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Interactive comment on "Modeling the chemical effects of ship exhaust in the cloud-free marine boundary layer" *by* R. von Glasow et al.

U. Pöschl

ulrich.poeschl@ch.tum.de

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The study by von Glasow et al. (Atmos. Chem. Phys. Discuss., 2, 525-575, 2002) is a very interesting attempt to resolve the physicochemical processes involved in the aging of ship exhaust plumes in the marine boundary layer. It strives to account also for processes occurring on short time-scales (seconds to hours), which are often neglected in the modelling of large-scale atmospheric chemistry.

The authors have applied a detailed photochemical box model and conclude that gas phase processes in the early stages of an exhaust plume, which are characterised by high concentrations of the emitted species, can significantly influence the overall impact of emissions. Moreover, they find that heterogeneous chemistry on background aerosol particles has a significant effect on gas phase chemistry. On other hand, they

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find only very small effects of freshly emitted combustion aerosol particles, which they separate into "partially soluble combustion particles" (organics and sulfate) and "soot particles".

I appreciate the clear messages of the paper, and following up on the Referee Comments (Atmos. Chem. Phys. Discuss., 2, S176-S179, 2002; Atmos. Chem. Phys. Discuss., 2, S270-S271, 2002) I think that the study is highly relevant for global atmospheric modelling and future research on the evolution of emission plumes.

For the modelling approach, results, and conclusions on aerosol chemistry, however, I would like to add a few caveats and suggestions for improvement:

Soot, which is technically defined as the black solid product of incomplete combustion or thermal decomposition of hydrocarbons, has no well defined chemical composition. It consists of graphite-like material (operationally defined as black or elemental carbon) and a significant fraction of organic compounds. The actual fraction and molecular structure of the organics contained in soot particles are highly variable and depend on combustion engine and fuel. Moreover semi-volatile species contained in the gas phase of an exhaust plume (organics, sulfuric acid, etc.) will not only lead to the formation of secondary particles but also condense onto primary soot particles. Thus the distinction between "partially soluble combustion particles" and "soot particles" appears questionable and should be regarded as a very rough approximation, even if it may be a practicable way of representing aerosol particle emissions from ships.

The reduced reactivity of freshly emitted combustion aerosol particles (soot, organics, etc.) relative to aged background aerosol particles seems a little surprising and might be due to incomplete representation of heterogeneous chemistry in the applied model. Heterogeneous processes occurring on the surface and in the bulk of aerosol particles are in general poorly characterized up to date, and there is a lack of reliable and representative measurement data and kinetic parameters. In particular, the time-dependence of uptake coefficients is often neglected or not understood well enough to allow an accurate description of the chemical evolution of an aerosol system on a time scale ranging from seconds to hours and days.

By now it has been widely recognized that one cannot simply take the next best uptake coefficient that has been measured in a laboratory experiment performed under certain conditions and on a certain time-scale, and use this value under atmospheric conditions (as has been done too often in the past). However, there is still a lack of clear distinction between surface and bulk processes and between (reversible) physical uptake and (irreversible) chemical reaction. Especially for solid and highly viscous liquid particles, surface processes including reversible adsorption and surface specific reactions are of major importance. Only after deconvolution of the physical transport processes (gas phase diffusion, adsorption, surface-bulk transfer and bulk diffusion) involved in the overall heterogeneous reaction, one can accurately describe the time-dependence of uptake coefficients and the chemical passivation of particles by consumption of reactants or potential catalytic sites (e.g. Pöschl et al., J. Phys. Chem. A, 105, 4029-4041, 2001, and references therein). Along these lines also the use of the terms "(reactive) uptake coefficient", "(mass) accomodation coefficient", "reaction probability", "sticking coefficient", etc. has been largely inconsistent.

It is of course not the task of a ship exhaust plume modelling study like the one discussed here, to resolve general problems in the description of atmospheric aerosol particle composition and reactivity. Nevertheless, I would suggest to consider the following aspects upon revision of the manuscript:

1) Point out more explicitly that the model results with respect to combustion aerosol particles (soot, organics, etc.) are highly uncertain due to a lack of reliable and representative input data (particle composition and reactivity).

2) Use the term "(effective) uptake coefficient" and symbol γ instead of the term "accommodation coefficient" and symbol α for the heterogeneous chemistry model input parameters described on pp. 535-536.

3) Outline how the input parameters were actually used to calculate the effects of heterogeneous chemistry on aerosol particles (rate equations).

Suggestion 2) is based on the assumption that the authors have calculated the loss rate of a given gas phase species (molecule cm^{-3} s^{-1}) by multiplying its average gas phase concentration (molecule cm^{-3}) with its "accommodation coefficient" and mean thermal velocity (cm s^{-1}) divided by 4, and with the aerosol particle surface area concentration (cm^{2} cm^{-3}).

Under these conditions it would be more appropriate to use the term "(effective) uptake coefficient", which does not discriminate between surface or bulk and physical or chemical processes, rather than the term "(mass) accommodation coefficient", which usually refers specifically to the physical transfer of a species from the gas phase to the (bulk) condensed phase. An "effective uptake coefficient" would implicitly take into account the effects of gas phase diffusion. It stands for the ratio of the flux of net uptake (molecule cm^{-2} s^{-1}) to the average gas kinetic flux (molecule cm^{-2} s^{-1}), i.e. the collisional flux obtained by multiplication of the average gas phase concentration with the mean thermal speed divided by 4. If the model explicitly described the effect of gas phase diffusion, it would be appropriate to use the term "uptake coefficient" defined as the ratio of the net uptake flux to the actual collisional flux to the surface. For a convoluted process including uptake of a reactive species and release of a reaction product back to the gas phase (i.e. heterogeneous chemical conversion), it would be suitable to use a term like (effective) reaction probability or conversion coefficient.

In any case it would be desirable to refine the applied terminology for aerosol chemistry, and to outline how the effects of heterogeneous reactions are actually calculated from the input parameters.

Interactive comment on Atmos. Chem. Phys. Discuss., 2, 525, 2002.