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Illustrating the benefit of using hourly monitoring data on secondary inorganic aerosol and its precursors for model evaluation

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Abstract

Secondary inorganic aerosol, most notably ammonium nitrate and ammonium sulphate, is an important contributor to ambient particulate mass and provides a means for long range transport of acidifying components. The modelling of the formation and fate of these components is challenging. Especially, the formation of the semi-volatile ammonium nitrate is strongly dependent on ambient conditions and the precursor concentrations. For the first time an hourly artefact free data set from the MARGA instrument is available for the period of a full year (1 August 2007 to 1 August 2008) at Cabauw, the Netherlands. This data set is used to verify the results of the LOTOS-EUROS model. The comparison showed that the model underestimates the SIA levels. Closer inspection revealed that base line values appear well estimated for ammonium and sulphate and that the underestimation predominantly takes place at the peak concentrations. For nitrate the variability towards high concentrations is much better captured, however, a systematic relative underestimation was found. The model is able to reproduce many features of the intra-day variability observed for SIA. Although the model captures the seasonal and average diurnal variation of the SIA components, the modelled variability for the nitrate precursor gas nitric acid is much too large. It was found that the thermodynamic equilibrium module produces a too stable ammonium nitrate in winter and during night time in summer, whereas during the daytime in summer it is too unstable. We recommend to improve the model by verification of the equilibrium module, inclusion of coarse mode nitrate and to address the processes concerning SIA formation combined with a detailed analysis of the data set at hand. The benefit of the hourly data with both particulate and gas phase concentrations is illustrated and a continuation of these measurements may prove to be very useful in future model evaluation and improvement studies. Based on our findings we propose to implement a monitoring strategy using three levels of detail within the Netherlands.

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1 Introduction

Secondary inorganic aerosol (SIA) contributes a large part of the particulate mass in Europe (e.g. Putaud et al., 2004). From these components nitrate is the dominant component in western and central Europe (Schaap et al., 2002). Moreover, during episodes with elevated levels of particulate matter nitrate concentrations are particularly high compared to other components (e.g. Putaud et al., 2004). In western and central Europe nitrate is mostly in the form of the semi-volatile ammonium nitrate (ten Brink et al., 1997; Schaap et al., 2002), whereas sodium nitrate may dominate in northern and southern Europe (e.g. Pakkanen et al., 1999). As such, particulate nitrate may be an important contributor to the aerosol direct effect over western and central Europe (Schaap et al., 2007). Furthermore, ammonium nitrate and its gaseous counterpart's ammonia and nitric acid play a key role in acidifying and eutrophying deposition over Europe (Simpson et al., 2006). The understanding of the formation, transport and fate of these components is crucial to assess their role in air quality and climate change and to reduce their effects.

Within the EMEP programme the concentrations of secondary inorganic aerosol is monitored to assess the ambient concentrations and their trend in Europe (Aas et al., 2010). Furthermore, the data are used for evaluation purposes of the regional modelling work performed under the convention and within the member states (e.g. Simpson et al., 2003; Schaap et al., 2004b; Stern et al., 2008). Although observations are required on the partitioning of the nitrogen species between the gas and aerosol phase, only a limited number of sites provide this information. Instead, a large set of daily total nitrate and ammonium data is available. Hence, the evaluation of a regional model is hampered as the partitioning between the gas and aerosol phase is hard to verify (Schaap et al., 2004b). The partitioning information is highly relevant as the non-linear nature of ammonium nitrate formation and the resulting uncertainties associated with the modelling affect the source receptor matrices which are used to develop cost effective mitigation strategies for Europe (Fagerli and Aas, 2008).

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At present, available long-term monitoring data on SIA components are obtained with the standard 24-h sampling of aerosol by filtration and subsequent chemical analysis. This is a straightforward procedure; however, the volatile character of ammonium nitrate and the reactivity of gaseous nitric acid make these filtration methods prone to artefacts (Slanina et al., 2001). The volatilisation artefact depends on the filter material and ambient meteorological conditions like temperature and relative humidity (Chow, 1995; Hering and Cass, 1999). The evaporation artefact leads to serious underestimation of the ambient concentrations, especially during summer (Schaap et al., 2004a; Vecchi et al., 2009). Despite of the evaporation artefact the actual nitrate concentration can also be overestimated depending on the filter type. Cellulose type aerosol filters, commonly used in Europe, retain nitric acid which is thus assigned to aerosol nitrate (Schaap et al., 2004a; Keck and Wittmaak, 2006). Denuder filter packs can be used to overcome these artefacts but their use is restricted to few sites in Europe as they are costly to operate on a daily basis. To overcome these problems two systems have been developed recently in Europe, the DELTA (Tang et al., 2009) and the MARGA (Ten Brink et al., 2007; Thomas et al., 2009). The DELTA is a low cost sampler to monitor SIA components and its gaseous counterparts at a low (monthly) temporal resolution. On the other hand, the online but more labour intensive MARGA system is able to provide data for secondary inorganic aerosol and its gaseous counterparts on an hourly time resolution. Consequently, the interpretation of long term data sets obtained with the MARGA system may provide new insight in the variability and behaviour of the components. Our goal here is to illustrate the added value of hourly concentration data on secondary inorganic aerosols and their precursors for model validation. We also propose a new monitoring strategy using a combination of the traditional and new instrumentation for the Netherlands for the purpose of model evaluation. Note that an in-depth evaluation of the model and consequent model improvement is outside the scope of this paper and will be reported in the future.

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As part of the Netherlands Research Program on PM (BOP; Matthijsen et al., 2009) and continued within EMEP intensive campaigns (Aas et al., 2010) a MARGA instrument was operated at Cabauw for a full year (Sect. 2). The LOTOS-EUROS model was applied to simulate the study period at hand (Sect. 3). The model results are confronted with the measurement data (Sect. 4) to provide insight in the model performance. In Sect. 4 results on daily and seasonal variation are presented and implications discussed. Finally, we discuss a combination of instruments suitable to monitor the SIA components at different levels of detail for the purpose of model evaluation.

2 Experimental

A MARGA instrument was operated between 1 August 2007, and 1 August 2008, at the Cabauw Experimental Site for Atmospheric Research (CESAR). CESAR (Russchenberg et al., 2005; http://www.cesar-observatory.nl) is the focal point of experimental atmospheric research in The Netherlands. The site is located in a rural area in the central part of Netherlands (51.97° N, 4.93° E). It hosts a comprehensive set of instruments for meteorology, radiation as well as atmospheric chemistry, providing an excellent basis to perform additional detailed measurements.

The MARGA (Monitor for AeRosols and Gases, Applikon Analytical BV) was used to obtain a full year data set of hourly integrated data of both inorganic aerosol composition and the precursor gas concentrations. MARGA is the commercialized version of the GRAEGOR system (Thomas et al., 2009). Measured were the gases NH_3, HNO_3 as well as the inorganic PM components NO_3, SO_4, and NH_4 (see Table 1). The sampling part of MARGA comprises a wet rotating annular denuder (WAD) for the collection of the precursor gases (Keuken et al., 1988) and subsequently a steam jet aerosol collector (SJAC) for the collection of the particulate matter (Khlystov et al., 1995). The resulting sample solutions were collected in multi channel syringe pump and per hourly cycle on line analyzed by an anion- and a cation chromatograph by direct injection. Li^+ and Br^- were added as internal standard. With respect to the cations in the GRAEGOR only NH_4^+ was measured, by means of selective membrane diffusion.

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The MARGA was located indoor while a Teflon coated PM_{10} (URG) inlet was mounted on the edge of the roof. The sampled air was drawn through a 2-m PE (polyethylene, 1/4" o.d.) tube towards the inlet of the WAD. A shielding PVC tube was used to maintain the sample tube wall temperature at ambient conditions by means of fan driven airflow in the PVC tube annulus preventing condensational losses towards the inner wall of the PE tube. The sampling height was 4 m. The site was visited once a week for service purposes. After validation data coverage of 84% was acquired as an average over the total suite of components, varying from 79% for HCl to 87% for NH_3. The detection limit was about 50 ng/m^3 for each component.

The quality of the method depends on the inaccuracy of the instrument itself (<10%) (Erisman et al., 2001; Slanina et al., 200; Weber et al., 2003) and the effect of the inlet system. The wall loss on a similar PE tube was investigated. A set of 3 used inlet tubes of the Dutch Automated Ammonia network were internally rinsed and the effluents were analyzed. Compared to the annual averaged concentration losses for 2-m length were calculated varying from 1 to 2% for SO_4, HNO_3+NO_3, HCl+Cl, Na and Mg. For NH_3+NH_4 a loss less than 0.1% was found.

Another way to perform quality control is through comparison with independent co-located data. At Cabauw PM_{10} samples were taken and analyzed at a regular interval of two days a week (Weijers et al., 2010). In Fig. 1 we compare the results of the filter samples to the corresponding daily mean value of the MARGA for nitrate, ammonium and sulfate. The results of the two methodologies for these components compared reasonably well with regression coefficients varying from 0.9 to 1.1, off sets less than 1 µg/m^3 and correlation coefficients (r^2) between 0.8 and 0.9. The differences are well within the uncertainty ranges of the methods applied and we concluded that the MARGA system functioned correctly throughout the measurement period. The volatilization artifact from the quartz filters is not obviously seen, because the majority of the filters were sampled at temperatures below 20 °C. The artifact becomes significant above 20 °C (Schaap et al., 2004a).

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3 Model simulation

We used the regional air quality model LOTOS-EUROS v1.3 (Schaap et al., 2008) to simulate the secondary inorganic aerosol distribution over Europe and the Netherlands in particular. The LOTOS-EUROS model is a 3-D chemistry transport model aimed to simulate air pollution in the lower troposphere. The model has been used for the assessment of particulate air pollution in a number of studies directed to PM (e.g. Schaap et al., 2004c; Stern et al., 2008; Manders et al., 2009) and its secondary inorganic components (Schaap et al., 2004b; Erisman and Schaap, 2004; Barbu et al., 2008). The model has participated frequently in international model comparisons addressing ozone (e.g. van Loon et al., 2007) and particulate matter (Cuvelier et al., 2007; Hass et al., 2003; Stern et al., 2008). For a detailed description of the model we refer to these studies. Here, we describe the most relevant model characteristics and model simulation used in this study.

Secondary inorganic aerosol formation in the model is represented through different pathways. The oxidation of SO_2 to sulphate and NO_x to nitric acid is described in the CBM-IV gas phase chemistry routine. Heterogeneous N_2O_5 hydrolysis is described according to Schaap et al. (2004b). Besides the oxidation of sulphur dioxide by the OH radical, another important oxidation pathway, in particular in winter, is the formation of sulphate in clouds. Due to insufficient data on clouds in the meteorological input, this process is difficult to explicitly represent in the current model. Therefore, it is represented with a first order reaction constant that varies with cloud cover and relative humidity, similar to the approach followed by Matthijsen et al. (2002). The sulphuric acid formed is assumed to condense directly and is neutralised by ammonia. When sulphuric acid is completely neutralised excess ammonia (further denoted as free ammonia) can react with nitric acid under formation of semi-volatile ammonium nitrate. This equilibrium is very sensitive to ambient conditions and the precursor concentrations (Ansari and Pandis, 1998) and is calculated in LOTOS-EUROS using ISORROPIA (Nenes et al., 1999). Note that the model does not include the formation of coarse mode nitrate through reaction of nitric acid with sea salt or dust.

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The model was run for the full campaign period using ECMWF meteorology. Emissions are taken from the GEMS emission database (Visschedijk et al., 2007). The model was first run for the full European model domain on the 0.5° lon×0.25° lat grid. Next, a nested run over the Netherlands, from 3 to 9° E and from 49 to 55° N, on a 0.125° lon×0.0625° lat resolution, about 7×7 km^2, was performed. We have used the results of the nested simulation to compare to the detailed measurement data on both the SIA components and its gaseous counterparts.

4 Results

4.1 Seasonal variation

The observed and modelled seasonal variation is compared in Fig. 2. Note that the panels show a year from January to December meaning that the 2008 data are put before those of 2007 to arrive at a figure that is easier to interpret. For nitrate, ammonium and to a lesser extent sulphate the month to month variability is captured, albeit that the levels are underestimated. The underestimation is on average 35% for nitrate and sulphate, and 25% for ammonium. Nitric acid shows a modelled distribution with a pronounced summer maximum, which is to our surprise not found in the measured data. Such a summer time maximum is observed in other countries (e.g. www.emep.int; Zimmerling et al., 2000; Perrino et al., 2001) so the different observed behaviour in the Netherlands needs further consideration. Furthermore, the observed ammonia levels are higher than those modelled. As Cabauw is located in an agricultural area with stables nearby, local contributions may affect the analysis. Hence, the scale at which LE is aimed is too coarse to properly account for ammonia in source regions. Hence, the comparison for ammonia should be interpreted with care (see discussion).

The comparison between the modelled and measured daily values for SIA (Fig. 3) shows that the model is able to capture a large part of the day to day variability in the observed concentrations. The correlation coefficients values are about 0.6 for NO_3 and NH_4 and around 0.40 for SO_4. Closer inspection reveals that low and moderately

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high concentrations and variability appear well estimated for ammonium and sulphate and that the underestimation predominantly takes place at the peak concentrations. For example, the four periods with sulphate concentrations above 10 µg/m^3 are not captured by the model and cause the lower correlation compared to nitrate. Hence, the formation of sulphate during these episodes that occur mostly in the winter/spring needs to be addressed further. For nitrate the variability towards high concentrations is much better captured and a systematic relative underestimation remains.

We have calculated the correlation between the SIA components in the model and the observations, see Table 2. In the model the anions are strongly correlated to ammonium with coefficients of 0.98 for nitrate and 0.88 for sulphate. Nitrate is more strongly correlated to ammonium than sulphate is. Also, nitrate and sulphate are less strongly correlated than each of them with ammonium. This pattern is also found for the MARGA data adding to the conclusion that the model is able to reproduce many features of the SIA components. However, it appears that the correlations are stronger in the model than in reality, which is explainable to the role of other cat-ions than ammonium in the atmosphere that are not accounted for in LOTOS-EUROS.

4.2 Seasonal variation

For the first time the LOTOS-EUROS model can be evaluated on an hourly resolution with both the particulate components as well as their gas phase counterparts which together determine the equilibrium for ammonium nitrate. The comparison of the hourly data is illustrated in the form of time series in Figs. 4 and 5. These time series show the general features as described above. In other words, they show the underestimation but good correlation for nitrate as well as the sulphate episodes not captured in spring. On the other hand, much more detail is visible in the time series and we notice that the model is able to reproduce many features, also at the intra-day scale.

To further investigate the behaviour of the model on an hourly basis we have compared the (annual) average diurnal variation against that in the measurements, see Fig. 6. The measured sulphate variation over the day is relatively flat, with a tendency

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to a daytime maximum. LOTOS-EUROS yields a flat distribution as well but has a tendency to a slight daytime minimum. We conclude that the formation of sulphate as well as the sinks should be investigated to improve the absolute level and especially the peak values rather than investigating the diurnal variability.

Although the absolute level of nitrate is underestimated the diurnal variation is rather well captured. Maximum concentrations occur in the early morning after a night time build up. Both the model and the observations show a daytime minimum, which is driven in the model by the increase in mixing layer height and the higher instability of ammonium nitrate at high temperatures. It appears that the decrease in nitrate (and also ammonium) in the early morning starts 1–2 h earlier than in the observations. This may be due to the three hourly meteorological data used by the model which are interpolated to acquire hourly values. Hence, the timing of the rise of the mixing layer is not well represented and occurs gradually between 6 and 9 a.m. in summer, whereas in reality it may be characterised by a more rapid mixing layer growth that occurs later in the morning.

The comparison for nitric acid and ammonia reveals an interesting picture. The model predicts a strong diurnal variation of nitric acid. In summer a strong daytime maximum is modelled up to an average concentration of about 3.5 $\mu g/m^3$. During winter, the model simulates much lower values than in summer with a daytime minimum, which is associated with a daytime maximum in ammonia. The measurements on the other hand yield a much lower dependency on season. The measured concentrations in summer are only little higher than in winter (Fig. 2). Moreover, the measurements indicate a flat diurnal variation in winter and only a slight daytime maximum in summer. For ammonia the diurnal variation is roughly in line with observations albeit that the absolute concentrations are too low as discussed above. The discrepancies between modelled and measured variability on the seasonal and the diurnal scale need to be addressed taking into account several (interacting) processes that influence the concentrations and their dependencies. Below we address the evaluation of the equilibrium assumption incorporated in the model in more detail.

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4.3 Testing the equilibrium module

We have identified that the model does not reproduce the seasonal and diurnal cycle of nitric acid. The lower modelled nitric acid concentrations than those measured indicate that, even with an underestimation of ammonia levels, the ammonium nitrate in the model is significantly more stable than in reality in winter. For the summer, it is difficult to draw conclusions on this aspect as the concentration product of the underestimated ammonia and the overestimated nitric acid may be more inline with the measured values. Hence, we have addressed the partitioning module in the model separately by confronting the predicted partitioning based on the measured total nitrate, total ammonium, sulphate and meteorological data to the observed partitioning. We include only data with a total ammonium to sulphate ratio above 3 to ensure the presence of free ammonia and ammonium nitrate formation.

In Fig. 7 we compare the modelled and measured diurnal cycle of nitrate and nitric acid for December and July. For December, the predicted nitric acid concentration by the equilibrium module is much lower than observed throughout the day, whereas nitrate is (by definition) overestimated by the same amount. This behaviour is observed for all months from October to April. In the other (summer) months, however, a different picture arises. During the night the predicted stability is too high, as for the winter period. During daytime, on the other hand, the predicted nitric acid concentration is much higher than measured. The same underestimation of nitrate indicates that the ammonium nitrate is too unstable in the equilibrium module. This interpretation is valid under the assumption that the ammonium nitrate is in the atmosphere in equilibrium with its gaseous counterparts. Thus, our results indicate that the equilibrium assumption is not valid and/or that the equilibrium module is not able to describe the partitioning correctly under the conditions encountered in the Netherlands.

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5 Discussion and conclusions

The one-year MARGA data set acquired at Cabauw provides a unique case for model validation. The detailed and highly resolved data provide new insights in the intra-day variability of the inorganic aerosol and its precursors. Therefore, they are highly useful for model evaluation. We have identified that the LOTOS-EUROS model underestimates the concentrations of secondary inorganic aerosols at Cabauw. Note that this is not consistent with earlier comparisons against Dutch monitoring data (e.g. Manders et al., 2009). This is explained by the consistently higher SIA concentrations measured in this study compared to those obtained from the national network (Weijers et al., 2010) against which our and other models have always been evaluated. Hence, the higher than expected levels of SIA combined with the possibility to evaluate the performance on a diurnal basis calls for a renewed attention to the modelling of SIA in the Netherlands.

The concentration of ammonium nitrate is sensitive to the sulphate concentration, concentrations of the precursor gases as well as the meteorological conditions (T, RH). This makes the diagnosis of the origin of an underestimation difficult as one needs to verify the source strengths of precursors, chemical production of sulphate and nitric acid, the equilibrium between ammonium nitrate and its gaseous counterparts as well as the sinks for all components involved. We have illustrated that the experimental data obtained within the campaign are very useful to evaluate the cycles of these components in the model. Evaluation of the seasonal and diurnal cycles showed that they are generally captured by the model for the particulates. On the other hand, the seasonal and diurnal variability of nitric acid in the model is much higher than in reality. The results hint at shortcomings in the equilibrium approach, among others. Though, an in-depth evaluation of the model and consequent model improvement is outside the scope of this paper, we have touched upon the modelling of the thermodynamic equilibrium in some more detail.

The MARGA observations were used to evaluate the calculated equilibrium between particulate ammonium nitrate and gaseous nitric acid and ammonia. We have found

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that the thermodynamic equilibrium module produces a too stable ammonium nitrate in winter and during night time in summer, whereas during the daytime in summer it is too unstable. Earlier studies have also identified an underestimation of the particulate nitrate concentrations during summer and daytime (Moya et al., 2001; Fisseha et al., 2006; Morino et al., 2006). In contrast, a number of studies have shown that the predicted equilibrium is generally in accordance with observations (Zhang et al., 2003; Takahama et al., 2004; Yu et al., 2005), though also in these studies significant discrepancies between measured and predicted partitioning have been observed. The reported results have been obtained over a range of pollution and climatic regimes. The contradicting results indicate that is necessary to further test thermodynamic gas-aerosol partitioning modules using experimental data for a wide range of climatic and pollution conditions.

The equilibrium module can be tested directly only when the equilibrium assumption is valid. Our results indicate that the equilibrium assumption is not valid and/or that the equilibrium module is not able to describe the partitioning correctly under the conditions encountered in the Netherlands. In the first case, the equilibrium should be calculated dynamically in the model to account for the impact of other processes on the concentrations. For example, it has been has been postulated that the relative abundant nitrate during daytime in summer may partly be due to transport of nitrate richer air from the upper parts of the boundary layer to the ground (Morino, et al., 2006).

The filter measurements (Weijers et al., 2010) indicate that the coarse mode nitrate concentrations can be significant in polluted marine air masses. The LOTOS-EUROS model does not incorporate the formation of coarse mode nitrate through reaction of nitric acid with sea salt (or dust). Incorporation of this process appears to be needed as it may contribute to the lowering of the underestimation of nitrate and (partly) the overestimation of nitric acid. Furthermore, the process would contribute to the lowering of the correlation between nitrate/sulphate and ammonium which is slightly too high in the model.

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Regional models tend to underestimate the ammonia concentrations at regional background sites. As Cabauw is located in an agricultural area local emission contributions for ammonia can not be excluded. Therefore, the presented comparison to the data is not representative due to the location in a "hotspot" area. Hence, for ammonia observations in nature areas or even cities should be used for validation. Due to the sensitivity of the ammonium nitrate formation to the ambient ammonia concentrations an hourly resolved MARGA dataset obtained in a nature area would be very useful to verify our conclusions on the equilibrium module and the variability in nitric acid. Note that new approaches to tackle long lasting challenges in ammonia modelling such as the incorporation of the compensation point in the deposition routine are under development. MARGA data may prove very useful to evaluate the impact of these approaches on ammonia concentrations as well as the associated particulate concentrations.

5.1 Recommendation for monitoring in the Netherlands

The issue of the representativeness of the monitoring data in combination with the different behaviour of pollutants as function of conditions highlights the need of measurement locations in different environments. The latter is generally recognised. We have shown the benefit of the hourly data with both particulate as well as gas phase concentrations and a continuation of these measurements may prove to be very useful in future model evaluation and improvement studies. However, the MARGA is labour intensive and its use is probably restricted to a number of sites of special interest. Hence, a monitoring strategy for SIA and its gaseous counterparts needs to find an optimal balance between the required information and the resources to obtain the data. Hence, a suite of methodologies should be applied. We propose a general combination of methodologies for the purpose of model evaluation for SIA, taking into account the requirements of monitoring for Particulate Matter and acidification and eutrophication.

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We propose to use a monitoring strategy within the Netherlands employing a combination of the MARGA system, a filter based approach used for the determination of $PM_{2.5}$ and PM_{10} mass concentration and a modified DELTA sampler. The DELTA (Tang et al., 2009) could be used as a backbone of the network. It provides monthly mean concentrations of the same species as the MARGA. However, Gehrig et al. (2009) have shown that losses may occur in the original tubing of the sampler. Hence, we propose to use the modified DELTA sampler (Gehrig et al., 2009) in combination with NaCl impregnations of the denuder and filter for the collection of nitric acid and nitrate. The latter is to avoid possible artefacts from absorption and consequent oxidation of HNO_2 (Pakkanen et al., 1999; Tang et al., 2009). This system is cost efficient and can be used at a significant number of sites in different environments. In addition, dedicated passive sampling for ammonia is very valuable to resolve the high gradients in this component over the country (Duyzer et al., 2001). Daily concentration data on the particulate components can be derived from the analysis of the samples taken for PM_x. Although these samplers are prone to losses of ammonium nitrate (Vecchi et al., 2009), the data are consistent with the PM measurements adding to the assessment of the mass closure for PM_x. Finally, at a small number of sites the MARGA system can be operated for detailed monitoring. These sites could also be used to test emerging measurement techniques such as optical techniques for measuring ammonia (von Bobrutzki et al., 2010). Simultaneous monitoring at these central sites is necessary to benchmark the performance of the systems against each other and to interpret the data from the full monitoring program.

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Table 1. Statistical summary of the measured concentrations between 1 August 2007, and 1 August 2008, at Cabauw. The average, standard deviation as well as median and quartiles are presented. N indicated the numer of (hourly) measurements.

	HNO_3	NH_3	NO_3	SO_4	NH_4
Average	0.63	9.0	5.9	3.1	2.4
Std	0.36	7.5	5.2	2.6	2.4
25 percentile	0.41	4.0	2.2	1.5	0.7
Median	0.56	6.8	4.2	2.4	1.6
75 percentile	0.74	11.9	8.2	3.8	3.3
N	7589	7603	7565	7500	7472

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Table 2. Comparison of the correlation (R) between the SIA components in the model and in the MARGA data.

	LE		MARGA	
	SO_4	NO_3	SO_4	NO_3
NH_4	0.88	0.98	0.75	0.93
NO_3	0.75		0.59	

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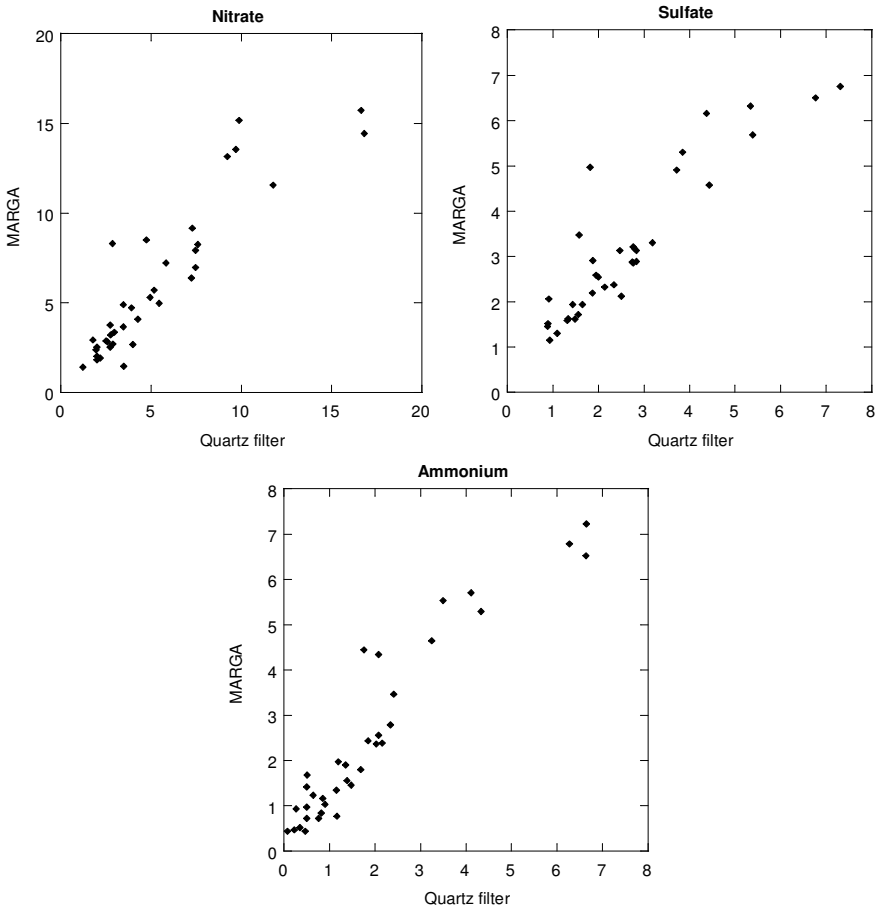

Fig. 1. Comparison between daily average concentrations (μg/m^3) of nitrate, sulfate and ammonium as obtained by the MARGA and co-located quartz filter samples.

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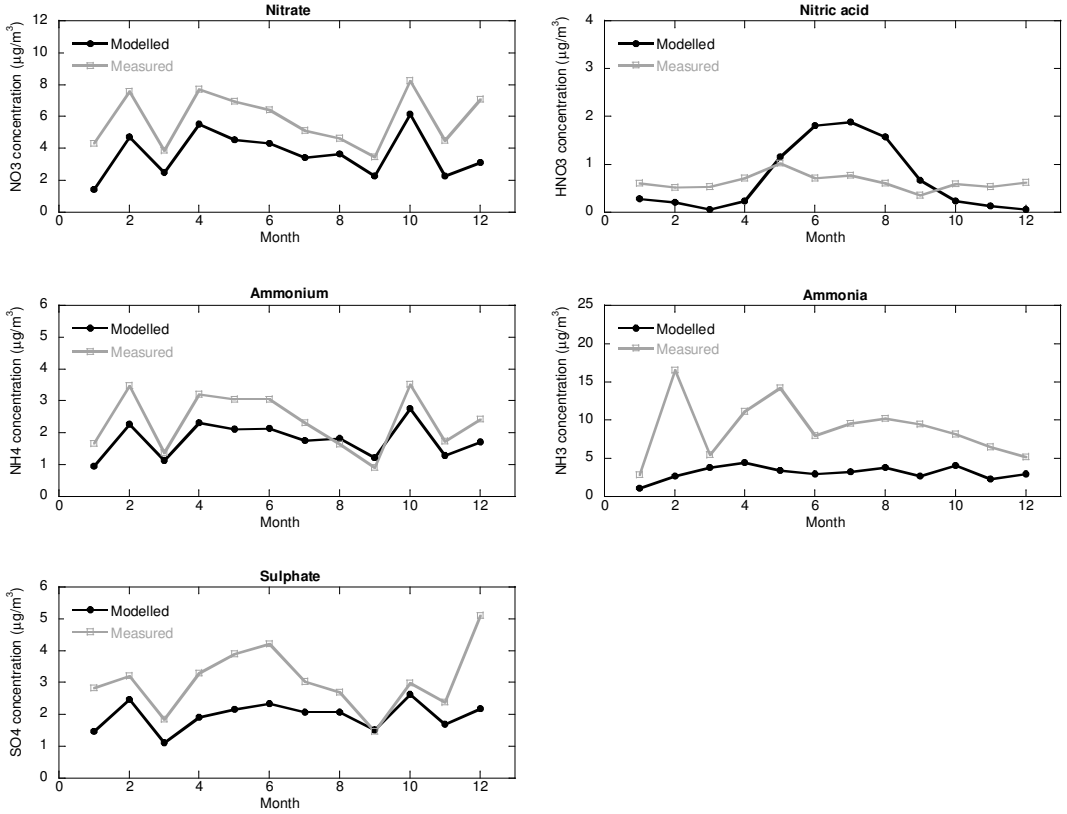

Fig. 2. Modelled and measured seasonal cycle for nitrate, sulphate, ammonium, nitric acid and ammonia. Note that for easy interpretation the data have been organised as if it was a year from January–December. Hence, the monthly means of January–July 2008, are put before the period August–December 2007.

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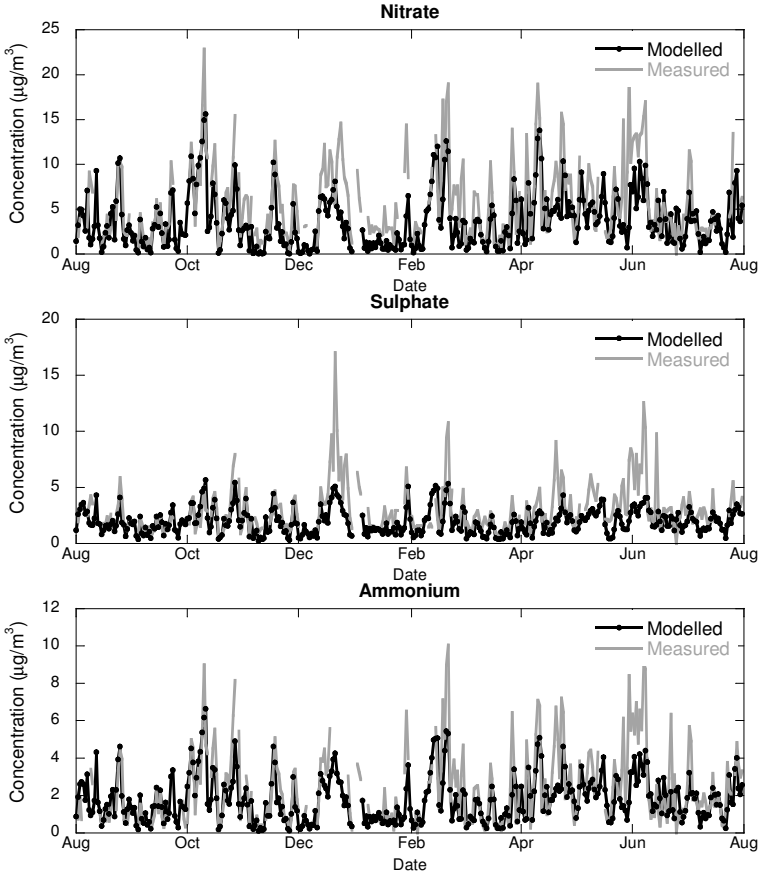

Fig. 3. Comparison of daily modeled (black) and measured (grey) concentrations of nitrate, sulphate and ammonium for the full year.

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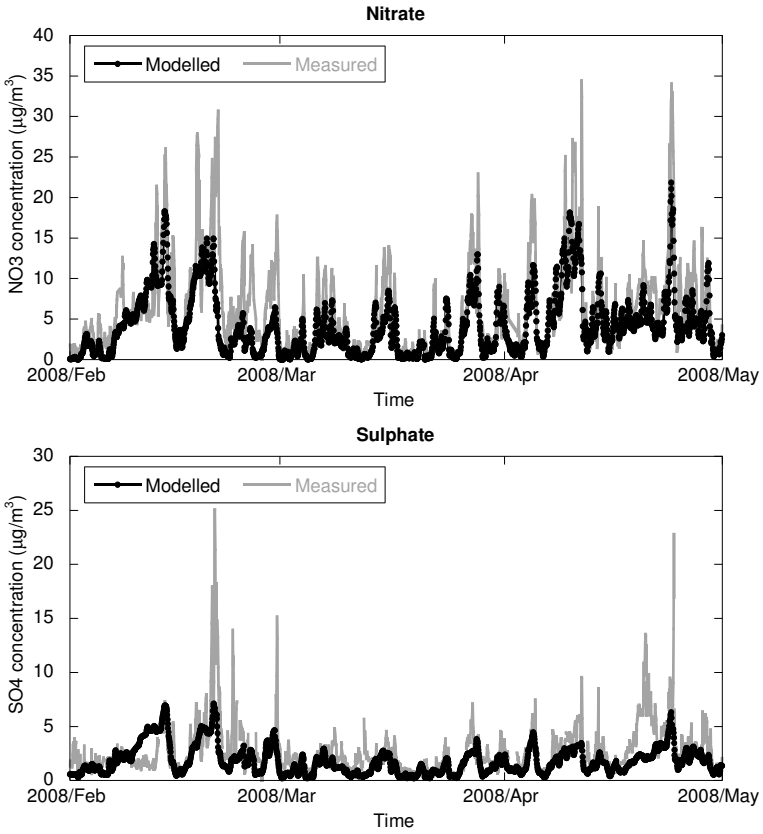

Fig. 4. Comparison of hourly modelled (black) and measured (grey) concentrations of nitrate and sulphate for February–March–April 2008.

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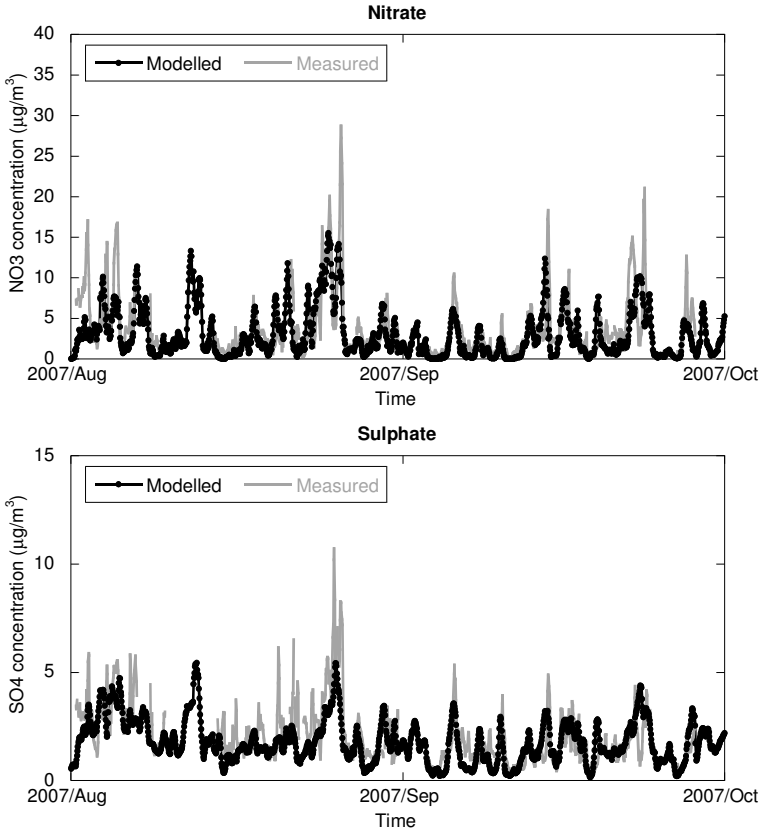

Fig. 5. Comparison of hourly modelled (black) and measured (grey) concentrations of nitrate and sulphate for August–September 2007.

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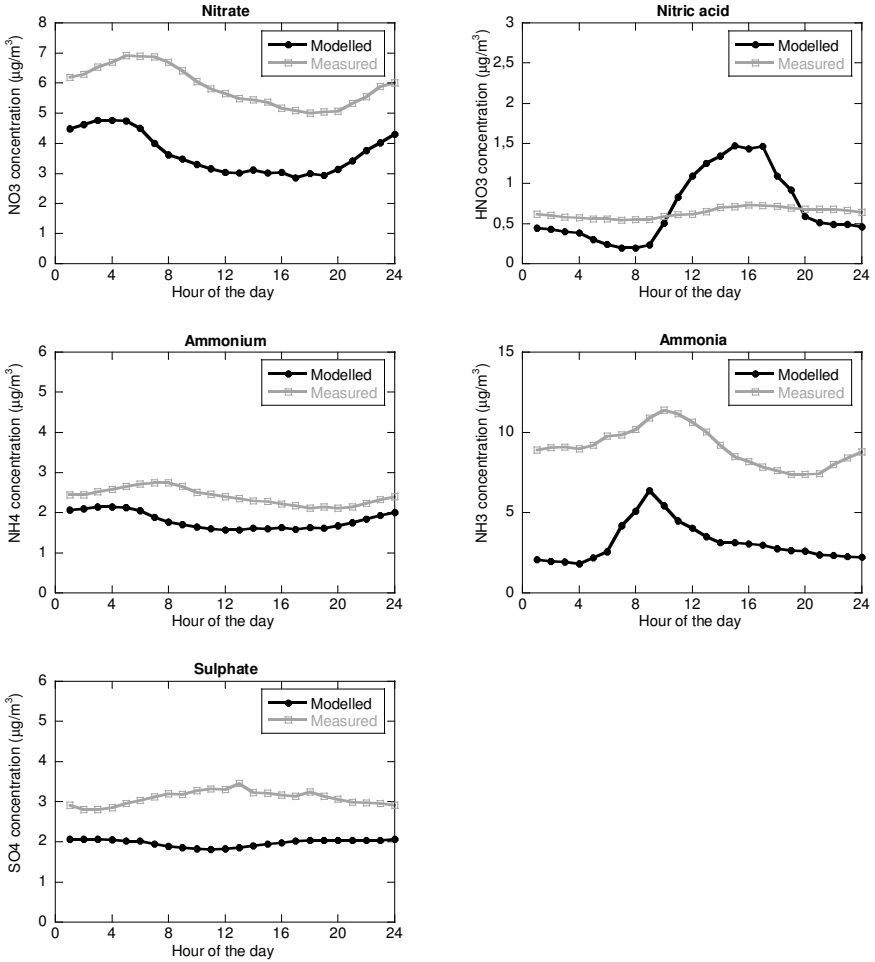

Fig. 6. Modelled and measured diurnal cycle for nitrate, sulphate, ammonium, nitric acid and ammonia.

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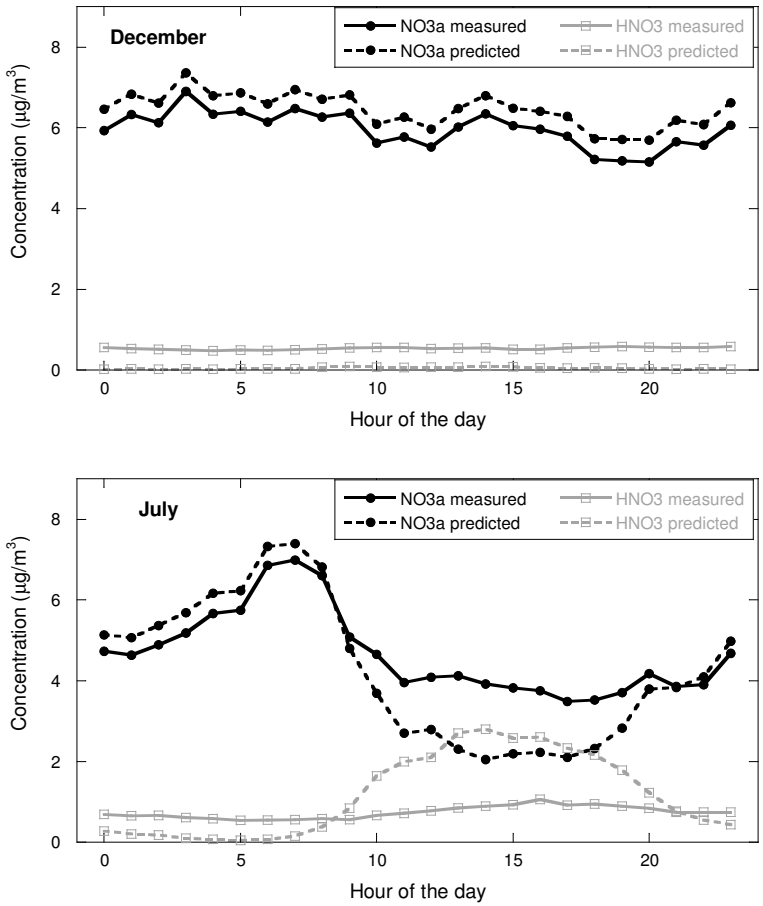

Fig. 7. Comparison between the predicted and measured partitioning of nitrate between the aerosol and gas phase for December (upper panel) and July (lower panel). For both months the average diurnal cycle is given. All hourly averages consist of at least 23 data points.

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