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Matthias, V.; Aulinger, A.; Quante, M.:

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ADAPTING CMAQ TO INVESTIGATE AIR POLLUTION IN NORTH SEA COASTAL REGIONS

V. Matthias, A. Aulinger, M. Quante
GKSS Research Centre, Institute for Coastal Research, Max-Planck-Strasse 1, 21502 Geesthacht
E-mail: volker.matthias@gkss.de, Tel. +49-4152-872346, Fax. +49-4152-872332

ABSTRACT

The Models-3 Community Multiscale Air Quality (CMAQ) model is setup on a 54 x 54 km² grid for Europe and on a smaller domain with a 18 x 18 km² grid for the North Sea region. In this paper we investigate the models ability to represent atmospheric pollution in North Sea coastal areas. Comparisons to NO_2 and PM_{10} measurements at selected EMEP sites are used for quality control for atmospheric concentrations. We use modeled nitrogen deposition fields and EMEP wet deposition measurements during January and July 2001 as a measure to test the deposition schemes. Better agreement between the model and the measurements was found for the nitrogen compounds in January, when on average NO_2 was overestimated by 18 % (measured: 3.52 µg N /m³, modeled: 4.16 µg N/m³), nitrate deposition was only slightly underestimated by 2 % and ammonia was underestimated by 44 %. In July, NO_2 levels are much lower than in January and the model underestimates the mean density by 35 % (measured 1.49 µg N /m³, modeled 0.97 µg N/m³). Wet deposition is also underestimated, but again the results for nitrate (-38 %) were in better agreement with the measurements than for ammonium (-57%). PM_{10} values are largely underestimated in January and July (by about 65 % on average), but this result was not surprising, because only anthropogenic emissions were considered. Nevertheless, especially in January high daily correlations (0.69 to 0.84) between the modeled dry PM_{10} and the measurements in Germany were found. This indicates that the aerosol transport pathways are captured quite well. The model has been expanded to represent also persistent organic pollutants (POPs). In this paper first results of deposition fields of the carcinogenic benzo(a)pyrene (B(a)P) are shown.

1. Introduction

Significant amounts of carcinogenic polyaromatic hydrocarbons (PAH's) are still emitted into the atmosphere and influence human health and the state of ecosystems. Many of these substances are bound to aerosol particles and their lifetime in the atmosphere is closely connected to particle wet and dry deposition. The three dimensional Eulerian model system CMAQ (Byun and Ching, 1999) can be used to model the atmospheric distribution of aerosols over time scales from several days to several months. The model system has to be evaluated carefully for its suitability to represent the most important aerosol path ways. The CMAQ modeling system already includes a detailed representation of atmospheric aerosols and it can be expanded to other substances. It can be conveniently linked to the MM5 mesoscale atmospheric model, which has been developed by the Pennsylvania State University and the National Centre for Atmospheric Research in Boulder, Colorado, USA (Grell et al, 1995) and which is used here to calculate the meteorological input fields. MM5 can be run with different parameterisation schemes for representing e.g. the planetary boundary layer, cloud microphysics and subgrid convective clouds.

The CMAQ model system has been extensively used and validated in the US (Russell and Dennis, 2000, Mebust et al, 2003, Arnold et al., 2003) but in Europe only recently some results for selected regions (mainly in Spain) were published (Garcia et al., 2003, Jimenez and Baldasano, 2004, San Jose et al., 2004). Therefore, it cannot be recommended to use the

model system without further testing in other regions of Europe and in different setups of the grid and the meteorological parameterisations of MM5. However, it is not the goal of this paper to perform a comprehensive validation of the model, this has already been done. Here, model for two months in 2001 (January and July) are used to examine the model results and compare them against ground based measurements.

The model system and the additions that have been included at GKSS Research Center are briefly described before the parameterisations used to derive the meteorological input fields are explained. The models ability to represent the gaseous pollutants in North Sea coastal areas is tested by comparisons to NO_2 measurements at selected EMEP stations. Modeled aerosol mass is compared to PM_{10} measurements which are also available within the EMEP network. Finally, nitrogen deposition fields in the North Sea area are given and compared to other model results and to the available EMEP measurements. First estimates of B(a)P deposition fields in January 2001 and July 2001 are also given.

2. CMAQ Model System

2.1. Chemistry transport model

CMAQ has been developed under the leadership of the Atmospheric Modeling Division of the EPA National Exposure Research Laboratory in Research Triangle Park, North Carolina, USA. The modeling system and its source codes are freely available for use by air quality regulators, policy makers, industry, and scientists to address multiscale, multi-pollutant air quality concerns. It includes a chemistry transport model that currently allows to simulate concentrations and deposition of the major air pollutants, particulate matter and mercury.

Because of its generalized coordinate system and its advanced nesting features CMAQ can be used to study the behavior of air pollutants from local to regional scales. A detailed description of the model system is given by Byun and Ching (1999).

The model includes gas phase, aerosol and aqueous chemistry. For the gas phase chemistry, the CB4 mechanism (Gery et al., 1989) is used. The aerosol is represented by three size modes (Aitken, accumulation and coarse mode), each of them is assumed to have a lognormal distribution. Secondary aerosols are generated by nucleation processes from its precursors nitrate, ammonium and sulfate, and also from terpenes. Heterogeneous chemistry is not considered, also sea salt was not included in the version 4.4 of the CMAQ model that was used here. However, the newer version 4.5 released in September 2005 treats also sea salt, which is of special importance for North Sea applications and which will be used for future studies.

At the Institute for Coastal Research of the GKSS Research Centre Geesthacht currently an addition to CMAQ is being developed to study the trans-boundary transport of PAHs and their deposition into coastal regions. In a first step the carcinogenic benzo(a)pyrene (B(a)P) is included in the aerosol portion of the model. B(a)P can be considered as primary substance in the group of polyaromatic hydrocarbons (PAHs), because it can be comparably easily measured and therefore a relatively large number of observations, which are also representative for other PAHs, is available for this substance. In the atmosphere, B(a)P will be almost completely connected to particles, therefore it is treated as an aerosol that can occur in either accumulation or Aitken mode. Chemical reactions of B(a)P are not considered up to now but they will be added in a further step. Atmospheric concentration and deposition are almost independent from this fact because on the time scales which are considered here B(a)P

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is insensitive to reactions in the atmosphere. The new mechanism is described in detail in Aulinger et al (2006).

The CMAQ model is setup on a 54 x 54 km² grid for Europe and on a nested smaller domain with a 18 x 18 km² grid for the North Sea region. Special emphasis is laid on the representation of the planetary boundary layer to capture vertical transport and dispersion of atmospheric air pollution in coastal environments, where special circulation patterns (e.g. land see breeze effects) can be of importance. Therefore, 30 vertical levels up to 100 hPa , with 20 levels below approx. 2500 m are used in a ? -coordinate system.

2.2 Emissions

In the Models 3 framework, emissions are generated with the emissions model SMOKE (Zitat). This model cannot be directly transferred to Europe because the geostatistical information, the speciation of the emissions and the temporal evolution of the emissions are different in Europe and are currently not available in the needed formats. The emissions that were used to derive the results presented in this paper were provided by the Institute for Energy Economics and the Rationale Use of Energy (IER), Stuttgart, Germany. They were calculated on the basis of EMEP and EPER annual country emissions and include the gaseous species NO_x, CO, SO_2, NH_3, and 35 NMVOCs in RADM2 speciation. Aerosol particles are given as PM_{10} and $PM_{2.5}$ primary emissions. The emissions are scaled down to the 54 x 54 km² and the 18 x 18 km² grids and a temporal development based on information about e.g. traffic, heating and industrial production is assumed. The IER emissions contain all anthropogenic sources described in the European inventories. The data was delivered with one hour resolution for the time period 1 January 2000 to 31 December 2000. For the 2001 model results, it was assumed that the emissions did not change compared to the year before. Details

on the emissions model of IER are described in Friedrich and Reis (2004).

B(a)P emissions are based on 1993 gridded emissions for the 50 x 50 km² EMEP grid (Pacyna, 1993). They form the newest available gridded data set on B(a)P emissions in Europe These emissions were interpolated to the 54 km and the 18 km grids. For each of the considered months they were kept constant in time, but according to measurements in industrial areas in the Czech Republic, emissions in January were assumed to be a factor of 2 larger than the annual average and in July they were assumed o be 0.09 times the annual average. Because the data is comprised with large uncertainties, it was not useful to construct an emission field with higher temporal and spatial resolution.

2.3 Meteorological Fields

The CMAQ chemical transport model can be run with meteorological fields defined on different types of grids. However, the most common procedure is to use the mesoscale meteorological model MM5, which can be directly linked to CMAQ via a Meteorology chemistry Interface Preprocessor (MCIP, Otte(1999)). MM5 is widely used and tested in the scientific community (Zitate) and also European groups use this model to derive meteorological input fields for their atmospheric chemistry models (EURAD zitat). The model can be run with several combinations of physical parameterisations, depending on purpose and grid resolution. For this study, MM5 was operated with the more sophisticated parameterisations. The microphysics scheme Reisner 2 includes ice, snow and graupel (Reisner et al., 1998). The Planetary Boundary Layer (PBL) processes are based on a scheme which is also used in the MRF model (Hong and Pan, 1996). It is based on the Troen and Mahrt (1986) nonlocal diffusion concept. A cumulus scheme that is formulated to allow also

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long term simulations is the Kain Fritsch 2 scheme (Kain and Fritsch, 1993). It considers conservation of mass, thermal energy, total moisture and momentum.

For initial and boundary conditions, NCEP reanalysis data on a 2.5° x 2.5° grid were used. To derive the meteorological fields for one month, the model was successively run on eleven 4-days-periods. From this period, the last three days were taken as input data for the CCTM. Each new run started at 0:00 UT on day 4 of the previous run. This procedure was chosen to achieve low discrepancies between the MM5 run and the reanalysis fields.

2.4. Initial and Boundary Conditions

Depending on the model setup, initial and boundary conditions can play an important role for the model results, particularly if the species under investigation can undergo long range transport or if special atmospheric conditions prolongate the atmospheric life time of some of the considered species.

In this case, initial conditions are of minor importance because the model was run for 32 days, starting one day before the first day of the month, and 24 hours spin up time are sufficient to keep the influence of the initial conditions low. In the whole domain, typical profiles were used as initial conditions.

Boundary conditions were also derived from typical profiles of the gaseous species CO, O_3, NO_2 and SO_2. These profiles can significantly influence the calculated atmospheric concentrations in the outer part of the large domain. For the inner domain, which is analysed in this paper, the influence of the boundary conditions is again small. The boundaries of the outer grid are at least at 900 km distance from the inner grid's boundaries.

3. Model Results

Main purpose of the model development at GKSS is the reconstruction of past PAH deposition patterns and predictions based on scenarios for the future. Before these questions can be addressed, the model, including emissions and meteorological fields should be tested for its ability to correctly reproduce atmospheric densities and deposition fields of some important species. We chose NO_2 as frequently measured gaseous species to represent the oxidation pathways of the model. Aerosols are represented by the total mass of all particulate species, which can be compared to ground level PM_{10} measurements. Nitrogen deposition fields are investigated over the North Sea, the main region of interest. Other model results and EMEP routine measurements (EMEP, 2005) at 14 different stations in Great Britain, France, Germany, Denmark, Sweden and Norway are used to test the simulation. We focus on results in the inner domain with 18 km horizontal resolution.

We calculated absolute differences (D) and relative differences (RD) between the model results (M) and the observations (O), so D = M-O, and RD = (M-O) / O. Correlation coefficients were calculated for time series of daily averages for NO_2 and PM_{10}. The nitrogen wet deposition, split into the contributions of nitrate and ammonium, were taken as monthly means.

Great care should be taken when modelled concentrations of atmospheric trace gases are compared to measurements at ground. In many cases, the measured value is not representative for the larger area which is represented by a model grid cell. On the other hand, the model

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results in a grid cell are not independent from the information in the neighbouring cells, i.e. the effective resolution of the model is usually coarser than the grid cell dimension implies. Additionally, measurements are mostly taken close to the ground (say at 2 m level), which is close to important sinks (the surface of trees, buildings, crops, etc.) and the emission sources (traffic, factories, buildings) while the models lowest layer is typically some dekameters thick (here 37 m). Because of these difficulties, we chose only the EMEP background stations for our intercomparisons, which are preferably in flat homogeneous terrain. A brief description of the stations is given in Table 1.

3.1 NO_2 Density

Tables 2 and 3 show the monthly mean NO_2 values measured at 10 EMEP stations together with the model results, the differences D and RD and the correlation coefficients (Corr) for the time series of daily mean values.

On average the model overestimates the NO_2 density by about 18 % (D = 0.64 µg N / m³) in January 2001. This is mainly caused by three stations (DE02, DE07 and NL10, see Figure 1 a)) in highly polluted areas where NO_2 values are on average 2.7 µg N / m³ higher than measured. The temporal development of the NO_2 daily means is captured quite well at 4 stations with correlation coefficients higher than 0.5 (see Figure 1 c)), another 3 stations show correlation coefficients between 0.33 and 0.4. At DE07 and DE09 almost no correlation was found.

In July, the mean NO_2 levels are much lower than in January. This is caused by the higher solar radiation and the subsequent photochemical processes which destroy NO_2. Additionally,

better vertical mixing at almost equal NO_x emissions result in lower atmospheric NO_2 density. Averaged over the 10 selected EMEP stations only $O = 1.49\ \mu g\ N\ /\ m^3$ are measured, the modeled values are even lower at $M = 0.97\ \mu g\ N\ /\ m^3$. The relative difference is larger than in January (RD = 35 %), and the observed correlations are usually poor (Corr = -0.31 to 0.52). The model particularly underestimates the NO_2 levels at the coastal stations DE01, DE09, DK08 and SE02 (Figure 1 b)) which points to special coastal effects which are not sufficiently captured by the model and which will be further investigated. The daily NO_2 values show only small day-to-day variations, which keeps the correlation coefficient low, but a pronounced diurnal cycle in July.

3.2. PM_{10} Density

To investigate the models ability to represent atmospheric aerosols and their main transport pathways, we also compared measured PM_{10} density with modeled values of dry and wet aerosol mass. The modeled aerosol mass consists of pure anthropogenic aerosol, because primary natural emissions of atmospheric aerosols (e.g. dust and sea salt) and biogenic emissions of aerosol precursors (e.g. terpenes from trees and crops in summer) are not considered. Therefore agreement cannot be expected, but day-to-day variations caused by transport and formation of anthropogenic aerosol will be reflected in the model results.

Tables 4 and 5 show the results for dry and wet PM_{10} in January and July, respectively. The wet PM_{10} values contain the whole water mass that has been taken up by the aerosols. At high relative humidity (RH) the water mass can be much higher than the aerosol mass because hygroscopic aerosols can increase by a factor of 2 or 3 in size due to water uptake at RH = 99 %.

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In January, this leads to much higher modeled PM_{10} (wet) values than observed, but because the measured values refer to a relative humidity of 50 %. They contain only small portions of water. The PM_{10} (wet) values can better be compared in July when the relative humidity is usually lower and the uptake of water by the aerosol particles is also much lower. Because of the high sensitivity of the wet aerosol mass to the relative humidity, it is more appropriate to compare the PM_{10} (dry) values to the measurements. However, the remaining water fraction of the measured aerosol mass at RH = 50 % will lead to some additional discrepancies between the model and the measurements.

Although the aerosol mass is largely underestimated by the model, the comparisons with the measurements at the German stations DE01, DE02, DE07 and DE09 show high correlation coefficients between 0.69 and 0.84 in January. In July they are lower (0.23 to 61) which might be caused by the fact that in summer the temporally highly variable solar radiation determines the aerosol formation by photochemical processes including the naturally emitted terpenes which are not included in the model runs shown here. In contrast in winter sea salt, which was also not included in these model runs, is the most dominant source of natural aerosols in North Sea coastal regions and they form temporally more stable background values depending on wind speed. Correlation coefficients decrease when the modeled wet aerosol mass is compared to the measurements.

An underestimation of the PM_{10} aerosol mass was also reported by Mebust et al. (2003) for comparisons of CMAQ model results to observations in the western US. They found averaged over 18 IMPROVE stations that modeled values were 30 % lower than the observations. At coastal stations, the model underestimated the observations by typically 50 %. These

discrepancies were attributed to the lack of wind blown dust and sea salt aerosols in the aerosol emissions.

3.3 Nitrogen Deposition

3.3.1 Modeled Deposition Fields

Because PAH deposition data is sparse, nitrogen deposition fields are used instead to test the reliability of the modelled B(a)P deposition. This is adequate because nitrogen wet deposition is dominated by aerosol deposition and this will also hold for B(a)P. If the most important processes causing nitrogen wet deposition are captured by the model, B(a)P deposition will also be correctly represented.

Nitrogen deposition fields were calculated for the outer domain comprising whole Europe and the North Sea area. Figure 2 displays the wet deposition fields in the North Sea area for nitrate and ammonium aerosols in January and July 2001. Because dry deposition measurements are not available, we restrict ourselves to the wet deposition. Additionally, the higher surface roughness over land will significantly increase the dry deposition and land based measurements will not reflect the situation over water. The wet deposition of atmospheric nitrogen is almost completely caused by deposition of ammonium and nitrate aerosols. Over the North Sea wet deposition is about 74 % of the total deposition, not dependent on season, which is in good agreement with de Leeuw et al. (2003) who found a fraction of 82 % wet deposition.

For ammonium (Figure 2 a and b), the main deposition areas are close to the source regions in the Netherlands, Germany and in July also in Great Britain. Significant gradients between land and water can be observed. The model reflects almost no seasonal trend over the North Sea, in January the ammonia based wet deposition of nitrogen is 0.38 mg/(m² d), in July it is 0.33 mg/(m² d). On the other hand, nitrate wet deposition is significantly higher in January than in July. The main deposition areas are closely connected to the precipitation pattern (e.g. in southern Norway and the south eastern North Sea). The source areas for the most important precursors NO_x are more widely spread than those for ammonia, which are highly concentrated in the Netherlands and north west Germany. There is only a small seasonal trend in NO_x emissions and the lower boundary layer height in winter leads to larger NO_x and HNO_3, and subsequently nitrate aerosol density close to the ground in winter. In contrast, ammonium emissions are very low in January and the effect of lower boundary layer heights does not lead to a significant increase of ammonium aerosol density and the related deposition.

The total amount of nitrogen deposition, including dry deposition is 1.1 mg N/m² in July 2001 and 2.0 mg N/m² in January 2001 over the North Sea. This is on average 70 % higher than the mean value of 0.9 mg N /m² reported by de Leeuw et al. (2003) for the whole year 1999. Agreement cannot be expected, because here only two months in a different year are modelled. Nevertheless it can be stated that the model results shown here reveal higher atmospheric nitrogen deposition than given by de Leeuw et al. (2003). As will be seen in the next section, EMEP measurements point to even higher nitrogen deposition than it has been modeled with CMAQ.

3.3.2 Comparison to EMEP stations

Comparisons of modeled deposition fields to wet deposition measurements contain several sources of uncertainty and have to be treated very carefully. The main reason is that the wet deposition is closely connected to the precipitation which also in small areas can be very inhomogeneously distributed. This makes direct comparisons at one station nearly impossible. However, if a number of stations are taken over larger areas one could expect that averaging effects reduce the deviations between model and measurements significantly.

Measured concentrations of ammonium and nitrate in rain water were used together with the precipitation measurements to estimate the wet deposition of atmospheric nitrogen at 13 EMEP stations which can be found in the inner model grid. The stations are briefly described in Table 1. Five station provided daily values, at another five stations, weekly totals and at three stations fortnightly totals could be used. This again leads to some uncertainty because large portions of the weekly deposition might result from only one day and this particular day might not be within the modeled time period of one month. Here, we summed all measurements that were available in a particular month except for 1 January 2001 at the three Danish stations that provide fortnightly totals.

We calculated the measured wet deposition by multiplying the reported concentrations in rain water with the precipitation and then we took the sums over all stations and the whole month of January and July, respectively. The results are displayed in Table 6.

In January, the mean precipitation is captured quite well (measured 84.5 mm/month, modeled 87.8 mm/month), however at particular stations the deviations between model and measurements can be more than 100 % (Fig 3 a)). Only small differences were found for the nitrate deposition which was on average 1.26 mg N/(m² d), the modeled value was 1.24

mg/(m² d). Larger differences were found for ammonium. Here the measurements (0.99

mg/(m² d))were on average almost 80 % larger than the modeled values (0.55 mg/(m2 d)).

The total wet deposition of atmospheric nitrogen in January 2001 was 10 % higher than the

modeled values.

In July the agreement is not that good. Although the average total precipitation is again

captured quite well (measured 80.4 mm/month, modeled 77.4 mm/month), the wet deposition

of atmospheric nitrate is significantly higher in the measurements (0.99 mg/(m2 d)) compared

to the model (0.61 mg/m2 d)). As in January, also the ammonium deposition is significantly

higher in the measurements (1.25 mg/(m2 d)) than in the model (0.54 mg/(m2 d)). It is known

that dry deposition of NH_3 can lead to a significant overestimation of the wet ammonium

deposition (Cape and Leith, 2002) in open gauge bulk collectors. This could explain a

significant part of the differences.

Figure 3 shows the deviations of the modelled precipitation (a), ammonium deposition(b) and

nitrate deposition (c) to the measurements at the different EMEP stations in January 2001.

Obviously, the quality of the precipitation information dominates also the deposition.

Precipitation is underestimated at the EMEP stations located close to mountainous areas

(NO01, NO08, GB14, FR09) while it is overestimated at most of the German stations and in

the Netherlands. With some exceptions this pattern can also be observed for the nitrate and

ammonium depositions. At SE02, precipitation is overestimated but both nitrate and

ammonium deposition are close to the measurements. On the other hand, at DE07 the amount

of precipitation is captured quite well while the nitrate deposition is largely overestimated.

The pattern is similar in July 2001 (Figure 4). Again the agreement of the modeled deposition to the measurements depends strongly on the precipitation. Precipitation is underestimated at NO01, NO08, GB14, FR09 and at DK05. Too high values can again be found at DE02, DE07 and SE02. This distribution is reflected in the depositions although both nitrate and ammonium deposition are lower in the model compared to the measurements at almost all stations. Here, an exception can be found at DE02, where both ammonium and nitrate depositions are larger in the model than observed.

Obviously, stationwise comparisons of wet deposition values are difficult and large deviations have to expected. Having the close connection to the precipitation pattern, which is usually very inhomogeneous, in mind, this is not surprising. The results presented here show that comparisons to measurements are useful if longer time series, even longer than the two months presented in this paper, and a larger number of stations that represent a complete area are used. We conclude that the precipitation in the North Sea area was captured quite well by the MM5 simulations. This led to nitrate deposition patterns which on average agree with EMEP measurements in January. Ammonium was underestimated in the model. In July both nitrate and ammonium deposition were underestimated by the model although the mean precipitation was again captured quite well. Several reasons for the discrepancies including the aerosol and chemistry modules of CMAQ, the emission fields (ship emissions are not considered here) and the representation of the planetary boundary layer depth are under investigation, but also the quality of the measurements, especially for ammonium has to be taken into account.

3.4 B(a)P Deposition Fields

Looking at B(a)P, its deposition is focused on eastern Europe, where also the main source regions are located. Nevertheless, significant deposition can also be found in the North Sea region (Figure 5). The pattern depends mainly on transport pathways and the precipitation distribution. This simulation is based on 1993 annual mean emissions due to a lack of more recent data, excluding ship emissions. Emissions have declined since then. Therefore, it can be expected that current deposition will be lower.

In the North Sea region, large gradients are observed between coastal and open sea depositions, because the main part is deposited close to the sources, i.e. the highly populated areas around London, Rotterdam, Antwerpen and the Ruhr Basin. This causes high depositions in the south west of the North Sea, lowest values are found in the north west of the North Sea. Because B(a)P emissions are closely connected to combustion processes for heating, the emissions are much lower in July and deposition is less than 3 % of the values in January.

The B(a)P deposition in the whole model domain is estimated to be 0.15 µg/(m² d) in January and 0.004 µg/(m² d) in July. For the whole year, the deposition will be about 0.077 µg/(m² d). Gocht (2004) collected annual values from measurements reported in the literature. They were mainly taken between 1998 and 2002 in rural regions in Germany, Sweden and France and show values between 0.004 and 0.038 µg/(m² d). Because B(a)P emissions have declined since 1993, it is expected that the model estimates are higher than the measurements suggest.

4. Conclusions

The Community Multiscale Air Quality (CMAQ) model was successfully adapted to North Sea coastal regions. The model has been set up on a new grid with 54 km grid spacing over Europe and an inner nest of 18 km grid spacing over the North Sea. Adequate meteorological fields were calculated with the MM5 mesoscale model for January and July 2001. Emission data in hourly resolution for 2001 calculated by IER Stuttgart was used for the simulation. The model shows better results in January than in July, when NO_2 density, nitrate and ammonium wet deposition are underestimated. Good agreement with observed NO_2 densities at 10 selected EMEP stations and of nitrate wet deposition at 13 stations was found for January 2001. Ammonium was also underestimated in January, but measurement uncertainties could account for a large part of this underestimation by the model.

Measured PM_{10} is largely underestimated because only anthropogenic emissions are considered in the model and it is well known that natural sources (e.g .sea salt and dust) account for the largest part of the atmospheric aerosol. Good correlation of the modeled dry aerosol mass with PM_{10} measurements in Germany show that the main transport pathways of anthropogenic aerosols are captured by the model.

It can be concluded that it is reasonable to apply the model to North Sea coastal regions to estimate the deposition of particle bound polyaromatic hydrocarbons in this part of Europe. Caused by the pronounced annual cycle of the emissions and the meteorological conditions in winter, B(a)P deposition in the inner model domain is much higher in January (0.15 µg/(m² d)) than in July (0.004 µg/(m² d)). The values are larger than the sparse observations reported in the literature, but emissions were reduced since 1993, the reference year for the B(a)P emissions that were used here.

Acknowledgements

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Figure captions

Fig 1: Color coded relative difference (-100 % - 100 %) between modeled and measured monthly mean NO$_2$ densities at 10 selected EMEP sites in January (a) and July (b) and color coded correlation coefficients (-1 – 1) of modeled and measured daily mean NO$_2$ densities at the same sites in January (c) and July (d).

Fig. 2. Modeled wet deposition (mg N/(m² d)) of aerosol bound ammonium (a and b) and nitrate (c and d) in January and July 2001 .

Fig 3: Color coded relative difference (-100 % - 100 %) between modeled and measured monthly mean precipitation (a), ammonium wet deposition (b) and nitrate wet deposition (c) at 13 selected EMEP sites in January 2001.

Fig 4: Color coded relative difference (-100 % - 100 %) between modeled and measured monthly mean precipitation (a), ammonium wet deposition (b) and nitrate wet deposition (c) at 13 selected EMEP sites in July 2001.

Fig 5: Modeled wet deposition (mg /(m² d)) of aerosol bound benzo-a-pyrene in January (a) and July (b) 2001.

Table 1. Brief description of the selected EMEP stations and the measured quantities that were used for the comparison with the CMAQ model results. If not explicitly mentioned, measurements are daily means.

Code	Station name	Latitude North	Longitude West	Altitude	Measured quantities
DE01	Westerland	54.93	8.31	12	NO_2, PM_{10}, Depos (weekly)
DE02	Langenbrügge	52.80	10.76	74	NO_2, PM_{10}, Depos (weekly)
DE07	Neuglobsow	53.17	13.03	62	NO_2, PM_{10}, Depos (weekly)
DE09	Zingst	54.43	12.73	1	NO_2, PM_{10}, Depos (weekly)
DK05	Keldsnor	54.73	10.73	10	Depos (fortnightly)
DK08	Anholt	56.72	11.52	40	NO_2, Depos (fortnightly)
DK22	Sepstrup Sande	55.08	9.60	60	Depos (fortnightly)
FR09	Revin	49.90	4.63	390	Depos
GB14	High Muffles	54.33	-0.81	267	Depos (weekly)
NL09	Kollumerwaard	53.33	6.28	1	NO_2, Depos
NL10	Vredepeel	51.53	5.85	28	NO_2
NO01	Birkenes	58.38	8.25	190	NO_2, PM_{10}, Depos
NO08	Skreadalen	58.82	6.72	475	NO_2, Depos
SE02	Rörvik	57.42	11.93	10	NO_2, Depos

Table 2: NO$_2$ density (µg N/m³) at selected EMEP sites and in the lowest layer of the closest model grid box. Average values in January 2001, absolute and relative differences and correlation coefficients for daily means.

Station	Meas.	Model	abs. diff. D	rel. diff. RD	correlation Corr
DE01	3.50	2.59	-0.91	-0.26	0.40
DE02	3.91	5.70	1.79	0.46	0.33
DE07	3.53	5.83	2.30	0.65	0.22
DE09	3.03	3.42	0.39	0.13	0.19
DK08	2.25	1.84	-0.40	-0.18	0.71
NL09	5.78	5.40	-0.38	-0.07	0.35
NL10	9.52	13.51	3.99	0.42	0.68
NO01	1.01	1.00	-0.01	-0.01	0.57
NO08	0.57	0.76	0.19	0.33	0.70
SE02	2.07	1.59	-0.48	-0.23	0.33
mean	**3.52**	**4.16**	**0.64**	**0.18**	

Table 3: NO$_2$ density (µg N/m³) at selected EMEP sites and in the lowest layer of the closest model grid box. Average values in July 2001, absolute and relative differences and correlation coefficients for daily means.

Station	Mean meas.	Mean model	Abs. diff.	Rel. Diff.	correlation
DE01	1.26	0.56	-0.70	-0.55	0.49
DE02	1.26	1.08	-0.18	-0.14	-0.13
DE07	1.28	0.96	-0.32	-0.25	0.38
DE09	1.37	0.75	-0.62	-0.45	-0.11
DK08	1.17	0.28	-0.89	-0.76	-0.31
NL09	1.57	1.67	0.10	0.06	0.52
NL10	5.44	4.05	-1.39	-0.25	0.19
NO01	0.39	0.22	-0.17	-0.44	0.07
NO08	0.30	0.25	-0.05	-0.17	-0.190
SE02	0.89	0.19	-0.70	-0.79	-0.11
mean	**1.49**	**0.97**	**-0.52**	**-0.35**	

Table 4: PM₁₀ density (µg N/m³) at selected EMEP sites (measured at RH = 50 %) and in the lowest layer of the closest model grid box excluding water (dry) and including water (wet). Average values in January 2001, absolute and relative differences and correlation coefficients for daily means.

Station	Mean meas.	Mean model	Abs Diff	Rel. Diff	Correlation
Dry					
DE01	27.1	5.5	-21.6	-0.80	0.82
DE02	28.5	9.0	-19.5	-0.68	0.69
DE07	27.7	9.1	-18.6	-0.67	0.80
DE09	30.3	7.8	-22.5	-0.74	0.84
NO01	6.9	1.9	-5.0	-0.73	0.47
mean	**24.1**	**6.7**	**17.4**	**-0.72**	
Wet					
DE01	27.1	35.3	8.2	0.30	0.23
DE02	28.5	89.8	61.3	2.15	0.68
DE07	27.7	101.0	73.2	2.64	0.57
DE09	30.3	57.4	27.1	0.89	0.29
NO01	6.9	13.6	6.7	0.97	0.21
mean	**24.1**	**59.4**	**35.3**	**1.47**	

Table 5: PM_{10} density (µg N/m³) at selected EMEP sites (measured at RH = 50 %) and in the lowest layer of the closest model grid box excluding water (dry) and including water (wet). Average values in July 2001, absolute and relative differences and correlation coefficients for daily means.

Station	Meas.	Model	abs diff D	rel. diff RD	correlation Corr
Dry					
DE01	17.0	4.5	-12.5	-0.74	0.23
DE02	13.3	5.0	-8.3	-0.62	0.26
DE07	11.5	4.4	-7.1	-0.62	0.61
DE09	14.1	4.1	-10.0	-0.71	0.34
NO01	8.5	1.9	-6.6	-0.78	0.42
Mean	**12.9**	**4.0**	**-8.9**	**-0.69**	
Wet					
DE01	17.0	11.8	-5.2	-0.31	0.16
DE02	13.3	8.9	-4.4	-0.33	0.12
DE07	11.5	7.2	-4.3	-0.38	0.60
DE09	14.1	7.7	-6.4	-0.45	0.34
NO01	8.5	6.0	-2.5	-0.30	0.29
Mean	**12.9**	**8.3**	**-4.6**	**-0.36**	

Table 6: Monthly mean deposition (mg N /(m² d)) of ammonium, nitrate and precipitation averaged over 13 selected EMEP sites and in the lowest layer of the corresponding model grid box. Values for January and July 2001.

	measured	modeled
January 2001		
NH$_4$ / mg N /(m² d)	0.99	0.55
NO$_3$ / mg N/(m² d)	1.26	1.24
Precipitation mm/month	84.5	87.8
July 2001		
NH$_4$ / mg N/(m² d)	1.25	0.54
NO$_3$ / mg N/(m² d)	0.99	0.61
Precipitation / mm/month	80.4	77.4

Fig 1: Color coded relative difference (-100 % - 100 %) between modeled and measured monthly mean NO$_2$ densities at 10 selected EMEP sites in January (a) and July (b) and color coded correlation coefficients (-1 – 1) of modeled and measured daily mean NO$_2$ densities at the same sites in January (c) and July (d).

Fig 2: Modeled wet deposition (mg N/(m² d)) of aerosol bound ammonium (a and b) and nitrate (c and d) in January and July 2001 .
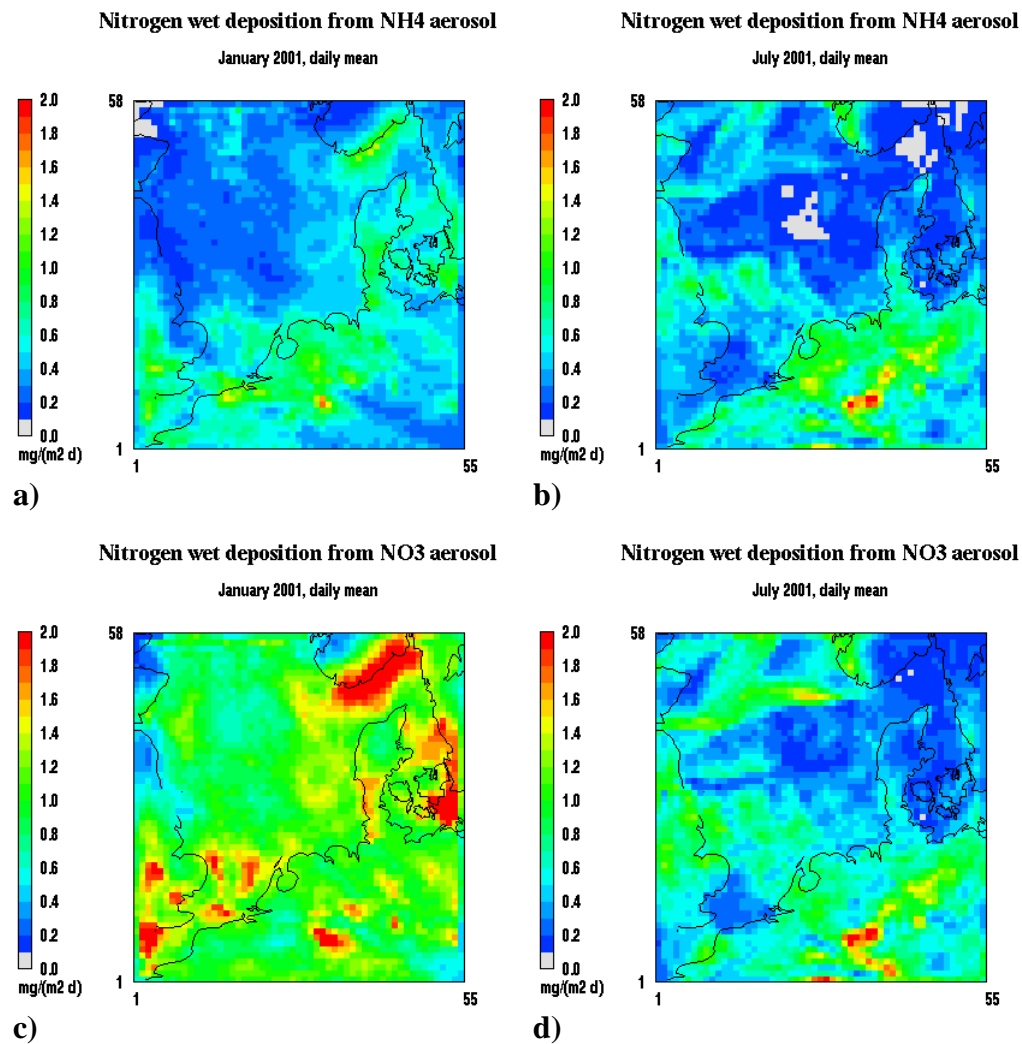

a)

b)

c)

d)

Fig 3: Color coded relative difference (-100 % - 100 %) between modeled and measured monthly mean precipitation (a), ammonium wet deposition (b) and nitrate wet deposition (c) at 13 selected EMEP sites in January 2001.
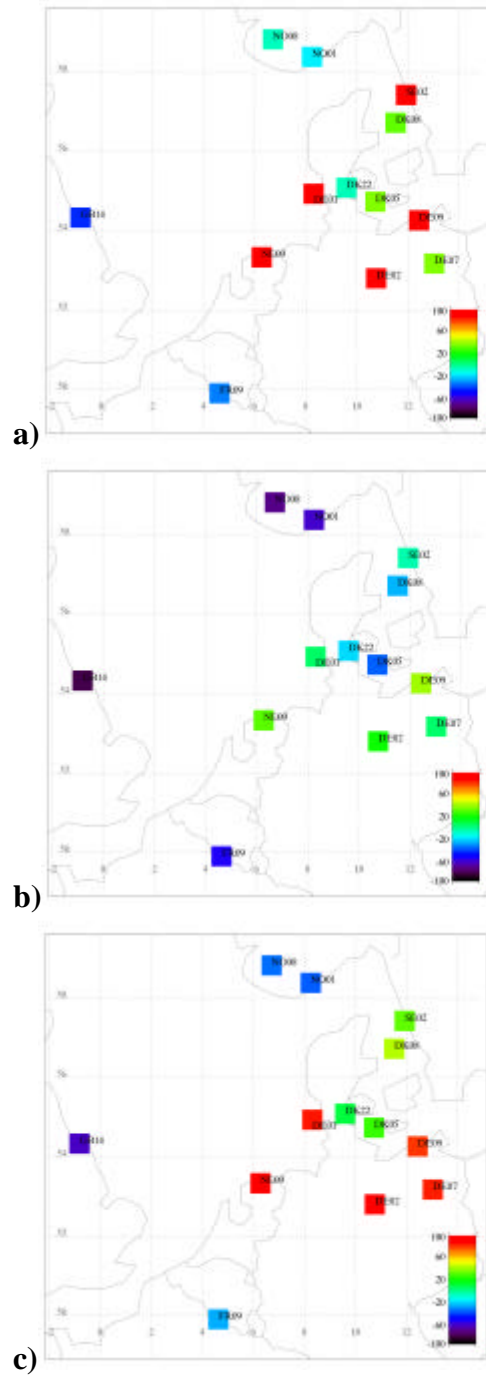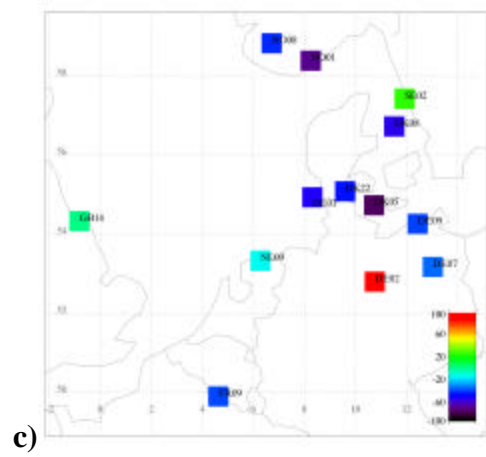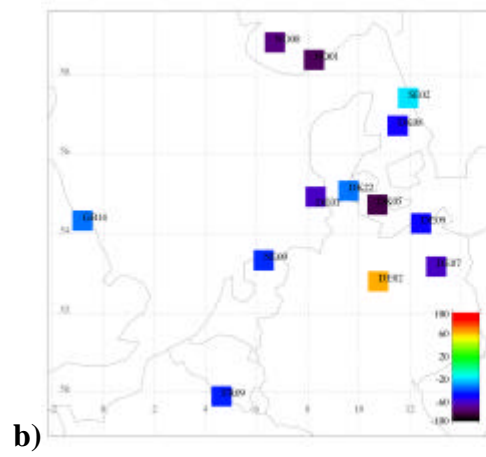

a)

b)

c)

Fig 4: Color coded relative difference (-100 % - 100 %) between modeled and measured monthly mean precipitation (a), ammonium wet deposition (b) and nitrate wet deposition (c) at 13 selected EMEP sites in July 2001.
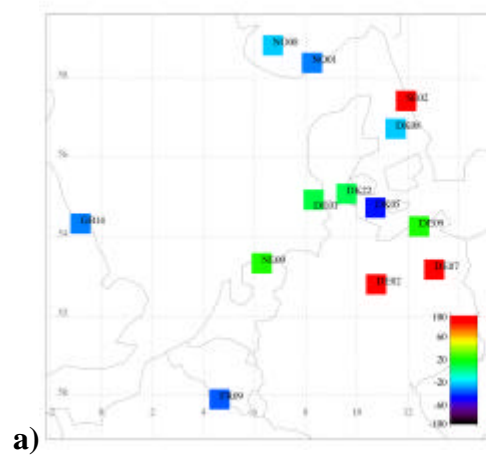

a)

b)

c)

Fig 5: Modeled wet deposition (mg /(m² d)) of aerosol bound benzo a pyrene in January (a) and July (b) 2001.