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Interactive comment on “High solubility of SO₂: evidence in an intensive fog event measured in the NCP region, China” by Q. Zhang and X. Tie

Anonymous Referee #2

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Zhang and Tie present observations of gaseous sulfur dioxide during 3 fog episodes in Tianjin, China. Based on observed, large decreases in SO₂ concentrations during fog, they argue that the effective solubility of SO₂ 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 SO₂ 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 SO₂. Fog pH, which is an important factor in determining the solubility of weak acids

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such as dissolved SO₂ 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 SO₂ solubility in fogs. For these reasons, further explained below, I recommend that the manuscript be rejected from any further consideration for publication in ACP.

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 SO₂, for example, the effective Henry's Law constant includes dissociation of dissolved SO₂ (H₂SO₃) to produce bisulfite (HSO₃⁻) and sulfite (SO₃²⁻). 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 SO₂ is between 100 and 1000 (no units provided, presumably M/atm), depending on pH values. In fact, the effective Henry's Law constant for SO₂ 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.

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 SO₂ are both highly relevant.

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

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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 H₂O₂ that is proposed here. The authors' approach inappropriately mixes fast, reversible equilibrium reactions with more permanent, often slower oxidation reactions.

4. Even if one chooses to take the authors' approach and include S(IV) oxidation by H₂O₂ 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 HSO₃⁻ and SO₃²⁻ 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 O₃ 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.

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 H₂O₂ is depleted from solution, other oxidants may become important (e.g., O₃). Ongoing production of H₂O₂ through gas and aqueous phase mechanisms may also be important. Are we to consider these phenomena, too, when determining effective SO₂ solubility? Or is it dependent solely on the initial H₂O₂ present? And why don't the authors treat the effective solubility of H₂O₂ in the same way they treat SO₂? Shouldn't H₂O₂ reaction with dissolved SO₂ 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."

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 SO₂ in fogs and clouds (see, for example, numerous papers coming out of fog studies in California's

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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.

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.

8. Equilibrium and rate constants depend on temperature. Did the authors consider temperature and its effects on SO₂ solubility, H₂SO₃ ionization, H₂O₂ solubility, and S(IV) oxidation by H₂O₂ in their analysis?

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