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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Illustrating the benefit of using hourly monitoring data on secondary inorganic aerosol and its precursors for model evaluation" *by* M. Schaap et al.

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Dear Editor, reviewers,

Below we like to respond to the review of manuscript ACP-2010-229 entitled "Illustrating the benefit of using hourly monitoring data on secondary inorganic aerosol and its precursors for model evaluation" by Martijn Schaap, Rene Otjes and Ernie Weijers. We would like to thank both reviewers for their time and effort reviewing the paper. We feel it has improved as a consequence of the constructive comments.

In the appendix we have listed all reviewer comments and addressed them.

We hope the revised manuscript is acceptable for publication and lives up to the standards of ACP.

Yours truly,

Martijn Schaap

Response to Referee #1 (Anonymous)

Introduction: Here you only describe the nitrogen SIA species as important, however sulphate is in many cases (episodes) the dominant SIA and it should be mentioned as well.

In the first sentence we address SIA as a whole including sulphate. In the next sentences we stress the regional importance of nitrate in north-western Europe. Though the reviewer is right that in some episodes sulphate may dominate, long term measurements indicate that nitrate generally dominates over sulphate in western Europe. We have added an extra reference "Weijers et al., 2011" that shows this for the Netherlands. To incorporate the sense that sulphate should not be forgotten we have modified the second sentence to read: "While in other regions sulphate might be more important, nitrate is the dominant component in western and central Europe (Schaap et al., 2002)."

When referring to the EMEP programme it is better to use a more official reference than an unpublished paper (Aas et at 2010), e.g. the EMEP monitoring strategy (ECE/EB.AIR/GE.1/2009/15) may be more appropriate.

We have added the suggested reference and kept the reference to Aas et al. (2010) as requested by Reviewer 2.

Experimental: Why is only nitrogen and sulphur species mentioned? The MARGA/GRAEGOR system also allow measurements of HCl , sea salts and base cations. I assume it is because the model does not include all these species? Nevertheless if more complete measurements has been undertaken it is important to men-

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tion. It could also be valuable to give an average concentration of all the species (in table 1) to illustrate the relative importance of i.e sea salt and base cations. This information is important when you want to discuss the importance of course nitrate (and sulphate).

The nitrogen and sulphur species were only mentioned as the paper did not consider the other species. The reviewer is right that more components are available, i.e. Na, Cl, HCl, HONO and SO2. However, the model does not include all these species (Cl, HCl). In the text (pg4) we have now mentioned the other species (pg 4) and added the statistics on these species in table 1.

Further the inlet system of the MARGA/GRAEGOR allows separating between PM10 and PM2.5. Why has the PM10 been used when the model only (?) includes fine particles? Is it because there is not a full year of PM2.5 measurements? But if there are periods with both PM10 and PM2.5 it would be nice to include some discussion of the difference to illustrate the difference between fine and coarse SIA.

In the current study the MARGA was used for PM10 only and no PM2.5 data were obtained. The reason was to keep the precision of the instrument as high as possible and, considering the long operation time, to reduce the amount of data gaps as the two sampling boxes would function as each others back-up. We have included this information in the paper. So, unfortunately, no analysis on fine and coarse nitrate can be given based on the MARGA data at hand. Note, that the model does contain coarse mode particles, i.e. sea salt and primary PMcoarse. However, the heterogeneous reaction of nitric acid with sea salt and dust are not included in the model, so no coarse nitrate formation occurs in the model.

Model simulation: It is only mentioned that coarse nitrate is not included. What about coarse sulphate?

Only primary coarse mode sea salt sulfate is included in the model. As given above, no secondary coarse mode sulphate is included.

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For the ammonia emissions, is it included any diurnal variations, or how is this (if it is) addressed in the model?

Ammonia emissions do have a prescribed seasonal and diurnal cycle and is discussed in detail in Schaap et al. (2004b). We have added this information to the text: “Seasonal and diurnal patterns were used to downscale the annual emission totals to hourly emissions for all primary components including ammonia as discussed in Schaap et al. (2004b; 2008).”

Results: Even though SO2 and NO2 is not mentioned, I assume these are measured at Cabauw as well. How well is these primary species addressed in the model?

SO2 concentrations are overestimated by the model, see e.g. Barbu et al. (2008). This may be due to a too slow conversion, but mixing issues, emission height distributions are not to be excluded. The secondary components are much less sensitive to these aspects. In case of NO2, the model is able to capture the gradients and concentrations levels over the Netherlands and NW-Europe quite well. Model results have been compared to in-situ data as well as OMI-NO2. Separate publications are in preparation.

The peak concentrations of sulphate in spring and winter are these sea salt related? The data has not been corrected for sea salt sulphur. Or can it be other coarse sulphate not included in the model? An ion balance test of these episodes may give some indications on this.

The episodes with high sulphate concentrations are measured in continental air masses, verified with back trajectories. Furthermore, sodium concentrations are very low during these episodes. The continental nature of the air masses is included in the text:”For example, the four periods with continental air masses containing sulphate concentrations above 10 μg/m3 are not captured by the model and cause the lower correlation compared to nitrate”. Primary sea salt contribution to sulphate was estimated to be 5% on average based on sodium as a tracer for sea salt and sea water composition. This contribution is much lower than the observed model to measurement

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bias. This information is given in the discussion on coarse mode nitrate and sulpfate that was added to the discussion section.

Discussion: You state that the regular Dutch measurements underestimate the SIA. First of all that is a bit strange statement/observation for sulphate since these measurements shouldn't be biased, though for NH4NO3 it is relevant. However this is in contradiction to the results seen in figure 1 where the regular measurements are in good agreement with the MARGA/GRAEGOR system.

The regular Dutch measurements before 2008 were obtained with a dedicated LVS system. These data are mentioned here and show the large difference. There is a separate report on this issue now as we refer to this work (Hafkenscheid et al., 2010). The filter data used here in Figure 1 were also obtained in the same BOP campaign and are described in detail by Weijers et al (2011). Cabauw is not a station at which SIA is monitored in the Netherlands, much to our disappointment! Some remarks clarifying the difference between lvs measurements, and Marga/PM10 filter measurements have been added.

In the strategy discussion it would be nice to include how your recommendations relate to other monitoring obligations/strategies in Europe, i.e. in UNE CE and EU.

We have mentioned the link to the EU-PM reference method. A complete strategy fulfilling all aims of all protocols and obligations is much more elaborate and outside the scope here. It may require additional sacrifices to meet available budget

Response to Referee #2 (E. Nemitz)

Major Scientific Comments Contribution from coarse aerosol The main problem of the intercomparison appears to me that this study compares model results for the inorganic fractions that are expected to be contained in PM1 with measurements of PM10. The latter contain coarse nitrate (balanced by sodium and, possibly, calcium) as well as sea salt sulphate. Although this is mentioned in the paper, the magnitude of the

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problem and the consequences are insufficiently explored and discussed throughout. The authors should investigate the charge balance in the measurements to investigate the importance of NaNO3. For example, in Dec the model appears to get the NH4+ concentration about right, while nitrate and sulphate are underpredicted. This implies a difference in the charge balance between model and measurements. The authors cite a report by Weijers et al. (2010), which incidentally I failed to find at www.pbl.nl, for the importance of coarse nitrate at this site, but I am aware that the MARGA measured, at least for some time, aerosol composition of PM2.5 and PM10 (as pointed out by Referee 1) and additional campaign-based measurements are available from a MARGA sizer and a MARGA / Aerosol Mass Spectrometer comparison. Thus, the authors should be able to quantify the importance of the coarse components at this site. Similarly, the authors need to discuss the potential effect of internal vs. external mixing on the equilibrium. For example, the higher NO3a measured during daytime in July (Fig. 7) may be due to the contribution of non-volatile NaNO3.

It is unclear to me, why the model does not treat coarse aerosol in its current form as these authors appear to have used the LE model before, e.g. to simulate Na in the NL (Manders et al., 2010).

Other components As pointed out by Referee 1, the MARGA provides measurements of other compounds, such as Na, SO2 and HCl (as mentioned on P 12346, but then not further used in the text). These time-series should further help elucidate the reasons for model / measurement discrepancies. For example, much of the HCl is thought to be derived from reaction of HNO3 with seasalt. Because HNO3 loss to sea salt is not treated in the model, the modelled HNO3 concentration may agree better with the sum of measured HNO3 and HCl? Performance for SO2 may shed light on the reasons why sulphate may be underestimated? The Na concentration should enable coarse sea salt sulphate to be quantified?

Boundary layer height. How good is the description of the boundary layer height in the model? If the model gets the baseline concentrations about right, but underpredicts the

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high episodes, this may be because the vertical resolution in the model is insufficient or the boundary layer height in the model is overestimated. The tall Cabauw tower and profiler measurements during the intensive campaigns at this site should provide information that could be used to investigate this influence. At the moment, the authors do not draw conclusions on weather model. measurement discrepancies are most likely related to the coarse mode, prediction of the boundary layer height, absolute and relative temporal pattern in emissions, the thermodynamic equilibrium model or kinetic constraints on evaporation / condensation. By taking into account further information on the importance of the coarse mode (see above), other compounds and the boundary layer height, the authors may be able to constrain the options further.

Local ammonia sources. If the site is affected by local ammonia sources (P12354, L4), this surely would affect the other concentrations also, if the equilibrium is as fast as is assumed in the model. What would be the consequences? By the way, NH3 concentration can be very variable in urban environments, due to kerb site increases related to emissions from catalytic converters.

Link to other EMEP work. I agree with Referee 1 that a further reference is needed to the EMEP work. However, the proposed reference to the Aas et al. (2010, in prep.) paper should not be dropped, because it integrates the work presented here with other work in the Special Issue. In fact, the authors may want to add links to some further papers in preparation for the EMEP Special Issue, such as Nemitz et al. (2010a, b), Twigg et al. (2010) as well as Mensah et al. (2009) and her paper in preparation for the APCD EUCAARI Special Issue. Is the long-term concentration time-series from the MARGA at Cabauw being written up separately? It would be useful to provide details on this.

Inconsistency with earlier Dutch model validation exercises. The authors fail to explain why the results from this study are inconsistent with the earlier work of Manders et al. (2009). Is this due to the characteristics to the Cabauw site, the measurement periods or instrumental issues? As pointed out by Referee 1, sulphate should not be lost from

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the filters.

The reviewer raises a number of important issues in his review. The modeling of particulate matter and secondary inorganic aerosol in particular is complex and dependent on many factors. The reviewer says “measurement discrepancies are most likely related to the coarse mode, prediction of the boundary layer height, absolute and relative temporal pattern in emissions, the thermodynamic equilibrium model or kinetic constraints on evaporation / condensation. By taking into account further information on the importance of the coarse mode (see above), other compounds and the boundary layer height, the authors may be able to constrain the options further.” We like to stress that this list is still limited. Additional processes that may be of higher importance than listed by the reviewer include cloud or multi-phase chemistry, particle dry deposition, neglecting of ammonia compensation point, effective emission height of large point sources, etc. The purpose of this paper is not to evaluate all these issues in detail. It would take the attention away from the message of the paper. Therefore, we have addressed one process, the thermodynamic equilibrium, in more detail. The reason is that the MARGA provides unique data for this issue. Moreover, a thorough evaluation should include at least several and preferably many stations with supporting data from additional networks and species. Hence, the full analysis is out of scope of this paper. Such analyses are ongoing and several publications are in preparation focusing on the separate issues. We have further highlighted this point in the second paragraph of the discussion. As the equilibrium is an important part of the paper, we have addressed the issue of coarse nitrate formation in the MS. We admit that the original MS only touches on this issue and that a more elaborate discussion was needed.

We have never included coarse nitrate as there was no means to verify the modeled concentrations. In the last years a few data sets with simultaneous PM2.5 and PM10 measurements provide a means to verify the model results. Hence, inclusion is planned in the near future. Note, that sodium nitrate may also be formed at the filter itself which complicates the evaluation.

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In the current study the MARGA was used for PM10 only and no PM2.5 data were obtained to keep the precision of the instrument as high as possible and to reduce the amount of data gaps. So, unfortunately, no analysis on fine and coarse nitrate can be given based on the MARGA data at hand. We have added a results section 5.3 dealing with the importance of sodium nitrate. In this paragraph we explore the potential amount of coarse mode nitrate and consider the molar balance between ammonium and SO4+NO3. A new figure were included to support the analysis and it was concluded that coarse nitrate may partly explain the observed gap during daytime in summer but not to the full extent. A significant role for sodium nitrate implicates that the indication that the modeled ammonium nitrate in winter is too stable is strengthened. In the discussion we put the findings in perspective of other studies in NL. The matter is complex and inclusion of the coarse mode nitrate in the model seems to be needed to fully address this issue.

Note that the MARGA-sizer was applied for sub-micron aerosol. Datasets with PM1 and PM10 are not available.

We have changed the reference to Weijers et al., 2010 to a new ACP paper on the BOP campaign by Weijers et al (2011).

Additional ammonia would shift the equilibrium (slightly) to the aerosol phase. Note that the analysis of the equilibrium module uses the measurements as input. In case of a non-equilibrium this and a kinetic constraint the quilibrium would “see” a lower concentration.

The inconsistency is due to instrumental issues as indicated in the text now.

Minor Scientific Comments Section 4.3. As pointed out later in Discussion, this approach (and the LE model) assume instantaneous equilibrium, while in reality there is a kinetic constraint on evaporation, while vertical exchange (including deposition) and subgrid variability linked to local sources helps to counteract the equilibrium.

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This is the reason why a follow-up study is conducted with a more detailed boundary layer model including chemistry. In that study both the mixing time scales and the time scale for attaining equilibrium are accounted for. We hope to finish this work this year.

Table 2. The correlation coefficient is insufficient for quantifying model skill and other metrices should be included (e.g. RMSE, bias).

Table 2 is directed to investigate the correlation between NO3 and SO4 with ammonium to see if sodium nitrate is important. This analysis is now expanded as discussed above. In the original paper we chose not to provide a detailed statistical evaluation as the data represent one station and we did not want deviate the attraction from the message that these kind of datasets are key to future model evaluation. We now provide the statistics but caution that for a single station statistical parameters can be misleading.

P12347, L16. A reference to the CBM-IV gas-phase module would be helpful.

For the modified the CBM-IV gas-phase mechanism we refer to the LOTOS-EUROS documentation (www.lotos-euros.nl).

P12348, L1. Was the standard version of the LE model used for this study or were any parameters already adjusted in light of the intercomparison results?

The standard operational version of LOTOS-EUROS v1.3 was used. There were no adjustments to the model code what so ever. Evaluations of model version v1.6 showed that this version yields nearly the same results as indicated here (1-2% differences). Hence, the evaluation is applicable to the versions of LOTOS-EUROS of the last 2-3 years.

Section 5.1. I agree with Referee 1 that the authors should not only make recommendations for Dutch monitoring, but also for the EMEP Measurement Strategy. In this context they may want to mention that long-term monitoring by MARGA has commenced at other European sites, such as Melpitz (EMEP/TFMM presentation), Helsinki, Auchen-

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corth (Twigg et al., 2010) and Harwell, UK.

Ofcourse, the same considerations apply to other countries in Europe. We have added a few lines to add this message and mention the new data sets that are becoming available. A recommendation for the complete monitoring strategy, on the other hand, is out of scope so we kept it at discussion of the strategy for SIA only.

Technical Comments The reviewer gave 13 hints to improve the English in the paper. All technical comments have been taken into account in the revised MS.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 12341, 2010.

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