

Reviewer 2

Zhang and Tie present observations of gaseous sulfur dioxide during 3 fog episodes in Tianjin, China. Based on observed, large decreases in SO<sub>2</sub> concentrations during fog, they argue that the effective solubility of SO<sub>2</sub> is high and outline a method for determining an effective Henry's Law constant that includes consideration of the reaction of dissolved sulfur dioxide with dissolved hydrogen peroxide. Unfortunately, the presented analysis adds little to the understanding of SO<sub>2</sub> solubility in atmospheric fogs. Solubility, an equilibrium concept, is confused with kinetic concepts, including aqueous S(IV) oxidation. Furthermore, the authors fail to include analysis of conventional approaches to determining effective Henry's Law constants for ionizing species such as dissolved SO<sub>2</sub>. Fog pH, which is an important factor in determining the solubility of weak acids such as dissolved SO<sub>2</sub> is barely mentioned. The authors also fail to consider (or reference) any of a long history of much more extensive field studies that have examined SO<sub>2</sub> solubility in fogs. For these reasons, further explained below, I recommend that the manuscript be rejected from any further consideration for publication in ACP.

We thank the reviewer for the careful reading of the manuscript and the useful comments. The paper is revised following the comments. Since all the comments are included in the following major concerns, we will answer the comments one-by-one in his/her concerns.

By considering the reviewer's valuable comments, we make major changes and the manuscript is reconstructed and significantly improved. For example, the term of effective Henry's Law constant makes confusion for readers, and we change this term to effective solubility coefficient of  $S_{\text{eff}}$ . Other important factors such as pH, S(IV) + O<sub>3</sub>, temperature are also included in the revised manuscript. The sensitivity related to the different pH and temperature is also analyzed. The revised paper has considerably more scientific merits than the previous version.

In addition to the improvement of the paper, we also add statement that the measurement of SO<sub>2</sub> in the intensive fog period provides very useful information for our understanding of the air pollution in this region. The measurement site is located in north China plain, in which there are large amount SO<sub>2</sub> emissions in this region, providing an unique information for showing the large amount of gas to aqueous phase conversion of SO<sub>2</sub> (from 20-40 to a few ppbv). In addition, during the fog period, there is a cascade formation of fogs in a few days. The gas to aqueous phase conversion of SO<sub>2</sub> showed a rapid response to the fog appearance. In this case, the measurement not only provides the amount of the gas/aqueous partitioning, but also the time evolution for the gas → aqueous conversion. Moreover, it also shows the time evolution from aqueous → back to gas phase conversion between two fog periods. In our understanding, this kind measurement is unique, and has not been presented in this region.

Major concerns:

1. Effective Henry's Law constants are commonly used for expressing the

solubility of gas phase species that undergo equilibrium reactions (e.g., ionization) in solution. In the case of SO<sub>2</sub>, for example, the effective Henry's Law constant includes dissociation of dissolved SO<sub>2</sub> (H<sub>2</sub>SO<sub>3</sub>) to produce bisulfite (HSO<sub>3</sub><sup>-</sup>) and sulfite (SO<sub>3</sub><sup>2-</sup>). This approach is clearly outlined, for example, in the 2006 classic text by Seinfeld and Pandis. Although the authors of the current manuscript cite this reference (actually the older, 1998 1st edition) in the discussion, they barely discuss the importance of these ionization reactions and the role that pH plays, except for a passing comment (lines 9-10, p. 2937) that the Henry's Law constant for SO<sub>2</sub> is between 100 and 1000 (no units provided, presumably M/atm), depending on pH values. In fact, the effective Henry's Law constant for SO<sub>2</sub> can be much higher for pH values commonly seen in fogs. Fig. 7.6 in Seinfeld and Pandis (2006), demonstrates effective solubility constants exceeding 100,000 M/atm at 298K for fog pH values approaching 7. Even higher constants are found at lower temperatures.

Res: We agree with the reviewer that there is a precise physical definition of the "Effective Henry's Law constant" which is applied to the total effect of standard Henry's Law constant and the effect of dissociation. According to the study by Chameides et al (1982), the effective Henry's Law constant is calculated by the following processes:



The standard Henry's Law constant of SO<sub>2</sub> ( $H_{\text{so}_2}$ ) is small (1.2 M atm<sup>-1</sup> with T=298K). However, SO<sub>2</sub> is undergone the following dissociation processes;



The effective Henry's Law constant of SO<sub>2</sub> can be expressed by

$$H_{\text{eff}} = H_{\text{so}_2} \times (1 + \text{eq1}/[\text{H}^+] \times (1 + \text{eq2}/[\text{H}^+])) \quad (1)$$

From this expression, it indicates that the effective Henry's Law constant is strongly dependent on the pH value. For example, the values of  $H_{\text{eff}}$  under different pH values can be calculated by Eq 1;

pH	3.0	4.0	5.0	6.0	7.0
$H_{\text{eff}}$	22	$2 \times 10^2$	$2 \times 10^3$	$2 \times 10^4$	$3 \times 10^5$ (M/atm)

From the above calculation, we note that with the pH values generally range from 10<sup>2</sup> to 10<sup>4</sup> when the pH ranges from 4 to 6. However, when the pH value is very low (3.0), the  $H_{\text{eff}}$  is very small (22), while when the pH value is very high (7.0), the  $H_{\text{eff}}$  can reach to a very high value (>10<sup>5</sup>). The value of 7 is generally out of the range for the pH values in the north China plain region (NCP). Even though the pH values are low in north China ranging between 5-5.5 (It was 5.13 in a heavy fog period in the site, private communication), the value of  $H_{\text{eff}}$  is still relatively low in NCP (ranges between 10<sup>3</sup> and 10<sup>4</sup>). These values cannot explain the high partitioning of

aqueous/gas of SO<sub>2</sub> (about 3.0 to 6.0) during the measurement period. In the revised manuscript, we will show the result of SO<sub>2</sub> under different pH values (4.0, 4.5, 5.0, 5.5, 6.0). All of calculations considerably underestimate the solubility of SO<sub>2</sub>. We will discuss more details regarding the sensitivity of SO<sub>2</sub> to pH values in the revised text. Thus, addition effects (such as aqueous phase reactions of SO<sub>2</sub>) must be considered to explain the result.

In the revised manuscript, we have included the above statement in the text. In order to avoid the confusion of the effective Henry's Law constant as we used in the original manuscript, we re-define the solubility of SO<sub>2</sub> with the consideration of aqueous reaction to be the "effective solubility coefficient of S<sub>eff</sub>."

2. Any study of soluble gas uptake and associated evaluation of Henry's Law solubility constants ought to include measurements in both the gas and aqueous phases. No aqueous phase composition measurements were made here. Measurements of fog pH and dissolved SO<sub>2</sub> are both highly relevant.

Res: This measurement includes valuable information for studying the solubility of SO<sub>2</sub> (such as the liquid water content (LWC), the visibility, temporal variability of SO<sub>2</sub>, and CO etc). For example, LWC is a key parameter to calculate the partitioning of aqueous/gas of SO<sub>2</sub>. Visibility can provide an indirect evidence for the occurrence and magnitude of the fogs. The simultaneous measurement of SO<sub>2</sub> and CO can be used to phase out the other effects (such as the meteorological conditions) on the large variability of SO<sub>2</sub>. As we discussed above, some information for pH values in this region are available (with uncertainties) for reference, which are used to estimate the solubility of SO<sub>2</sub> in the revised manuscript. In order to reduce some uncertainties of the effect of pH values, we conduct several sensitive studies for arranging the pH values from 4.0 to 6.0. All these statements and calculations are added in the revised paper.

3. Henry's Law solubility is an equilibrium concept. Effective Henry's Law solubility constants generally incorporate effects of additional, reversible, equilibrium transformations that occur due to fast reactions in solution. Most of these are cases of fast acid-base equilibria (e.g., deprotonation of carbonic acid) although the concept is sometimes used to represent fast, reversible formation of other equilibrium species (e.g., gem diol formation in the case of dissolved HCHO). Effective solubility has not traditionally been used to describe additional, non-reversible reactions, such as the aqueous S(IV) oxidation by H<sub>2</sub>O<sub>2</sub> that is proposed here. The authors' approach inappropriately mixes fast, reversible equilibrium reactions with more permanent, often slower oxidation reactions.

We partially answer this question in Question 1. In order to avoid the confusion for readers, we don't use the term of effective Henry's Law for studying the measured large solubility of SO<sub>2</sub>. We think that **effective solubility coefficient of S<sub>eff</sub>** in the revised paper will avoid the confusion and also the equilibrium concept as points out by the reviewer.

4. Even if one chooses to take the authors' approach and include S(IV) oxidation

by H<sub>2</sub>O<sub>2</sub> as part of effective solubility, the authors' treatment of this approach is not sound. The proposed reactions (R1-R4) do not include effects of pH. Formation of HSO<sub>3</sub><sup>-</sup> and SO<sub>3</sub><sup>2-</sup> must be included. At high pH (higher than ~5.5), one also must include aqueous S(IV) oxidation by ozone, a pathway that was inappropriately dismissed by the authors in the manuscript. Even in polluted environments in China, fog pH is sometimes high enough that O<sub>3</sub> is an important aqueous S(IV) oxidant. Other pathways (e.g., oxidation of S(IV) by molecular oxygen catalyzed by Fe and Mn) should also be included.

We agree with the reviewer that another aqueous phase reaction (S(IV) with O<sub>3</sub>) may also be important for this approach, especially under high pH value condition. In the revised manuscript, we have included both the important reactions of SO<sub>2</sub>. By considering the effect of pH on the calculation, we calculate both the reactions for the solubility calculation under different pH values (ranging from 4.0 to 6.0).

5. Including oxidation reactions also poses the question about how slow must a reaction be to be excluded from analysis. Even when pH is low (<5), as H<sub>2</sub>O<sub>2</sub> is depleted from solution, other oxidants may become important (e.g., O<sub>3</sub>). Ongoing production of H<sub>2</sub>O<sub>2</sub> through gas and aqueous phase mechanisms may also be important. Are we to consider these phenomena, too, when determining effective SO<sub>2</sub> solubility? Or is it dependent solely on the initial H<sub>2</sub>O<sub>2</sub> present? And why don't the authors treat the effective solubility of H<sub>2</sub>O<sub>2</sub> in the same way they treat SO<sub>2</sub>? Shouldn't H<sub>2</sub>O<sub>2</sub> reaction with dissolved SO<sub>2</sub> also enhance its effective solubility? This is not included in R5. My opinion is no, but if one follows the logic in this manuscript, I think one would have to argue "yes."

One part of the concerns has been answered by the response of Question 4. In the revised manuscript, we show that the roles of both the reactions under different pH values. Regarding the application for H<sub>2</sub>O<sub>2</sub>, we think that this approach is only suitable for the lower soluble species of the reactors. By looking the main equation, one can see that the soluble coefficient cannot be enhanced for the larger soluble species, such as H<sub>2</sub>O<sub>2</sub>.

6. The authors do a startlingly poor job of providing readers of the article with references to appropriate peer-reviewed literature on the subject at hand. Many papers have been published over the last 30 years on uptake and reaction of SO<sub>2</sub> in fogs and clouds (see, for example, numerous papers coming out of fog studies in California's Central Valley or Italy's Po Valley). None are cited in the reference list. In fact, only 11 citations are provided in total. 6 of these (more than half) are self-citations.

We agree with reviewer. In the revised manuscript, we add more references, which are relevant to this study. We think that this also improves the quality of the manuscript.

7. The first paragraph of section 3.2 further mixes concepts of equilibrium and kinetics (rates). The equilibrium solubility of a species is not directly determined by the diffusion rate for transport of gas-phase molecules into water (listed item 1). This diffusion rate is important, rather, for determining

the timescale to approach equilibrium. Equilibrium represents a balance between rates (e.g., the rate of gas uptake is equal to the rate of material leaving the droplet back to the gas phase). Similar problems exist for items (2) and (3) as stated in the listing in this paragraph.

According to the reviewer's comments, we revise this part of text by taking the comment of the reviewer.

8. Equilibrium and rate constants depend on temperature. Did the authors consider temperature and its effects on SO<sub>2</sub> solubility, H<sub>2</sub>SO<sub>3</sub> ionization, H<sub>2</sub>O<sub>2</sub> solubility, and S(IV) oxidation by H<sub>2</sub>O<sub>2</sub> in their analysis?

In the revised paper, we add some calculation by changing temperature. This analysis is also included in the uncertainty analysis along with the changes in different pH values.