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Atmospheric
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Discussions

Interactive comment on “A Lagrangian model with simple primary and secondary aerosol scheme 1: comparison with UK PM$_{10}$ data” *by* K. M. Emmerson et al.

Anonymous Referee #2

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This paper presents a modelling study in which a Lagrangian model is updated to include a simple representation of emissions and secondary formation of airborne particulate matter. The model is tested by its ability to simulate PM10 concentrations observed at one urban and two rural sites in the UK, using data for selected months.

The paper addresses a topic of high importance, and studies of this type in which ambient aerosol measurements are used to test and validate model performance are definitely required to allow assessment of understanding of aerosol sources and how they should be represented in atmospheric models.

Although this paper aims to do this, the "simple" treatment developed by the authors does indeed contain many simplifications, assumptions and shortcomings, and apparently fails to take account of some relevant information which has become available in recent years. It is maybe not surprising, therefore, that the simulated PM10 concentrations fail to match those observed, generally being significantly underestimated. The results show that the simple treatment is inadequate, and do serve to demonstrate that the successful representation of (in particular) secondary organic aerosol formation is a highly complex and challenging problem. However, the discussion of those aspects of the treatment which require improvement is not satisfying, particularly in view of a number of published studies in recent years which are not cited.

The paper therefore requires some considerable improvement before it should proceed to a full ACP publication. Although I recognise that it is probably unfair to request revised calculations following significant modifications to the treatment of a number of elements of the model (given that the authors only claim a simple treatment), the extent of the simplifications within the context of the literature must be better discussed and assessed, and indeed the simplifications themselves need to be better described. In this respect, the citations for key aspects of the emissions, chemistry and gas-to-aerosol transfer (where more detailed justification and description are presumably available) are largely to reports or papers which are not easily available to the wider scientific community. The series of comments listed below identifies some specific points that need to be addressed.

Comment 1: speciation of organic emissions: The report "PORG (1997)" is cited as the source of the speciation of anthropogenic non-methane VOC applied. That report does not contain a full emissions inventory, but only a listing of emission totals for a limited series of light hydrocarbons. Not only is this incomplete from an SOA-precursor point of view, but even this list significantly exceeds those for which the chemistry is actually represented in the CiTTyCAT model, according to Evans et al., (2000) (and allowing for the inclusion of "xylene" chemistry as part of the present study). Given that it was therefore necessary to lump emissions into the limited series of representatives in the chemistry scheme, it is not clear why the authors did not make use of the

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comprehensive NMVOC speciation reported by the UK NAEI, which is updated each year and freely available on the internet. This would have allowed potentially important SOA-precursor compounds, such as the full suite of aromatics, to have been represented more appropriately, rather than the contributions of most of them being omitted (which is apparently the case).

In the case of the biogenic emissions, apart from the obvious simplification of constant emissions density over the UK, it is not clear why only 50% of the monoterpene emissions were represented as alpha-pinene. Given that monoterpenes are isomeric hydrocarbons which are all reactive and are generally SOA-precursors, it would seem that (in the absence of available chemistry for other terpenes) the full monoterpene emissions should have been represented as alpha-pinene. It appears, therefore, that the emissions of both anthropogenic and biogenic SOA-precursors are probably under-represented in the present study.

Comment 2: organic chemistry: The new chemistry included for "xylene" and alpha-pinene is attributed to a report of Jenkin (1996), and is stated to be a subsection of the Master Chemical Mechanism (MCM) reported by Jenkin et al. (1997). The MCM development paper of Jenkin et al. (1997) specifically treats only the degradation of non-aromatic VOC, and does not include any monoterpenes. It therefore seems unlikely that mechanisms appearing in Jenkin (1996), as used in the present study, are a subsection of the MCM.

The description of alpha-pinene chemistry suggests that OH-initiated oxidation is the major route to pinonic acid formation. However, this must be highly dependent on the concentration of NOx (favoured at low NOx), whereas the pinonic acid formation from the ozone-initated chemistry does not depend on NOx concentration.

It is stated that "xylene and toluene have reasonably well established reaction mechanisms". The mechanisms for aromatic hydrocarbons have been notoriously difficult to elucidate and validate, and are even now not fully understood (e.g. Calvert et al., 2002 and references therein). They were certainly not well established at the time of the citations given in the present study.

Comment 3: gas-to-aerosol transfer: The process of SOA formation is assumed to involve one condensable product formed from each of toluene, xylene and alpha-pinene, by a mechanism requiring supersaturation. This is an inadequate and out-of-date representation. General understanding from the results of chamber and theoretical studies is consistent with SOA formation involving multiple products, and with species being associated with the aerosol phase when the gas phase concentrations are substantially below saturation. The classic work of Odum et al. (1996) demonstrated that chamber SOA yields could be interpreted in terms of absorptive partitioning of notional products into a condensed organic phase, following the theory of Pankow (e.g. Pankow, 1994; Seinfeld and Pankow, 2003). Subsequent work using estimated parameters for real (i.e. observed) products of alpha-pinene ozonolysis confirmed the applicability of the approach, but required product vapour pressures to be artificially lowered to account for the observed yields of SOA (Cocker et al., 2001). This and more recent work (e.g. Jang et al., 2002; Kalberer et al., 2004) has shown that condensed phase reactions assist the transfer of material from the gas phase. Based on current understanding, therefore, the representation of gas-to-aerosol transfer used in the present study would be expected to underestimate SOA formation.

Other comments

Page 3134, HNO3 formation: The discussion of sources of HNO3 needs to make it clear that reaction (4) is a gas phase reaction generating gaseous HNO3, whereas reaction (3) is mainly an aerosol surface reaction generating nitrate aerosol directly.

Page 3134, H2SO4 formation: Presuming that reactions (6) and (7) are the only fates for HSO3 and SO3 represented in the mechanism (they usually are), the rate determining step in H2SO4 formation is reaction (5). Contrary to the statement made, the inclusion of a further heterogeneous reaction of SO3 with liquid water will have no effect

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on the H2SO4 formation rate.

Page 3136, lines 16-20: Secondary aerosol will mainly "condense" onto existing aerosol. The choice of different deposition velocities for the primary and secondary aerosol components needs to be better justified and explained (indeed the deposition velocity for primary aerosol is not actually given).

Page 3136, model calculations: There is no clear statement about the frequency of the model calculations, although from the figures it appears that only one trajectory per day was considered. If this is the case, the arrival time should be given, and similar information should be provided concerning the observational data, i.e. is each observation a daily average, or an hourly average for the arrival time of the calculation? Given the simplicity of the model (i.e. it can be run quickly), and the frequency of the observational data, it is a shame that a greater arrival frequency was not considered.

Page 3136, benchmark composition: It seems inappropriate to use the same benchmark PM10 composition for the urban site and the rural sites, because the primary/secondary ratio must be greater at the urban location.

Page 3137, line 24: Rather than to identify "pinonic acid" as a specific contribution to the aerosol, it would seem more appropriate to call this the "secondary biogenic component", given that pinonic acid is (presumably) only a representative condensable species.

References not already cited

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