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Interactive comment on “Chinese SO_2 pollution over Europe – Part 2: Simulation of aerosol and cloud condensation nuclei formation” *by* V. Fiedler et al.

Anonymous Referee #1

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General Comments – This paper presents a box model simulation of how CCN numbers in an aerosol size distribution are modified by the nucleation, coagulation and condensation of oxidized SO2 during a 9-day period. The main conclusion, that CCN concentrations increase with time as SO2 oxidizes and the size distribution matures (coagulates), is nothing "new" or different from well-accepted physics in this area. It is way overconfident and even absurd to claim that a simple box model that ignores a wide range of physiochemical processes can "explain" the observed SO2 1 ppb plume. I have a bigger problem with the "trajectory" model put forth in Part 1 of this study, which links the observed SO2 to a China source. The aerosol growth and nucleation model contains so many gross simplifications that it becomes a somewhat academic study

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that says little about the 1 ppb SO2 that was actually measured. The box model is interesting, and will teach graduate students or scientists outside of this research area about the qualitative details of aerosol growth and the competition between nucleation and condensation to existing particles as SO2 oxidizes, but its conclusions are self evident: Adding 2 ppb sulfate to a size distribution by either nucleating new particles or adding mass to existing particles will increase CCN concentrations. Even without sulfate formation, existing aerosol spectra will coalesce and "grow" more CCN as the size distribution "ages". Any quantitative numerical values about the rate of CCN increases are so specific to the highly unrealistic conditions of this particular simulation that they are essentially meaningless in terms of interpreting the plume that was measured. Nor is it possible to make generalizations about aerosol behavior from this study that are not already well established.

I can only recommend formal publication after several major revisions where the obvious deficiencies of this study are at least addressed in a simple manner.

Specific Comments and Technical Corrections

1. The last few sentences of the abstract are not really appropriate conclusions of this study. This study really didn’t consider clouds and precipitation processes or radiative properties of clouds. In fact cloud processes were totally neglected in the parcel model formulation. These last few sentences should be relegated to a minor footnote of a discussion portion of the text.

2. The authors have totally neglected all cloud-related physiochemical processes. It is scientifically ludicrous to suggest that one is somehow simulating reality over a nine-day period with such a grave omission. There are four effects associated with clouds that will STRONGLY influence sulfur concentrations over 9 days: 1) aqueous chemistry; 2) scavenging; 3) radiative effects (increased photolysis above clouds); and 4) vertical mixing. The authors cannot address nearly ANY of these effects in anything closely resembling their current box model approach. They need to just give up the no-

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tion that they are somehow simulating something that might have happened in the real atmosphere. Their box model is so unrealistic, it can only be used as an "educational" tool to help readers gain an understanding of a few processes. This could be acceptable for publication with all the proper acknowledgements of the serious simplifications invoked.

2a. Aqueous chemistry: It is well established from acid rain research days that on average about 50% of sulfate formed globally is converted to sulfate in clouds via aqueous-phase reactions. Here the authors totally neglect aqueous-phase processes, which is not necessarily bad, since this almost seems to be the design of this study. However, the only way SO2 can be lifted to 5-7 km is in a cloud, so aqueous chemistry MUST have occurred sometime after emission. Maybe the authors are considering only what happens AFTER the SO2 is "vented" out of a convective cell at 5-7 km somewhere above China, and maybe there was absolutely NO cloudy conditions along a 9-day trajectory towards Europe from China, but this is extremely unlikely. In order to justify that there was absolutely NO cloud encounter along a trajectory for 9 days would be to prove it with observations. It is highly unlikely that cloud and condensation conditions were never encountered given the Rh record. Periods of high Rh are usually associated with scattered cloud conditions.

2b. Scavenging: If a cloud was encountered along the trajectory, larger aerosols would have been activated to form cloud drops, further aqueous-phase SO2 oxidation would have occurred, and larger drops would have settled out of the cloudy air, most likely evaporating in air below the simulated parcel. There should be some mechanism of aerosol removal from the size spectra when Rh is high.

2c. Photolysis effects: The authors suggest that their trajectory is ABOVE cloud tops along its entire path. If so, then it is well known that photolysis rates would be ENHANCED significantly (up to a factor of 2), leading to double the HO concentrations during periods when the air parcel floats above clouds. Including this effect could lead to some interesting aerosol nucleation effects that would enhance the conclusions of

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this paper.

2d. Mixing effects: The primary mechanism by which air is exchanged between the polluted boundary layer and the free troposphere is in convective updrafts which are ubiquitous over midlatitudes. These intermittent mixing events will lead to significant dilution, diffusion, and mixing of new air into the "air parcel" into which the convection penetrates. This is part of a much more serious problem of "parcel box" models in general. Parcel "box" models do not allow air outside the parcel to have any impacts at all on the processes being simulated in the "closed" parcel. This is a serious deficiency of this study that renders any numerical quantitative results moot with respect to their comparisons with measurements, especially over simulation periods greater than a day or more. The neglect of diffusion and dilution and mixing of other air into the parcel seriously limits the ability of this model to accurately simulate reality over time periods over which these processes dominate ($<$1 day).

3. pg 2766, line 5, discussion of Fig. 1: The caption should contain information about the time (year, month, day, time) and approximate location of the observations. The note that averages are over "30 points" should be expressed as a more meaningful spatial and temporal average. Is this a 10-minute average? Is this an average over one km?

4. pg 2766, line 20: Use of 9-day back trajectories. I realize this is not the main purpose of this paper under review, but the use of the backward trajectory Lagrangian particle model for such a long time period is highly questionable. Trajectories provide only limited information about recent history of "air parcels", especially in environments where any mixing, turbulent diffusion, convective clouds, or even shear are present. Nearly all of these effects are ubiquitous throughout the troposphere. Maybe the authors can provide some evidence that there is no turbulence or convection along a 9-day path in the middle troposphere, but their own results suggest that this is not true (there is a plume of "north American" air that somehow "mixes" up to 2 km. Running backwards trajectories in environments where there is any mixing at all (even molecular diffusion!)

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is scientifically absurd. The second law of thermodynamics makes it conceptually and mathematically impossible to somehow "undo" diffusion. For example, if a convective cloud system disperses a polluted boundary layer uniformly throughout a troposphere column, it is IMPOSSIBLE for one to start with the uniformly-mixed ("after") convective event and then go backwards in time to put the uniform pollution back into the confined boundary layer. The only way you MIGHT be able to do this is if you had the full information about the time-varying GRADIENTS of all tracers throughout, meaning you would need a full 3-D model with everything (all physics, all sources). Backward trajectories (with NO MIXING ALLOWED) can only provide cursory evidence about where air may have originated. The whole concept of "isolated" air parcels retaining their identity WITHOUT MIXING is absurd, especially on time scales of more than a day or two. In reality, the air measured off the coast of Ireland contains a mixture of air that was influenced with anthropogenic sulfur emissions over a broad area upwind of the measurement location. I don’t doubt that China is probably a significant source for this particular plume, but unless a detailed fully- 3D global model is used, one cannot make quantitative assessments of source attributions using BACKWARD Lagrangian trajectories. The real proof that air originated from China at this measurement location should be demonstrated using FORWARD trajectories. All of the backward trajectory information presented in Part 1 of this paper is unnecessary, but I can understand its use as an intermediate phase of the investigation.

5. pg 2768, line 2: Forcing the "box" model to match concentrations at the measurement location, then "back" calculating what concentrations were 9 days previous really pushes the limits of credibility, considering the GROSS simplifications of this box model. Precise diffusion and mixing along the trajectory path will be impossible to specify for this study, and there are limitless possibilities to arrive at the "final" (observed) concentration if any additional known physical or chemical process were even crudely included. For example, the authors should have included even minor background diffusion of outside air into the parcel, which would contribute a significant dilution of the Chinese plume that would reduce concentrations 10-fold or more over these time

scales. If they ran their own particle trajectory model FORWARD in time from China, they would see this incredible dilution effect along a trajectory path. In order to compare with observations, dilution MUST be included in this parcel aerosol model.

6. pg. 2768, line 7, description of parcel model conditions. The physical characteristics of the parcel model MUST be specified in a figure. Is this really an "adiabatic" parcel? Is the water vapor mixing ratio held constant? If so, what is it? Please provide a graph of the temperature, pressure, and H2O mixing ratio throughout the 9 days.

7. pg 2768, line 16, changing parcel conditions. H2O mixing ratio will change only due to convective mixing into this "parcel" (which invalidates the premise of "parcel" model), or condensation and rainout. Both involve clouds. However, clouds are neglected, resulting in an inconsistent study. How and why are temperature and Rh changing in this study? The only way these properties can change is if there is some mixing, diabatic heating or other physical mechanism. Whatever is causing temperature or humidity to change will also modify the calculated size distributions. Either the parcel has to be considered adiabatic, and potential temperature and water vapor mixing ratio are held constant throughout the 9 days, or some diabatic effects have to be included that influence the size distributions of particles being simulated. If the adiabatic assumption is invoked, the parcel model becomes meaningless for interpreting measurements.

8. pg 2768, line 27, "sinusoidal" variation. This isn’t "semi-sinusoidal" since it goes to essentially zero for about 12 hours each day. A better description: "undergoes a secant-like daytime diurnal variation"

9. pg 2770, description of figs7-8: Why are there "skips" and other irregularities in this nucleation rate mid-morning? Why the bumps and other strange behavior on other plots? These must be numerical artifacts associated with discrete bins?

10. pg 2771, line 28: some awkward English. Should say "Particle concentration tripled". Also, the nucleation rates calculated by this model are known to be significantly higher than other models, and are also above or near the higher ranges of several

laboratory measurements (e.g. Hanson & Lovejoy 2006 J. Phys Chem A vol 110 p9525, doi:10.1021/jp062844w). The authors should do a study LOWERING their nucleation rates by a factor of 100-1000. This would probably show some sensitivity that isn't evident here.

11. Pg 2773, line 15: The paper would benefit from some further technical description. I've always been interested in how the "swelling" effects (absorption of water vapor, increasing the size of "dry" aerosol "cores") are accounted for in aerosol size distribution models. I assume the aerosol sizes noted in all figures of this paper are DRY aerosol sizes. Is this the case? If so, this should be noted in figure captions and in the text. The actual aerosol sizes in the air as it floats around at a time-varying Rh will grow and contract as it maintains its equilibrium with ambient water vapor, right? The "critical" activation CCN "diameters" shown in Fig. 10 cover a wide range of "dry" aerosol masses, and I think the "Diameters" shown here are "dry" diameters, right? If so, the note in the caption about sulfate H2O CCN is inappropriate. Please clarify whether these diameters are "dry" (pure condensed sulfate) or "equilibrium" (wetted aerosols, sulfate + water) diameters. My back-of-envelope calculation from classic cloud physics texts suggests that the equilibrium sizes of the "critical" activated CCN are about a factor of 10 higher than the sizes shown on this figure.

12. Minor comment: All figure captions first describe the figure on the right, then the left. Most readers read from left to right. Please describe figures from left to right.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 2763, 2009.

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