

## ***Interactive comment on “Contributions of anthropogenic and natural sources of sulfur to SO<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>(g) and nanoparticle formation” by D. D. Lucas and H. Akimoto***

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### **General comments**

The manuscript presents results obtained with a chemistry and transport model of the global sulfur cycle, with a particular focus on the origin and fate of sulfur emitted from different sources. The chemical and physical processes which the sulfur species undergo after emission are accounted for, including the formation of sulfuric acid from gas phase oxidation of SO<sub>2</sub>, and the subsequent nucleation of sulfate aerosol particles from the gas phase. By tagging and tracking the sulfur emitted from different sources (anthropogenic, oceanic, volcanic etc.), the authors are able to identify and quantify the influence of the these sources on different regions and processes, or in turn, to tell

which source is relevant for the sulfur burden in a given region, or for a given process in that region. This is an elegant and meaningful approach to elucidate the inner workings of the sulfur cycle.

The presented work is innovative and its results intriguing, and while burdened by many uncertainties, advance our understanding of the sulfur cycle and of its components, and thereby of the Earth's atmosphere and climate. The assumptions made and methods used, as well as the presentation and discussion of the results and conclusions are generally sound, with a few issues: In particular, the discussion of the contribution of anthropogenic SO<sub>2</sub> emissions to nanoparticle formation seems problematic, as I explain below. I recommend that the authors address and resolve these issues prior to publication of the manuscript in ACP.

## Specific comments

### Subsection 2.1 "Model description":

Here it would help the reader to understand the modeling approach if slightly more details on the model setup were given: How is the initial dynamic state of the model specified? What is the modeled time period? Is there a model spin-up time? Are the annual averages calculated from a particular model year, or are they multi-year annual averages?

### Section 5: "Contributions to nanoparticle formation"

I find the discussion of the contribution of SO<sub>2</sub> from different sources to nanoparticle formation problematic. The authors state that

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*In order to better understand the impacts of human activities on the climate system, it is important to quantify the number of new atmospheric NPs that can be formed from anthropogenic SO<sub>2</sub>. Sulfur emissions to the atmosphere increased by about a factor of four from preindustrial to modern times ...*

It should be noted here that the proper approach to assess the contribution of anthropogenic SO<sub>2</sub> to ultrafine aerosol production rates would be to run one model simulation representing pre-industrial and one industrial conditions, and to evaluate the difference of the resulting aerosol nucleation rates. The two simulations would have to use at least different SO<sub>2</sub> emission rates and aerosol loads (surface area concentrations), as these are the most relevant parameters for H<sub>2</sub>SO<sub>4</sub> concentrations, which in turn determine aerosol nucleation rates.

However, in the present work, the authors attempt to quantify the impact of anthropogenic SO<sub>2</sub> emissions on the aerosol nucleation rate just from an industrial simulation. The authors discuss their approach on pages 7700 and 7701 of the manuscript, which I refer to in the following.

Since the aerosol nucleation rates (often) depend non-linearly on H<sub>2</sub>SO<sub>4</sub> concentrations, a higher H<sub>2</sub>SO<sub>4</sub> in industrial times due to anthropogenic SO<sub>2</sub> emissions may lead, loosely speaking, to a total nucleation rate that consists of three contributions: The original non-anthropogenic contribution, the anthropogenic contribution, and a contribution that reflects the enhancement of the nucleation rates by the presence of H<sub>2</sub>SO<sub>4</sub> from the other source (cross terms). The authors attribute the cross terms symmetrically to the two sources, and conclude that

*... the proportions of the tagged H<sub>2</sub>SO<sub>4</sub>(g) tracers are preserved during NP formation ...*

While this holds for the mass of the tagged tracers that are converted from the gas

phase into new aerosol particles, I would not apply this approach to determine the enhancement of the number of particles formed due to the increase in  $\text{SO}_2$  since pre-industrial times:

Let us assume that  $[\text{H}_2\text{SO}_4]_n$  and  $[\text{H}_2\text{SO}_4]_a$  are the gas phase concentrations from natural and anthropogenic sources, respectively, based on a simulation of the industrial period, and that the nucleation rate  $J$  is cubic in the gas phase sulfuric acid concentration,

$$J([\text{H}_2\text{SO}_4]) = \alpha[\text{H}_2\text{SO}_4]^3 \quad , \quad (1)$$

with some constant  $\alpha$ . Then an approximation of the nucleation rate in pre-industrial times would be

$$J_{\text{natural}} = \alpha[\text{H}_2\text{SO}_4]_n^3 \quad , \quad (2)$$

while the total, industrial period nucleation rate is

$$J_{\text{total}} = \alpha([\text{H}_2\text{SO}_4]_a + [\text{H}_2\text{SO}_4]_n)^3 \quad . \quad (3)$$

I argue that the increase in the aerosol nucleation rate due to anthropogenic  $\text{SO}_2$  emissions from pre-industrial to industrial times is better estimated from

$$J_{\text{total}} - J_{\text{natural}} = \alpha([\text{H}_2\text{SO}_4]_a^3 + 3[\text{H}_2\text{SO}_4]_a^2[\text{H}_2\text{SO}_4]_n + 3[\text{H}_2\text{SO}_4]_a[\text{H}_2\text{SO}_4]_n^2) \quad , \quad (4)$$

as opposed to the equations on page 7701. There are at least two approaches to resolve this issue:

- A) Conduct a pre-industrial model run and analyze the change in aerosol nucleation rates from the pre-industrial to the industrial time. This would make the manuscript very strong.
- B) If A is not possible, estimate the increase of aerosol nucleation rates from the difference  $J_{\text{total}} - J_{\text{natural}}$ , where  $J_{\text{total}}$  is the total nucleation rate in the industrial-period model run, and  $J_{\text{natural}}$  the nucleation rate only from the  $\text{H}_2\text{SO}_4$  that originates from non-anthropogenic sources. This may lead to an overestimation of

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the effect, however, because the  $\text{H}_2\text{SO}_4$  concentrations from non-anthropogenic sources in the industrial-period model run are determined by the adopted aerosol surface area concentrations, which may be higher than the pre-industrial ones.

**Page 7683, line 7:**

*Even though the  $\text{SO}_2$  levels associated with anthropogenic emissions are sufficient for forming nanoparticles, the higher temperatures and aerosol loadings at the emitting sites effectively impede nanoparticle formation.*

Doesn't this mean that the  $\text{SO}_2$  levels are in fact insufficient to form nanoparticles?

**Page 7684, line 23:**

*The condensation rate (pathway R2) is estimated as a first-order loss process using a Fickian diffusion formulation and prescribed aerosol surface areas.*

Where do these prescribed aerosol surface areas come from? Since these aerosol surface areas remove  $\text{H}_2\text{SO}_4$  from the gas phase and therefore influence the calculated gas phase  $\text{H}_2\text{SO}_4$  concentrations and aerosol nucleation rates, and thereby constitute an essential model input, they should be described in more detail.

**Page 7684, line 25:**

*The condensation calculations are detailed in Lucas and Prinn (2005), and have been slightly altered (rates lowered by 25 %) to account for overestimated aerosol surface areas in the originally prescribed fields.*

More details should be given here as well: Why is it known that the aerosol surface areas are overestimated? What is the rationale for the 25 %? Why not reducing the surface area concentrations by 25 %, as opposed to the condensation rates?

**Page 7687, line 2:**

*The anthropogenic source of sulfur is defined using the 1995 annual average surface emissions of SO<sub>2</sub> ...*

This neglects the very strong seasonal cycle of SO<sub>2</sub> emissions and lower tropospheric concentrations Rasch/et-al-2000. Why is it a good assumption to neglect the annual cycle in SO<sub>2</sub> emissions?

**Page 7688, line 19:**

*Because existing aerosols are also removed by clouds and precipitation during convective processing, convective outflow regions in the free troposphere can provide optimal conditions for producing nanoparticles. Observations in the remote marine atmosphere are consistent with this picture (Clarke et al., 1998b), though additional measurements are needed.*

I would suggest to slightly change the wording here, since the observations are not at all required to be consistent with the picture referred to, but the picture should be consistent with the observations. In fact, it might be possible that the observations of very high concentrations of ultrafine particles in the outflow regions of convective clouds were made first, and prompted the idea that lifting and processing of MBL air by convective clouds into the middle and upper troposphere is driving aerosol nucleation aloft.

## Technical corrections

### Page 7695, line 7:

... *dramtically* ...

Dramatically.

### Page 7698, line 16:

*The annual and zonal average rates of producing atmospheric nanoparticles by ...*

Check the wording.

## References

[Rasch et al.(2000)Rasch, Barth, Kiehl, Schwartz, and Benkovitz] Rasch, P. J., Barth, M. C., Kiehl, J. T., Schwartz, S. E., and Benkovitz, C. M.: A description of the global sulfur cycle and its controlling processes in the National Center for Atmospheric Research Community Climate Model, Version 3, *J. Geophys. Res.*, 105, 1367–1386, 2000.

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