate mass burden estimations. This is particularly true for MIPAS, as the spectral bands measured by MIPAS saturate at high SO_2 concentrations. The inclusion of it in this paper provides a contrast compared to previously published total burden estimates derived from SO_2 decay timescale estimates..."

Finally, we have reworked Section 6 and updated Table 2 to include our own exponential fit-derived estimates of the total SO_2 burden. Please see the revised document for the changes.

l.400: '...and should be considered when analyzing volcanic SO2 with OMI'

I would suggest to add here: 'and other nadir-sounding instruments'.

Thank you for the suggestion; this text was added.

l.413-417: eruptions with ash

The eruption of Puyehue in June 2011 was also rich in ash. Have you tried to inspect that one for any effects on SO2 lifetime? (e.g. Griessbach et al., 2016, doi:10.5194/amt-9-4399-2016)

Thank you for the comment, as it is a good point. We considered other eruptions during the time period of overlap between MLS and MIPAS. However, we focus here on three specific eruptions in this paper because they were large enough to allow for a calculation of the e-folding time of SO_2. Puyehue, as well as other notable eruptions during this time period such as Grimsvotn had too weak and noisy of a signal, particularly in the MLS data, to calculate the decay rate. As we are interested in comparing MLS and MIPAS, we leave these smaller eruptions out of the analysis.

l.424: 'Our work suggests that the current SO2 data reported by available observational products are subject to significant uncertainty when examining the stratospheric lifetime of volcanic SO2 and suggests that more precise data is needed if chemical mechanisms and SO2 mass loading following an eruption are to be elucidated using observed decay times.'

On one hand, I support this statement, particularly considering the imminent loss of limb-sounding capabilities for stratospheric SO_2 observations, which will create a significant gap in our ability to monitor the stratosphere. On the other hand, I find the statement somewhat overly general. As noted in the manuscript, each observational technique has specific advantages and limitations in quantifying stratospheric SO_2. Therefore, to effectively evaluate and refine models, it may be more appropriate to tailor comparisons to align with the strengths of each dataset. For example, model results could be compared directly with nadir and MLS data closer to the eruption time, while comparisons with IR limb-sounding datasets might be more suitable for periods several weeks after the eruption.

Thank you for the suggestion. We have modified the last paragraph (lines 523-527 in the revised manuscript) to read as follows:

> "Our work suggests that the current SO_2 data reported by available observational products are subject to significant uncertainty when examining the stratospheric decay of volcanic SO_2. The varying strengths and shortcomings of the different observational products should be accounted for when using them to determine chemical mechanisms and SO_2 mass loading. Furthermore, the forthcoming loss of MLS (the only limb-sounding SO_2 instrument in operation) will leave a significant gap in our ability to monitor the stratosphere."