Dynamic model evaluation for secondary inorganic aerosol and its precursors over Europe between 1990 and 2009

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Abstract

In this study we present a dynamic model evaluation of the chemistry transport model LOTOS-EUROS (LOng Term Ozone Simulation - EURopean Operational Smog) to analyse the ability of the model to reproduce observed non-linear responses to emission changes and interannual variability of secondary inorganic aerosol (SIA) and its precursors over Europe from 1990 to 2009. The 20 year simulation was performed using a consistent set of meteorological data provided by RACMO2 (Regional Atmospheric Climate MOdel). Observations at European rural background sites have been used as reference for the model evaluation. To ensure the consistency of the used observational data stringent selection criteria were applied including a comprehensive visual screening to remove suspicious data from the analysis. The LOTOS-EUROS model was able to capture a large part of the seasonal and interannual variability of SIA and its precursors' concentrations. The dynamic evaluation has shown that the model is able to simulate the declining trends observed for all considered sulphur and nitrogen components following the implementation of emission abatement strategies for SIA precursors over Europe. Both, the observations and the model show the largest part of the decline in the 1990's while smaller concentration changes and an increasing number of non-significant trends are observed and modelled between 2000-2009. Furthermore, the results confirm

former studies showing that the observed trends in sulphate and total nitrate concentrations from 1990 to 2009 are lower than the trends in precursor emissions and precursor concentrations. The model well captured these non-linear responses to the emission changes. Using the LOTOS-EUROS source apportionment module trends in formation efficiency of SIA have been quantified for four European regions. The exercise has revealed a 20-50% more efficient sulphate formation in 2009 compared to 1990 and an up to 20% more efficient nitrate formation per unit nitrogen oxide emission, which added to the explanation of the non-linear responses. However, we have also identified some weaknesses to the model and the input data. LOTOS-EUROS underestimates the observed nitrogen dioxide concentrations throughout the whole time period, while it overestimates the observed nitrogen dioxide concentration trends. Moreover, model results suggest that the emission information of the early 1990's used in this study needs to be improved concerning magnitude and spatial distribution.

1 Introduction

Atmospheric input of sulphur and nitrogen components may decrease biodiversity in vulnerable terrestrial and aquatic ecosystems through eutrophication and acidification of soils and fresh water (Bobbink et al., 1998). The major sources of sulphur and reactive nitrogen in the atmosphere are sulphur dioxide (SO_2) and nitrogen oxide (NO_x) emissions from fossil fuel combustion and ammonia (NH_3) emissions from agricultural activities. Although these gases may themselves be removed from the atmosphere by dry deposition or rainout, they are the precursor gases for SIA (sulphate (SO_4^{2-}), nitrate (NO_3^-) and ammonium (NH_4^+)). The latter provides a means for long-range transport of reactive nitrogen on a continental scale causing negative ecosystem impacts far away from their major source areas. In addition, SIA contributes a large portion of particulate matter concentration throughout the European domain (Putaud et al., 2010). Especially ammonium nitrate (NH_4NO_3) concentrations are shown to be particularly enhanced during days with PM10 concentrations up or above the EU (European Union) daily limit value (e.g. Weijers et al., 2011). Moreover, SIA are involved in climate change by affecting the radiation balance of the earth (Forster et al., 2007). Recent studies show that short term climate mitigation aimed at reducing black carbon may be effective, provided that the climate impact of the co-emitted SIA precursors does not cause a net cooling impact (Bond et al., 2013). Hence, a thorough understanding of the SIA budget is required to

inform policy makers and to devise mitigation strategies that are effective for biodiversity, climate change and human health.

To combat the adverse impacts on biodiversity and human health a series of international conventions and agreements were implemented. The Convention on Long-range Transboundary Air Pollution was adopted in 1979 and the related Gothenburg Protocol establishing emission ceilings for sulphur oxides (SO_x), NO_x, volatile organic compounds (VOCs) and NH_3 for 2010 negotiated by the EU Member States together with Central and Eastern European countries, the United States and Canada was accepted in 1999 (UNECE, 1999). The National Emissions Ceiling Directive (NECD 2001/81/EC) was introduced in 2001 (EC, 2001) setting national emission ceilings for the EU countries for 2010 and 2020. The implemented mitigation measures have led to significant emission reductions (Grennfelt and Hov, 2005). According to the European Environmental Agency (EEA) (2012), SO_x emissions have decreased by 75%, NO_x emissions by 42% and NH_3 emissions by 28% in the EEA-32 group of countries from 1990-2010. As part of the conventions air pollution monitoring networks have been implemented over Europe providing a long-term observation facility to be able to assess the effectiveness of the implemented air quality management. Although the substantial emission reductions of SO_x, NO_x and NH_3 are largely reflected in the trends of pollutant concentrations and wet deposition fluxes, the responses were found to be non-linear (e.g. Lövblad et al., 2004; Fagerli and Aas, 2008; Tørseth et al., 2012; Harrison et al., 2014). These studies highlighted that for SIA and its precursors the implemented emission mitigation measures did not completely meet the expected concentration reduction. Hence, understanding of the non-linear responses is important to be able to provide robust policy support.

Chemistry transport models (CTMs) are used to analyse potential emission reduction strategies and quantify their effectiveness. Before the CTMs can be used to inform policy development they need to be evaluated. Dennis et al. (2010) introduced a comprehensive evaluation framework in which four types of model evaluation are identified: operational, diagnostic, dynamical and probabilistic evaluation. Operational model evaluations have been performed within a huge number of studies using standard statistical and graphical analysis to determine how the model results compare with observations (e.g. Appel et al., 2011, Thunis et al., 2012). Diagnostic model evaluation, focussing on the description of an individual process or component in the model has also been subject of many studies (e.g. Fahey and Pandis, 2003; Redington et al., 2009; Banzhaf et al., 2012). Recently, probabilistic or ensemble based evaluation has gained popularity as the ensemble mean of a group of models shows mostly the best model performance in comparison to observations (Vautard et al.,

2007; McKeen et al., 2005). Dynamic model evaluations, in which the ability of the modelling system to capture the observed responses to changes in emissions or meteorology is analysed, have only been performed in a few studies so far (e.g. Berglen et al., 2007).

CTMs need to be able to capture non-linear responses of the emission-concentration and emission-deposition relationship as well as interannual variability over the last 15-20 years to provide confidence in the use of CTMs for regulatory purposes (Civerolo et al., 2010). Colette et al. (2011) investigated the capability of six state-of-the-art chemistry transport models to reproduce air quality trends and interannual variability of ozone (O_3), nitrogen dioxide (NO_2) and PM10 for the time period of 10 years from 1998-2007. They concluded that the models captured most of the important features to justify their implementation for future projections of air quality provided that enough attention is given to their underestimation of interannual variability. Fagerli and Aas (2008) found that the EMEP (European Monitoring and Evaluation Programme) model's response for nitrogen in air and precipitation to emission changes over Europe from 1980-2003 is reasonable. The results indicated a lack of trends in total nitrate (TNO_3: sum of aerosol nitrate and gaseous nitric acid) concentrations despite NO_x emission reductions and it was concluded from the model simulations that this non-linear behaviour can partly be attributed to a shift in the equilibrium between nitric acid (HNO_3) and NH_4NO_3 towards particulate phase, which was caused by SO_2 emission reductions. However, the model simulations could not be performed using a consistent meteorological data set for all simulated years. Civerolo et al. (2010) performed an 18-year CMAQ (Community Multi-scale Air Quality) simulation (1988-2005) over the north-eastern United States enabling the investigation of spatial patterns and seasonal variations, but also on long-term trends of SO_4^{2-} and NO_3^- in the presence of emissions changes and meteorological variability. The results suggested that the modelling system largely captured the long-term trends in sulphur and nitrogen compounds. While the seasonal changes in sulphur compounds were also captured, the model did not reproduce the average seasonal variation or spatial patterns in NO_3^-.

Former studies suggest that the non-linear response of pollutant concentrations to emission changes can be attributed to the differing magnitude of emission reduction for the different substances (Løvblad et al., 2004; Fagerli and Aas, 2008) inducing shifts in the atmospheric chemistry and equilibrium between gas- and particulate phase, which determine the gas to particle conversion. These non-linearities have been also identified in short term modelling studies that focus on the sensitivity of SIA formation to precursor emission reductions (e.g. Erisman and Schaap, 2004; Redington et al., 2009; Derwent et al., 2009; Banzhaf et al., 2013). State of the art labelling

approaches (Yarwood et al., 2007; Wagstrom et al., 2008) can be applied to track the source allocation for secondary aerosols and its precursor gases to study the response of atmospheric chemistry to emission changes. However, long-term simulations including a source apportionment have not yet been performed due to the high computational burden. Kranenburg et al. (2013) introduced a source apportionment module for the operational CTM LOTOS-EUROS, which enables long-term simulations with source attribution to investigate possible trends in the gas to particle formation efficiency that accompanied the changes in emission levels over time. We aim to evaluate the LOTOS-EUROS model for its ability to model the trends in SIA concentrations and, at the same time, investigate the non-linearity in SIA formation.

In this study a model run of 20 years from 1990 to 2009 was performed with a horizontal grid resolution of 0.50° longitude x 0.25° latitude over Europe using the CTM LOTOS-EUROS (section 2.1.1). The model explicitly accounts for cloud chemistry and aerosol thermodynamics. The model run is based on emissions for 1990, 1995, 2000, 2005 and 2010 provided by the International Institute for Applied Systems Analysis (IIASA) (section 2.1.2) and a consistent 3 hourly meteorological data set from 1990 to 2009 obtained from the regional climate model RACMO2 (section 2.1.2) of the Royal Netherlands Meteorological Institute (KNMI). The modelled concentrations of SIA and its precursors are compared to observations at rural background sites (section 2.2). By means of an operational (section 3.1) and a dynamic evaluation (section 3.2) we identify shortcomings and limitations of the model system and input data that need to be improved or considered when using the applied set up for future emission scenarios. In order to enable the analysis of trends in gas to particle conversion and residence time of the involved species the source apportionment module of LOTOS-EUROS (section 2.1) has been used to trace the amount of SIA formed per unit emission of SO_2, NO_x and NH_3 for 4 different regions over Europe from 1990-2009 (section 3.3). The results are discussed and conclusions are drawn in section 4.

2 Methods and data

This investigation focuses on SIA and its precursors (SO_2, NO_x and NH_3) over the time period 1990 to 2009. Although the focus is on this 20 year long period we have also investigated the trends in concentrations for the shorter time periods 1995-2009 and 2000-2009 because emission reductions did not proceed linearly and in line with each other from 1990-2009. By considering several time periods we could assess the sensitivity of the trend to the different time periods. Furthermore, the

amount of available observations increased for the later periods, which made a broader assessment of the results possible.

In the following subsections the applied model and model set-up, the used observations and the statistic tools we have used to evaluate the model and calculate and assess the observed and modelled trends are described.

2.1 Simulation description

2.1.1 Model description LOTOS-EUROS

LOTOS-EUROS is a 3D chemistry transport model. The off-line Eulerian grid model simulates air pollution concentrations in the lower troposphere solving the advection-diffusion equation on a regular lat-lon-grid with variable resolution over Europe (Schaap et al., 2008). In this study, model version 1.8 was used.

The vertical transport and diffusion scheme accounts for atmospheric density variations in space and time and for all vertical flux components. The vertical grid is based on terrain following vertical coordinates and extends to 3.5 km above sea level. The model uses a dynamic mixing layer approach to determine the vertical structure, i.e. the vertical layers vary in space and time. The layer on top of a 25 m surface layer follows the mixing layer height, which is obtained from the meteorological input data that is used to force the model. The height of the two reservoir layers is determined by the difference between model top at 3.5 km and mixing layer height. If the mixing layer extends near or above 3.5km, the top of the model exceeds the 3.5 km according to the above-mentioned description. The horizontal advection of pollutants is calculated applying a monotonic advection scheme developed by Walcek et al. (2000).

Gas-phase chemistry is simulated using the TNO CBM-IV scheme, which is a condensed version of the original scheme (Whitten et al, 1980). Hydrolysis of N2O5 is explicitly described following Schaap et al. (2004). LOTOS-EUROS explicitly accounts for cloud chemistry computing SO_4^{2-} formation as a function of cloud liquid water content and cloud droplet pH as described in Banzhaf et al. (2012). For Aerosol chemistry LOTOS-EUROS features the thermodynamic equilibrium module ISORROPIA2 (Fountoukis and Nenes, 2007). Dry Deposition fluxes are calculated following a resistance approach as described in Erisman et al. (1994). Furthermore, a compensation point approach for NH_3 is included in the dry deposition module (Wichink Kruit et al., 2012). The wet

deposition module is based on precipitation rates using simple scavenging coefficients for the below cloud scavenging of gases (Schaap et al, 2004) and particles (Simpson et al, 2003).

In LOTOS-EUROS, the temporal variation of the emissions is represented by monthly, day-of-the-week and hourly time factors that break down the annual totals for each source category. An included biogenic emission routine is based on detailed information on tree species over Europe (Koeble and Seufert, 2001). The emission algorithm is described in Schaap et al. (2009) and is very similar to the simultaneously developed routine by Steinbrecher et al. (2009). Sea salt emissions are described using Martensson et al. (2003) for the particles <1μm and Monahan et al. (1986) for the coarser particles.

LOTOS-EUROS includes a source apportionment module, which enables tracking the source contribution of a set of sources through the model system. The emissions can be categorized in several source categories (e.g. countries or sector) and labelled accordingly before the model is run. The total concentration of each substance for each time step and in each grid cell is modelled as before, but next to this, the fractional contribution of each label to every species is calculated. During each process, the new fractional contribution of each label is defined by calculating a weighted average of the fractions before the process and the concentration change during the process. The labelling routine is only implemented for chemically active tracers containing C, S or N (reduced and oxidized) atoms, as these are conserved and traceable. The source apportionment module is extensively described in Kranenburg et al. (2013).

The LOTOS-EUROS model has participated in several international model inter comparison studies addressing O_3 (Hass et al, 1997; Van Loon et al, 2007; Solazzo et al., 2012a) and particulate matter (Cuvelier et al, 2007; Hass et al, 2003; Stern et al, 2008; Solazzo et al., 2012b) and shows comparable performance to other European models.

2.1.2 Model setup

A model run of 20 years from 01.01.1990 to 31.12.2009 has been performed on a domain covering Europe (35°N-70°N; 10°W-40°E) with a horizontal resolution of 0.50° longitude x 0.25° latitude on a rectangular regular latitude-longitude grid (ca. 25x25 km^2). As described above the lowest dynamic layer is the mixing layer, taken from the meteorological input.

The simulation was forced with a consistent meteorological data set from 1990 to 2009 obtained from the regional climate model RACMO2 (Lenderink et al., 2003; Van Meijgaard et al., 2008) of the

KNMI. At the boundaries the simulation was driven by meteorology from ERA-Interim reanalysis (Dee et al., 2011). Nudging of meteorological data has not been performed for the model runs and RACMO2 is only constrained by the lateral boundary conditions. RACMO2 has a horizontal resolution of 0.44° with 114 points distributed from 25.04°W to 24.68°E longitude and 100 points from 11.78° S to 31.78° N latitude in the rotated grid. The South Pole is rotated to 47°S and 15°E. In the vertical, 40 pressure levels were used. As described in Manders et al. (2012) the horizontal projection of RACMO2 fields on the LOTOS-EUROS grid was carried out by bi-linear interpolation. The vertical projection of RACMO2 profiles on the much coarser LOTOS-EUROS vertical grid was achieved by mass-weighted averaging of those RACMO2 model layers that were fully or partially contained in each of the LOTOS-EUROS model layers. At the applied resolution RACMO2 uses a model time step of 15 min and output for coupling with LOTOS-EUROS was generated every three hours. RACMO2 has been included in ensemble studies with other regional climate models (Kjellström and Giorgi, 2010; Kjellström et al., 2010; Vautard et al., 2013; Kotlarski et al., 2014) and has been successfully applied to force LOTOS-EUROS in earlier studies (Manders et al., 2011; Manders et al., 2012; Mues et al., 2013).

Lateral boundary conditions in LOTOS-EUROS were taken from climatological background concentrations for gases and aerosols. For a number of components we follow the EMEP method (Simpson et al., 2003) based on measured data, in which simple functions were derived to match the observed distributions. Some aerosol species are set to constant at the boundaries. NH_3 boundary conditions are neglected. SO_4^{2-} is assumed to be fully neutralised by ammonium. Nitrate values are assumed to be included in those of HNO_3 (derived following Simpson et al. (2003)) and are zero as well. The climatology fields did not include windblown dust going back to 1990. Hence, dust from e.g., wind erosion, agricultural land management and resuspension by road transport has been neglected, as it does not contribute to the here investigated substances. For O_3 we have used the climatological dataset by Logan (1999), derived from O_3 sonde data. For the interpretation of the model results we need to keep in mind that there are no trends in boundary conditions considered over the investigated 20 year period.

The emissions applied in this study were provided by IIASA. The data was generated using RAINS (Regional Air pollution INformation and Simulation) model output for 1990-2000 and GAINS (Greenhouse gas and Air pollution INteractions and Synergies) model output for 2000-2010. A description of the RAINS model and the GAINS model can be found in Amann et al. (1999) and Amann et al. (2011), respectively. Annual total emissions were provided per country, per sector and

per SNAP (Selected Nomenclature for Air Pollutants) code for 1990, 1995, 2000, 2005 and 2010. A linear interpolation was performed to fill in the emissions of the years within the delivered ones. Figure 1a shows the trends in SO_2, NO_x and NH_3 emissions in the EU-27 member States including Norway and Switzerland (= EU-27+) for 1990 to 2010 in % with 1990 as reference derived from the applied final emission inventory. The corresponding absolute annual total emissions of SO_2, NO_x and NH_3 of the EU27+ member States for 1990, 1995, 2000, 2005 and 2010 are presented in Table S1 in the Supplement. The emissions have decreased over Europe for all considered components. The slope of the decrease in Figure 1a has been computed using a standard linear least square method. Most emission reduction was achieved for SO_2 with a negative trend of -3.9% a^{-1} (a: annum) leading to a decrease of more than 70% from 1990 to 2010. NO_x emissions have been decreased by somewhat less than 50% in the same time period (-2.52% a^{-1}) followed by NH_3 emissions with a decrease of somewhat less than 20% from 1990 to 2009 (0.85% a^{-1}). In Figure 1a we present results for the emission trends since 1990 for the EU-27+ member States as a whole. While it is known that emission changes from 1990 to 2009 differed significantly from region to region, precise information on the spatial distribution of the emissions for the early 90s is lacking. Although EMEP provides information on changes in the emission distribution from the early 1990s onwards we used the TNO MACC (Monitoring Atmospheric Composition and Climate) (Denier van der Gon et al., 2010; Pouliot et al., 2012) spatial distribution of emissions for the year 2005 for the entire time period of investigation. We believe that current emission allocation proxies are more reliable than the ones used in the 1990s. Furthermore, the EMEP emission information for the 1990s is only available on a resolution of 150x150 km^2, which is much lower than the resolution of the applied MACC distribution and is therefore not expected to provide an improvement. Annual emissions from international shipping per sea and per sector were provided by the Centre on Emission Inventories and Projections (CEIP). Figure 1b shows the trends in SO_2 and NO_x International Shipping emissions for 1990 to 2010 in % with 1990 as reference. Included are the Baltic Sea, the North-East Atlantic Ocean, the North Sea, the Mediterranean Sea and the Black Sea. NO_x emissions have increased over the whole time period 1990 to 2009 for all seas while SO_2 emissions have increased for the North-East Atlantic Ocean, the Mediterranean Sea and the Black Sea. In the Sulphur Emission Control Areas of the North Sea ("NOS" in Figure 1b) and the Baltic Sea ("BAS" in Figure 1b) SO_2 emissions have increased from 1990 to 2005 and decreased thereafter due to improved fuel quality. The absolute annual total emissions of SO_2 and NO_x (summed over all included seas listed above) for 1990, 1995, 2000, 2005 and 2010 are given in Table S1 in the Supplement.

In order to analyse the trends in gas to particle conversion and residence time of the involved species the LOTOS-EUROS source apportionment module was applied. We defined 5 labels for tracking 10 kilo tons (ktons) of SO_2, NO_x and NH_3 emissions from either one of these. The labels were defined to represent the following geographical areas:

1. The Netherlands and Belgium
2. Baltic Sea (international shipping)
3. Czech Republic
4. Romania
5. Rest

Ten ktons of precursor emission were chosen, as it is certainly smaller than the single country annual total emissions for 2009. Note that the 10 ktons are chosen arbitrary as tracking any other fraction of the emissions would give the same results due to the labelling approach used (Kranenburg et al., 2013). In practice, for each year the 10 ktons are normalized to the total emissions. The obtained fraction is applied to all emissions in the country and allocated to the respective label. Together with the simulation of each substance in each grid cell on hourly basis, the fractional contribution of each of the above labels to every substance, including SO_4^{2-}, NO_3^- and NH_4^+, is calculated. By means of the latter the amount of SIA formed from the 10 ktons of precursor gases can be derived for each label and possible trends in gas to particle conversion within the time period 1990 to 2009 can be analysed.

2.2 Observations

In the following subsections we describe the in-situ surface observations that were used to evaluate the LOTOS-EUROS model and to derive the observed trends in SIA and its precursors concentrations (Section 2.2.1) and the observations used to compare to the meteorological input data provided by RACMO2 (Section 2.2.2).

2.2.1 Species concentrations

The European EMEP observational network is devised for trend assessment (EMEP/CCC, 2001; Hjellbrekke and Fjæraa, 2011). The EMEP data is validated through a quality assurance/quality control process involving the individual institutions responsible for the different sites and the EMEP-

CCC as documented by several reports available on the EMEP website (www.emep.int). Data was downloaded from the EBAS repository (http://ebas.nilu.no/, download in autumn 2012). However, only a few selected stations per country are included in the network. In addition to the EMEP sites, the stations of AirBase (European AIR quality database), the public database of the EEA, were added to the observational data set (http://airbase.eionet.europa.eu/, download in autumn 2012). The latter are not specifically devised for trend assessment but have been used in several studies on long-term trends (e.g. EEA, 2009; Colette et al., 2011; Wilson et al., 2012). The data reported to AirBase are quality controlled and checked prior to submission by the countries that provide the data.

This study is aimed to investigate the transboundary trend of concentrations in the European background following emission changes all over Europe from 1990-2009. Hence, only rural background stations are included in the applied observational data set. The analysis is based on daily observations. The consistency of the observational data set used for the trend assessment and the operational and dynamical model evaluation was ensured by the implementation of three selection criteria derived from the guidelines of the EEA (EEA, 2009; Colette et al., 2011):

1. The annual coverage of data must be larger than 75 %
2. With criterion No. 1 fulfilled, at least 80% of the annual time series must be available
3. Passing a visual screening of the data

For each time period (1990-2009, 1995-2009 and 2000-2009) a separate data subset of stations within the model domain (35°N-70°N; 10°W-40°E) was built based on the selection criteria described above. As we also address relative trends within this study we consider it important to have the first year of each time period covered. Hence, only stations that could provide the requested 75% data coverage for the first year of the time period were included in the corresponding subset.

Finally, a visual screening of the time series of daily observations for all species and at all stations that had passed the selection criteria described above was performed. Surprisingly many defective time series have been identified. The corresponding stations have been removed from the subsets. The most frequently reasons for removal from the data set were high detection limits throughout the time series leading to disappearing concentration regimes, high amounts of implausible outliers/peaks and constant value signals over long time periods. The data reliability is further discussed in section 4.

It was found that due to a lack of data the analyses of NH_3 observations could not be included in the study. However, total ammonia (TNH_4: sum of aerosol ammonium and gaseous ammonia)

observations were included in the trend assessment as considerably more stations with TNH_4 observations than with NH4 observations were available. The latter was also the case for TNO_3 and NO_3. Hence, the considered observed components within this study are SO_2, SO_4^{2-}, NO_2, TNO_3 and TNH_4. In the Supplement, Figure S1 to Figure S3 show maps of the locations of the observational sites used for the analysis for the different components and the different time periods. Table 1 summarizes the number of stations for the different species and subsets before and after the visual screening. The number of discarded stations is highest for SO_2 and NO_2. For both components a large part of the considered stations are from AirBase passing through a less stringent quality control process than EMEP stations.

Due to a lack of long-term monitoring sites within Great Britain, France, Spain and the Mediterranean region within the monitoring networks used in this study the majority of sites for SO_2 and NO_2 observations is located within central Europe accompanied by several sites in northern and eastern Europe. For both components no southern European station and in the case of NO_2 no western European station was available for comparison for the 20 years period. For the time period 1995-2009 an increasing number of eastern and western European stations and in the case of SO_2 one southern European station passed the selection criteria. For TNO_3 and TNH_4 additionally to the lack of long-term observations in southern and western Europe, a lack of observations in central Europe was found and the few available sites are located in northern and eastern Europe. Stations in NH_3 hot spot regions like e.g. the Netherlands or the Po valley did not pass the data selection criteria for any of the time periods. Also for SO_4^{2-} no southern European station was available for 1990-2009. The available stations are distributed over Western, Eastern and Northern Europe with most stations being located in Northern Europe. For 1995-2009 central and eastern European stations and one southern European station could be included in the analysis. We would like to stress that the stations at which SO_2 and SO_4^{2-} concentrations are investigated may partly differ.

Finally, for the time period 2000-2009 few southern European stations could be included in the analysis of all considered components. Furthermore, Figure S4 in the Supplement shows for each component those stations that pass the data selection criteria for all considered time periods.

2.2.2 Meteorological observations

Selected parameters of the RACMO2 model are compared to observations to be able to assess the ability of the model to capture the observed meteorological seasonal, annual and interannual

variability. For the evaluation, data of the European Climate Assessment and Dataset (ECA&D) project (Klok and Klein Tank, 2009) is applied. The project was initiated by the European Climate Support Network (ECSN) and is funded by and coordinated at the KNMI. A compilation of daily observations obtained from climatological divisions of national meteorological and hydrological services, observatories and research centres throughout Europe and the Mediterranean are included in the database. The data series of observations is combined with quality control and analysis of extremes via climate change indices (Klein Tank et al., 2002).

Daily observed series of 4 parameters that affect atmospheric chemistry have been extracted from the dataset for the years 1990 to 2009 for evaluation purposes: Temperature (at 2 meter), relative humidity (at 2 meter), wind speed (at 10 meter) and precipitation. For each parameter a selection of stations was extracted so that, if available, central, northern, eastern, southern and western European stations were included in the analysis to also enable a regional consideration. For relative humidity no northern European stations could be included and western European stations were rare concerning observations of relative humidity and wind speed. In total 206 stations were selected for the evaluation of modelled temperature, 113 stations for the evaluation of modelled relative humidity, 246 stations for the evaluation of modelled wind speed and 240 stations for the evaluation of modelled precipitation. The observed station data is compared with model data at the nearest gridpoint.

2.3 Statistical measures and methods for evaluation and trend assessment

For the evaluation of the used meteorological input provided by RACMO2 and the resultant concentrations simulated by LOTOS-EUROS three statistical measures have been applied to assess the ability of the models to reproduce the observed values:

1. Correlation coefficient r

$$r = \frac{\sum_{i=1}^{n}(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2 \sum_{i=1}^{n}(y_i - \bar{y})^2}} \qquad \text{Equation 1}$$

2. Root mean square error (RMSE)

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(x_i - y_i)^2} \qquad \text{Equation 2}$$

3. Bias

$$BIAS = \frac{1}{n}\sum_{i=1}^{n}(x_i - y_i) \qquad \text{Equation 3}$$

where x is the model output vector and y its observation counterparts. Each vector has n elements and $\bar{x}$ and $\bar{y}$ represent their mean value. The correlation coefficient (Equation 1) has been applied to assess the simulated temporal variability and the RMSE (Equation 2) and bias (Equation 3) to assess the simulated absolute values. The evaluation of RACMO2 and LOTOS-EUROS fields is based on daily averages.

The trends in concentrations are computed using annual averages based on daily data. The slope is calculated using a standard linear least square method. Within this study we computed only linear trends and the computation of non-linear trends (Konovalov et al., 2010) or piecewise linear trends (Carslaw et al., 2011) has not been performed. To assess the significance of the trend a Mann-Kendall test at the 95% confidence level is performed (Kendall, 1976; Hipel and McLeod, 2005).

3 Results

3.1 Evaluation of model results

3.1.1 Evaluation of meteorological fields

The applied meteorological input data has been compared to observations to be able to assess the ability of RACMO2 to reproduce the observed meteorological annual, interannual and seasonal variability. In order to limit the length of this article only an abridgement of the performed evaluation is shown here. Four parameters that considerably impact atmospheric chemistry are shown: Temperature (at 2 meter), relative humidity (at 2 meter), wind speed (at 10 meter) and precipitation. The evaluation is based on daily data for the 20 years period. Table 2 summarizes the number of

stations, the mean correlation coefficient, the observed mean and RMSE and bias. As an example Figure 2 shows the 60-days moving average of the four parameters averaged across all available German stations from 1990-2009. The 60-days moving average was chosen to be able to plot the whole time series in one graph and, at the same time, to be able to see variability in the time series.

As the mean correlation coefficient of 0.97 in Table 2 shows the model captures very well the temporal distribution of temperature for the considered time period. Figure 2a shows that the interannual variability (presented here for 66 German stations) is simulated fairly well too. Warm summers like in 2003 and 2006 and cold winters like the one in 1995/1996 are well reproduced by RACMO2. However, the bias and also the corresponding graph in Figure 2 indicate a slight underestimation of the temperature during wintertime in central Europe. The performance of the model has also been assessed regionally for Northern, Eastern, Southern, Western and Central Europe separately (not shown here). The underestimation during wintertime was found to be most distinct for southern and least distinct for northern Europe, which is consistent with findings in van Meijgaard et al. (2012) and Kotlarski et al. (2014).

As Figure 2b illustrates, RACMO2 captures the interannual variability of the relative humidity at 61 German stations less well than that of the temperature (Figure 2a). A regional assessment of the model performance over Europe has revealed that the latter is most evident at southern European stations. Also, the model overestimates the relative humidity during wintertime at a large number of sites in Europe. The latter was again found to be most distinct at southern European stations and may be connected to the underestimation of the temperature during wintertime. Relative humidity is a difficult quantity to evaluate, in particular in areas or during episodes with high values of relative humidity (>95%). However, a mean correlation coefficient of 0.66 at 113 European stations (see Table 2) indicates that the observed temporal variability is satisfactorily simulated by the model.

The temporal variability of the wind speed is also satisfactorily simulated with a mean correlation coefficient of 0.68 over 246 European stations (see Table 2). Figure 2c displays the mean 60 days moving average of wind speed for 59 German stations for the investigated time period. The graph indicates that although the timing is well simulated the model tends to overestimate the wind speed in central Europe. In central and eastern Europe the overestimation was found to be present throughout the whole year. In northern and southern Europe RACMO2 overestimates wind speed solely during wintertime while it tends to slightly underestimate wind speed during summertime.

Figure 2d shows the mean 60 days moving average of precipitation for 1990-2009 at 66 German stations. The figure shows that the interannual variability is modelled satisfactorily in central Europe

although it is slightly underestimated. Dry years like 1996, 2003 and 2006 are well reproduced by the model. RACMO2 underestimates summertime precipitation in southern Europe while it tends to overestimate wintertime precipitation in northern and central Europe, which was also found by van Meijgaard et al. (2012) and Kotlarski et al. (2014). Generally, moving from daily to monthly or annual precipitation sums (not shown here) RACMO2 results compare better to the observed values. Mean correlation coefficient, RMSE and bias have been calculated at 240 European stations (see Table 2). The mean correlation of 0.48 indicates that considering the high temporal variability of precipitation RACMO2 simulates the observed timing reasonably well.

For the CTM calculation it is more important to capture the occurrence of precipitation than to capture its intensity and duration with the meteorological driver as wet deposition is a very efficient removal process. Therefore, at each of the 240 stations it was investigated on which percentage of days of the 20 years period the model is able to simulate the observed rain occurrence (rain: yes; rain: no). In the following a correct modelled rain:yes or rain:no is referred to as 'hit'. To account for unphysical small amounts of drizzle that often occur in climate models, daily accumulated precipitation below 0.5mm was considered as no rain. The results are summarised in Table 3. At 205 out of 240 stations the model is able to correctly simulate the rain occurrence on more than 70% of the days from 1990-2009.

Although some shortcomings in the meteorological input fields were found the outcome of the evaluation of RACMO2 has shown that the model is capable of satisfactorily reproducing the observed magnitudes and meteorological annual, interannual and seasonal variability of the investigated parameters.

3.1.2 Concentrations in air

The summary of the statistical evaluation based on daily pairs of observed and measured concentrations at the stations that have been selected to be used for the trend assessment (see Section 2.2.1) is given in Table 4 for the 1990-2009, 1995-2009 and 2000-2009 time periods. For the validation of the model more sites become available for the later time periods. To be able to compare the model performance for different time periods Table 5 shows the statistical evaluation for 1990-2009 and 2000-2009 when using the same subset of stations per component for both time periods (i.e. considering only those stations that passed the selection criteria presented in Section 2.2.1 for both of these time periods). Figure 3 shows the 60-days moving average concentrations averaged across the

selected stations for each component for the time period 1990-2009. Besides the time series the average seasonal variation is given for this same 20 year time period.

The modelled time series of SO_2 presented in Figure 3a shows that LOTOS-EUROS underestimates the observed SO_2 concentrations in the period 1990-1997, while for later years there appears to be a small bias at these stations. The latter is also reflected in an improved RMSE and bias (in relation to the observed mean) for the 2000-2009 time period compared to the 1990-2009 time period when considering the same subset of stations for both time periods (see Table 5). Throughout the time series the year-to-year variability is captured well by the model, as is the seasonal variation presented in Figure 3b. The mean correlation coefficient of 0.6 for SO_2 for 1990-2009 (see Table 4) suggests that the model is able to reproduce part of the observed day-to-day variability throughout the time period.

Figure 3c and 3d reveal that the concentrations of SO_4^{2-} are systematically underestimated by LOTOS-EUROS throughout the whole time period. The underestimation is most distinct from 1990-1997, which appears to be related to the underestimation of SO_2 in the same period. Analysis of the individual sites showed that the sites located in eastern and central Europe largely determine the underestimation for both components as northern European stations show much better comparison. We speculate that the models' underestimation of SO_2 and SO_4^{2-} concentrations in the 1990s could be connected to the lack of a good representation of the change in emission structures in the power sector in eastern and parts of central Europe in the 1990s as a consequence of the fall of the Berlin wall and political changes associated with the liberalisation of the Eastern Bloc's authoritarian systems as discussed below. A striking feature in the comparison for SO_4^{2-} is the inability of the model to reproduce the magnitude of several spring episodes that occurred in e.g. 1996, 2003 and 2006. Although for some of these episodes the model is able to capture the timing, it is not able to reproduce the peak values. These episodes are characterized by very stable conditions across central Europe and some have been studied in detail (e.g. Stern et al., 2008; Banzhaf et al., 2013). A model comparison by Stern et al. (2008) has shown that also other state of the art models were not able to simulate the peak values in early spring 2003. It is unclear if the underestimation is connected to a lack of SO_2-to-SO_4^{2-} conversion or an overestimation of turbulent mixing leading to too high deposition and vertical mixing.

The mean correlation coefficient of 0.46 (see Table 4) for SO_4^{2-} for 1990-2009 indicates that the day-to-day variability is not very well captured by the model throughout the time period. The mean correlations for the secondary species SO_4^{2-}, TNO_3 and TNH_4 presented in Table 4 and Table 5 with

values between 0.4 and 0.5 for the different time periods are lower than those found in former LOTOS-EUROS model evaluation studies showing mean correlations of 0.5 to 0.7. Further analysis of the time series has revealed that when correlations are low the modelled temporal distribution at a station is often shifted by just one day compared to the observed distribution. One possible reason for the lower correlations compared to former evaluation studies of the model could be that the meteorological input fields used in this study have been generated without nudging of meteorological data while the LOTOS-EUROS standard meteorological input includes the assimilation of surface meteorological data.

On average, the model underestimates NO_2 concentrations by about 15%. Figure 3e shows that the overall bias is distinct in the first three years of the time series and becomes small in the years afterwards. After 2000 the bias between modelled and observed NO_2 starts to increase again and becomes increasingly larger towards 2009. The seasonal cycle presented in Figure 3f is well simulated and the interannual variability is satisfactorily reproduced. Also, the temporal correlation coefficient (>0.6) for these stations throughout the series illustrates that LOTOS-EUROS captures the day-to-day variability reasonably well. The higher mean correlation coefficients for NO_2 and SO_2 compared to those of SO_4^{2-}, TNO_3 and TNH_4 we attribute to a less strong emission signal in the secondary species concentrations.

At the few northern European sites where long term time series (1990-2009) of TNO_3 concentrations were available the seasonal cycle and the interannual variability are well simulated by LOTOS-EUROS (see Figure 3g and h) and the bias is very small. Moreover, some TNO_3 episodes are well captured by the model. Also for TNH_4 concentrations, presented in Figure 3i, the bias at the few northern European sites that exhibited time series for 1990-2009 is small. However, a major shortcoming in the TNH_4 modelling is clearly visible in the average seasonal cycle (see Figure 3j). The model overestimates TNH_4 concentrations during wintertime (Oct-Jan) and tends to underestimate during late spring and early summer. Moreover, the maximum concentration is modelled to be in March, whereas the observed maximum occurs in April. The lack of a good representation of the seasonal cycle in the NH_3 emissions is a likely cause for this feature.

3.2 Trends in concentrations

The observed and modelled trends are illustrated in Figure 4 and Figure 5. Figure 4 shows scatter plots of the observed versus modelled trend for the studied components at the considered stations for

the 3 different time periods. It is labelled in the graphs if the observed and/or modelled trends are significant (method used described in section 2.3): (+) implies that the observed and the modelled trends are significant, (o) implies that the observed trend is non-significant while the modelled trend is significant, (o) implies that the observed trend is significant while the modelled trend is non-significant and (o) implies that the observed and the modelled trends are non-significant. Table 6 summarizes for each component the resultant observed and modelled absolute and relative median trends for the three considered time periods. For comparison, in Table S2 in the Supplement, the observed and modelled absolute and relative median trends are also given considering the same subset of stations (per component) for all time periods to extract the impact of changing number and location of included sites. However, Table S2 only includes SO_2, NO_2 and SO_4^{2-} as for TNO_3 and TNH_4 the number of sites (4 and 3, respectively) was considered to be too low for a trend assessment.

Figure 5 shows the observed and modelled trends of the annual mean SO_4^{2-}, TNO_3 and TNH_4 concentrations, their 5^{th} and 95^{th} percentile and the corresponding trend lines for the 1990-2009 time period. Solid lines refer to significant trends and dashed lines refer to non-significant trends (only found for the TNO_3 5^{th} percentile).

3.2.1 Observed trends

Figure 4 illustrates that the observed SO_2, SO_4^{2-} and NO_2 concentrations show significant negative trends at the majority of stations for the time periods 1990-2009 and 1995-2009. For NO_2 a significant positive trend for 1995-2009 was observed at two stations located in Estonia at the shore of the Baltic Sea. For TNO_3 and TNH_4 the majority of trends is significant negative for the 1990-2009 time period while for 1995-2009 the observed trends are non-significant at all stations (TNO_3) or at the majority of stations (TNH_4). Note that for TNO_3 and TNH_4 the few considered station are located in northern and eastern Europe due to a lack of long-term observations in the other regions. The trends in TNO_3 in hot spot areas like the Netherlands may differ. For all components, the relative amount of stations with non-significant trends increases when moving from 1990-2009 (SO_2: 0%; SO_4^{2-}: 0%; NO_2: 11%; TNO_3: 33%; TNH_4: 14%) to 1995-2009 (SO_2: 5%; SO_4^{2-}: 18%; NO_2: 21%; TNO_3: 100%; TNH_4: 50%) to 2000-2009 (SO_2: 52%; SO_4^{2-}: 86%; NO_2: 72%; TNO_3: 75%; TNH_4: 80%). This increasing number of non-significant trends when moving to the later time periods has also been found when considering the same subset of stations per components for all time periods, i.e. considering only those stations that fulfilled the selection criteria for all three time periods (not shown here). For the time period 2000-2009 Figure 4 shows that the observed trends are non-significant at the majority of stations for all considered components. We would like to stress that this

does not necessarily imply that there is no trend present in the data of these stations for 2000-2009 but 10 years may be too short to infer statistically significant trends.

Table 6 shows that for all components the observed median absolute negative trends decrease moving from 1990-2009 to 2000-2009 (absolute decrease in TNO_3 trends in the 3rd decimal place). For SO_2 and NO_2 the decrease of the observed absolute negative trends from 1990-2009 to 1995-2009 is less strong than the decrease from 1995-2009 to 2000-2009. Table S2 in the Supplement shows that the latter features also apply when considering the same, but smaller, subset of stations per components for all time periods. Furthermore, comparing the observed median relative trends in SO_4^{2-} concentrations to those of SO_2 shows that the trends in SO_4^{2-} are lower for all considered time periods. We are aware that the stations at which SO_2 and SO_4^{2-} concentrations are investigated partly differ. However, the spatial distribution of sites over Europe for SO_2 is comparable with that for SO_4^{2-} (see Figures S1-S4 in the Supplement) and we assume that rural background stations represent the regional scale atmospheric composition, so that the same conditions are represented by the two sets. Therefore we think that comparison of the relative trends of both components is maintainable.

Finally, the sensitivity of the resultant observed median trends to the selection criteria introduced in section 2.2.1 has been tested. The results for the 1990 to 2009 time period are presented in the Supplement showing that increasing the length of the annual time series (at least 80% of the considered time period was the criterion given in section 2.2.1) has a minor impact on the resultant median trend.

3.2.2 Modelled trends and comparison to observed trends

As the results in Table 6 (and Table S2) show the model is able to well simulate the decrease in the absolute median negative trend for SO_2, SO_4^{2-} and NO_2 when moving from 1990-2009 to 1995-2009 to 2000-2009. Also, the model is able to reproduce the lower relative trends of observed SO_4^{2-} concentrations compared to those of SO_2.

The model simulates significant negative trends in SO_2, NO_2 and SO_4^{2-} concentrations at most station locations for 1990-2009 and 1995-2009 (see Figure 4), which coincides with the observed trends for these time periods. However, the model underestimates the negative trends in concentrations for SO_2 at several stations and for SO_4^{2-} at most stations while it overestimates the negative trends in NO_2 concentrations at the majority of station locations. For all considered time periods the deviation of the modelled trends in SO_2, SO_4^{2-} and NO_2 concentrations from the observed trends were found to be

most distinct at eastern European stations and stations in north-eastern Germany (e.g. the three outliers in Figure 4b correspond to trends at two stations in Czech Republic and one station in eastern Germany) and least distinct at northern European station locations (not shown here). For the time period 2000-2009 the model well simulates the low negative median trends in SO_2 and SO_4^{2-} concentrations (see Table 6) but Figure 4 reveals that the model simulates significant negative trends at most station locations while non-significant trends were observed. The latter is also valid for modelled and observed NO_2 concentration trends. As for the 1990-2009 and 1995-2009 time periods the model overestimates the trends in NO_2 concentrations for the 2000-2009 time period.

As Figure 5 a illustrates, the strong observed negative trend in SO_4^{2-} concentrations is mostly driven by the high observed concentrations in the beginning of the 90s. The latter high observed concentrations could not be reproduced by the model. The 5th percentile, which represents the background concentrations, and its significant negative trend are well captured by the model. The negative trend of the 95th percentile, which represents the high concentration range (the peak SO_4^{2-} concentrations), is considerably underestimated by the model. The model satisfactorily captures the temporal distribution of the interannual variability but there is a substantial negative bias between modelled and observed value. This shows that the models inability to capture the observed trend in SO_4^{2-} is driven by the underestimation of the high range of concentrations.

Also for TNO_3 and TNH_4 shown in Figure 5b and Figure 5c the deviation from the observed values is most distinct in the 95th percentile while the interannual variability is well simulated by the model. Figure 4 shows that the model well reproduces the low trends in TNO_3 concentrations at the majority of considered sites for all time periods while for TNH_4 the model tends to underestimate the observed concentration trends. Furthermore, for both components, TNO_3 and TNH_4, the increased relative number of non-significant trends when moving from the 1990-2009 to the 2000-2009 time period is well captured by the model at most stations.

3.3 Trends in SIA formation

The previous section has revealed that the observed relative trends in SO_4^{2-} concentrations are lower than those of its precursor gas SO_2. Furthermore, the analysis of the LOTOS-EUROS simulation has shown that this non-linear effect was well reproduced by the model. Hence, the LOTOS-EUROS source apportionment module was used to further investigate the observed and modelled non-linearity. Therefore 10 ktons of SO_2, NO_x and NH_3 emissions, respectively, have been tracked for

1990 to 2009 for 4 different labels, which were chosen to be 4 different regions: The Netherlands and Belgium (NLBE), the Baltic Sea (BAS), Czech Republic (CZE) and Romania (ROM). By means of the labelling we can determine how much SIA was formed per unit emission during the time period from 1990 to 2009. The results of the source attribution are presented in Figure 6. Figure 6a shows the SO_4^{2-} concentration (solid lines) formed per unit emission normalized to that of 1990 for the different labels for 1990 to 2009. A trend line (dashed line) is added for all labels. For all considered regions the SO_4^{2-} formation efficiency increases from 1990 to 2009. Following the Mann-Kendall Test at a 95% confidence level the positive trends are significant for all labels. To investigate if the identified increase is a matter of climate change we re-run the model for 1990, 1995, 2000 and 2009 using the emissions for the corresponding year but the meteorology of 2005. The results are added to Figure 6a as accordingly coloured dots for each label. Most dots are located on or close to the corresponding trend line. The latter indicates that the increase in SO_4^{2-} formation efficiency is induced by the change in emissions from 1990 to 2009. The increase is most distinct for the region NLBE with a 61% more efficient SO_4^{2-} formation in 2009 compared to 1990 followed by CZE (+60%), BAS (+31%) and ROM (+28%). The major driver for the increased SO_4^{2-} formation efficiency in the model has been an increasing neutralisation of cloud acidity and thus pH over time as diagnosed from the model run.

SO_4^{2-} formation is a sink for SO_2 concentrations and therefore the increase in SO_4^{2-} formation efficiency explains that the decrease in SO_2 concentrations is larger than expected solely from the decrease in SO_2 emissions. Figure 6b displays the decrease in SO_2 quantity per unit SO_2 emission showing a negative trend for the time period 1990 to 2009 for all considered labels. However, for the Baltic Sea (BAS) the trend from 1990 to 2009 is not significant following a Mann-Kendall Test at the 95% significance level.

Figure 6c reveals a decrease in NH_4^+ formation per unit NH_3 emission for the labels NLBE, CZE and ROM with a reduction of -22% (ROM) to -33% (NLBE and CZE) for 2009 compared to 1990. Following a Mann-Kendall Test at the 95% significance level the trend is significant for these labels. BAS is not included in the figure as there is no NH_3 emission from shipping on the Baltic Sea.

The changes in NO_3^- formation efficiency from 1990 to 2009 are lower than for SO_4^{2-} and NH_4^+ (see Figure 6d). A significant trend has been found for the label NLBE showing an increase in NO_3^- formation efficiency with an increase of +22% from 1990 to 2009. In the next section the results of the labelling exercise are further discussed.

4 Discussion and Conclusions

In this study we presented a dynamic model evaluation of the LOTOS-EUROS CTM to analyse the ability of the model to reproduce the non-linear responses to emission changes and interannual variability of SIA and its precursors over Europe from 1990 to 2009. This study presents the first evaluation of the model system over such a long time period.

With respect to the study design we feel that the simulation of the whole period is a strong point as opposed to using one or several key meteorological years to study the impact of emission changes as it is difficult to choose a meteorological year that is representative for an average year throughout Europe. In addition, through the reanalysis with RACMO2 we have used a consistent set of meteorological data to drive the model for the whole period. The major activity needed to improve the study design is associated with the emission information for the early nineties. Improvements are especially needed for the eastern European countries. Emission estimates for 1990 are relatively uncertain (Granier et al., 2011) as much of the information currently used to estimate emissions is not available (at the same quality) for 1990. Moreover, we have simply used the spatial allocation of the TNO-MACC-2005 dataset and scaled the emission totals per sector back to those of 1990. As a result, the (spatial) representation of e.g. the industrial infrastructure and location of power plants, especially in eastern and parts of central Europe in the period 1990-2000 will not be correct as the infrastructure here during this period still resembled the pre-1990 period. The improvement needed here is highlighted by the higher underestimation of the pollutants in the first years of the study period. One could use the spatial allocation of emission inventories built in the nineties to overcome these problems partly. Making a small compromise on the spatial resolution of the data may not be a large problem as model resolution does hardly affect the performance of CTMs for regional assessments (Schaap et al., *in prep.*).

In the present model set-up, trends in boundary conditions were not considered, although background concentrations are expected to change from 1990 to 2009. We believe that the impact of using time-variant boundary conditions would be most relevant for O_3 levels, which also affect the formation of SIA. Time-variant lateral boundary conditions could be extracted from a global model simulation. Hogrefe et al. (2011) studied the uncertainties associated with chemical boundary conditions from a global model, showing that the representation of the interannual variability of O_3 concentrations was improved when time-variant boundary conditions were used. However, biases in the global simulations significantly affected the O_3 simulations throughout the modelling domain with adverse impact on the simulated O_3 trends.

Complementing the EMEP monitoring data with those of AIRBASE has increased the number of stations with valid time series, especially for the precursor gases. Our visual screening of the measurement data revealed that a large fraction of the stations with long time series were not useable as data quality was obviously an issue. The most frequent peculiarities were shifts in the concentration level, many implausible peaks of short duration, constant value signals over prolonged time periods or concentration regimes below the detection limit. Most problems were associated to time series of SO_2. The number of defective time series was highest for the 1990's and decreases considerably towards 2009. A lack of a long-term time series for southern and parts of western and eastern Europe hampered an evaluation across the full European domain. Furthermore, for concentrations of NO_3^- and NH_4^+ there is a lack of observations with separation between gas- and aerosol-phase. Additional efforts for data mining within European countries could yield larger observational basis for evaluation of the time period. Moreover, generation of a centralized dataset for the specific purpose of evaluation long-term trends could be a means to improve the data quality by incorporation of expertise from the data providers.

The operational model evaluation showed that the seasonal variability as well as the interannual variability are satisfactorily simulated for all components. Within a multi-model trend assessment study Collette et al. (2011) presented the ability of 6 state of the art CTMs to simulate the seasonal cycle of amongst others SO_2, SO_4^{2-}, NO_2, TNO_3 and TNH_4 concentrations at European rural background stations for the time period 1998-2007. A qualitative comparison of our model results to those presented in Collette et al. (2011) shows that LOTOS-EUROS performs comparatively well in simulating the observed seasonal cycles. Operational model evaluations within AQMEII (Solazzo et al., 2013) and EURODELTA (e.g. Vautard et al., 2009; Schaap et al., *in prep.*) showed that LOTOS-EUROS model skill is in line with those of models like EMEP and CHIMERE. Although LOTOS-EUROS was able to capture a large part of the observed variability in the considered sulphur and nitrogen compounds from 1990-2009, some shortcomings have been identified.

A systematic underestimation of SO_4^{2-} concentrations is observed throughout the whole study. This could be connected to a lack of good representation of clouds, which is needed for the recently implemented cloud chemistry scheme (Banzhaf et al., 2012; Wichink Kruit et al., 2012). The method used to pass the information of the liquid water content vertical distribution from the vertically high resolved meteorological driver to LOTOS-EUROS running on 5 vertical layers may need further improvements. Furthermore, uncertainties in NH_3 emissions (magnitude, space and time) may play an important role as NH_3 provides the neutralising capacity of cloud droplets and constrains cloud

water acidity. Cloud pH regulates the oxidation pathways of SO_2 and therewith the formation efficiency of SO_4^{2-} (Fowler et al., 2007). According to EMEP (2009), the uncertainty in magnitude of annual NH_3 emission totals amounts about ±30% in Europe. Furthermore, the seasonal and diurnal variation in NH_3 emissions are still uncertain and may differ regionally as a function of climatic conditions and in time due to changing agricultural practices and regulations (Geels et al., 2012) which is not accounted for in most state of the art CTMs including LOTOS-EUROS. The underestimation of springtime episodes for SO_4^{2-} connected to stable atmospheric conditions is observed in several years. It has not yet been solved if the underestimation is induced by a lack of SO_2-to-SO_4^{2-} conversion or too high deposition and vertical mixing due to an overestimation of turbulent mixing. In a case study for 2003 this feature was identified to be a common challenge for European CTMs as meteorological drivers tend to fail to represent these stable weather conditions satisfactorily (Stern et al., 2008).

Despite the mentioned shortcomings in the representation of the sulphur components, the model captures the non-linearity observed in the response to the emission changes. Investigating the observed trends at the EMEP monitoring sites between 1980 and 2009, Tørseth et al. (2012) showed that SO_2 trends indicate larger reductions than the reductions of SO_2 emissions while those of SO_4^{2-} concentrations are comparatively lower. These findings are very close to our analysis incorporating AIRBASE stations and earlier analyses by e.g. Løvblad et al. (2004). Fagerli and Aas (2008) presented an investigation on the observed trends of nitrogen from 1980-2003 at EMEP sites showing that the trends in TNO_3 concentrations were significantly lower than the trends in precursor emissions which matches the outcome of the here presented study. Using a source apportionment module trends in formation efficiency of SIA have been quantified adding to the explanation of the non-linearities described above. The exercise revealed an increase of SO_4^{2-} formation efficiency and a decrease in NH_4^+ formation efficiency for all regions considered. The major driver for the increased SO_4^{2-} formation efficiency in the model was the increasing neutralisation of cloud acidity and thus pH over time. The modelled trend is supported by the observed increase in precipitation pH during the last decades (Løvblad et al., 2004; Tørseth et al., 2012). Hence, the pH dependent aqueous-phase SO_4^{2-} formation by O_3 is more effective (Redington et al., 2009; Banzhaf et al., 2012; 2013). In addition, the H_2O_2/SO_2 ratio increases which also leads to more efficient formation. Finally, the simultaneous NO_x and SO_2 emission reductions may lead to increased OH levels, which counteract the SO_4^{2-} reduction as the rate of homogeneous oxidation of SO_2 is increased (Tarrasón et al., 2003; Derwent et al., 2009). The decrease in NH_4^+ formation efficiency is related to the overall decrease in

SO_4^{2-} concentrations from 1990 to 2009, which leads to less ammonium sulphate ($(NH_4)_2SO_4$) formation. The strong decrease in SO_4^{2-} concentrations from 1990-2009 increases the availability of NH_3 for the formation of NH_4NO_3 (Tarrasón et al., 2003; Fagerli and Aas, 2008; Harrison et al., 2014). Hence, this could explain the change in NO_3^- formation efficiency for the Benelux region. Another reason for changes in the NO_3^- formation efficiency could be a change in the oxidant levels (Fowler et al., 2005; Fagerli and Aas, 2008). A decrease in NO_x emissions leads to a decrease of O_3 titration and therewith to an increased rate of NO_2 to NO_3-conversion. The increased rate of NO_2 to NO_3-conversion could also be induced by higher availability of oxidants that previously were consumed in the oxidation of SO_2 or other pollutants. A more detailed budget analysis is advised to study the changes in chemical regime.

Furthermore, LOTOS-EUROS underestimates the observed NO_2 concentrations on average by 15% throughout the whole time period. The underestimation is induced by modelled concentrations at central and eastern European stations while the model performs considerably better at northern European stations. Part of the underestimation may be explained by the measurement devices used in the networks. Oxidized nitrogen compounds such as HNO_3, PAN (peroxyacyl nitrate) and other organic nitrates can significantly interfere with the measurements by contributing to the NO_2 signal (Steinbacher et al., 2007). In the beginning of the 90s again the uncertainties in the emission input may explain part of the bias in NO_2 concentrations. After 2000 the bias increases inducing an overestimation of the observed negative trend in NO_2 concentrations by the model. It has been investigated if the decrease in model performance after 2000 is connected to the increased NO_2/NO ratio of traffic emissions by comparing simulations with 3% and 20% direct NO_2 emissions from diesel fuelled vehicles. These runs showed a slight increase in the rural background close to large cities (up to 2 %), whereas in more remote areas NO_2 levels declined by about 0.5% due to the faster oxidation to HNO_3. Hence, this effect does not contribute to the mismatch between observed and modelled trends. The model inter-comparison study by Collette et al. (2011) has shown that 4 out of 6 models underestimate NO_2 concentrations at European rural background stations for the time period 1998-2007. Moreover, three of these models also show stronger trends than observed. A recent study using satellite retrieved NO_2 columns by OMI and in-situ data for the period 2005-2012 also showed lower trends in observations than in the European emission inventories (Curier et al., 2014). Hence, more research is needed to assess if the mismatch in the NO_2 trend is a model issue or if it can be attributed to too strong declines in the emission data.

The implemented emission abatement strategies for SIA precursors have led to concentration reductions over Europe even though for some secondary species the achieved concentration reduction is lower than corresponding precursor reductions would suggest. The LOTOS-EUROS model is able to capture most of the seasonal and interannual variability of SIA and its precursors' concentrations and their non-linear responses to emission changes for the time period 1990-2009. The largest part of the decline is observed in the 1990's. Smaller concentration changes and more non-significant trends are observed and modelled between 2000-2009. The smaller, non-significant trends between 2000-2009 do not necessarily imply that there is no trend present in the data, but only that we are not sure at the 95% confidence level (Nuzzo, 2014). It highlights that the validation of emission trends remains a challenge, in particular the ability to separate relatively smaller trends from interannual variability (Koumoutsariset al., 2008; Voulgarakis et al., 2010).

This study has revealed many interesting features and resulting research questions that can be approached making further use of the 20 years model simulation. Specific attention is needed to address the trends in NO_x and tackle the underestimation in SO_4^{2-} and other pollutants in eastern Europe. As a next step we will analyse the ability of the model to reproduce the trends modelled for O_3 as new analyses have shown shifts in seasonal variability over time (Parrish et al., 2013). Moreover, trends in wet and dry deposition should be investigated to further complement the budget analysis. We have found that the trends for SIA are emission-driven. Next, a quantification of trends induced by meteorological variability as reported by Andersson et al. (2007) is planned. Furthermore, special attention in further investigations will be given to uncertainties in the emission input by performing sensitivity studies on emission timing (dependency on meteorology etc.). The here presented study could be seen as an exploratory exercise for the re-analysis of the 1990-2010 period with several model systems within the UNECE-EMEP taskforce on measurement and modelling (TFMM).

In short, we presented a successful dynamic model evaluation of the LOTOS-EUROS CTM aimed at secondary inorganic aerosol formation in Europe between 1990 and 2009. In general, the model is able to capture the non-linearity as detected in the observations. A source apportionment analysis has confirmed that changes in the formation efficiency due to changes in the chemical regime are at the basis of this non-linearity.

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Table 1. Number of stations of the applied observational dataset per component and time period before and after the visual screening of the observed time series.

Species	Time period	Passed data availability criteria	Passed visual check of daily observations
SO_2	1990-2009	51	23
	1995-2009	88	40
	2000-2009	133	60
NO_2	1990-2009	57	37
	1995-2009	98	64
	2000-2009	167	112
TNO_3	1990-2009	9	9
	1995-2009	9	9
	2000-2009	18	16
TNH_4	1990-2009	7	7
	1995-2009	8	8
	2000-2009	16	15
SO_4	1990-2009	15	15
	1995-2009	23	22
	2000-2009	28	28

Table 2. Statistical comparison between measured and modelled meteorological parameters using daily observations at European observational sites. The number of considered stations, mean correlation, observed mean, RMSE and bias are given.

Evaluation	Temperature	Relative humidity	Wind speed	Precipitation
Number of stations	206	113	246	240
Mean correlation	0.97	0.66	0.68	0.48
Observed mean	286.06 K	78 %	3.82 m s^{-1}	1.82 mm
RMSE	2.82 K	11 %	1.87 m s^{-1}	4.52 mm
Bias	-1.47 K	2 %	0.35 m s^{-1}	0.04 mm

Table 3. Percentage of daily rain occurrence hits of the RACMO2 model from 1990 to 2009 at 240 European observational stations

Hits	# stations
h < 60%	0
60% ≤ h < 70%	35
70% ≤ h < 80%	156
80% ≤ h < 90%	48
h ≥ 90%	1

Table 4. Statistical comparison between measured and modelled concentrations using daily observations. The number of considered stations, mean correlation, observed mean, RMSE and bias are given for each component and each time period.

Period	Evaluation	SO_2	NO_2	SO_4	TNO_3	TNH_4
1990-2009	number of stations	23	37	15	9	7
	mean correlation	0.60	0.65	0.46	0.46	0.48
	observed mean ($\mu g/m^3$)	3.86	15.97	2.77	0.56	1.35
	RMSE ($\mu g/m^3$)	6.01	8.66	2.86	0.61	1.21
	Bias ($\mu g/m^3$)	-0.44	-2.43	-0.88	0.04	0.03
1995-2009	number of stations	40	64	22	9	8
	mean correlation	0.58	0.62	0.40	0.44	0.44
	observed mean ($\mu g/m^3$)	4.00	14.19	2.46	0.46	1.17
	RMSE ($\mu g/m^3$)	6.49	8.58	2.27	0.54	1.05
	Bias ($\mu g/m^3$)	-0.67	-2.58	-0.66	0.12	0.03
2000-2009	number of stations	60	112	28	16	15
	mean correlation	0.45	0.61	0.40	0.48	0.40
	observed mean ($\mu g/m^3$)	3.34	14.12	2.16	0.60	1.38
	RMSE ($\mu g/m^3$)	5.01	9.37	1.95	0.6	1.18
	Bias ($\mu g/m^3$)	-0.69	-3.77	-0.58	0.12	0.21

Table 5 Statistical comparison between measured and modelled concentrations using daily observations at those stations that passed the selection criteria presented in Section 2.2.1 for the 1990-2009 and 2000-2009 time period. The number of considered stations, mean correlation, observed mean, RMSE and bias are given for each component.

Period	Evaluation	SO_2	NO_2	SO_4	TNO_3	TNH_4
all	number of stations	15	33	11	4	3
1990-2009	mean correlation	0.62	0.67	0.47	0.49	0.54
	observed mean ($\mu g/m^3$)	4.19	17.05	2.53	0.40	0.77
	RMSE ($\mu g/m^3$)	6.15	8.93	2.75	0.54	0.77
	Bias ($\mu g/m^3$)	-0.57	-2.53	-0.85	0.12	0.07
2000-2009	mean correlation	0.52	0.67	0.40	0.46	0.47
	observed mean ($\mu g/m^3$)	2.16	15.23	1.85	0.38	0.66
	RMSE ($\mu g/m^3$)	2.48	8.09	1.75	0.49	0.70
	Bias ($\mu g/m^3$)	-0.03	-2.87	-0.49	0.10	0.11

Table 6. Number of stations and derived observed and modelled absolute (µg m^{-3} a^{-1}) and relative (% a^{-1}) median trends for the considered components and time periods.

Period	Evaluation	SO_2	NO_2	SO_4	TNO_3	TNH_4
1990-2009	number of stations	23	37	15	9	7
	Observed abs. median trend	-0.34	-0.36	-0.16	-0.01	-0.03
	Modelled abs. median trend	-0.33	-0.45	-0.07	-0.01	-0.01
	Observed rel. median trend	-4.88	-1.85	-3.55	-1.57	-2.18
	Modelled rel. median trend	-4.16	-2.44	-2.36	-1.33	-1.61
1995-2009	number of stations	40	64	22	9	8
	Observed abs. median trend	-0.28	-0.30	-0.10	-0.01	-0.02
	Modelled abs. median trend	-0.23	-0.44	-0.06	-0.01	-0.02
	Observed rel. median trend	-5.14	-1.67	-3.34	-1.23	-1.77
	Modelled rel. median trend	-4.98	-2.46	-2.57	-1.54	-1.18
2000-2009	number of stations	60	112	28	16	15
	Observed abs. median trend	-0.13	-0.14	-0.05	-0.01	-0.02
	Modelled abs. median trend	-0.12	-0.28	-0.05	-0.01	-0.01
	Observed rel. median trend	-4.45	-1.12	-2.63	-1.45	-0.98
	Modelled rel. median trend	-5.10	-2.17	-2.37	-1.66	-0.66

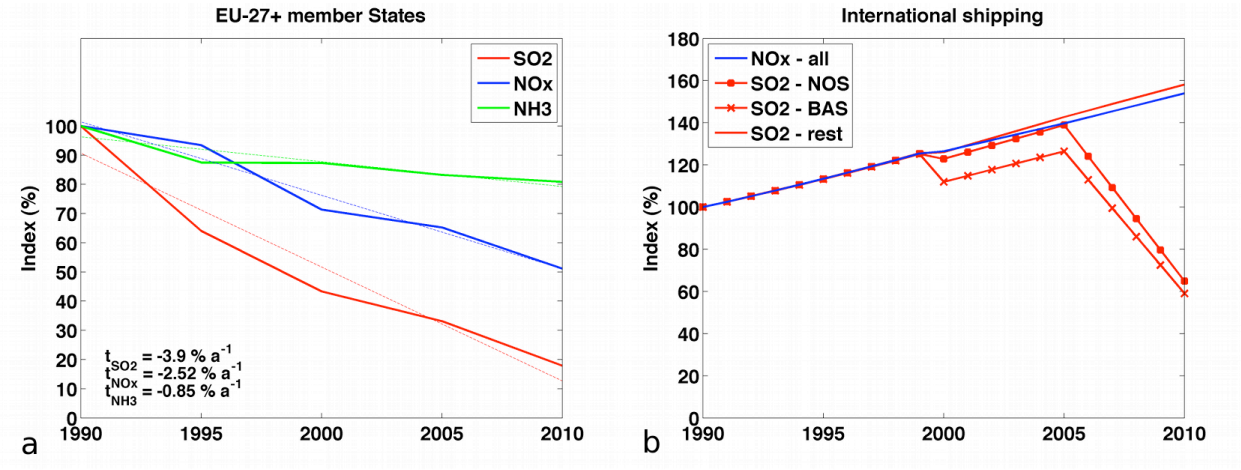


Figure 1. Emission trends of (a) SO_2, NO_x and NH_3 in the EU-27+ member States and (b) SO_2 and NO_x in International Shipping for 1990 to 2010 in % with 1990 as reference. The thin lines in (a) show the average trend computed over the entire period and the decrease per year is displayed as text.

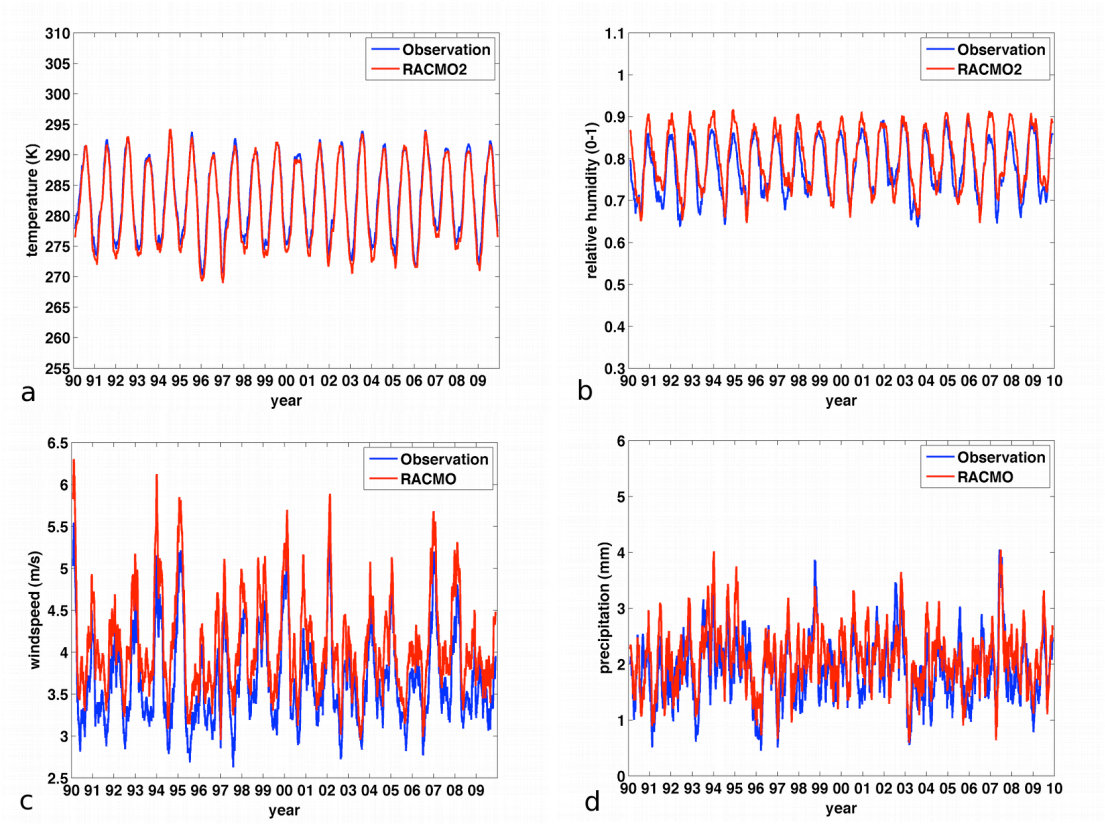
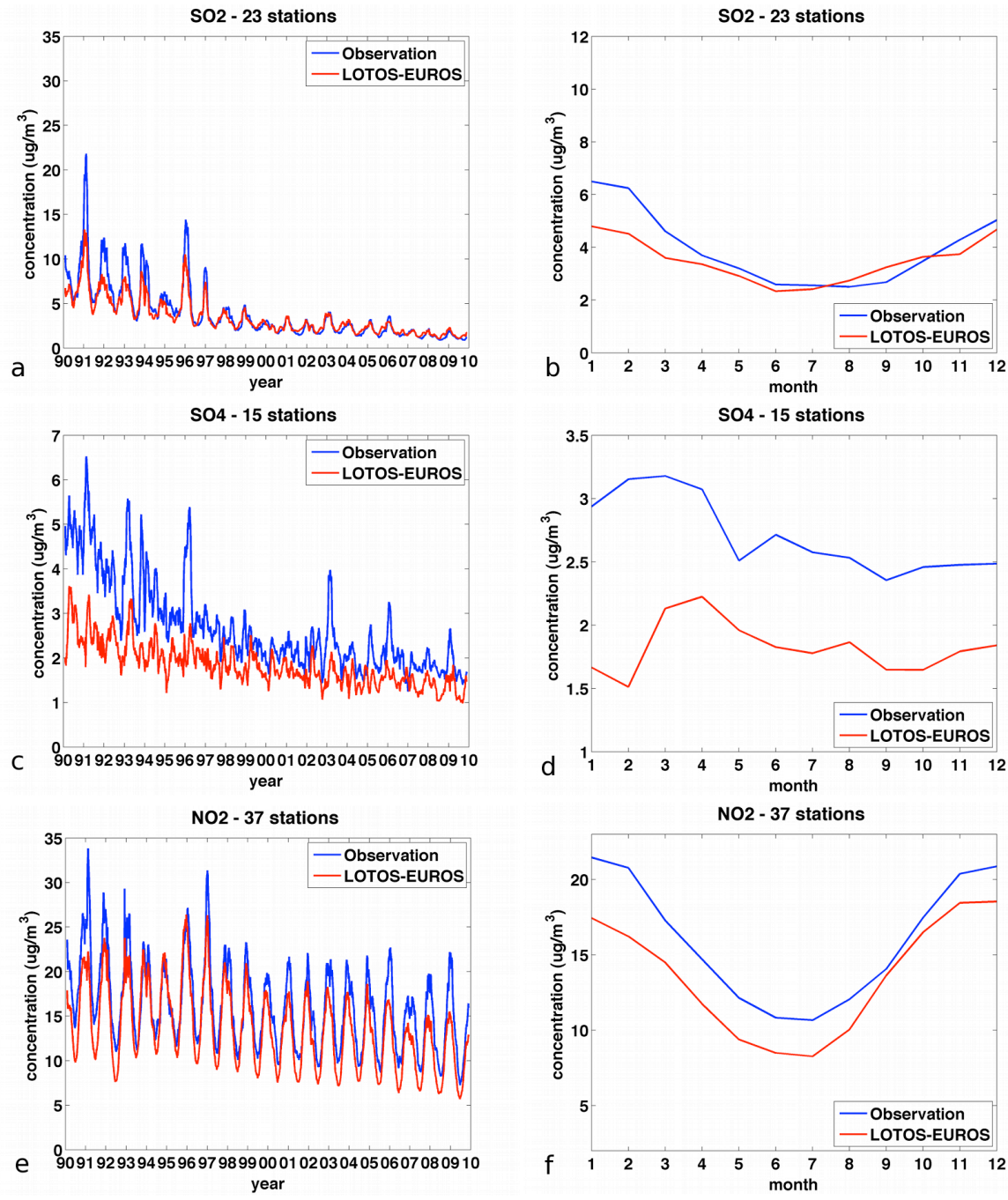


Figure 2. Mean 60 days moving average of (a) temperature, (b) relative humidity, (c) windspeed and (d) precipitation at 66, 61, 59 and 66 German observational sites, respectively, from 1990-2009.


SO2 - 23 stations
Observation
LOTOS-EUROS
concentration (ug/m3)
year
a
SO2 - 23 stations
concentration (ug/m3)
month
b
SO4 - 15 stations
c
SO4 - 15 stations
d
NO2 - 37 stations
e
NO2 - 37 stations
f

1

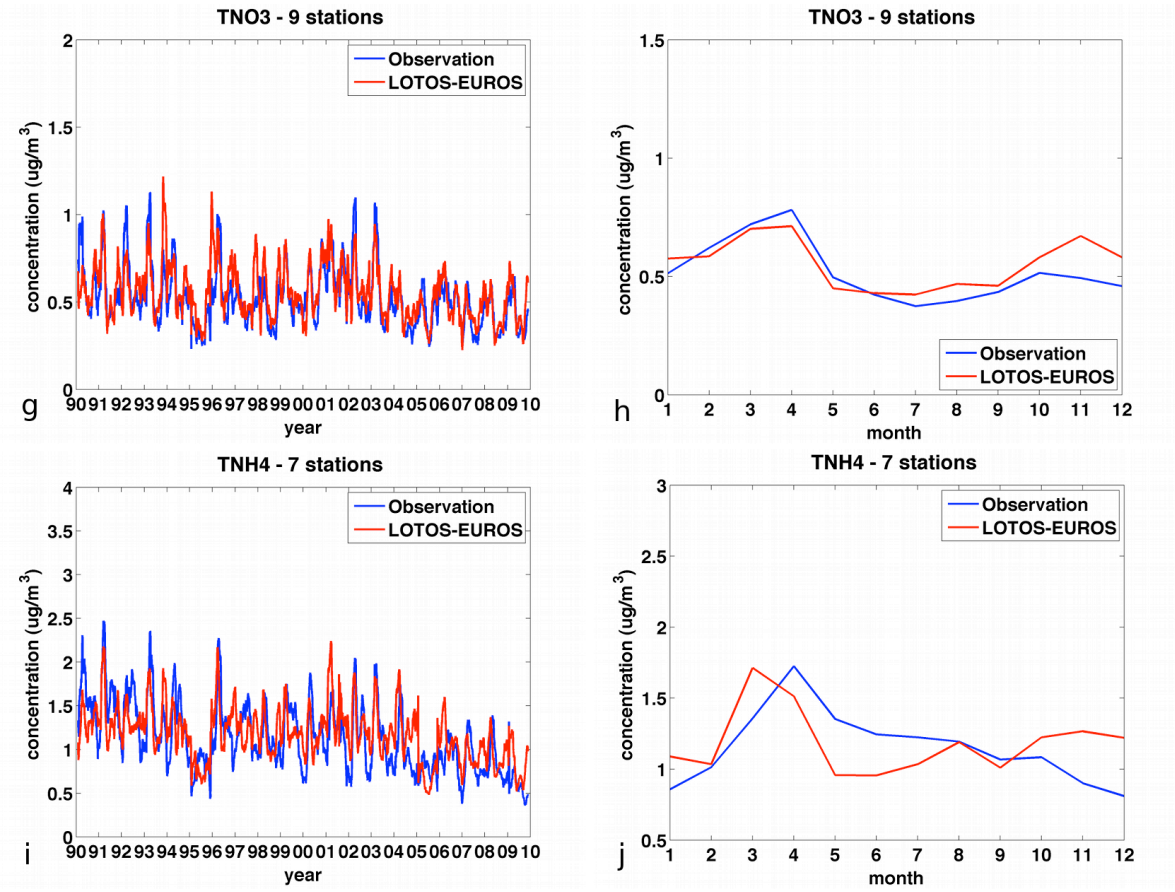
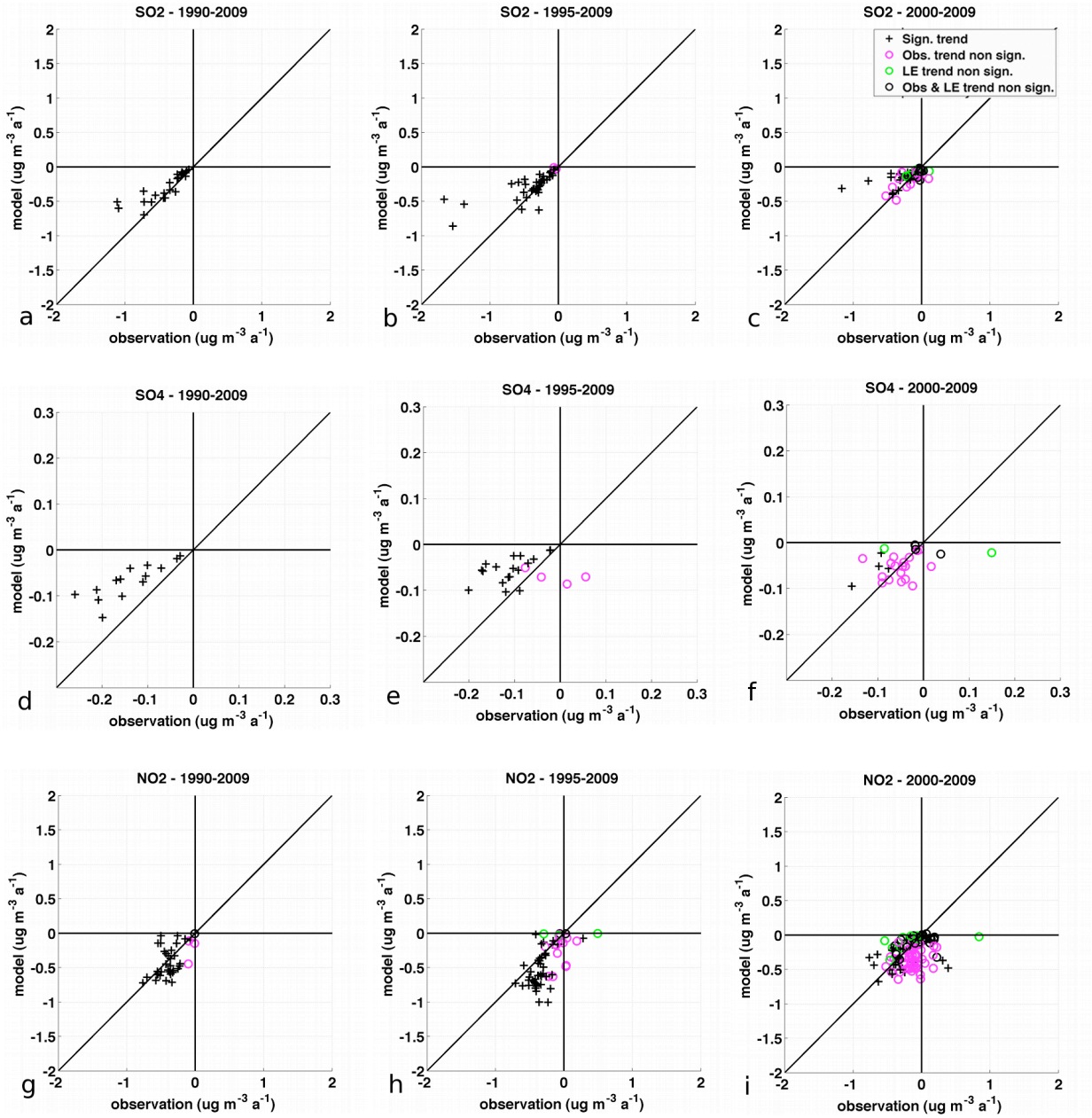


Figure 3. Mean 60 days moving average (left panel) and seasonal cycle (right panel) of (a-b) SO_2, (c-d) SO_4^{2-}, (e-f) NO_2, (g-h) TNO_3 and (i-j) TNH_4 for the time period 1990-2009. The number of considered stations is given in the figure captions.


SO2 - 1990-2009
SO2 - 1995-2009
SO2 - 2000-2009
Sign. trend
Obs. trend non sign.
LE trend non sign.
Obs & LE trend non sign.
SO4 - 1990-2009
SO4 - 1995-2009
SO4 - 2000-2009
NO2 - 1990-2009
NO2 - 1995-2009
NO2 - 2000-2009
model (ug m-3 a-1)
observation (ug m-3 a-1)
a
b
c
d
e
f
g
h
i

1

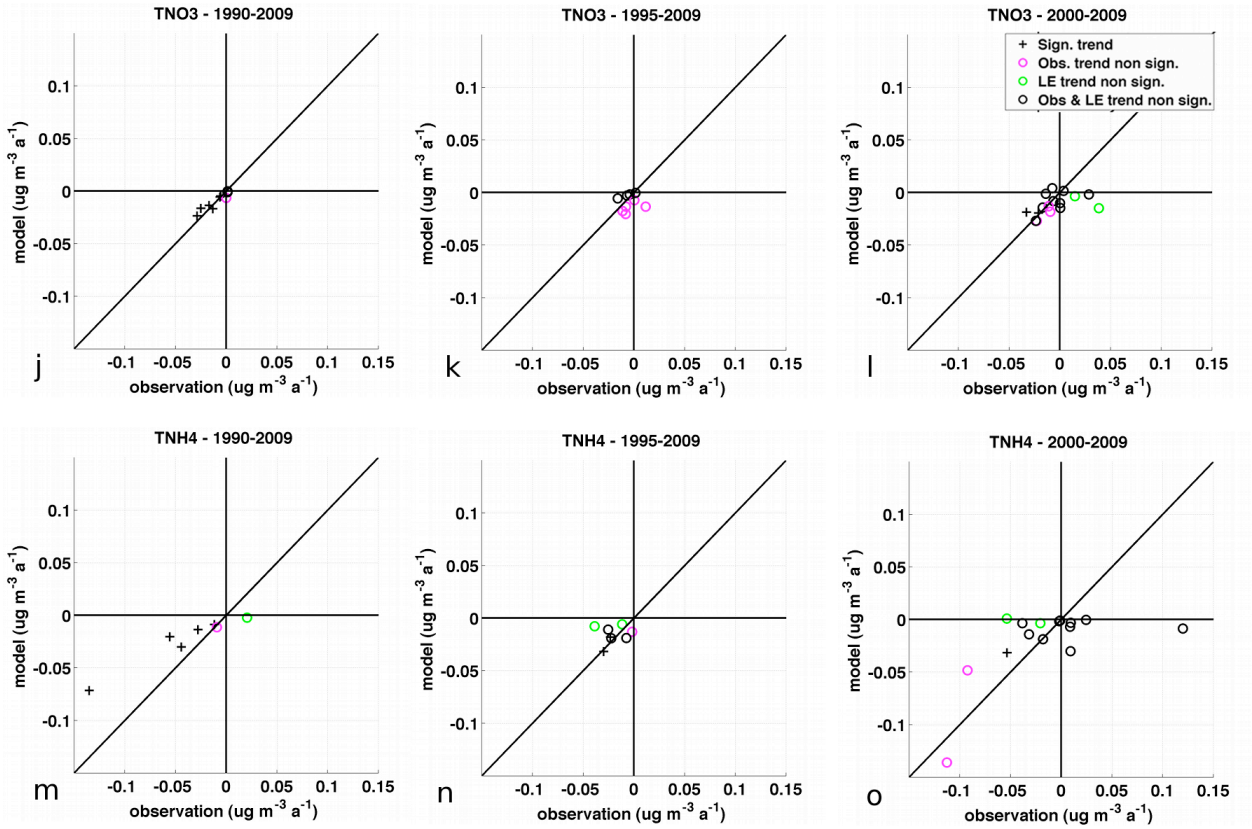


Figure 4. Scatter plots of the observed versus modelled trends for the studied components at the considered stations for the three different time periods. At each individual station the marker (described in the legend on the top right of the plot) indicates if the observed and/or modelled trend is significant following the Mann-Kendall test at a 95% confidence level.

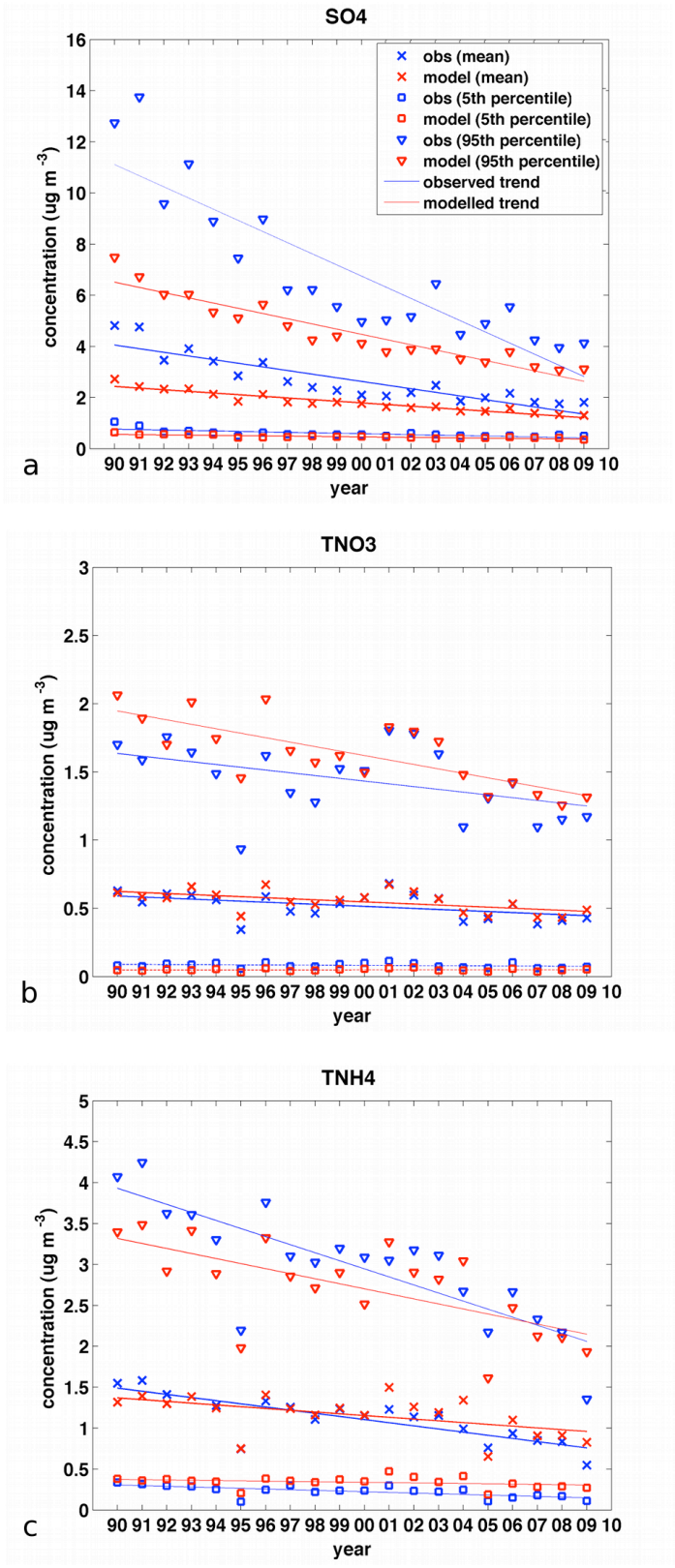


Figure 5 Observed (blue) and modelled (red) annual mean (crosses), 5th percentile (squares) and 95th percentile (triangles) and corresponding trend line of (a) SO_4^{2-}, (b) TNO_3 and (c) TNH_4. Solid lines indicate a significant and dashed lines a non-significant trend.

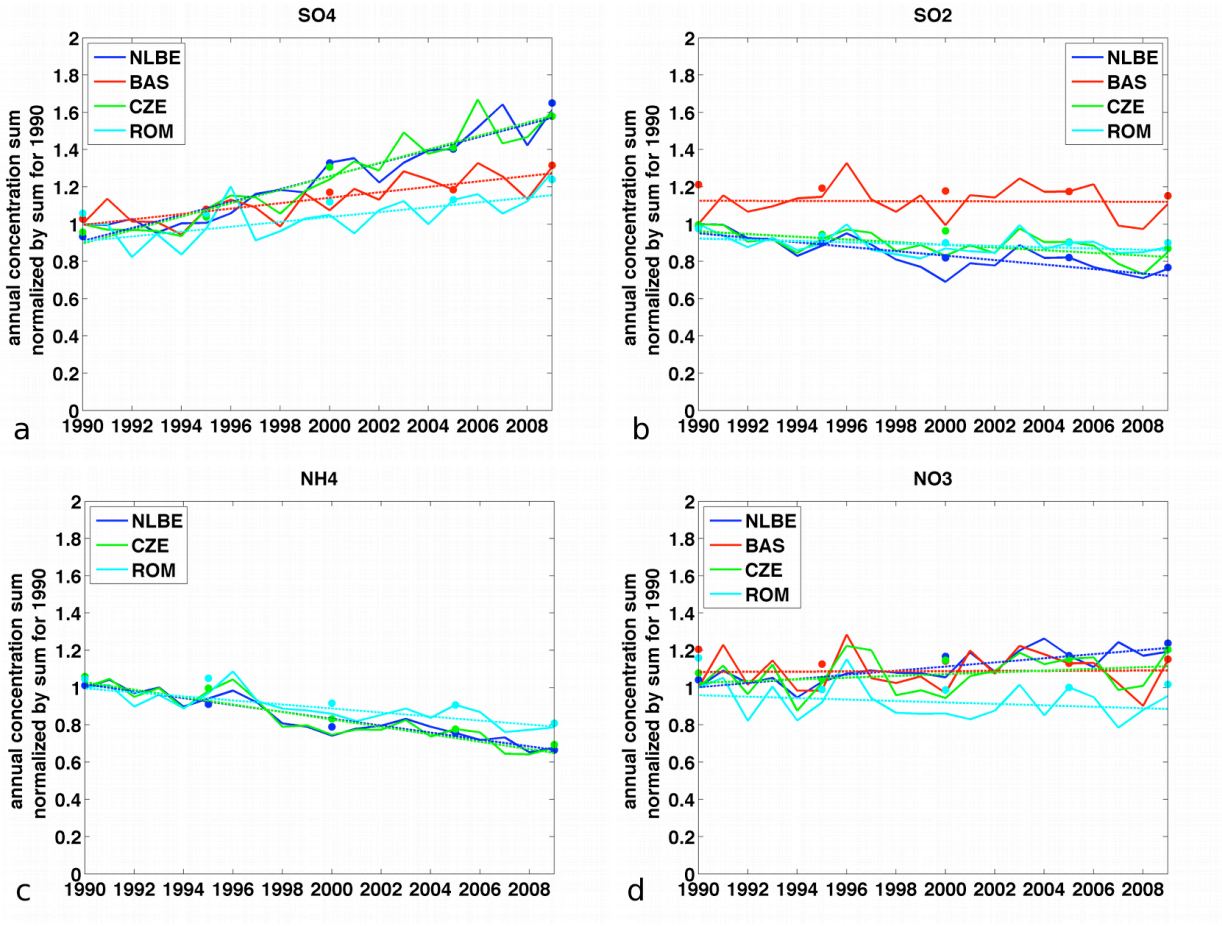


Figure 6 Amount of (a) SO_4^{2-}, (c) NH_4^+ and (d) NO_3^- (solid lines) formed from 10 ktons of SO_2, NH_3 and NO_2 emissions, respectively, relative to the amount formed in 1990, for the different labels as indicated by the colours, for the entire time period 1990 to 2009. Panel (b) shows the resultant SO_2 per unit SO_2 emission for each label for the 1990 to 2009 time period. The corresponding trend lines are presented as dashed lines. The dots denote results for the runs forced with 2005 meteorology.