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Atmospheric
Chemistry
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Discussions

Interactive comment on "Importance of the organic aerosol fraction for modeling aerosol hygroscopic growth and activation: a case study in the Amazon Basin" *by* M. Mircea et al.

Anonymous Referee #1

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General Comments

The work presented by Mircea et al., addresses a very important topic, which is highly relevant to the atmospheric chemistry and physics community, i.e. the importance of the organic aerosol fraction for modeling aerosol hygroscopic growth and activation. The authors show how the knowledge of water-soluble organic compounds (WSOC) and the associated physical and chemical properties (e.g. solubility, surface tension, molecular composition and degree of dissociation of WSOC) affect the hygroscopic growth and activation of the aerosol obtained during the SMOCC activation field exper-

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iment carried out in Rondônia, Brazil, over a period encompassing the dry (biomass burning) season to the onset of the wet season (September to mid-November, 2002). The authors derive new parameterizations for the CCN spectra, which take the associated physical and chemical properties into account.

The authors conclude that detailed knowledge of the chemical composition of the organic soluble fraction and the related properties, such as solubility, is mandatory to describe appropriately the aerosol water uptake in sub- and supersaturated regimes for aerosols containing a large amount of organic matter. They further conclude that the agreement between the predicted and measured DGFs is substantially improved with respect to the case where the WSOC is considered infinitely soluble, if the limited solubility of organic model compounds is taken into account, and, that the uncertainties in the definition of organic model compounds related to the solubility and the molality in solution have a greater impact on DGF prediction than on CCN prediction.

I recommend publication at ACP after the authors have addressed all specific comments.

Specific Comments (in addition to those given by referee 2)

(1) Line 10-14, page 5256. Citation unclear:
The approach of Zhou et al. (2002) and Rissler et al. (2004) applied to data from the SMOCC campaign (Vestin et al., 2005 2) showed a tendency to underestimate the measured CCN concentrations with increasing supersaturation, while Zhou et al. (2002) and Rissler et al. (2004) showed good agreement between predicted and measured CCN.

Should read (?):
..., while Roberts et al. (2001, 2002) showed good agreement between predicted and measured CCN.

(2) Line 28, page 5256:

There is no need to introduce a modified Raoult's term that takes into account the contribution of WSOC. It is sufficient just to account for the additional number of moles from WSOC in the summation. I therefore suggest omitting "modified Raoult's term" through out the text. See comment (5) on Eq. (1).

(3) Line 11-13, page 5260:
Please include the following reference and change to:
The concentration of inorganic ions (NH+4, Na+, K+, Ca2+, Mg2+, Cl-, NO-3, SO-2 4) was determined, besides real-time measurements of ammonia, acidic trace gases and water-soluble inorganic aerosol species (Trebs et al., 2004), by ion chromatography (IC) as described in Fuzzi et al. (2005).

Trebs, I., F. X. Meixner, J. Slanina, R. Otjes, P. Jongejan, and M. O. Andreae, Real-time measurements of ammonia, acidic trace gases and water-soluble inorganic aerosol species at a rural site in the Amazon Basin, Atmos. Chem. and Phys. 4, 967-987, 2004.

(4) Line 16-19, page 5261:
Reformulate second sentence to:
"Therefore, the equilibrium theory of Köhler (1936), which describes the equilibrium size of a droplet as a function of water saturation ratio, can be used to determine the DGF and CCN spectrum."

The so called Köhler equation only implicitly depends on the chemical composition through the total number of moles of solute (n$_s$) and the associated number of moles of water (n$_w$), as well as the surface tension of the (mixed) solution (σ). However, identical Köhler curves can be obtained for different chemical compositions, if these compositions yield the same number of moles and surface tension.

This can be readily seen from the most primitive form of the Köhler equation, which can be readily derived from thermodynamic principles, i.e.

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$S=p/p_s=a_w \exp(2\sigma V_m/RTr)$, with $a_w=f_w x_w$, and $x_w = n_w/(n_w + n_s)$.

The required information about the composition is limited to the water activity (a_w) and surface tension (σ) of the growing droplet. V_m is the partial molecular volume of water. The water activity (a_w) depends only on the mole fraction of water (x_w) and a correction factor (f_w, known as the activity coefficient), which accounts for non-ideality of (concentrated) solutions, either due to ion-ion interactions or (the unknown degree of) dissociation of the electrolytes.

Note that the relation between droplet radii and the required equilibrium saturation or supersaturation (respectively the increase in vapour pressure) was already expressed by the two equations of Thomson (1824-1907), later Lord Kelvin and that from this relation it can easily be seen that for a given amount of solute the principle characteristics of the vapour pressure is proportional to the droplet radii (which however depends on S), i.e:
$p(r)/p_0-1 = const_1\ 1/r - const_2\ 1/r^3$

(5) Eq. (1), page 5262:
According to (2) the additional summation over organic compounds is not needed, as the physical properties (and variables) are the same. One term is sufficient. The summation can also account for WSOC (e.g. sum over i, with $i=i_{inorg}+j_{org}$).
Please change Eq. (1) accordingly.

(6) Line 14, page 5263:
Time averages should be treated with care, since they are especially crucial for saturation relative humidities; the average values are then lower than the actual values and might therefore not allow for CCN activation. Averages of CCNs, etc. should be fine however.
Please clarify what was averaged and what was used as model input.

(7) Line 25, page 5263:
How relevant are other potassium compounds in addition to potassium sulfate? Are

there any indications for either potassium or ammonium nitrate in the fine fraction? In case not, briefly mention why.

(8) Line 23-24, page 5268:
You state that "the solubility of compounds is a potential key parameter for modeling aerosol growth at 90% RH". You have mentioned solubility already four times, but not explained how you account for the solubility in your model. Do you simply mean the difference between the droplet (D) diameter and the diameter of the insoluble aerosol residue (DN) in Eq. (1)? Please clarify.

(9) Line 10-12, page 5270:
You state that "the knowledge of the soluble and insoluble aerosol fractions may explain why some large aerosol particles grow less than much smaller particles", which is actually well known. The question is to which extend consists a droplet of an insoluble core and what is its diameter. Please discuss how to estimate the insoluble aerosol fractions, i.e. DN for modeling.

(10) Line 20, page 5270:
Typo, or reference missing for "(citation)" ...

(11) Line 26-27, page 5271:
Sentence not complete. Please reformulate.

(12) Line 8-11, page 5276:
This conclusion directly follows from the primitive form of the Köhler equation; see comment (4).

(13) Line 12-13, page 5277:
You state "Such parameterizations can be further used in large-scale models to simulate the cloud formation and evolution during dry, transition and wet periods."

Not really, because not only the parameter space is too small but also because of missing feedbacks between aerosol/CCN formation and cloud formation. The parameters (required for Eq. 3) would be needed for various regions and conditions, which actually require detailed knowledge of emissions of primary particles and secondary processes, thus requiring a more rigorous thermodynamic treatment. However, in the near future the CCN predictions might become feasible also in large-scale models based on the latest thermodynamic models that are recently developed and published.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 5253, 2005.