Atmos. Chem. Phys. Discuss., 5, S5722–S5735, 2005
www.atmos-chem-phys.org/acpd/5/S5722/
European Geosciences Union

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Atmospheric transport and deposition of Indonesian volcanic emissions" *by* M. A. Pfeffer et al.

M. A. Pfeffer et al.

Received and published: 1 March 2006

Given on the following pages is an itemized list of the reviewers comments, our responses, and the changes we have made. The sections and paragrpahs in our responses refer to the revised manuscript. We appreciate the detailed and thoughtful comments provided by the reviewers, which have contributed to a greatly improved manuscript.

Anonymous Referee #1

1) Since there are 95 volcanoes in the model domain, does this complicate the analysis of the correlation between the meteorological variables and the SO2 loss rates for any given volcano (V)?

Yes it does. We do not feel confident in highlighting results for any individual volcano, because of the large number of active volcanoes in the region and the relative coarseness of our modeling grid (1/2o.) This is why we have shown our results as box plots (Figures 5,6,10) and discuss the trends of the Indonesian volcanoes as a group rather than individually. In some cases two volcanoes are within the same grid box, and in several cases emissions from other volcanoes are transported into the grid box where other volcanoes reside.

Section 4.1, 2nd paragraph: The environmental conditions in this study are unique for Indonesia. There are a large number of active volcanoes close to each other, potentially resulting in overlapping plumes. The transport of SO2 from other volcanoes into grid boxes under consideration produces a complication for the analysis of the SO2 loss rates.

2) If I understand the model correctly, the SO2 emissions from any given volcano (V) are subject to losses by oxidation, deposition and transport. However, would there also be emissions from neighboring volcanoes reaching into the plume at V+2?

Yes, in some cases this is the situation. We addressed this by removing volcanoes from our calculations that had influence from other volcanoes.

Section 2.2, 3rd paragraph: For some volcanoes, the SO2 loss rate calculation resulted in a negative or null value. A negative value indicates an increase in the concentration of SO2 at ‘‘V+2” compared with ‘‘V”. This can occur when ‘‘V+2” contains SO2 released or transported into the grid box from another volcano. A null value can occur when the wind direction is so variable that the emissions are predicted in the first step to be transported away from the grid box ‘‘V” and in the second step returned to it, for a net distance of 0. In both of these situations, the calculated SO2 loss rates have been excluded from further consideration.

Section 3.1, last paragraph: Between locations ‘‘V+1” and ‘‘V+2” (an average distance of 70-120km from the volcanoes) the sum of the column burden of SO42- and the daily

ACPD

5, S5722–S5735, 2005

dry deposition of SO2 is greater than the loss of SO2. This apparent incongruity can be explained by the transport of SO2 from other volcanoes into grid box "V+2".

3) Could this mask the correlations between the SO2 loss rates and the meteorological variables, despite the fact that you have removed points where the concentration difference between V and V+2 was null or negative? Some discussion related to this concern would be helpful. If you repeated the correlations for a few of the volcanoes, assuming any given volcano to be the only one active in the domain, would this change your results?

The correlations were calculated using all of the volcanoes that were not excluded due to being obviously influenced by other volcanoes, and the results are plotted as box plots to show the variations amongst the individual volcanoes. Given the coarseness of the model, we cannot make clearer statements about how much the volcanoes influenced each others plumes. See the response to 1).

5) You mention that the major tropospheric chemical reactions for SO2 oxidation are used in the model. It would help the work if you explicitly stated these equations, and likewise gave the equations used for deposition. This would help the reader to understand if the oxidation or deposition processes are linked to meteorological variables in the model.

Section 2, 1st paragraph: Dry deposition is dependent on friction velocities and ground level atmospheric stability Wesley89. Wet deposition is dependent on precipitation rate, mean cloud water concentration, and compound solubility Walcek86. And Within the model, sulfate can be produced by the gas phase oxidation of SO2 by OH. or the aqueous phase oxidation of SO2 via five chemical reactions: by H2O2, O3, peroxyacetic acid (PAA), or methylhydrogenperoxide (MHP), or via catalysis by Fe3+ or Mn2+ (see Walcek86 and references therein).

6) Have there been any eld studies to examine the correlation between SO2 loss rates and meteorological variables?

ACPD

5, S5722–S5735, 2005

Section 1, paragraph 6: A field study examining the influence of variable meteorological factors on volcanic sulfur was performed by Fujita03. They observed that the wet deposition of SO42- and the percentage of sulfur deposited as SO42- increased with increasing precipitation. McGonigle04 attempted to determine what meteorological parameters are the most important for influencing the loss of SO2 from volcanic plumes by performing repeated scans of SO2 column concentration using ground-based differential optical absorption spectroscopy (DOAS). They measured the plume of Masaya volcano for several days during the dry season and found that time of day (i.e. insolation strength), relative humidity, and temperature had no significant impact on the measured SO2 flux rate.

9) Reference to previous, related studies that model the atmospheric transport and deposition of volcanic emissions could be added to the introduction. Also, mention if there have been any previous studies on the impact of meteorological variables on the transport and deposition of volcanic emissions. This will show that your work is a new contribution.

See response to question 6). Section 1, paragraph 6: We have addressed the question of the influence of meteorological conditions on volcanic plume SO2 loss using an atmospheric chemistry model. We have exploited this technique to hold the modeled volcanic emissions constant, thus removing the inherent natural variability of volcanic emission rates. This enables us to study what variations in atmospheric transport are due to changing atmospheric conditions rather than due to changes in the volcanic activity. The modeling technique also allows us to study a much longer time period (1 year), consider different seasons, and to perform statistical comparisons between the SO2 loss rate and the varying meteorological conditions. Modeling also enables us to calculate what portion of SO2 lost from the volcanic plume is due to the different loss mechanisms: oxidation, deposition, or transport out of the plume, as well as to consider volcanic emissions additional to SO2.

10) Also, in the introduction, could you add a sentence or two to explain the principle

ACPD

5, S5722–S5735, 2005

of the COSPEC instrument. Also in the introduction, the reference to fumarolic gas sampling, plume particle sampling, and remote sensing might be clearer if you mention the instruments that are used.

We have cited Stoiber (1983) as the reference on using COSPEC to monitor volcanic plumes and included a reference for Pfeffer et al (2006) as they apply many ground based volcanic emission instruments.

Section 1, paragraph 3: SO2 has been the most monitored volcanic emission because the concentration of SO2 within a volcanic plume is typically orders of magnitude greater in concentration than what is found in background ambient air. For the past few decades the majority of volcanic SO2 observations have been performed with the Correlation Spectrometer (COSPEC), which measures the flux of emitted SO2 (e.g. Stoiber83). And In addition to ground-based remote sensing (including COSPEC), fumarolic gas sampling and plume particle sampling (e.g. Pfeffer06) have contributed to an improved understanding of the variations in time and between different volcanoes of emission compositions and strengths and, to a lesser extent, about processes occurring within volcanic plumes.

11) Since the paper calls into question the validity of the assumption of a constant [PbCl2]/[SO2] ratio (PbCl2 being much more soluble than SO2), you might state explicitly if this metal was one of those examined in the previous observational studies that are referenced in the introduction. Also, you might comment on how the solubility of the other compounds that are commonly assumed to be constant to SO2 compares to PbCl2.

Section 1, paragraph 3: Some volcanic compounds are particularly environmentally important because they are released in extremely small quantities by other sources. For example, volcanoes may be responsible for 11 % of the total global emissions of Cr, and species including Hg, Ni, Cu, and As each contribute more than 5 % (Nriagu89, corrected by Mather03). Considering the volcanic contribution to natural

ACPD

5, S5722–S5735, 2005

(non-anthropogenic) emissions, species including Cd, Ni, Hg, and Pb contribute more than 15 % to the global natural emissions of each. And Section 2.2, paragraph 4: The ‘‘PbCl2 Experiment” was conducted to observe the transport and deposition pattern of PbCl2, a highly soluble compound released by volcanoes in relatively large concentrations (e.g. Delmelle03).

12) Looking at the figures, in Figure 4, for the observational data, there appears to be a trend in that the loss rates are lower for volcanoes that are higher into the troposphere. Your data does not show this trend. Could you comment on this?

We see no trend between loss rates and height in atmosphere. From the observational data, at an elevation of approximately 3000 m, the entire range of SO2 loss rates have been observed. See Figure 4.

13) Figure 5 show correlations with wind speed, did you also consider wind direction?

We did not consider wind direction, except in terms of the seasonal variations of wind, when in the north monsoon season the winds come mainly from China and in the south monsoon season the winds come mainly from the Indian Ocean and Australia. During the intermonsoon seasons the winds are very weak and variable in direction.

14) In Figure 6, in the seasonal comparison, are you able to explain why the loss rate is greatest in the summer in light of the meteorological variables?

We have modified Figure 6 to show the corresponding seasonal wind speeds, to show that this is the reason for the greatest loss rates in south monsoon season. See Figure 6 and Section 3.1, paragraph 5: The only season with a significantly higher mean SO2 loss rate is the south monsoon, which is distinguished by the strongest wind speed.

15) Could you consider the correlation of the loss rate with precipitation?

We plotted the seasonal precipitation with SO2 loss rates, but found no correlation.

17) Also, could you give an atmospheric loss rate for PbCl2?

ACPD

5, S5722–S5735, 2005

Section 3.2, 2nd paragraph: While SO2 is calculated to have an annual mean loss rate of 1.1 x 10-5 s-1, or an e-folding rate of approximately 1 day, PbCl2 is calculated to have a loss rate of 5.3 x 10-5 s-1, or an e-folding rate of approximately 0.2 day.

19) Perhaps it would help your discussion to make the point that dry deposition is a less efficient removal process than wet deposition and therefore solubility is an important factor in a domain that is quite moist.

Section 4.1, 2nd paragraph: The strong year-round solar radiation and high rainfall of Indonesia promotes the rapid oxidation of SO2 to sulfate and the rapid deposition of sulfate.

21) Figure 11 does not entirely convince one that the downward trend in the ratio is really enough to prevent one from choosing to approximate the ratio as a constant. Particularly, since you are using innitely soluble PbCl2 is an extreme case. An overestimation at 30 km of around 5% or less does not seem too large. Maybe you could comment on why an error of this magnitude would be of concern. The rapid wet deposition of a soluble species assumes that there is frequent precipitation perhaps if the volcano was in a drier domain, solubility would be even less of an issue. You could mention something in regard to the relative abundance of precipitation in your domain compared to other volcanic regions.

We agree that an overestimation of around 5 % is actually not that large in comparison with the other sources of error in plume observations, and have changed our conclusions accordingly. See response to question 19).

23) In the introduction, you say that over distances up to 30km, the ratio to SO2 is assumed to be constant. Since the distances of V+1 and V+2 are greater and you only have three points, can you really trust the interpolation to 30km? Could a higher model resolution help to make this point better?

A higher model resolution could possibly make this point better, but our simulations still

ACPD

5, S5722–S5735, 2005

allow us to study this question. We trust the extrapolation back to 30 km because our result is not based on only three points, but on actually 90 volcanoes times 3 points.

24) On Figure 11, the values for the mean ratio at V+1 and V+2 (89.3 and 83.2 ug/g) do not seem to agree with the lines drawn on the plot, check this. Also, does the Pb/S ratio of 245 ug/g given in Table 3 agree with the PbCl2/SO2 ratio given at V from Figure 11 (107.7ug/g)?

See Figure 10. We have changed the units in Figure 10 to be ug/g to be consistent with the text. This should make it easier to see that the lines are indeed at the mean ratios. And Section 4.2, 3rd paragraph: The ratio of 107.7 &#65533;g PbCl2 / g SO2 is equivalent to 160.5 &#65533;g Pb / g S. This differs from the 245 &#65533;g Pb / g S defined as the ratio of Pb / S in the primary volcanic emissions (Table 3) because of SO2 released by other volcanoes and transported into grid box "V".

26) The conclusion should mention that the results and conclusions are specic to this Indonesian volcano domain. The high density of volcanoes in the domain gives SO2 sources in many grid boxes, and that might possibly affect the correlation of loss rates with meteorological phenomena. Also, temperature and relative humidity might not vary much in this domain so perhaps one needs to be careful in making this conclusion too broad. The conclusions in regard to solubility are also specic to this domain with its inherent precipitation patterns. The wording of the present conclusion might be too broad. State that this result was specic to the Indonesian domain.

This is a very important point, thank you. Section 4.1, 2nd paragraph: The environmental conditions in this study are unique for Indonesia. There are a large number of active volcanoes close to each other, potentially resulting in overlapping plumes. The transport of SO2 from other volcanoes into grid boxes under consideration produces a complication for the analysis of the SO2 loss rates. The strong year-round solar radiation and high rainfall of Indonesia promotes the rapid oxidation of SO2 to sulfate and the rapid deposition of sulfate. The conclusions drawn in this study about the atmospheric

ACPD

5, S5722–S5735, 2005

loss of volcanic SO2 are only applicable to this region and should be extrapolated to other volcanic regions cautiously.

27) Also, mention the limit on the distance that the field workers would assume this ratio to be constant.

Section 4.2, last paragraph: Based on this mean rate of decay, we estimate that calculations (e.g. based on COSPEC measurements) which assume a constant [X]/[S] ratio as found in fumarolic gases will result in a 6 % underestimation of the emission flux of highly soluble species at 30km distance away from a volcanic vent; at 100km, this would grow to an 18 % underestimation. Our results indicate that the assumption of a constant ratio between SO2 and other, highly soluble species such as PbCl2 is justified at distances where COSPEC is usually performed.

28) Table 1 Could you mention in the text the criteria that distinguishes whether a volcano is called continuous or sporadic?

Section 2.1, 1st paragraph: The inventory established for this work contains both continuous and sporadic volcanic emissions. Continuous emissions include passive degassing as well as long-lasting diffusive eruptive emissions while sporadic emissions include short-lived eruptions (typically stronger than continuously erupted emissions).

29) Table 4 Could you add a sentence or two in the text to say how one determines the percentage of S in peat that can be attributed to volcanoes, and is there much uncertainty with this method?

Section 4.3, 3rd paragraph: The potential volcanic contribution to the peat S has been calculated on the basis of what percentage of the peat S could be attributed to the deposition of volcanic S.

31) Figure 10 Did you say why you choose to multiply by 4082?

Caption to Figure 9: To show the S and Pb on the same scale, the Pb has been multiplied by 4082, the inverse ratio of Pb / S in Indonesian fumarolic gases.

ACPD

5, S5722–S5735, 2005

Referee #2 Martina Halmer

32) However, I suggest the authors should consider to consult a native English speaker to signicantly improve the readability of the manuscript.

The first author is American. We have attempted to improve the clarity and readability of the manuscript.

34) Page 11863 Line 9: I do not agree with the numbers taken from Andres and Kasgnoc (1998). It seems to be a misinterpretation of the original source. I suggest to reassess the percentage values in the paper again.

Section 1, 2nd paragraph: It was calculated by Andres98 that only 1 % of volcanic SO2 is released sporadically, while 99 % is released continuously.

Quoting Andres and Kasgnoc (1998) to demonstrate we are citing correctly: page 25,254: Thus the sum of the measured SO2 fluxes from continuously and sporadically emitting volcanoes is 26,400 Mg/day or 9.66 Tg/a. On an annual basis, sporadically emitting volcanoes account for less than 1% of this total.

35) Page 11863 Line 12: There are as well other and more recent estimates considering volcanic plumes reaching the stratosphere such as Halmer and Schmincke (2003) The impact of moderate scale explosive eruptions on stratospheric gas injections. Bull Volc. (e.g., 54 eruptions/yr inject gas into the atmosphere while ca. 14 eruptions/yr out of the 54 can inject their gas into the stratosphere (Fig. 6), a much higher percentage than the 12 eruption(s)/yr postulated by Simkin (1993)(Halmer and Schmincke (2003)).

Section 1, 2nd paragraph: Violent eruptions can inject volcanic emissions past the tropopause with generally at least one to two stratosphere-reaching eruptions per year (Simkin93 Bluth97).

The estimate of 1-2 stratosphere-reaching eruptions per year as in Simkin (1993) is based on the historical record of volcanic eruptions >= VEI 4. The estimate of up to 14 stratosphere-reaching eruption per year as in Halmer and Schmincke (2003) is based

ACPD

5, S5722–S5735, 2005

on assuming that all eruptions in a year can reach 10 km elevation. According to a table provided in Bluth et al (1997), over the 15 years from 1979-1994, only 18 eruptions had max. tephra heights >= 15 km and 26 eruptions had max. tephra heights >= 10 km- leading to an estimate of 1-2 stratosphere-reaching eruptions per year. Not all eruptions will reach 10 km, leading to the lower estimate.

37) Page 11868 Line 13: The index of Schnetzler et al (1997) underestimates the SO2 emission as shown by Halmer et al (2002). Halmer et al (2002) calculated a SO2 emission based on the original VSI (Schnetzler et al., 1997) and multiplied the values of the original VSI with a factor of approximately 2 to match the values of measured SO2 emission. The VSI is based on the quantity of volcanic SO2 produced by explosive eruptions and is scaled in different degrees of SO2 emission (in kilotons, kt = 109 g) based on the VEI scale. Schnetzler et al. (1997) developed the VSI using the relationship of the average sulfur dioxide emission and the VEI of volcanic eruptions for their index. Then modied the VSI by the factor 2 because it signicantly underestimated the quantity of degassed SO2. In some extraordinary sulfur rich eruptions such as El Chich&#65533;n (1982) the modied VSI still slightly underestimates the SO2emission. The index is quite appropriate, however, for average sulfur rich eruptions. Then related the eruption frequency to VEI from 1900 to 1972 for the time series analyses prior to 1972 and determined the annual eruptive activity for each VEI category. Multiplying the new VSIvalue (average quantity of SO2 degassed during an explosive eruption scaled with VEI) by the number of annual eruptions results in a total annual global volcanic SO2 emission from explosive eruptions for a certain year. The annual global volcanic SO2 emission from 1972 to 2000 was rst calculated with the original VSI by Schnetzler et al. (1997). The result was then compared with our estimate of global volcanic SO2 emission based on 50 directly monitored volcanoes and the 310 extrapolated volcanoes. Halmer et al. (2002) modied the VSI by a factor of 2 for calculating the SO2 emissions by volcanic eruptions prior to the period of monitoring by COSPEC and TOMS because the original VSI calculates a minimum quantity of the SO2 emission based on the 50 directly monitored volcanoes. The modied VSI is very useful to

ACPD

5, S5722–S5735, 2005

quantify the sulfur yield of volcanic eruptions and is used as a base for our minimum estimate of the quantitative volatile input into the stratosphere for historic eruptions, especially from 1900 to 1971. Currently, there is a paper under revision from Halmer and Schmincke (2005) considering two new indices called Volcanic Gas input into the Atmosphere (VGA) as well Volcanic Gas input into the Stratosphere (VGS). If the authors are interested I can provide them with a copy of the submitted manuscript.

Section 2.1, 2nd paragraph: Indexes estimating the amount of SO2 released due to each VEI class have been developed by Schnetzler97, the volcanic sulfur index ‘‘VSI”, and by Halmer02, the ‘‘modified VSI”. In this study, we have applied the VSI.

We chose to apply the VSI from Schnetzler et al. (1997) for the sporadic eruptive volcanic emissions. The values of sulfur released by arc volcanoes provided in Schnetzler et al. (1997) were based on TOMS satellite observations of 54 eruptions from 1978-1994. Their values are best for eruptions $>$ VEI 4, because TOMS is best at observing large eruptions. The modified VSI proposed by Halmer et al (2002) is based on 50 COSPEC and TOMS measurements from 1972-2000. They found that an approximate doubling of the VSI proposed by Schnetzler et al (1997) fit these TOMS and COSPEC observations better. The advantage of the Halmer et al (2002) approach over that of Schnetzler et al (1997) is the inclusion of COSPEC data in addition to TOMS data. Because Halmer et al. (2002) do not provide tables of the primary measurement data they used to develop the modified VSI and both Halmer et al. (2002) and Schnetzler et al. (1997) use TOMS data in their calculations, we must assume that the proposed modified VSI fits the COSPEC data better than the original Schnetzler et al. (1997) VSI based only on TOMS data. COSPEC is most accurate for smaller eruptions, so it follows that the modified VSI of Halmer et al. (2002) is probably more accurate for eruptions of VEI 0-3 and the VSI of Schnetzler et al. (1997) is probably more accurate for eruptions of VEI 4-7.

38) Page 11869 Line 4: You should add the reference or an explanation for the chosen percentages of SO2 and SO42

ACPD

5, S5722–S5735, 2005

Section 2.2, 1st paragraph: The volcanic emissions were released into the model as 96 % SO2 and 4 % SO42-. The assumption of an initial presence of some sulfate at the source to account for immediate oxidation processes is common in atmospheric chemistry modeling (e.g. Stier05).

39) Page 11871 Line 23: You compare volcano height together with the height of volcanic plumes. I do not believe that you really can set this into a simple relation with each other since there seems to occur no signicant agreement in between those two types of data (Figure 4).

Caption from Figure 4: Modeled SO2 loss rates (yellow squares) are plotted against the actual height of each volcano and measured SO2loss rates from Oppenheimer98 are plotted against the observed plume height.

In the model experiment, volcanic emissions are released at the height of the volcano, hence the modeled plume height = actual volcano height.

40) Page 11872 Line 11: Most of your volcanoes are located on the Southern Hemisphere, therefore I would suggest that you want to use either only months or add as well the Southern Hemispheric seasons instead of the Northern Hemispheric seasons. This might be important to understand changes in meteorological parameters.

This is a good point. We have changed the names of the seasons. Section 3.1, 5th paragraph: SO2 loss rates have been calculated for each month and season based on the monsoonal winds: north monsoon (December - March); April/May intermonsoon (April - May); south monsoon (June - September); and October/November intermonsoon (October - November).

41) Page 11874 Line 1: There occurs a huge variance in your data of Table 4 between measured S and modeled S. The range is larger than 1 magnitude between measured and modeled data. Further, the percentage of volcanic S increases with increasing distance, but there is no satisfying explanation given in the manuscript.

ACPD

5, S5722–S5735, 2005

See Table 4. The variation in the measured sulfur content of the peat samples (398 4412 kg/km2-yr) is much greater than the variation of the modeled volcanic S deposition (215 285 kg/km2-yr). This is because the modeled volcanic S deposition is quite homogeneous at distance from the volcanoes and there are huge uncertainties in the measurement of S in peat. The volcanoes are not the only source for S in the peat. We find that the comparison of the modeled volcanic S deposition with the peat samples demonstrates that the model experiment is realistically accomplished because they are within the same orders of magnitude, and the volcanic S is a fraction of the measured S in the peat. The percentage of volcanic S in the peat does not increase with increasing distance- at 153 km there is 28 - 72% volcanic S, at 160 km 6 15 %, and at 396 km 23 59 %. There is no observable trend.

42) Page11874 Line 14: You should explain in more detail that the assumption of similar C14 ages for close by peat cores to the analysed core could be another important source of error, which might be incorporated into the model later on.

Data from the peat samples is not used in the model, but is used for comparison with the model results. Section 4.3, 2nd paragraph: Peat core samples had both total S and 14C age measured, or had only total S measured and were very close to another peat sample where 14C was measured. S values from portions of the peat cores that were dated to be less than 150 years old were not included in the average as these S values may have been influenced by human activity.

All of the recommended changes to the sentences have been considered and many have been included, improving the manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 11861, 2005.