

Comment on acp-2021-788

Anonymous Referee #2

Referee comment on "Contribution of the gas-phase reaction between hydroxyl radical and sulfur dioxide to the sulfate aerosol over West Pacific" by Yu-Wen Chen et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-788-RC2>, 2022

This paper investigates the contribution of the gas-phase oxidation of SO₂ to the mass concentrations of sulfate aerosols over the West Pacific. The authors used airborne and surface measurement data obtained during the EMeRGe-Asia campaign. They proposed a new approach to derive the fraction of OH that reacted with SO₂ (SO₂ oxidation rate fraction) using the concentrations of trace gases and their rate constants with OH, and estimated the contribution of the gas-phase oxidation of SO₂ to sulfate. The data presented in this paper are valuable, and the scope of this paper is appropriate for ACP. However, I do not recommend the publication of this paper in its present form because of the lack of robust conclusions.

(1) Assumptions and approximations

The key point of this study is the new approach to estimate the contribution of the gas-phase oxidation of SO₂ to sulfate. My major concern is that there are too many assumptions and approximations, which affect the robustness of the estimates. Here are the assumptions and approximations to obtain Equation (13) and the major conclusions.

(i) The total OH reactivity of VOCs is proportional to the sum of the OH reactivity of CH₄, CO, NO_x, and SO₂.

(ii) The scaling factor "t" for the VOC-OH reactions is ignored.

(iii) The O₃ concentration is representative of the oxidizing capacity of the observed air masses.

(iv) The contribution of the CH₄-OH reaction is ignored.

(v) NO_y is composed of NO_x and PAN in daytime.

(vi) The slope of sulfate versus SO₂ oxidation rate fraction was due to the gas-phase reactions and the intercept was due to transport from other regions and/or aqueous-phase reactions.

The key oxidants responsible for the aqueous-phase reactions (H₂O₂ at all pH and O₃ at higher pH) are expected to show positive correlations with the oxidizing power in the air masses, and therefore the slope may not be exclusively due to the gas-phase reactions. The positive correlations of sulfate versus SO₂ oxidation fraction may represent that air masses containing high SO₂ yielded high sulfate. Unfortunately, potential uncertainties due to these critical assumptions and approximations are not discussed, and therefore the major conclusions are not convincing.

(2) The normalization by O₃

The r² values in Figure 1 increased by the O₃ normalization method. However, the rationale for the O₃ normalization is not well described. The ratio of [SO₂]/[O₃] would be largely affected by the background O₃, and the interpretation would not be straightforward. The normalization is generally done by inert tracers such as CO after subtracting the background.

(3) Introduction

The introduction section is poorly written. I would recommend that the authors should thoroughly review the current understanding of the budget of sulfate aerosols in the troposphere rather than describing the well-known reaction mechanisms of SO₂ (both the gas-phase and aqueous-phase).