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Atmospheric Chemistry and Physics Discussions

Interactive comment on "A parameterisation of the soot aging for global climate models" *by* N. Riemer et al.

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The authors of this paper present an interesting study devoted to the aging process of soot particles in the atmosphere, and I complement the authors for taking up such an important and difficalt task This process is one of the key uncertainties governing the burden and effects of BC. Hence, the associated time scale is under scientific discussion. The authors present two simulations including a description of aerosol dynamics for a small region over Germany. Two cases were selected to address the time scale associated with BC aging. The simulations were used to derive a simple parameterization. The major result of the study is that during daytime the time scale is in the order of a few hours, whereas during the night a timescale of 10-40 hours is found. In addition the authors argue that nitrate plays an important role in the aging of BC (in winter).

In my opinion the paper contains interesting results and an insight in the processes

involved in the aging of BC. However, it is my feeling that the timescales derived in this paper depend strongly on the chosen conditions, which makes the derived parameterization uncertain. In addition, since nitrate is suggested to play an important role the parameterization presented has a limited applicable area, i.e. ammonium nitrate rich areas, and will not be representative for the entire globe. Therefore, I do not recommend to accept the paper in its present form for ACP and propose a major revision of the paper, away from developing a parameterization and towards focussing on the processes involved and that it gives an overview of the difficulties associated with the quantification of the aging time scale. The presented simulations could then be used as case studies to illustrate these. Below, I would like to discuss the paper in more detail.

Detailed discussion:

The following picture on the time scale is derived in the paper. In summer during the daytime the aging process is fast due to the effective photochemical formation and subsequent condensation of H2SO4. In the night time the aging time scale is in the order of 10-40 hours because coagulation limits the aging rate. In winter, ammonium nitrate is effectively formed during the day in the model, whereas H2SO4 formation is limited. Assuming that the authors distributed the NH4NO3 over the modes as function of the sulphate concentration in these mode, small amounts of sulphate condensed on the BC causes a lot of nitrate to be associated with the BC and aging goes fast, e.g. 1 hour. During the night sulphate and nitrate formation cease and like in summer coagulation limits the aging

Coagulation limited conditions:

The night time aging time scales are governed by coagulation. Therefore the time scale depends strongly on the background aerosol levels during the night (SO4, NO3, NH4 etc). In Figure 7 the composition of the aerosol is shown. The concentrations of sulphate in the model are very low. Moreover, BC to sulphate ratio is much higher than

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observed in rural locations in Germany, especially in winter when there is much more BC than SO4 around in the model. The low SO4 levels, which underestimate the average ambient levels by about a factor 4 to 10 for summer and winter respectively, may cause the life time of BC during the night to be considerably shorter than calculated. There is another issue related to the life time calculated conditions where the rate is limited by coagulation. In reality, more sources contribute to BC than diesel cars alone, although they contribute a large fraction of the emissions in densely populated areas. In addition, primary organic carbon is not included in the model, which also makes a large contribution to the accumulation mode aerosol, affection the coagulation rates. The uncertainties in the modeled concentrations is high, which make the derived life time of BC with respect to coagulation very uncertain.

Condensation limited conditions:

During the day in summer the life time is limited by condensation. As for SO4, the low background concentrations may also be valid for SO2, which means that H2SO4 production during the day may be underestimated in summer. If so, the higher H2So4 levels cause a higher total amount available for condensation. This would enhance the aging. However, higher background concentrations of SO2 and SO4 (as well as missing aerosol species) would also result in a more effective condensation on the mixed aerosol modes, slowing the aging process. The influence of higher background levels on the condensation of H2SO4 should be discussed.

Aging by nitrate formation:

With respect to the aging of nitrate I would like to raise two issues. The first governs the model assumptions to represent the process. The second is the influence of the hydrolysis of N2O5 on nitrate formation. The paper does not describe how nitrate is involved in the aging. Especially, the assumptions used to distribute the nitrate over the aerosol modes needs to be addressed. A method often found in the literature is that the nitrate calculated in the equilibrium module is distributed over the modes as function

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of the SO4 concentration in the modes. The validity of this assumption needs to be addressed. Moreover, such an assumption causes the aging rate to be dependent on the ratio of sulphate in the hydrophobic BC mode to the sulphate in the internally mixed modes. Hence, given the uncertainties in the modeled SO4 levels I wonder how accurate these rates are and if there is not an artificial aging going on due to the assumption on the nitrate distribution. It is stated that ammonium nitrate in winter is formed during daytime (page 9). However, previous studies by the authors show that during the night time nitrate or nitric acid is effectively formed due to the hydrolysis of N2O5 on aerosol surfaces. Moreover, since photochemistry is inactive during winter this process probably accounts for the majority of the nitrate formed in the atmosphere. Therefore, I would expect that the influence of nitrate would be predominantly during the night, in winter but to a lesser extent also in summer. This is in contradiction with the statements in the paper. This issue should be discussed and resolved.

Applicability parameterization:

If nitrate indeed plays an important role in the aging of BC, the applicability of the derived parameterization is limited to those parts of the world where ammonium nitrate levels are substantial. This feature should be discussed.

Influence of clouds:

The winter scenario used in this study is not typical for a pollution episode in western Europe. Westerly winds are associated with cloudy and rainy conditions. The cloud and wet deposition processes as well as cloud chemistry (SO2 to SO4) associated with these conditions are not included in the model. To my opinion a discussion of the influence of cloud processes on the aging time scale should be included in the paper.

Conclusion:

The aging rates presented in the paper are associated with very high uncertainties since they depend strongly on the chosen casesTo my opinion the proposed ageing

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scheme is not generally applicable, and do not improve the description of the aging process in less detailed models. However, the study performed by the authors reveals interesting and publishable results. It shows the variability associated with the aging rate. Too my knowledge the importance of nitrate is highlighted for the first time. Furthermore, the study was performed with a state of the art model. Hence, I do not think that the study can easily be improved since the choice of the case(s) would determine the results. Therefore, a systematic discussion of the results, the sensitivities and especially the uncertainties in key assumptions would be a valuable contribution to the literature. In addition to the issues already discussed by the authors, the issues in my review should certainly be included in a discussion.

Minor remarks:

In the method description the initialization and boundary conditions of the model setup should be described. In the method description and further on page 6 it is stated that H2SO4 and Organics are the condensable species. However, how nitrate is involved in the aging is not explained. Especially, the assumptions used to distribute the nitrate over the aerosol modes needs to be addressed.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 2089, 2004.