Atmospheric
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Discussions

Response of secondary inorganic aerosol concentrations and deposition fluxes of S and N across Germany to emission changes during high PM$_{10}$ episodes in spring 2009

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Abstract

In this study, the response of secondary inorganic aerosol (SIA) concentrations to changes in precursor emissions during high PM_{10} episodes over Central Europe in spring 2009 was investigated with the Eulerian Chemistry Transport Model (CTM) REM-Calgrid (RCG). The model performed well in capturing the temporal variation of PM_{10} and SIA concentrations and was used to analyse the different origin, development and characteristics of the selected high PM_{10} episodes. SIA concentrations, which attribute to about 50 % of the PM_{10} concentration in north-western Europe, have been studied by means of several emission scenarios varying SO_2, NO_x and NH_3 emissions within a domain covering Germany and within a domain covering Europe. It was confirmed that the response of sulphate, nitrate and ammonium concentrations and deposition fluxes of S and N to SO_2, NO_x and NH_3 emission changes is non-linear. The deviation from linearity was found to be lower for total deposition fluxes of S and N than for SIA concentrations. Furthermore, the study has shown that incorporating explicit cloud chemistry in the model adds non-linear responses to the system and significantly modifies the response of modelled SIA concentrations and S and N deposition fluxes to changes in precursor emissions. The analysis of emission reduction scenarios demonstrates that next to European wide emission reductions additional national NH_3 measures in Germany are more effective in reducing SIA concentrations and deposition fluxes than additional national measures on SO_2 and NO_x.

1 Introduction

Particulate matter has adverse impact on public health (Pope et al., 2007, 2008). The European Commission established directives regarding PM_{10} concentration level to avoid, prevent or reduce harmful effects on human health (European Commission, 2008). The analysis of observations reveals that the current EU limit values for PM_{10} are still exceeded over large parts of Europe (EEA, 2012) indicating a continued

need for further implementation of abatement strategies. Secondary inorganic aerosol (= SIA: SO_4^{2-}, NO_3^- and NH_4^+) originating from gaseous precursors such as SO_2, NO_x and NH_3 (Fountoukis and Nenes, 2007) involves an important fraction of PM_{10}. Experimental studies have shown that in the rural background the average PM_{10} is dominated by SIA contribution (Van Dingenen et al., 2004; Putaud et al., 2004). Moreover, during PM episodes the fraction of SIA is higher than on average (Weijers et al., 2011). After removal of SIA and its precursors from the atmosphere they contribute to eutrophication and acidification of soils and water bodies with harmful effects to vulnerable ecosystems (Bobbink et al., 1998).

SIA is dominated by ammonium-sulphate and ammonium-nitrate salts (Putaud et al., 2010). The precursor gases NO_x and SO_2 are oxidised to form HNO_3 and H_2SO_4, respectively. Ammonium-sulphate and ammonium-nitrate are then formed when nitric acid and sulphuric acid are neutralised by NH_3. In contrast to ammonium-sulphate, ammonium-nitrate is a semi-volatile component (Nenes et al., 1999). NH_3 preferentially neutralizes sulphuric acid due to its low saturation vapour pressure. If abundant NH_3 is available, ammonium-nitrate may form. The thermodynamic equilibrium between gas and aqueous aerosol phase is determined by temperature, relative humidity and the ambient concentrations of sulphate, total nitrate and total ammonia (West et al., 1999). In addition, NH_3 constrains cloud droplet pH, which regulates the oxidation pathway of SO_2 and therewith the formation efficiency of sulphate (Fowler et al., 2007). Furthermore, the dry deposition velocities of NH_3 and SO_2 are connected (Fowler et al., 2001). Hence, emission reductions of gaseous SIA precursors lead to shifts in the equilibrium and affect the formation, residence time and removal of sulphur and nitrogen compounds and result in a non-linear response of the SIA concentrations (Fagerli and Aas, 2008). The impact of the complex interactions varies seasonally and regionally over Europe with changing emission regime.

Among emission changes of SO_2, NO_x and NH_3, responses to NH_3 emission changes show the largest non-linear behaviour (Tarrasón et al., 2003). Former studies over Europe regarding responses of ambient PM levels to SO_2, NO_x and NH_3 emission

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reductions indicate that a decrease of NH_3 emissions may entail a high reduction potential for SIA and therewith PM concentrations and deposition fluxes of S and N (e.g. Erisman and Schaap, 2004; Derwent et al., 2009; Redington et al., 2009; Matejko et al., 2009). Pinder et al. (2007) found that reducing NH_3 emissions may offer significant cost savings compared to further controls on SO_2 and NO_x (in the US). In contrast, other studies indicated that for regions in which SIA formation is SO_2- and HNO_3-limited due to high NH_3 concentrations, a decrease in SO_2 and NO_x emissions may result in a large reduction of SIA concentrations and deposition fluxes of S and N (Pay et al., 2012; de Meij et al., 2009). Further research is needed to consider and include the impact of the non-linear system described above in current PM_{10} mitigation strategies.

So far, investigations on the impact of emission reductions of precursors SO_2, NO_x and NH_3 on SIA or PM concentrations focussed on long-term trends (Fagerli et al., 2008; Fowler et al., 2005; Lövblad et al., 2004; Erisman et al., 2003), on the analysis of one specific year (Tarrasón et al., 2003; Derwent et al., 2009) or on separate months (Erisman and Schaap, 2003; Renner and Wolke, 2010; de Meij et al., 2009), but not on specific periods with elevated PM_{10} levels. During the last decade, springtime high PM_{10} episodes were repeatedly reported in large areas over Europe with PM_{10} concentrations above $100\,\mu g\,m^{-3}$ (e.g. 2006, 2007, 2009 and 2011). Springtime is marked by periods of fair weather with medium temperatures combined with high NH_3 emission due to incipient agricultural action leading to high NH_3 availability, which enhances SIA formation. In this study, the development and characteristics of two high PM_{10} episodes over Central Europe in spring 2009 are studied and the response of modelled SIA concentrations to changes in the precursor emission during these high PM_{10} episodes is investigated. With respect to the latter the sensitivity of modelled SIA concentrations to changes in NH_3 emissions is investigated. Furthermore, SIA concentrations are calculated for different scenarios with varying SO_2, NO_x and NH_3 emissions, simultaneously. A critical question for national policy makers is how much exposure reduction of the population can be achieved by national measures versus generic European measures. We define measures in the German national domain and

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compare the impact with European wide measures. Therefore, for each scenario, two cases were simulated: in the first case the emission scenarios were only applied to the model domain covering Germany, and in the second case, the emission scenarios were also applied to the European model domain which provides the boundary conditions for the national domain. Besides SIA concentrations, also deposition fluxes of S and N are included in the analysis. Deposition fluxes are important sinks for SIA and the air concentrations of its precursor gases.

In the following section, the model and observations are described. A detailed overview of the model set up and the performed emission scenarios is given. In Sect. 3, the investigation period is described. In the subsequent section (Sect. 4) the characteristics of the PM episodes in spring 2009 and results of the model evaluation and the emission scenarios are presented. The results are discussed and conclusions are drawn in Sect. 5.

2 Methods and data

2.1 Model description and set-up

The Eulerian grid model REM-Calgrid (RCG) simulates air pollution concentrations solving the advection-diffusion equation on a regular lat-lon-grid with variable resolution over Europe (Beekmann et al., 2007; Stern, 2006). RCG is offline-coupled to the German Weather Service operational NWP model COSMO-EU (Schättler et al., 2008). The vertical transport and diffusion scheme accounts for atmospheric density variations in space and time and for all vertical flux components. For the horizontal advection of pollutants the advection scheme developed by Walcek (2000) is used. Gas phase chemistry is simulated using an updated version of the photochemical reaction scheme CBM-IV (Gery et al., 1989), including Carter's 1-Product Isoprene scheme (Carter, 1996), as described in Gipson and Young (1999). Furthermore, RCG features thermodynamic equilibrium modules for secondary inorganic aerosols (ISORROPIA:

Nenes et al., 1999) and organic aerosols (SORGAM: Schell et al., 2001). RCG includes modules to treat the emissions of sea salt aerosols (Gong et al., 1997) and wind blown dust particles (Claiborn et al., 1998; Loosemore und Hunt, 2000). Dry Deposition fluxes are calculated following a resistance approach as proposed by Erisman
5 et al. (1994).

For this study, a research version of RCG was used as described in Banzhaf et al. (2012). It includes enhanced physical and chemical descriptions of scavenging processes and sulphate production as a function of cloud liquid water content and cloud/rain droplet pH. Cloud droplet pH is estimated using the concentrations of the
10 (strong) acids and bases including the buffering by bi-carbonate (through CO_2). For the formation of sulphate in cloud water the oxidation of dissolved SO_2 by hydrogen peroxide and ozone are simulated. Sulphate formation and wet scavenging can either be calculated using modelled droplet pH or using a constant droplet pH. Banzhaf et al. (2012) showed that a modelled droplet pH gives a better model performance and
15 better model consistency concerning air concentrations and wet deposition fluxes than a constant pH. The RCG wet deposition scheme distinguishes between in-cloud and below-cloud scavenging of gases and particles. The applied scheme integrates wet deposition throughout the column.

The model runs for spring 2009 were performed on a domain covering Germany
20 (47.2° N–55.1° N; 5.4° E–15.7° E), in the following referred to as "German domain" (= GD), with a horizontal resolution of approximately $7 \times 7 \, \text{km}^2$ and 20 vertical layers up to 5000 m. An RCG run covering Europe (35.1° N–66.3° N; 10.2° W–30.8° E), in the following referred to as "European domain" (= ED), provided the boundary conditions. Emissions for Germany were taken from a national inventory for the year 2005 (Appel-
25 hans et al., 2012; Builtjes et al., 2010) and combined with the European TNO-MACC data set for the same year (Denier van der Gon et al., 2010; Kuenen et al., 2011). The spatial distributions of the total annual NH_3, SO_x and NO_x emissions of the German domain are presented in Fig. 1. The distributions illustrate that emission regimes vary significantly. Agricultural ammonia-rich areas are situated in the Northwest and South-

east of the domain. The SO_x emissions are located in the industrial areas whereas NO_x emissions are highest in urbanised regions and transport corridors.

2.2 Model runs

To investigate the mitigation potential of emission reductions of precursor gases SO_2, NO_x and NH_3 on SIA concentrations and S and N deposition fluxes, a base case simulation and three reduction scenarios have been performed:

1. reducing NH_3 emissions only,

2. reducing SO_2 and NO_x emissions simultaneously and

3. reducing SO_2, NO_x and NH_3 simultaneously

The emission reduction scenarios are listed and labelled in Table 1. All model runs have been performed using modelled droplet pH. To study the impact of national measures compared to Europe wide mitigation efforts, all reduction scenarios have been performed twice:

1. emissions have been reduced within the German domain only (scenario denoted by GD) and

2. emissions have been reduced within the German and within the European domain lowering the boundary conditions (scenario denoted by ED).

For simplicity, the emission reductions to assess national or regional measures were applied to the whole "German" zoom domain. Inevitably, this domain comprises parts of neighbouring countries and seas. As for the land area, around two thirds of the emissions in the GD domain is from Germany itself (see Table 2).

To study the model sensitivity to ammonia emission changes in more detail, additional scenarios have been performed in which ammonia emissions have been varied on the German domain 20 %-stepwise from −60 % to +40 %. The emission scenarios

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are listed and labelled in Table 3. To study the sensitivity to model results to the variable pH in cloud water, which has often been neglected in previous studies, the sensitivity runs have been performed twice:

1. applying modelled droplet pH and

2. applying a constant pH of 5.5.

Finally, to study the impact of long-range transport the -40% NH_3 scenario has been performed on the German domain (scenario denoted by GD) and on the European domain implying emission reduction within the German and the boundary conditions (scenario denoted by ED)

2.3 Observations

AirBase (European AIR quality database, http://airbase.eionet.europa.eu/) provides PM_{10} air concentrations for a large number of European measurement stations. For the evaluation of RCG, PM_{10} model results have been compared to daily averages of PM_{10} at 42 rural background stations in AirBase spread over Germany. A comparison to 63 suburban background stations in AirBase over Germany has also been included.

Data from the national German monitoring network (UBA, 2004) are used for evaluation of COSMO-EU precipitation and RCG wet deposition fluxes. Precipitation sampling is performed by using wet-only collectors (Firma Eigenbrodt, Germany). Weekly total precipitation and wet deposition fluxes for 11 stations spread over Germany were available. At time of writing no quality controlled SIA measurement data for Germany were available. Measurement data of sulphate, nitrate and ammonium for three observational sites (Vredepeel, Kollumerwaard, Valthermond) close to the German border were supplied by the Dutch "National Institute for Public Health and the Environment" (http://www.rivm.nl). The locations of all stations are shown in Fig. 2.

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3 Investigation period

3.1 Meteorological Situation

The investigation period was 24 March to 28 April in spring 2009. The mean temperature over central Europe in spring 2009 was according to German Weather Service up to 3 K higher than the mean of the reference period of 30 yr (1961–1990). In April this temperature anomaly was even more than 4 K. In Germany, in April 2009 the mean temperature of 11.9 °C was 4.5 K higher than the mean of the reference period. April 2009 was announced as the warmest April since the beginning of comprehensive weather observations 120 yr ago. Sunshine duration was 62 % above average while regionally precipitation amounts were far below average with extremes like the station Berlin-Buch with only 1 mm in April. This extreme warm, dry and sunny weather in April 2009 was related to high-pressure systems with rather stable air conditions and little atmospheric mixing.

3.2 PM_{10} concentrations

Stable air conditions lead to high PM_{10} levels (Mues et al., 2012; Demuzere et al., 2009). For April 2009 the mean PM_{10} concentration over all German UBA rural background stations was 25 % higher than the mean over the previous 9 yr (2000–2008) (UBA, 2010). The EU limit for daily mean PM_{10} (= 24 h average above 50 $\mu g\,m^{-3}$) was exceeded on 9 to 12 days within this month at most stations in Belgium and the Netherlands and at several stations in Germany. There were two main high PM_{10} episodes within the investigation period, one from about 2 to 7 April and another one from about 11 to 16 April. Figure 3 shows the daily mean PM_{10} concentration distribution over Germany on the peak days of each episode derived by Optimal Interpolation of observations. PM_{10} daily mean concentrations above 100 $\mu g\,m^{-3}$ were measured at several stations in Central Europe within both episodes. On the 13 April, daily mean PM_{10} concentrations of around 150 $\mu g\,m^{-3}$ were measured at rural background stations in North-

Rhine Westphalia in the west of Germany. In both episodes the fraction of SIA was very high with measured daily mean SIA concentrations of up to above $70 \, \mu g \, m^{-3}$. In this study, the extremely high concentration levels and their origin during these episodes are investigated, which is highly relevant for mitigation purposes.

4 Results

4.1 Model performance

Figure 4a shows a scatterplot of the modelled daily mean PM_{10} concentrations of the base run compared to observations at 42 rural background stations spread over Germany. The corresponding statistics are given in Table 4. The model performs well with a correlation of 0.75. The model tends to overestimate low PM_{10} values and underestimate the high peaks. The bias of $+2.95 \, \mu g \, m^{-3}$ (observed mean $22.56 \, \mu g \, m^{-3}$) indicates a slight overall overestimation by the model. A comparison of modelled PM_{10} concentrations to 63 suburban background stations (not shown here) led to slightly higher daily mean PM_{10} concentrations (observed mean $27.01 \, \mu g \, m^{-3}$) than for the rural background stations with a similar correlation coefficient of 0.71. The RMSE for the comparison with the suburban background stations is higher than for rural background stations, which is related to a higher frequency of peak values. Figure 4b shows the time series of PM_{10} daily means at station Westerwald-Herdorf. The model nicely reproduces the temporal variation of PM_{10} concentrations in the investigation period. However, as already recognised in the scatter plot, the model tends to underestimate peak values and overestimate low values.

Figure 5a shows modelled daily mean SIA concentrations compared to measurements at 3 Dutch observational sites. The model performs well with a correlation coefficient of 0.76. The bias of $-2.10 \, \mu g \, m^{-3}$ indicates a slight overall underestimation of SIA concentrations by the model. Similar as the PM_{10} concentrations, the SIA concentrations in the high concentration range are underestimated by the model.

In Fig. 5b, time series of the SIA components SO_4^{2-}, NO_3^- and NH_4^+ at station Kollumerwaard (NL) are presented. The high correlation coefficients for SO_4^{2-}, NO_3^- and NH_4^+ in Table 4 indicate that the model captures the temporal variability of SIA concentrations well. The model tends to overestimate SO_4^{2-} concentrations and underestimate NO_3^- concentrations while NH_4^+ concentrations are simulated well for the considered period. The correlations for the precursor gases SO_2 and NO_2 (NH_3 concentration measurements were unfortunately not available for Germany in 2009) show that RCG is able to capture the temporal variability of the analysed species concentrations. Surface SO_2 concentrations tend to be overestimated by RCG, while NO_2 concentrations tend to be underestimated.

Total wet deposition fluxes of SO_x, NO_y and NH_x for the investigation period are compared to observations at 11 UBA sites spread over Germany. The model performance concerning wet deposition fluxes is summarised in Fig. 6. The corresponding statistics are given in Table 4. The spatial correlations between model results and observations are high with values of 0.82, 0.80 and 0.74 for SO_x, NO_y and NH_x, respectively. The bias indicates that SO_x and NH_x wet deposition fluxes are underestimated by the model while NO_y is slightly overestimated. Figure 6d shows the performance of the meteorological driver for precipitation at the 11 wet deposition measurement sites. The spatial correlation is 0.57.

Although some shortcomings can be identified, the overall performance is satisfactory and in line or better than in previous studies (e.g. Stern et al., 2008; Solazzo et al., 2012). The model is able to capture main variability of component concentrations and deposition fluxes in space and time.

4.2 Origin and characteristics of the PM_{10} episodes in spring 2009

The model evaluation in Sect. 4.1 has shown that RCG performs well in simulating the temporal and spatial variation of SIA and PM_{10} concentrations within the investigation

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period. Thus, RCG is used to investigate origin and characteristics of the high PM_{10} episodes in spring 2009.

4.2.1 First episode (2–7 April 2009)

Since the end of March, a high-pressure system over northern Central Europe de-
termined the weather pattern over the investigation area. In northern France and
northern Netherlands the stagnant air conditions led to accumulation of SIA precur-
sor gases enhancing local SIA formation in the beginning of April. SIA was dominated
by ammonium-nitrate due to the elevated NO_x levels originating from road transport
and shipping activities and high NH_3 emission levels originating from local agricultural
action. On 4 April, a trough moving in from the west passing the British Islands trans-
ported the polluted air masses – containing high SIA and high NO_x concentrations –
towards Germany. Passing ammonia-rich areas, further ammonium-nitrate formation
occurred within the humid air mass. The polluted air mass hit Germany in the late
morning hours of 4 April and spread out over the country in the following hours. Fig-
ure 7a shows modelled average SIA concentrations of the base run for the 4 April.
Average SIA concentrations exceed $45 \, \mu g \, m^{-3}$ that day. We would like to stress that
the spatial distribution of modelled SIA concentrations in Fig. 7a compares well to the
spatial distribution of observed PM_{10} concentrations on 4 April shown in Fig. 3a. On
the 5 April a high-pressure system built up over northern Germany. The stagnant air
conditions led to accumulation of pollutants that have been transported to Germany
(mainly SIA and precursor NO_x) during the 4 April and local pollutants. As a result SIA,
again dominated by ammonium-nitrate, originating from local formation in Germany on
the 5 April added up to the SIA originating from long-range transport. Modelled hourly
SIA concentrations exceed $70 \, \mu g \, m^{-3}$ on 5 April.

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4.2.2 Second episode (11–16 April 2009)

From 11 to 16 April a ridge over Central Europe led to warm weather and stagnant air conditions over Germany. The latter resulted in pollutant accumulation and enhanced local SIA formation over western Germany due to high precursor emissions in the Ruhr-Area and its surrounding. On the 13 and 14 April western Germany was situated on the very western border of the ridge with very stagnant conditions favouring the built-up and local formation of SIA and precursor levels. Different from the first episode, ammonium-nitrate did not dominate the SIA concentrations, but ammonium-sulphate and ammonium-nitrate levels are equally high. The model simulations show that ammonium-sulphate was mainly formed during daytime when temperatures were high (above 25 °C) while ammonium-nitrate was mainly formed during night time and early morning hours with moderate temperatures (10–15 °C) and high relative humidity (80–90 %). Figure 7b shows modelled average SIA concentrations for the 13 April. In North-Rhine Westphalia, in the west of Germany, average SIA concentrations exceed a daily average of $60\,\mu g\,m^{-3}$. Again, the spatial distribution of modelled SIA concentrations in Fig. 7b compares well to the spatial distribution of observed PM_{10} concentrations on 13 April shown in Fig. 3d.

The analysis using RCG shows that the high SIA concentrations are of different origin for the two episodes. Within the first episode SIA was mainly formed outside of Germany while within the second episode SIA mainly originated from local sources within Germany. This will be further discussed in Sect. 5.

4.3 Emission scenarios

4.3.1 Sensitivity of SIA concentrations to ammonia emission changes

Figure 8 presents a time series of daily mean sulphate, nitrate and ammonium concentrations at station Westerwald-Herdorf. The station location is marked (x) on the map on the upper right hand side. The station is situated in the western part of Germany and

was hit by both episodes. Figure 8 includes 3 different runs: base run, -40% NH3$_{GD}$ run and $+40\%$ NH3$_{GD}$ run. The figure again illustrates that the first episode around 4 April was dominated by ammonium-nitrate while during the second episode around 12 April ammonium-sulphate and ammonium-nitrate levels are equally high.

All SIA components clearly show a dependency on ammonia emission changes whereas mean concentrations increase compared to the base run when ammonia emissions are increased and vice versa. Sulphate concentrations are sensitive to changes in ammonia emission as ammonia affects droplet pH and consequently the rate of sulphate formation. Also, changes in ammonia emissions affect the availability of "free ammonia" and hence affecting the formation of ammonium-nitrate. The comparison of Fig. 8a and b shows that the nitrate concentrations are affected to a higher extent by changes in ammonia emissions than sulphate concentrations with an increase of up to 42 % relative to the base run during the high PM$_{10}$ episodes for the $+40\%$ NH3$_{GD}$ run and a decrease of up to 60 % relative to the base run for the -40% NH3$_{GD}$ run.

The sensitivity of SIA concentrations to ammonia emission changes for the German domain scenarios (GD) is small on the 4 and 5 April, but much larger on the 12 and 13 April. These different sensitivities illustrate the importance of transport for the first episode and the local built up for the second episode. The non-linearity observed in the responses is further addressed below.

4.3.2 Reduction scenarios

The impact of 3 different emission reduction scenarios for 2 domains (GD and ED) on the mean modelled SIA concentration and total deposition flux in the German domain is presented in Fig. 9. The change in the average SIA concentration and deposition fluxes compared to the base run refers to averages over the German domain. Figure 9a and b show the results for emission reductions in the German domain and Fig. 9c and d show the results for emission reductions in the European domain. The plots on the left side show the SIA concentrations and the plots on the right side the total deposition fluxes.

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GD emission reduction impact on SIA concentrations and total deposition fluxes

Figure 9a shows that the air concentrations of particulate sulphate, nitrate and ammonium decrease for all performed emission reduction scenarios compared to the base run. The mean SIA concentrations are reduced by -4.6%, -12.6% and -15.8% for the -NOx-SO2$_{GD}$, -NH3$_{GD}$ and -NH3-NOx-SO2$_{GD}$ scenario, respectively. This indicates a non-linear behaviour considering the corresponding precursor reductions. Sulphate concentrations are reduced by $-0.26\,\mu g\,m^{-3}$ (-5.7%) and $-0.27\,\mu g\,m^{-3}$ (-5.9%), within the -NOx-SO2$_{GD}$ and the -NH3$_{GD}$ scenario, respectively. The -NH3-NOx-SO2$_{GD}$ scenario leads to a reduction of $-0.48\,\mu g\,m^{-3}$ (-10.5%) in sulphate concentrations. This is less sulphate reduction than the reduction sum of scenario -NOx-SO2$_{GD}$ and -NH3$_{GD}$. Nitrate is only slightly reduced within the -NOx-SO2$_{GD}$ scenario ($-0.19\,\mu g\,m^{-3}$) but is significantly reduced within the -NH3$_{GD}$ scenario ($-0.91\,\mu g\,m^{-3}$). With a reduction by $-1.0\,\mu g\,m^{-3}$ the reduction within the -NH3-NOx-SO2$_{GD}$ scenario is also for nitrate less than the reduction sum of scenario -NOx-SO2$_{GD}$ and -NH3$_{GD}$. The later non-linearity can also be observed for ammonium concentrations, with reductions of $-0.14\,\mu g\,m^{-3}$, $-0.41\,\mu g\,m^{-3}$ and $0.50\,\mu g\,m^{-3}$ for the -NOx-SO2$_{GD}$, -NH3$_{GD}$ and -NH3-NOx-SO2$_{GD}$, respectively.

Figure 9b shows that other than for SIA concentrations the reduction scenarios do not only result in reductions in deposition fluxes. Reduced nitrogen dry deposition fluxes are slightly increased compared to the base run when NO_x and SO_2 emissions are reduced. Due to the reduction of SO_2 and NO_x, less ammonia is consumed for the neutralisation of nitrate and sulphate leading to a higher concentration, lower transport distances and thus higher deposition within the country. A similar effect is observed for oxidised nitrogen deposition when ammonia is reduced. Within the -NH3$_{GD}$ scenario the total deposition of oxidised nitrogen is increased by 11.9%.

For the same scenario reduced nitrogen total deposition is reduced by -33.8% due to higher HNO_3 air concentrations following the decrease in ammonium-nitrate formation introduced by NH_3 emission reductions. As the deposition velocity of HNO_3 is high,

HNO$_3$ dry deposition fluxes increase. As the decrease in reduced nitrogen is larger than the increase in oxidised nitrogen, the total N deposition is still reduced for the -NH3$_{GD}$ scenario by -15.2 % while total deposition of S is reduced by -6.5 %. For the -NH3-NOx-SO2$_{GD}$ scenario all components' wet and dry deposition fluxes are reduced (total deposition of S by -18.9 % and N by -20.3 %). For the -NOx-SO2$_{GD}$ scenario the reduction of total S deposition amounts to -13.9 % and that of total N deposition to -4.4 %. Comparing the resultant deposition fluxes of the scenarios -NOx-SO2$_{GD}$ and -NH3$_{GD}$ to those of scenario -NH3-NOx-SO2$_{GD}$ shows that S and N deposition fluxes react more linearly on the emission changes than the SIA concentrations.

German domain vs. European domain emission reductions

Figure 9c and d show the change in average German domain SIA concentrations and deposition fluxes resulting from the scenarios on the European domain. Concentrations of SIA are reduced by -23.1 %, -21.9 % and -39.1 % for the -NO$_x$-SO2$_{ED}$, -NH3$_{ED}$ and -NH$_3$-NO$_x$-SO2$_{ED}$ scenario, respectively. The reduction in sulphate concentrations within the German domain changes significantly from GD to ED scenario. The -NH3-NOx-SO2$_{ED}$ scenario is less effective in reducing SIA concentrations than the results of the scenarios -NO$_x$-SO2$_{ED}$ and -NH3$_{ED}$ would suggest if linearity would be assumed. The deviation from linearity is larger for the ED runs than for the GD runs in Fig. 9a. The least difference in reduction amount and reduction fraction of the different SIA compounds between GD and ED runs show the -NH3$_{GD/ED}$ scenarios.

The latter is also valid for the deposition fluxes. The -NH3$_{GD/ED}$ scenarios show least differences between GD and ED runs and the deviation from linearity is larger for the ED runs than for the GD runs. Also for the deposition fluxes the change in S compounds is most significant between GD to ED runs. The total S deposition is reduced by -42.6 %, -8.7 % and -47.5 % and the total N deposition by -8.8 %, -19.8 % and -29.9 % for the -NO$_x$-SO2$_{ED}$, -NH3$_{ED}$ and -NH$_3$-NO$_x$-SO2$_{ED}$ scenario, respectively.

4.3.3 Response to ammonia emission changes

Following the findings of Sect. 4.3.2 the response of SIA concentrations and S and N deposition fluxes to ammonia emission changes has been further investigated. The applied emission scenarios are summarised in Table 3.

Figure 10a shows base case average SIA concentration of the investigation period. Average SIA concentrations were highest in and around the Ruhr Area. Figure 10 shows the absolute (b) and relative (c) SIA reduction compared to the base case when reducing NH_3 by 40 % on the German domain. The highest absolute reduction of average SIA concentrations of more than $3\,\mu g\,m^{-3}$ is achieved south of the Ruhr Area where average SIA concentrations were high. The highest relative reduction amounts up to 22 % in the south-western part of the domain. The comparison of absolute and relative SIA reduction to the NH_3 emission map in Fig. 1c clearly shows that the NH_3 measure leads to highest SIA reduction in areas with moderate and low NH_3 emission densities. In ammonia-rich areas in north-western and south-eastern Germany the reduction is less distinct, however, still amounts to more than 10 %.

In Fig. 11a, the change in average modelled SIA concentration within the German domain is plotted against the stepwise change in the NH_3 emissions using modelled droplet pH (solid line) and a constant pH of 5.5 (dashed line). A polynomial curve was fitted through the data. The response of SIA concentrations on NH_3 emission changes is non-linear. The larger the reduction of the NH_3 emissions gets, the more effective the reductions in the SIA concentrations are. The change in average modelled SIA concentration amounts $-2.7\,\mu g\,m^{-3}$ for the -60 % NH_3 run compared to the base run when applying a modelled droplet pH. When a constant pH of 5.5 is used, a decrease in the mean modelled SIA concentration of $-2.3\,\mu g\,m^{-3}$ is obtained. Hence, the model simulates NH_3 emission reductions to be about 20 % more effective using a modelled droplet pH. A reduction of NH_3 emissions leads to reduced neutralisation of cloud acidity and consequently to less sulphate production, which is not accounted for using a constant droplet pH.

Figure 11b shows the average total SO_x, NO_y and NH_x deposition within the German domain. The response of SO_x, NO_y and NH_x total deposition fluxes on ammonia emission changes is non-linear, similar as for the SIA concentrations. Only marginal changes in total SO_x deposition occur when ammonia emissions are varied and a constant droplet pH is used. Applying a modelled droplet pH total SO_x deposition varies with varying ammonia emissions. As for the sulphate concentrations, the reason is the missing feedback between ammonia concentrations and droplet pH. NO_y total deposition shows no dependency on droplet pH. However, ammonia emission reductions result in an increase of the total NO_y deposition. Ammonia emission reduction leads to less ammonium–nitrate formation and hence to higher HNO_3 concentrations. The latter results in a dominant increase of HNO_3 dry deposition, which increases NO_y deposition fluxes. Reducing ammonia emissions leads to a decrease of the total NH_x deposition flux and vice versa for increased ammonia emissions. Reductions of the total NH_x deposition flux are larger for the model runs using a constant pH than for the model runs using a modelled droplet pH. This is because a decrease in ammonia emissions leads to a decrease of the droplet pH. Hence, ammonia is wet scavenged more effectively and the decrease in NH_x deposition is less effective.

5 Discussion and conclusions

In this study the response of modelled SIA concentrations to changes in precursor gas emissions during two high PM episodes over Central Europe in spring 2009 has been investigated. The applied CTM, i.e. RCG, performed well in capturing the temporal variation of the PM_{10} and SIA concentrations. The model was successfully used to analyse the origin, development and characteristics of the investigated episodes.

The two SIA episodes were of different origin. For the first episode SIA was mainly formed outside the German domain. Hence, changes in ammonia emissions within the German domain did not impact SIA concentrations in Germany as severely as changes on the European domain. Within the second episode the sensitivity of SIA concentra-

tions to changes in ammonia emissions in the German domain indicated that the high SIA concentrations originated from local sources within the German domain. The response of modelled SIA concentrations and connected deposition fluxes to precursor emission changes was non-linear. The response was found to be more linear for total deposition fluxes of sulphur and nitrogen than for SIA concentrations. Our knowledge on the constituents' non-linear relationships and interactions needs to be further improved and ideally implemented in our models to be able to assist policy-makers to develop sustainable mitigation strategies and adapt the latter to seasonal and spatial variations in the emission pattern (West et al., 1999; Tsimpidi et al., 2007). Hence, models with linearised chemistry (e.g. OPS (Operational Priority Substances) model; Van Jaarsveld, 2004) are not suitable for this purpose.

The impact of national measures compared to Europe wide mitigation efforts has been studied by means of several reduction scenarios with decreased emissions within the German domain only or within the European domain. As long range transport is important and important source areas are located upwind of Germany, decreasing emissions on the European domain (ED scenarios) is more effective in reducing SIA concentration and total deposition flux than reducing emissions on the German domain only (GD scenarios) for all performed emission scenarios. The difference between GD and ED scenarios is more severe for pollutants that are to a large extent affected by long-range transport as e.g. SO_2. This outcome confirms that a European wide mitigation strategy is essential to achieve substantial pollutant concentration reductions.

As NH_3 is more local than SO_2 and NO_x the effectiveness of NH_3 emission reduction shows the least difference between GD and ED scenario. Sulphate and nitrate concentrations are only slightly reduced when reducing emissions of SO_2 and NO_x simultaneously on the German domain. Although SO_2 German domain emissions are reduced by 50 % the resultant sulphate reduction is slightly less than the reduction in sulphate when NH_3 emissions are reduced by 40 %. The latter reduction in sulphate concentrations results solely from a reduced neutralisation of cloud acidity. Moreover, the simultaneous NO_x and SO_2 emission reductions lead to increased OH levels, which

counteract the sulphate reduction as the rate of homogeneous oxidation of SO_2 is increased (Tarrasón et al., 2003; Derwent et al., 2009). Additionally, the NO_x reduction is partly compensated by an increase in ammonium-nitrate due to the SO_2 emission reduction. Furthermore, the increase in OH levels also reduces the nitrate response as

5 it leads to an increased conversion of NO_x to HNO_3 counteracting for the decrease in NO_x (Fagerli et al., 2008). In contrast, nitrate is significantly reduced as soon as NH_3 emissions are reduced. The results demonstrate that national NH_3 measures in addition to EU wide efforts in Germany are more effective to reduce SIA concentrations and deposition fluxes than additional national measures on SO_2 and NO_x.

10 The potential of control strategies concerning SIA and PM reduction is strongly connected to the specific emission regime of the investigation area. We have found that NH_3 measures lead to highest SIA reduction in areas with moderate and low NH_3 emission densities. In these regions SIA formation is limited by the availability of NH_3 while in ammonia-rich areas SIA formation is limited by HNO_3 as even following a reduction

15 of NH_3 a sufficient amount of NH_3 remains to neutralize the available HNO_3.

The non-linear response in the emission-concentrations and the emission-deposition relationship has been subject of several investigations over Europe in the past two decades. Pay et al. (2012) suggested that control strategies concerning SIA in north-western Europe should focus on reductions of SO_2 and NO_x emissions. However, the

20 conclusion was drawn based on the analysis of the indicators "free ammonia", "S-ratio" (Hass et al., 2003) and "G-ratio" (Ansari and Pandis, 1998) which do not include all sensitivities, e.g. OH interactions which contribute to non-linearities in the sulphur and oxidised nitrogen budget (Tarrasón et al., 2003; Derwent et al., 2009). However, our findings are in line with earlier studies for different European regions (e.g. Renner and

25 Wolke, 2010; Derwent et al., 2009; Erisman and Schaap, 2004; Builtjes et al., 2010) showing that NH_3 emission reduction measures maintain a high reduction potential for SIA and therewith PM_{10} concentrations. The response of SIA concentrations on NH_3 emission changes was found to be non-linear with an increasing SIA reduction effectiveness with increasing reduction of NH_3 emissions. The latter was also found

in the German PAREST project (Builtjes et al., 2010). In addition to the SIA reduction stated by former studies, this study accounted for an additional sulphate reduction due to a reduced neutralisation of cloud acidity when NH_3 emissions are decreased through the variable droplet pH approach (Banzhaf et al., 2012) as suggested by Redington et al. (2009). The incorporation of the explicit cloud chemistry adds more non-linearity to the system. All SIA components are sensitive to ammonia emission changes when using a modelled droplet pH, while the change in SIA concentrations results solely from changes in nitrate and ammonium concentrations when assuming a constant droplet pH.

Although RCG simulates the temporal development of the PM episodes well, some shortcomings of the model have been found. The model was not able to capture the PM_{10} peaks, which is partly due to missing components in the modelled PM budget. In contrast, low PM_{10} levels are simulated too high. As the latter is not the case for the overall SIA concentrations, the reason for overestimation likely originates from the primary fraction. It was found that this overestimation is connected to high levels of wind blown dust for high wind speed conditions. As high PM levels during the investigation period occur at low wind speeds, high concentrations of wind blown dust do not occur during these episodes. The slight overestimation of sulphate concentrations can be partly attributed to an overestimation of modelled droplet pH leading to a too high rate of sulphate formation. Next to the buffering by carbon dioxide the effects of other buffering systems such as sea salt, mineral dust and organic components (Deguillaume et al., 2009) are not accounted for when modelling droplet pH (Banzhaf et al., 2012). In contrast to the sulphate concentrations, the nitrate concentrations are underestimated by RCG. This is partly connected to the overestimation of sulphate, which leads to a lower rate of ammonium-nitrate formation. Furthermore, evaluations of the applied equilibrium module ISORROPIA (Nenes et al., 1999) have indicated diverse shortcomings within the approach concerning the equilibrium between nitric acid and particulate ammonium nitrate (e.g. Schaap et al., 2011; Morino et al., 2006; Fisseha et al., 2006). The uncertainty in ammonia emission inventories in space and

time (Geels et al., 2012) leads to an additional uncertainty in the modelled nitric acid-ammonium nitrate-equilibrium and the overall modelled SIA formation. Next to the uncertainty in space and time according to EMEP (2009) the uncertainty in magnitude of absolute annual ammonia emission values amounts about ±30 % in Europe. As non-linearities are to a large extent controlled by ammonia, the uncertainty in ammonia emissions severely impacts the modelled SIA budget. Also the correlations for the precursor gases SO_2 and NO_2 in air are encouraging as they show the ability of the model to capture the temporal variability of the analysed species concentrations. However, RCG tends to overestimate SO_2 concentrations, while NO_2 concentrations tend to be underestimated. As former studies have shown primary pollutants – like SO_2 and NO_2 (which can be considered as almost primary pollutant as it is formed rapidly from emitted NO) – are more difficult to model (Vautard et al., 2009). The evaluation of modelled SO_x, NO_y and NH_x wet deposition fluxes indicated a good model performance with correlation coefficients between 0.74 and 0.82. The improvement of the spatial representation of precipitation of the meteorological driver may lead to a better representation of modelled wet deposition fluxes.

To further improve the performance of RCG, several options are singled out (1) inclusion of coarse nitrate from the reaction of HNO_3 with soil and sea-salt particles (Pakkanen, 1996), (2) accounting for the co-deposition of SO_2 and NH_3 (Flechard et al., 1999) within the deposition routine, and (3) incorporation of the compensation point in the RCG dry deposition scheme (Wichink Kruit et al., 2010). The implementation of these processes may add further interdependencies and non-linear responses. The resultant variations in the response to emission changes need to be identified and understood.

This study confirmed the important role of NH_3 when considering reductions of SIA concentrations and deposition fluxes of sulphur and nitrogen compounds. The NEC Directive and the Gothenburg protocol provide national emission ceilings for SO_2, NO_x, NH_3 and VOC. Following the latest current legislation baseline, according to Amann et al. (2012), SO_2 and NO_x emissions will decrease significantly from 2010–2030 in the EU-27 (SO_2: ∼ −70 %; NO_x: ∼ −65 %) and Germany (SO_2: ∼ −45 %; NO_x: ∼ −65 %)

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compared to 2005 emissions. NH_3 emissions are expected to increase for the EU-27 ($\sim$ +2 %) and for Germany ($\sim$ +11 %). However, results of a "maximum technically feasible reduction" (MTFR) scenario show that available measures could reduce NH_3 emissions significantly for the EU-27 ($\sim$ −30 %) and Germany ($\sim$ −35 %) compared to the current legislation baseline. The latter reveals that the NH_3 reduction potential might not be fully utilised yet. Next to the reduction potential the cost-effectiveness of measures needs to be considered. In Europe, costs for air pollution control including the costs for the current legislation baseline are significantly lower in the agricultural sector (which includes $\sim$ 95 % of the total NH_3 emissions) than in other sectors, where stringent emission control is already in force (Amann et al., 2011, 2012; Appelhans et al., 2012; Builtjes et al., 2010). Future negotiations for further emission reductions over Europe should focus on further implementation of sustainable and cost-effective NH_3 measures.

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Table 1. Overview of performed emission reduction scenarios and their set-up.

Emission Scenarios	pH modelled	pH constant	German domain (GD)	European domain (ED)
base run	×	–	×	×
−40 % NH3	×	–	×	×
−20 % NOx −50 %SO2	×	–	×	×
−40 % NH3 −20 % NOx −50 %SO2	×	–	×	×

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Table 2. Total annual "German" and "German domain" SO_x, NO_x and NH_3 emissions and the ratio of "German" emissions to "German domain" emissions.

Emissions	SO_x (t a^{-1})	NO_x (t a^{-1})	NH_3 (t a^{-1})
German domain emissions	979 800	2 402 052	876 200
German emissions	561 580	1 543 970	606 880
German emissions/German domain emissions	0.57	0.64	0.69

Table 3. Overview of performed ammonia emission sensitivity scenarios and their set-up.

Emission Scenarios	pH modelled	pH constant	German domain (GD)	European domain (ED)
−60 % NH3	×	×	×	−
−40 % NH3	×	×	×	×
−20 % NH3	×	×	×	−
base run	×	×	×	−
+20 % NH3	×	×	×	−
+40 % NH3	×	×	×	−

Table 4. Statistical comparison between measured and modelled concentrations and wet deposition fluxes at different stations (see Fig. 2) for the investigation period. Observed mean, as well as BIAS, RMSE and correlation are given.

Concentrations and wet deposition fluxes	Observed mean	RMSE	BIAS	Correlation
PM_{10} concentration (rural background)	$22.56\,\mu g\,m^{-3}$	$10.36\,\mu g\,m^{-3}$	$2.95\,\mu g\,m^{-3}$	0.75
PM_{10} concentration (suburban background)	$27.01\,\mu g\,m^{-3}$	$12.61\,\mu g\,m^{-3}$	$1.28\,\mu g\,m^{-3}$	0.71
SIA concentration (rural background)	$17.55\,\mu g\,m^{-3}$	$8.88\,\mu g\,m^{-3}$	$-2.10\,\mu g\,m^{-3}$	0.76
SO_4^{2-} concentration (rural background)	$3.4\,\mu g\,m^{-3}$	$2.6\,\mu g\,m^{-3}$	$1.3\,\mu g\,m^{-3}$	0.63
NO_3^- concentration (rural background)	$11.7\,\mu g\,m^{-3}$	$6.3\,\mu g\,m^{-3}$	$-3.5\,\mu g\,m^{-3}$	0.76
NH_4^+ concentration (rural background)	$4.1\,\mu g\,m^{-3}$	$2.16\,\mu g\,m^{-3}$	$0.17\,\mu g\,m^{-3}$	0.73
SO_2 concentration (rural/suburban background)	$3.9\,\mu g\,m^{-3}$	$5.4\,\mu g\,m^{-3}$	$2.9\,\mu g\,m^{-3}$	0.62
NO_2 concentration (rural/suburban background)	$15.0\,\mu g\,m^{-3}$	$8.8\,\mu g\,m^{-3}$	$-4.5\,\mu g\,m^{-3}$	0.65
SO_x wet deposition	$102.27\,mg\,m^{-2}$	$45.9\,mg\,m^{-2}$	$-32.2\,mg\,m^{-2}$	0.82
NO_y wet deposition	$50.10\,mg\,m^{-2}$	$19.2\,mg\,m^{-2}$	$7.3\,mg\,m^{-2}$	0.80
NH_x wet deposition	$40.91\,mg\,m^{-2}$	$23.4\,mg\,m^{-2}$	$-11.6\,mg\,m^{-2}$	0.74
Precipitation	$50.75\,mm$	$29.4\,mm$	$2.5\,mm$	0.57

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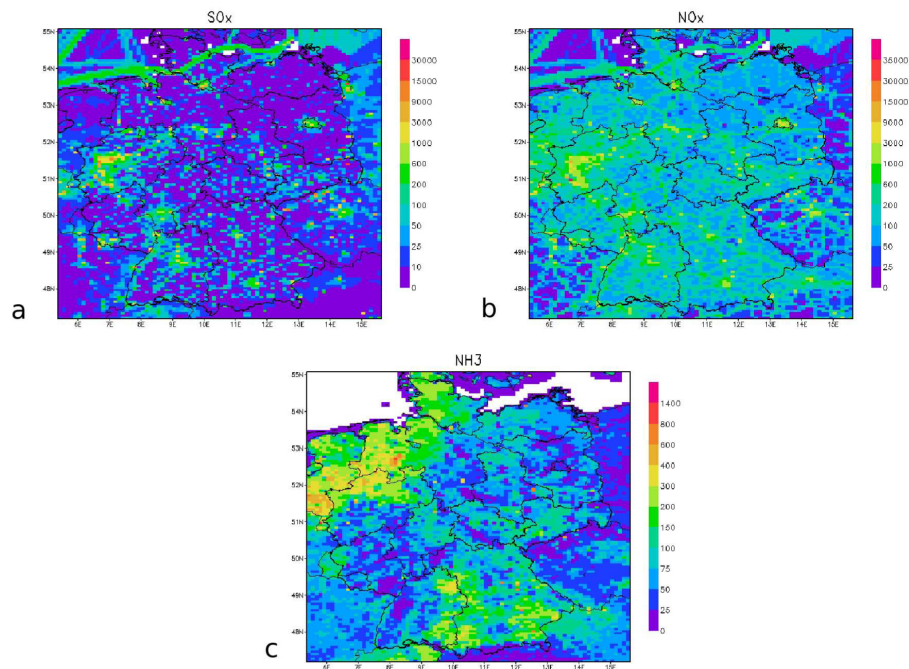
Fig. 1. Spatial distribution of the total annual **(a)** SO_x, **(b)** NO_x and **(c)** NH_3 emissions in $t\,a^{-1}\,cell^{-1}$.
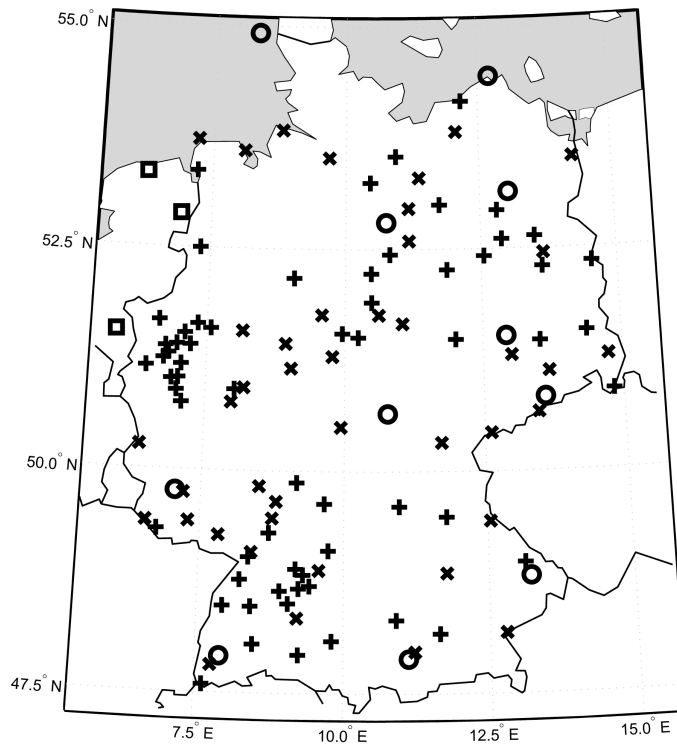
Fig. 2. Map of observational station locations: PM$_{10}$ concentrations (rural background) (×), PM$_{10}$ concentrations (suburban background) (+), SIA concentrations (□), wet deposition fluxes (○).
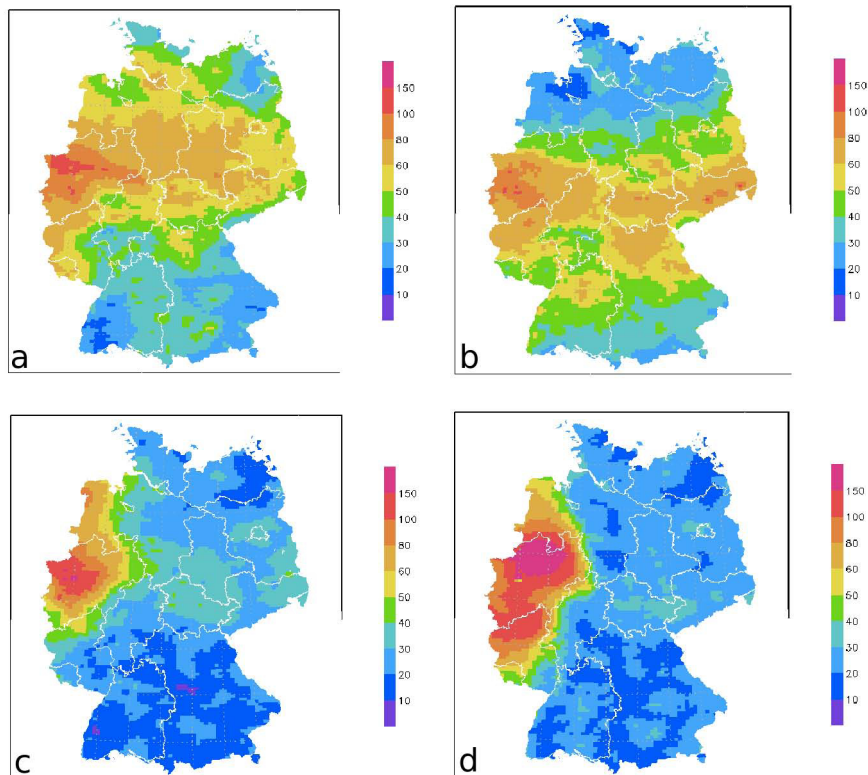
Fig. 3. Daily mean PM$_{10}$ concentrations in µg m^{-3} on **(a)** 4 and **(b)** 5 April 2009 and **(c)** 12 and **(d)** 13 April 2009 derived by Optimal Interpolation of observations.
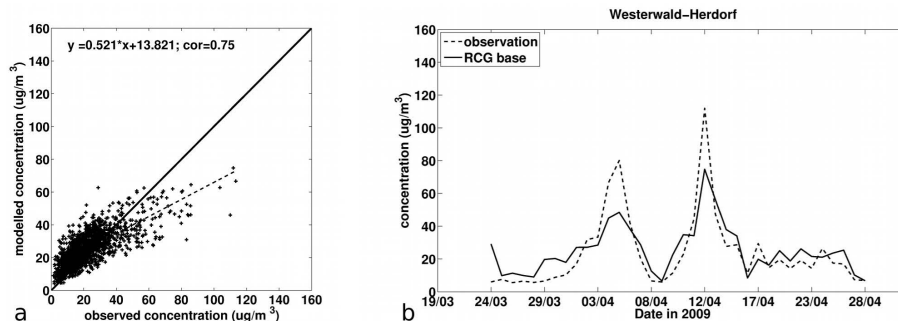
Fig. 4. Daily mean modelled PM_{10} concentrations **(a)** versus observations at 42 Airbase sites and **(b)** versus observations at Airbase site Westerwald-Herdorf.
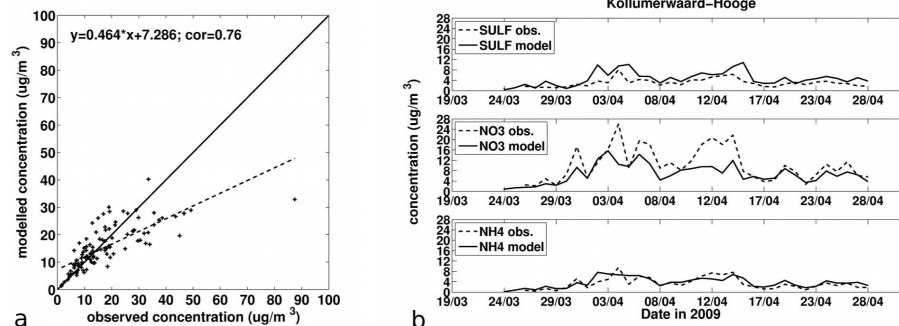
Fig. 5. Daily mean modelled SIA concentrations **(a)** versus observations at 3 RIVM sites and **(b)** versus observations at station Kollumerwaard.
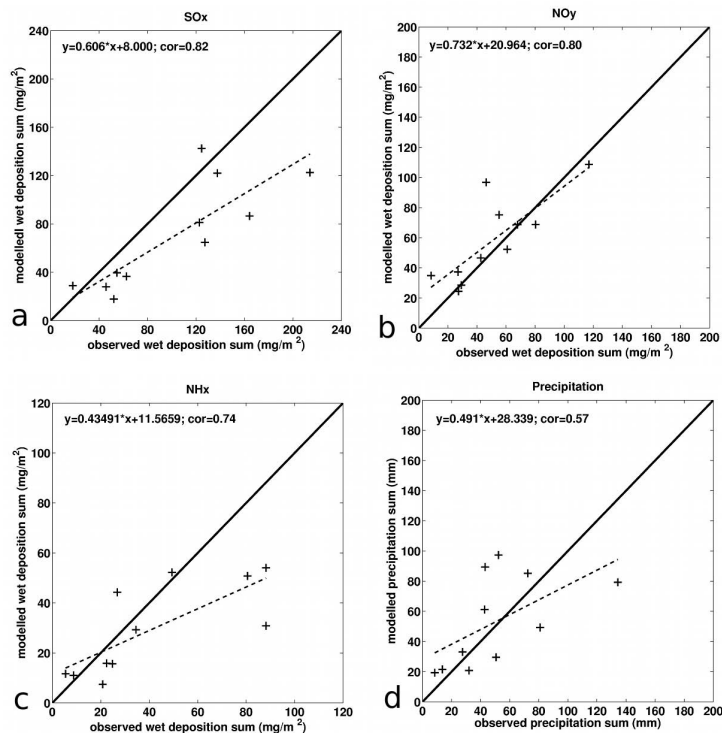
Fig. 6. Modelled wet deposition sum of **(a)** SO_x, **(b)** NO_y, **(c)** NH_x and **(d)** total precipitation for the investigation period versus observations at 11 UBA sites.
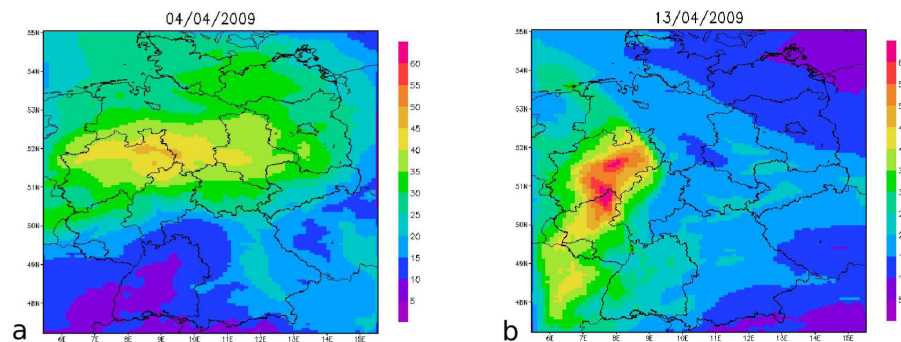
Fig. 7. Modelled mean SIA concentration of the base run for **(a)** 4 April 2009 and **(b)** 13 April 2009.
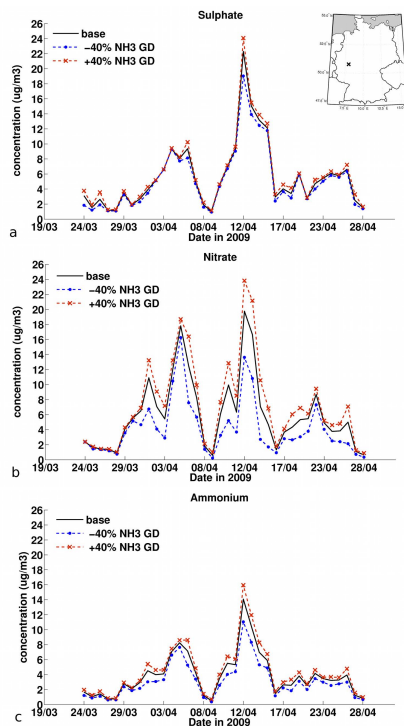
Fig. 8. Daily mean **(a)** sulphate, **(b)** nitrate and **(c)** ammonium concentration at station Westerwald-Herdorf for different ammonia emission scenarios.

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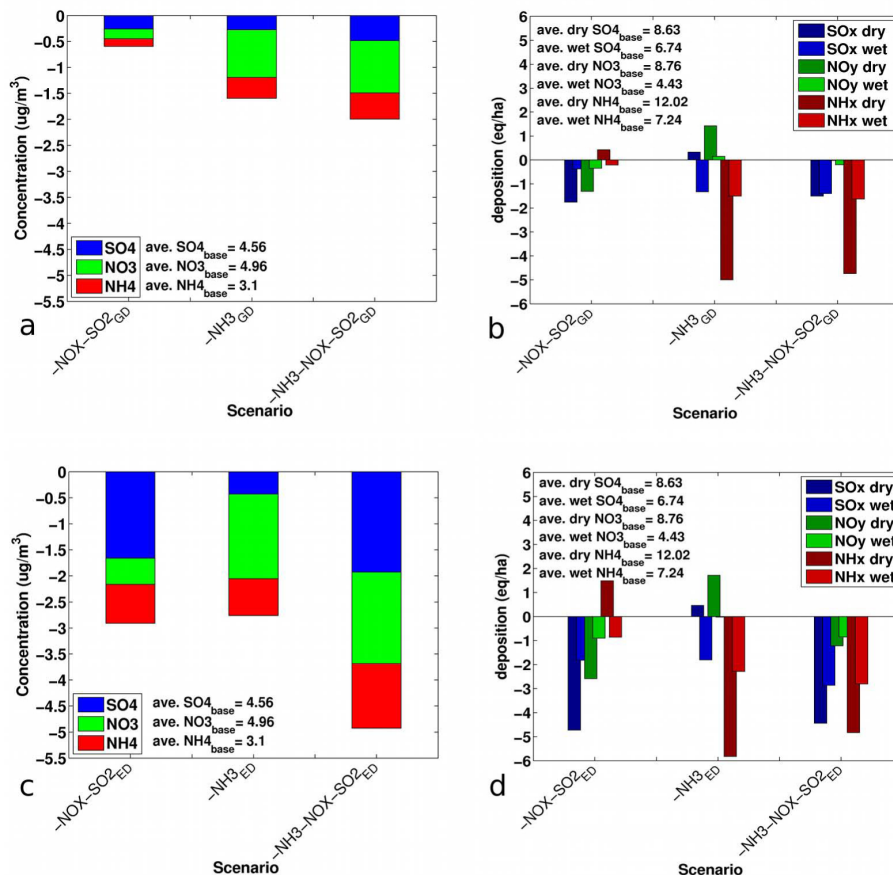
Fig. 9. Mean modelled **(a)** SIA concentration and **(b)** total deposition flux for different emission scenarios on the German domain excluding the boundary conditions and **(c, d)** the German domain including the boundary conditions.

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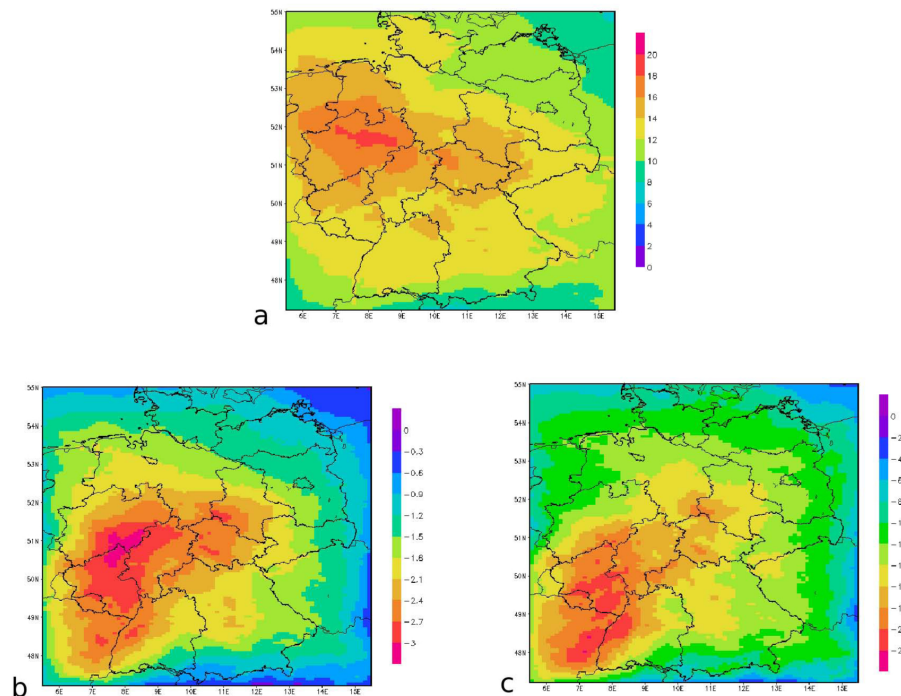
Fig. 10. (a) Base case mean SIA concentration ($\mu g\,m^{-3}$) of the investigation period and **(b)** absolute and **(c)** relative SIA reduction by means of the −40 % NH3 GD scenario compared to the base case.
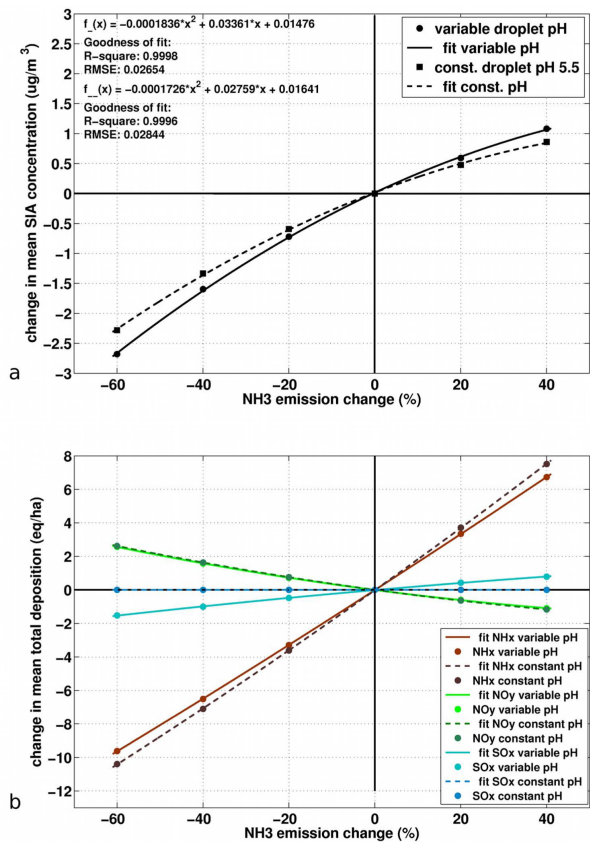
Fig. 11. Response of **(a)** the mean modelled SIA concentration and **(b)** the mean modelled SO_x, NO_y and NH_x total deposition in the German domain to ammonia emission changes using a variable (solid line) or constant (dashed line) droplet pH.