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An approach to temporally disaggregate Benzo(a)pyrene emissions and their application to a 3D Eulerian atmospheric chemistry transport model

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Abstract To simulate the atmospheric fate of air pollutants it is at first necessary to know the emission rates that describe the release of pollutants into ambient air. For benzo(a)pyrene emission data are currently only available as yearly bulk emissions while the simulation models typically read emissions in time steps of one hour. Because residential heating is by far the most important source for benzo(a)pyrene we developed a method to temporally disaggregate these bulk emission data using the linear dependency of benzo(a)pyrene emission rates stemming from residential combustion on ambient temperature. The resulting time dependent hourly emission rates have been used in a chemical transport model to simulate concentrations and deposition fluxes of benzo(a)pyrene in the year 2000. The same simulations were repeated with constant emission rates and emission rates that varied only seasonnaly. By comparing the three emission cases with monthly measurements of air concentrations the characteristic and the benefit of our disaggregation approach is illustrated. The simulations with disaggregated emissions fitted best to the measurements. At the same time the spatial distribution as well as the yearly total deposition was notably different with each emission case even though the yearly total emissions were kept constant.

1 Introduction

Benzo(a)pyrene belongs to the group of polycyclic aromatic hydrocarbons (PAHs). These are semivolatile, lipophilic persistent organic pollutants (POPs), which originate primarily from incomplete combustion of organic material. Surveys have revealed that a variety of PAHs possess a high carcinogenic potential to animals and humans

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(Agency for Toxic Substances and Disease Registry, 1995) and are bio-accumulated in the food chain. They can be transported over long distances in the atmosphere resulting in a widespread distribution across the earth, including regions where they have never been used. Due to their toxic and ecotoxic characteristics they pose a threat to humans and the environment, and therefore the international community has called for actions to reduce and eliminate the release of POPs, such as the Protocol to the United Nations Economic Commission for Europe (UNECE) Convention on Long-range Transboundary Air Pollution (CLRAP) on POPs. Benzo(a)pyrene (B(a)P) is one of the best investigated PAHs both because of its severe toxicity and its relatively good availability to measurements. In our study it was for this reason used as a marker for carcinogenic PAHs. Because of its low vapor pressure and its affinity to organic matter it occurs in the atmosphere bound to particles rather than in its gaseous form. The deposition of particles depends significantly on the weather conditions why it is crucial to know the meteorological conditions that prevail during B(a)P emission events to determine whether it is deposited near the sources or can be transported further away.

By using a 3D Eulerian model it is possible to study the atmospheric transport and deposition of PAHs over Europe in high spatial and temporal resolution. In contrast to measurements modeling studies can also investigate concentrations and depositions in former and future times using different emission scenarios. The model results must of course thoroughly be evaluated and compared to measurements wherever possible. Our research group uses the Community Multiscale Air Quality (CMAQ) Modeling System developed under the leadership of the US Environmental Protection Agency (Byun and Ching, 1999; Byun and Schere, 2006) as basic model and extended it to treat semivolatile POPs, in particular PAHs. The release of PAHs into the environment is highly dependent on human activities whereas their distribution over e.g. Europe is driven by their physical-chemical characteristics and meteorological conditions. Thus, to investigate the pathways of PAHs and to assess the threat they may pose to particular ecosystems it is indispensable to apply proper emission data and meteorological fields together with a sophisticated chemical transport model.

The most comprehensive data base for emission data in Europe is the "WebDab" data base maintained by the Co-operative Program for Monitoring and Evaluation of the Long-range Transmission of Air pollutants in Europe (EMEP) and UNECE. Countries that signed the Convention on Long-Range Transboundary Air Pollution (CLRTAP) are committed to report their total annual emissions of the main pollutants, aerosols and selected heavy metals and POPs to UNECE. The experts at EMEP do a great effort to compile these data and complete them where officially reported data is missing. Despite of this, emission data for B(a)P is very sparse and the data is connected with large uncertainties. The EMEP/EEA air pollutant emission inventory guidebook (European Environment Agency, 2009) for collecting and reporting emission data reveal that the emission factors for some activities or processes causing B(a)P emissions vary within orders of magnitude. While emissions for the main pollutants are disaggregated temporally by means of emission models on the basis of emission activities no such models exist for B(a)P or any other PAHs. In this paper an approach to create temporally disaggregated B(a)P emissions as input for a chemistry-transport model is presented.

2 CMAQ chemistry-transport model

CMAQ is a 3D Eulerian regional model which was in our case configured for the European continent. The entire model domain is split into an outer domain that covers Europe from the Mediterranean Sea to the North Polar Sea and from Iceland to Western Russia with a grid cell size of 54x54 km. It comprises 30 vertical layers up to a minimum pressure level of 100 hPa.The CMAQ chemistry-transport model (CCTM) was mainly designed for classical air pollutants like SO_2, NO_x, O_3, and particulate matter (PM). In our model version we chose the option to use the CB-IV chemical mechanism (Gery et al, 1989) combined with aqueous and aerosol chemistry routines that takes into account the atmospheric reactions of the main pollutants including the production of photo-oxidants as well as the formation of secondary organic and inorganic aerosols both of which are crucial for the fate of B(a)P in the atmosphere. At GKSS the CB-IV mechanism was extended to cope with the degradation of B(a)P in the gas phase and adsorbed to particles (Aulinger et al, 2007). Thereby, special emphasis was laid on considering the mass transfer of B(a)P between the gaseous and the particulate phase. The partitioning of the compound between the gas and the particle phase as well as its distribution between the Aitken, accumulation and the coarse particle mode is dependent on temperature and particle surface, mass of organic aerosols and aerosol water content in each mode. The physical-chemical properties of B(a)P which determine the partitioning are hence its liquid vapor pressure, octanol-air partitioning coefficient and Henrys Law constant. In the current version of our B(a)P module gaseous B(a)P is degraded by photolysis and by reactions with OH and ozone radicals. However, owed to the fact that B(a)P occurs at temperatures prevailing in middle Europe mainly bound to aerosols the degradation reactions in the gas phase are of minor importance for the fate of B(a)P. Even if the degradation reactions of particle bound B(a)P is orders of magnitude slower than those of the gaseous form (Esteve et al, 2006) the heterogeneous reactions are an important sink. According to Kwamena et al (2007) the decisive heterogeneous reaction is that with gaseous ozone which has been implemented in the CCTM.

To drive the transport and deposition mechanisms of the CCTM several meteorological parameters are required which are calculated with the meteorology-chemistry interface processor (MCIP) (Otte, 1999) from variables provided by a meteorological model. To calculate the meteorological variables for the simulation year 2000 we used NCAR's fifth generation mesoscale atmospheric model (MM5) (Grell et al, 1995). The quality of the meteorological data and their applicability to CMAQ for Europe has been tested and the results are described in a separate paper (Matthias et al, 2009b). For the simulations presented here the boundary conditions of the main pollutants were taken from MOZART (Horowitz et al, 2003) model results for the year 2000. The data has a spatial resolution of $1° \times 1°$ and a temporal resolution of one day. It includes the gas phase species O_3, O, O^1D, CO, NO, NO_2, SO_4, HO_2, OH, PAN, HCOH, isoprene, terpenes and HNO_3. The modelled concentrations of these species were interpolated to the boundary of the outer CMAQ domain. However, as the MOZART data vary only day by day and the model input frequency is one hour the data had also to be temporally interpolated. Intercontinental transport of aerosol particles was not considered. Further, we had no knowledge of B(a)P concentrations outside the model domain why the boundary concentrations for B(a)P were set in a way that avoids a concentration gradient through the border. Initial conditions are set once to average winter concentrations found on 25 December the year before the annual run started. By this spin-up
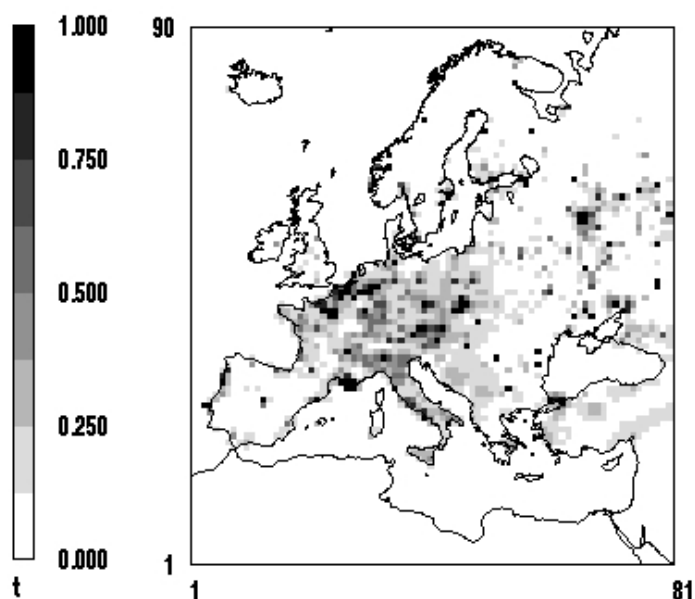
Fig. 1 Accumulated emissions of B(a)P in 2000 in tones

time of seven days the influence of the initial conditions is kept very low. For a detailed description of how to set up and run CMAQ refer to Byun and Ching (1999).

3 Emissions

The format in which emissions are reported by the CLRTAP member countries usually include yearly bulk emissions separated in emission sectors like residential heating or traffic. In case the reported data are not complete they are completed by emission experts at EMEP. To be used in an Eulerian model they have to be gridded, i.e. interpolated to the grid cells of the model domain. This is in a simple way done by using the population density in the different grid cells as weighting factors. More sophisticated methods involve different interpolation methods for different emission sectors. To distribute emissions from the sector "residential heating" the population density driven interpolation can be used while for distributing emissions from the sector "road traffic" it is recommendable to use rather the vehicle density as weighting factor. Emissions from certain point sources can be directly allocated to the grid cell where the point source is located without interpolation.

3.1 Benzo(a)pyrene emission inventory

In the framework of a research study at TNO (The Netherlands Organisation for Applied Scientific Research TNO) an European emission inventory of B(a)P and other POPs containing yearly bulk emissions for the year 2000 was compiled (Denier van
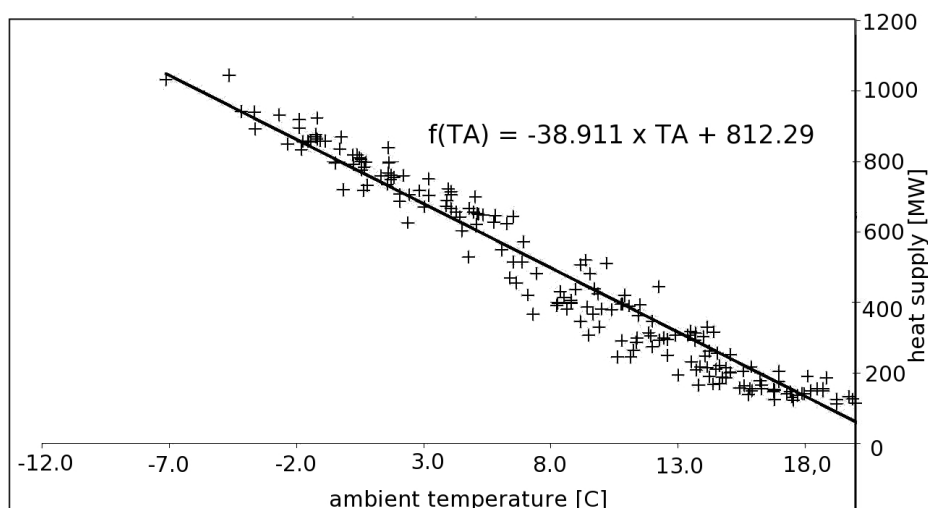
Fig. 2 Heat supply in dependence of ambient air temperature two-day means (DIN 4108) 01.01.2005 31.12.2006

der Gon et al, 2005). The base for this inventory were officially reported country emissions. In addition, the authors of that study created a reference data base derived from emission activities and emission factors which they used to complete and correct the official data where this appeared advisable to them. The resulting emission inventory was kindly provided to us in a gridded version projected on the 50x50 km polar stereographic EMEP grid and separated into the emission sectors public power and heat, residential combustion, industrial combustion and processes, road transport, non-road transport, solvent and product use, waste incineration and agriculture. For creating the gridded data the population density and information about point sources were considered. Residential combustion accounted for the by far largest contribution of B(a)P emissions followed by industrial combustion and processes and road transport. The contribution of the remaining sectors was nearly negligible. In order to be applicable to our model domain these data were interpolated to the CMAQ grid with the inverse distance weighting method ensuring conservation of mass (Figure 1).

3.2 Temporal disaggregation of Benzo(a)pyrene emissions

Because according to Denier van der Gon et al (2005) more than 80% of the B(a)P emissions emanate from residential combustion a strong dependence of the emissions on season is expected. Unfortunately, the data base does not give any information on the temporal evolution of the emissions. Thus, the straightforward way to use the emissions with CMAQ is to keep the emission rate (in g/s) constant for each model time step. Baart et al (1995) proposed to apply a factor of 1.2 to the emissions in fall and winter and 0.8 in spring and summer to take into account the seasonal variations.

In our approach to gain hourly variable B(a)P emissions we pursued different strategies for the different emission sectors. Emissions from residential combustion were directly linked to the ambient temperatures in each grid cell. In a research study conducted by Vattenfall Germany (Beecken, 2007) about district heating at Hamburg,

Germany, it was shown that the quantity of heat that is supplied to consumers is linearly dependent on the ambient temperature up to a maximum of $18°C$ where the supplied heat reaches a minimum and remains constant (Figure 2). By dividing the function values of the heat-temperature function by the minimum supplied heat of 130 KW and assuming that the B(a)P emissions are directly proportional to the supplied heat we derived equation 1 to calculate a daily average emission rate E_d as a multiple of the minimum emission rate E_{min} for each grid cell in case the temperature is below $T_{lim} = 18°C$ (equation 1). Thus, E_{min} has the value 1.0 as the heat-temperature curve has been normalized to the minimum heat supply which is by definition corresponding to the minimum emissions. The temporal pattern of the emissions is, then, independent of the minimum emissions in the grid cell. The not normalized emission rates depend, of course, on the number of inhabitants, the heating devices and the type of fuels used all of which is different in each grid cell. This information is, however, comprised in the yearly total emissions as contained in the TNO data base. For this reason the standardized time resolved emissions were rescaled by means of the the quotient of the total annual emissions and the sum of the daily emissions calculated with equation 1 in that grid cell (equation 2). Thus, the yearly total emissions in each grid cell remained constant while the daily emissions were varying with the ambient temperature. With l_d as the multiple of E_{min} on day d and T being the ambient temperature in $°C$:

$$T \geq T_{lim} \rightarrow E_d = E_{min}$$
$$T < T_{lim} \rightarrow E_d = E_{min} \times (-0.2208 \times T + 6.0385) = E_{min} \times l_d \qquad (1)$$

$$E_{d,0} = \frac{E_0}{\sum_{d=1}^{366} E_d} \times E_d \qquad (2)$$

E_0 are the total annual emissions in a certain grid cell as derived from the TNO emissions inventory, E_d are the calculated emissions on day d scaled so that E_{min} equals 1.0 and $E_{d,0}$ are the rescaled emissions on day d; n is the number of days of the year, i.e. 366 for the year 2000. With k equal to the number of days when the daily mean temperature is below T_{lim} follows:

$$E_{d,0} = \frac{E_0}{\sum_{d=1}^{k} E_{min} \times l_d + \sum_{d=1}^{n-k} E_{min}} \times E_d = \frac{E_0}{E_{min} \times (\sum_{d=1}^{k} l_d + n - k)} \times E_d \quad (3)$$

Thus, if T is equal to or higher than T_{lim}:

$$E_{d,0} = \frac{E_0}{\sum_{d=1}^{k} l_d + n - k} \qquad (4)$$

And if T is lower than T_{lim}:

$$E_{d,0} = \frac{l_d \times E_0}{\sum_{d=1}^{k} l_d + n - k} \qquad (5)$$

Hence, the rescaled emission rate on day d is independent of the minimum emission rate in the grid cell. It is however dependent on the number of days k with temperatures below T_{min}. The larger k becomes the smaller the calculated emission $E_{d,0}$ will be – remember that l_d cannot be smaller than 1. This means that if in a grid cell the temperature falls frequently below the minimum the higher emissions are dispersed

Table 1 Changes in monthly B(a)P emissions in the model domain in tones

	January	July	Difference
standard	105	24.0	81.0
Slope -50%	93.2	31.5	61.7
Slope +50%	111	20.3	90.7
T_{min} +10%	101	25.1	75.9
T_{min} -10%	110	22.6	87.4
Slope -50%, T_{min} -10%	95.7	31.2	64.5
Slope +50%, T_{min} +10%	106	21.9	84.1
Slope -50%, T_{min} +10%	91.2	31.8	59.4
Slope +50%, T_{min} -10%	118	18.2	99.8

over a larger number of days and the difference between warmer and colder periods is smaller than in grid cells where the minimum temperature is rarely reached.

Even if the linear dependence between heat and temperature is valid the very heat-temperature curve that we derived from the Vattenfall study is strictly speaking only valid for the community heating at Hamburg in the years 2005-2006. The slope and the minimum temperature could of course vary at other places and in other years. The better the houses are insulated the lower the minimum temperature will be because people will more likely turn on the heating only at low outside temperatures. At the same time, the higher the efficiency of the heat production and the smaller the losses during the heat transport to the heating devices the smaller the slope of the heat-temperature curve will be. For this reason we varied these two parameters in order to test the influence of the uncertainties in the heat-temperature relationship on the generated emissions time scheme. We compared emission data created with the original heat-temperature curve to emission data where the slope was varied by 50% and the minimum temperature by 10%. We considered 50% variation of the slope and 10% variation of the minimum temperature plausible. However, to our knowledge the Vattenfall study is the only one of this type, so we could not verify our assumption. Table 1 illustrates how the seasonal variations of the emissions are affected when the slope and T_{min} are increased or decreased. As a simple measure to estimate this effect we compared the difference between total B(a)P emissions in January as representative for winter emissions and July as representative for summer emissions. "Standard" denotes the values we got from the original heat-temperature curve. For the original heat-temperature curve this difference summed up over the entire model domain is 81 tons. If the slope of the curve is increased by 50% the difference between the emissions in January and July rises to 90.7 tons and it goes down to 61.7 tons if the slope is decreased by 50%. Varying T_{min} doesn't have a large influence. With T_{min} equal to 19.8°C 75.9 tons more are emitted in January than in July and with T_{min} equal to 16.2°C the difference is 87.4 tons. The reason why increasing the minimum temperature decreases the seasonal variation is that the higher the temperature for switching on the heating is the higher the number of heating days will be and vice versa (equation 5). Consequently, the largest deviation from the standard curve would occur if the slope is increased while the minimum temperature is decreased or vice versa. This is however the most unlikely case because if the heat production is very efficient in a certain country the standard for insulating the buildings will also be relatively high, expectedly. We therefore decided to regard the curve with slope +50% as the maximum positive deviation and the curve with slope -50% as the maximum negative deviation

from the original curve. Thus, maximum positive deviation means that in the cold months emissions could be up to 11% lower or they could be up to 31% higher in the warm months that leads to a difference of 90.7 tones. The case with maximum negative deviation resulted in emissions being 6% higher in January and 15% lower in July resulting in a difference of 61.7 tons. Obviously, the possible underestimation of the difference between January and July caused by a smaller slope is more effective than the overestimation caused by a larger slope (Table 1).

Although less important than the temperature dependent seasonal variations the emissions in the sector residential combustion are also subject to weekly and daily cycles. To account for the weekly and daily cycle the same scaling factors were used that are commonly applied in emission models for CO emissions because CO emissions reflect to a large extent the heating activities. In particular it is an indicator for the quality of combustion and thus a good indicator for PAH production (European Environment Agency, 2009). Factors for industrial combustion and processes as the second important sector follow only weekly but no diurnal or seasonal cycles. They were also derived from CO emissions. Emissions from the sector road transport were assumed to show the same temporal evolution as the NO_x emissions in the same grid cell. They are also only subject to weekly and diurnal but not to seasonal variations. The remaining emissions are kept temporally invariant for simplicity reasons.

3.3 Emissions of the main pollutants, aerosols and biogenic substances

An emission inventory of the gaseous species NO_x, SO_2, CO, NH_3 and 35 non-methane volatile organic compounds as well as PM10 and PM2.5 was purchased from the Institute for Energy Economics and the Rational Use of Energy (IER), Stuttgart, Germany. The inventory contains gridded data for the inner and outer CMAQ domain in hourly resolution for the year 2000. As base served the annual country emissions from the EMEP data base and the European Pollutant Emission Register (EPER). Experts at IER interpolated these data to our model domain under consideration of population density, roads and industrial plants and took also care about the temporal disaggregation of the emissions. Details on the emissions model of IER are described in Friedrich and Reis (2004).

Emissions of the biogenic chemicals isoprene and terpenes that are the most important precursors of secondary organic aerosols were taken from the POET data base while emissions of particulate organic matter and elemental carbon was derived from the Global Fire Emissions data base. Dust was considered using the Aerocom emission data sets for the year 2000. These data sets are usually used for global models and are typically given as monthly averages on a $1° \times 1°$ grid. For our purposes we interpolated them spatially first to the outer and subsequently to the inner domain and temporally down to daily varying emissions.

4 Model Results and discussion

The focus of this study was to test the influence time-variant B(a)P emissions have on the simulation results of the CMAQ runs for the year 2000 and whether our approach of the above described procedure of temporal disaggregation yields satisfactory simulation results. Therefore, we carried out model runs with CMAQ using three different emission

Table 2 Description of emission scenarios

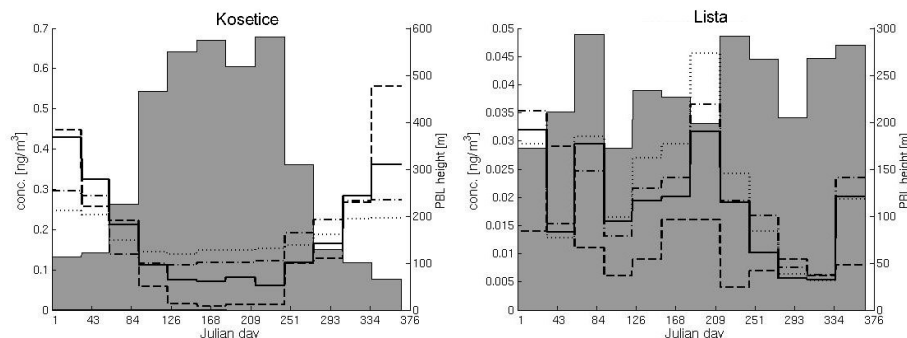| case a	constant emissions (all sectors)
case b	seasonally varying emissions (all sectors)
case c	temperature dependent emissions (residential heating)
	weekly cycle (residential heating, road traffic, industry)
	diurnal cycle (residential heating, road traffic, industry)

Fig. 3 Comparison of modeled planetary boundary layer height and concentrations: Dashed lines are measured concentrations, dotted lines simulated with case a, dash dotted simulated with case b, solid lines simulated with case c and filled plot is the PBL height

cases (Table 2) one with constant B(a)P emissions rates all over the year (case a), one with only seasonality considered according to the factors 1.2-0.8-0.8-1.2 for winter-spring-summer-fall as proposed by Baart et al (1995) (case b) and one with temporally disaggregated B(a)P emissions according to our approach (case c) including also daily and weekly variations. The emissions of the other substances and particles were the same for each run.

4.1 Comparison of simulated concentrations with measurements

To evaluate the model performance ground level B(a)P concentrations measured in 2000 at five measurement stations of the CLRTAP consortium were compared to modeling results. The data are stored in the WebDab data base and can be obtained via the EMEP internet site (www.emep.int). They are provided as monthly or yearly mean concentrations. The stations at Aspvreten and Rörvik in Sweden are assumed to measure rural background concentrations. Also Košetice, Czech Republic is labeled as background station. However, it is probably more influenced by emission sources than the Swedish stations. Pallas, Finland and Lista, Norway are remote from sources and assumed to measure global background. In addition, we received data of two stations in Germany from the German Environmental Agency (UBA). The suburban station at Radebeul near Dresden provided two-day average measurements and the rural station at Bornhöved provided weekly averages.

Already with constant emissions (case a) at most measurement stations the simulated near ground concentrations follow a seasonal variation similar to that found in the measurements. This emphasizes that the concentrations are not only dependent on emissions but also on meteorological conditions. The annual cycle of concentrations

Table 3 Correlations between PBL height and measured or simulated ground level concentrations

station	measured	case a
Rörvik, SE, rural, monthly means	-0.76	-0.29
Aspvreten, SE, rural, monthly means	-0.15	-0.26
Pallas, FI, remote, monthly means	-0.49	-0.77
Košetice, CZ, rural, monthly means	-0.85	-0.89
Lista, NO, remote, monthly means	-0.39	-0.11
Bornhöved, DE, rural, weekly means	-0.63	-0.52
Radebeul, DE, suburban, 2-day means	-0.54	-0.53

reflects to a large extent the annual variation of the planetary boundary layer height (PBL height). In winter when the PBL height is low the concentration of chemicals increases in comparison to summer when the PBL height is higher causing the concentration of chemicals to decrease (Figure 3). The main part of atmospheric B(a)P is mostly deposited near the sources or degraded within a few hours after emission while a minor part is available for large scale transport. Therefore, the best agreement between measurements and model, provided the emission pattern is simulated in a realistic way, can be found at stations in the vicinity of source regions. Consequently, the correlations are lower at the rural and remote background stations even if they are still high. As an example, the Pearsons correlation coefficient r between measured and modeled monthly mean concentrations at Košetice was 0.88 while it was -0.85 between measured concentrations and the monthly average PBL height that has been derived from the meteorological model. At the same time r between PBL height and simulated concentrations was -0.88. Also, correlations between measured concentrations, simulated concentrations and simulated PBL height were found at Radebeul, Bornhöved, Pallas and Rörvik. The reason that no correlations could be found at Aspvreten and Lista may be that the PBL height at these coastal stations was not reproduced correctly by the model (Table 3). Coastal processes are hardly satisfactory captured with the grid resolution of 54x54 km^2 (Colby Jr, 2004). As quality criteria for comparing measured and simulated concentrations we chose the index of agreement (IOA) because it considers both the correlation and the bias (equation 6).

$$IOA = 1 - \frac{\sum_{i=1}^{N}(Cp_i - Co_i)^2}{\sum_{i=1}^{N}(|Cp_i - \overline{Cp}| + |Co_i - \overline{Co}|)^2} \quad (6)$$

Here Cp_i and Co_i refer to the observed (Cp_i) and predicted (Co_i) values. Thus, it allows for estimating sensitivity toward difference in observed and predicted values as well as proportionality changes. The IOA ranges from 0.0 (theoretical minimum) to 1.0 (perfect agreement between observed and predicted values) and yields the degree to which model predictions are error-free. As expected, when time-variant emissions are used in the model the index of agreement generally increases (Table 4). Overall, the best agreement between measured and simulated values is achieved when the highly resolved emissions are applied (case c). The best agreement as well as the most significant improvement can be seen at Košetice. This station is obviously well suited for comparison with the model results for two reasons: Firstly it lies within a region with several sources nearby without being influenced by one particular source, and the grid cell it is located in is probably homogeneous with respect to terrain and emission sources. Good agreement was also found at Bornhöved that lies also in a homogeneous

Table 4 Index of agreement between measured and modeled concentrations for all three emission cases

station	case a	case b	case c
Rörvik, SE, rural, monthly means	0.47	0.58	0.61
Aspvreten, SE, rural, monthly means	0.11	0.16	0.2
Pallas, FI, remote, monthly means	0.45	0.5	0.44
Košetice, CZ, rural, monthly means	0.55	0.76	0.94
Lista, NO, remote, monthly means	0.33	0.4	0.4
Bornhöved, DE, rural, weekly means	0.7	0.72	0.75
Radebeul, DE, suburban, 2-day means	0.4	0.41	0.44

grid cell and a significant improvement between case a and case c was found at Rörvik that may be strongly influenced by time dependent emitting sources. Considering the fact that Pallas and Lista are remote stations with very low concentrations the IOA of around 0.4 is acceptable. Concentrations close to the detection limit are likely to have an increased analytical error and further all processes that determine the transport and degradation of the substance cause the simulation to become more uncertain the longer the molecules travel to reach the measurement station. The fact that no improvement between the different emission cases can be seen at the remote stations is probably due to the fact that fluctuations of emissions loose their influence far away from the sources. Poor agreement was found for the station at Aspvreten. This measurement station is close to Stockholm, the capital of Sweden. The B(a)P emissions inventory shows high B(a)P emissions for the grid cell Stockholm lies in and consequently the modeled B(a)P concentrations are quite high also in the neighboring grid cells including that of Aspvreten. Either the grid resolution of the model is too coarse to resolve the effect that Aspvreten is not heavily influenced by the emissions from Stockholm or the emission inventory largely overestimates the emissions here. Similar effects at this station are also reported by Shatalov et al (2005) for results of the EMEP model (Gusev et al, 2005). Radebeul lies in the vicinity of the city of Dresden. Therefore we would have expected a better agreement than that at the remote stations. Even if the correlation is good the measured concentrations are underestimated by a factor of approximately 3. This underestimation is plausible because this station is quite close to Dresden and most likely influenced by high emissions from the city that are not resolved in the model and the gridded emissions. Nonetheless, the good agreement at most of the test sites confirms that the atmospheric transport processes are mostly modeled correctly.

In chapter 3.2 it was estimated that due to uncertainties in calculating the temperature dependent emission rates the emissions in case c could vary between +31% and -15% in warm months or between +6% and -11% in cold months. In the vicinity of sources the changes of ground level concentrations are nearly linearly connected to variations of emissions. Košetice and Radebeul represent stations that lie near emission sources. At Košetice, with case c the average concentration in January was 61% higher than with case a and 31% higher than with case b. In July the concentration with case c was 58% lower than with case a and 48% lower than with case b. At Radebeul the difference between case c and a was +48% and +24% between case c and b in January, and -48% between case c and a and -30% between case c and b in July. Considering the uncertainty in case c emissions the differences between the scenarios would even be larger.
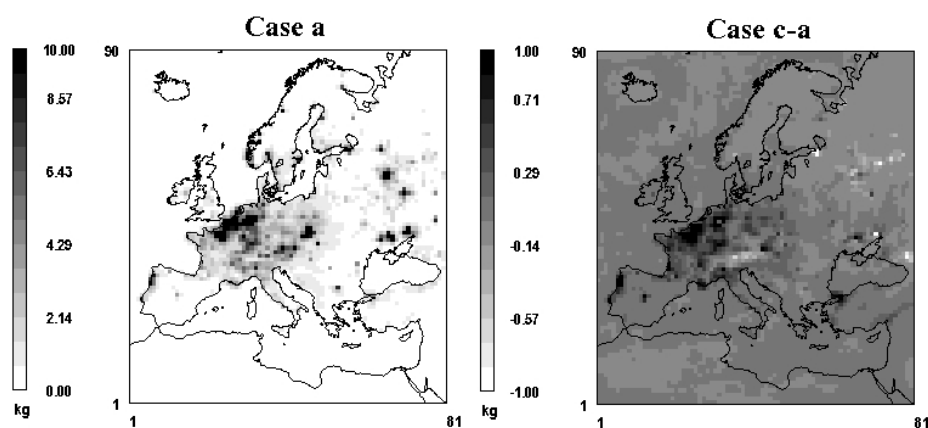
Fig. 4 Total annual depositions in kg per grid cell for simulations with constant emissions (case a) and differences between simulations with constant or temperature-dependent emissions (case c-a)

4.2 Influence of time-variant emissions on deposition fluxes

It appears reasonable that the monthly differences are more pronounced and agree better with the measurements with realistic time-variant emission scenarios at least at those stations that are close to sources. However, in all emission cases the annual total emissions remained the same. An important question to answer was if differences of the yearly total depositions into certain receptor regions could be seen caused by annually varying emissions.

Generally, it is evident that the highest B(a)P concentrations and deposition fluxes occur in regions where also high emission rates can be observed. This is the case in densely populated areas like the Rhine-Ruhr area in Germany, and especially in regions where coal and oil are burned without efficient purification of the exhaust gases like the greater Moscow area. At the same time, the deposition rates are also determined by precipitation rates because wet deposition is the dominant sink for atmospheric B(a)P and other PAHs (Matthias et al, 2009a). In polluted areas the differences between case c and case a reach more than 10% in some grid cells (Figure 4). No such differences could be observed in regions with little to no B(a)P emissions. The total B(a)P emissions in the Rhine-Ruhr area were in 2000 about ten tones. This resulted in a deposition rate of 301 mg/ha for the year 2000 averaged over this area when using constant emission ratios throughout the year (case a). Over the Baltic Sea without any emissions ship emissions are not considered so far the average deposition rate for 2000 was 18 mg/ha which sums up to 740 kg direct atmospheric input of B(a)P into the Baltic Sea. B(a)P is transported mainly from middle and eastern European regions in northern direction towards the Baltic Sea where it is scavenged by rain water. The deposition rate into the North Sea also neglecting ship emissions was about 10 mg/ha. The highest deposition rates would be expected in that case where high emission rates and thus high air concentrations coincide with high precipitation rates because deposition of particulate species is approximately proportional to precipitation and their concentration in air. As an example Figure 5 shows the monthly concentrations and precipitation over the Baltic Sea. It was raining the most in October, November and December. With constant

Table 5 Annual deposition rates in mg/ha for selected regions

	North Sea	Baltic Sea	Rhine-Ruhr
case a	10.6	18.0	301
case b	11.9	19.1	314
case c	11.4	18.9	322
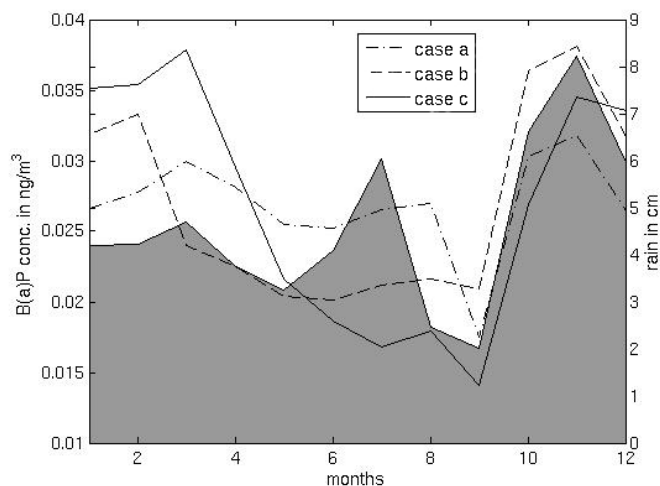
Fig. 5 Comparison of the average precipitation averaged over the Baltic Sea (filled plot) with the monthly average near ground concentration of B(a)P simulated with the three different emision cases

emissions (case a) the differences in B(a)P concentrations between summer and winter were smaller than with time-variant emissions (cases b and c). For this reason the annually averaged deposition fluxes were higher with time-variant emissions than with constant emissions (Table 5). Because of loss by degradation and deposition during the transport the deposition rates were significantly higher in source regions (Rhine-Ruhr) than over sea. The difference between maximum and minimum deposition rates were nearly the same in all three areas. In the Rhine-Ruhr area case c with the temperature dependent emission files showed the largest deposition rates. In contrast to this the highest deposition rates over sea resulted with the only seasonally varying emissions of case b because the average concentrations between October and December were the highest with case b. Case c emissions include also daily variability. This means that more B(a)P is emitted at daylight when also more ozone is in the troposphere and degradation of B(a)P takes place. This effect is, however, very small as shown by Bewersdorff et al (2009).

5 Conclusion

By means of numerical modeling the transport and deposition of B(a)P as a model PAH over Europe in 2000 with three different emission scenarios was studied. Model

runs with constant emissions all over the year allow assessing the influence of the meteorology on the concentrations and depositions. Concerning the ambient air concentrations the boundary layer height plays an important role. The deposition is to a large extent driven by precipitation because wet deposition is the most relevant deposition path. As B(a)P is mainly emitted by heating devices and wood burning it is necessary to consider seasonal differences to create realistic emissions. Comparison of simulation results with measured concentrations indicate that the proposal by Baart who uses 50% higher emissions in the colder months (Baart et al, 1995) is already a good approximation. The main purpose of our investigations was to show the benefit of linking the emissions linearly to the ambient temperature. On the one hand the comparison with measurements indicate that these model results fit even better to the measurements. In regions with strong emissions sources the differences in ambient concentrations and deposition rates is evident. On the other hand the differences remote from sources are small and, when comparing the differences of values averaged over larger areas and long timescales, the differences lie within the uncertainty of the emissions. Nevertheless it was shown that linking the B(a)P emissions to the ambient air temperature appears to yield realistic emissions and, above all, allows to account for regional differences in temporal emission schemes.

References

Agency for Toxic Substances and Disease Registry (1995) Toxicological Profile for Polycyclic Aromatic Hydrocarbons (PAHs). Tech. rep., Public Health Service, US Department of Health and Human Services, Atlanta, GA, USA

Aulinger A, Matthias V, Quante M (2007) Introducing a partitioning mechanism for PAHs into the community multiscale air quality modelling system and its application to simulating the transport of benzo(a)pyrene over europe. Journal of Applied Meteorology 46(11):1718–1730

Baart RC, Berdowski JJM, Jaarsveld JA (1995) Calculation of atmospheric deposition of contaminants the north sea. Tech. Rep. TNO-MEP - R 95/138, TNO Institute of Environmental Sciences, Energy Research and Process Innovation, Schoemakerstraat 97, P.O. Box 6011, 2600 JA Delft, The Netherlands

Beecken J (2007) Pilotprojekt KWK-Optimierung, Teilbericht des Netzes des Forschungsprojektes KWK-Optimierung. Tech. rep., Vattenfall Hamburg

Bewersdorff I, Aulinger A, Matthias V, Quante M (2009) The effect of temporal resolution of PAH emission data on transport and deposition patterns simulated with the Community Multiscale Air Quality modelling system (CMAQ). Meteorologische Zeitschrift 18(1):41–53, , doi 10.1127/0941-2948/2009/351

Byun D, Ching J (1999) Science Algorithms of the EPA Models-3 Community Multiscale Air Quality Modeling System. Epa/600/r-99/030, US Environmental Protection Agency, Office of Research and Development, Washington DC

Byun D, Schere K (2006) Review of the Governing Equations, Computational Algorithms, and Other Components of the Models-3 Community Multiscale Air Quality (CMAQ) Modeling System. Applied Mechanics Reviews 59:51–77

Colby Jr FP (2004) Simulation of the New England sea breeze: The effect of grid spacing. Weather Forecast 189:277–285

Denier van der Gon H, van het Bolscher M, Visschedijk A, Zandveld P (2005) Study of the effectiveness of UNECE Persistent Organic Pollutants Protocol and cost of possible additional measures. Phase I: Estimation of emission reduction resulting from the implementation of the POP Protocol. TNO report B& O-A R 2005/194, TNO, Laan van Westenenk 501, P.O. Box 342, 7300 AH Appeldoorn, The Netherlands

Esteve W, Budzinski H, Villenave E (2006) Relative rate constants for the heterogeneous reactions of NO2 and OH radicals with polycyclic aromatic hydrocarbons adsorbed on carbonaceous particles. Part 2: PAHs adsorbed on diesel particulate exhaust SRM 1650a. Atmospheric Environment 40(2):201–211

European Environment Agency (2009) EMEP/EEA air pollutant emission inventory guidebook 2009. Technical report 6/2009, European Environment Agency, Kongens Nytorv 6, DK - 1050 Copenhagen K, Denmark, DOI DOI 10.2800/23924

Friedrich R, Reis S (2004) Emissions of air pollutants. Springer, Berlin Heidelberg New York

Gery MW, Whitten GZ, Killus JP, Dodge MC (1989) A photochemical kinetics mechanism for urban and regional scale computer modeling. J Geophys Res 94:12,925 – 12,956

Grell G, Dudhia J, Stauffer DR (1995) A Description of the Fifth-Generation Penn State/NCAR Mesoscale Model (MM5). NCAR Technical Note 398, NCAR, Boulder, Colorado, USA

Gusev A, Mantseva E, Rozovskaya O, Shatalov V, Strukov B, Vulykh N (2005) Persistent organic pollutants in the environment. EMEP Status Report 3/2005, Norwegian Institute for Air Research, Kjeller, Norway

Horowitz LW, Walters S, Mauzerall DL, Emmons LK, Rasch PJ, Granier C, Tie X, Lamarque JF, Schultz MG, Tyndall GS, Orlando JJ, Brasseur GP (2003) A global simulation of tropospheric ozone and related tracers: Description and evaluation of MOZART, version 2. J Geophys Res 108(D24):4784, doi:10.1029/2002JD002853

Kwamena NOA, Staikova MG, Donaldson DJ, George IJ, Abbatt JPD (2007) Role of the aerosol substrate in the heterogeneous ozonation reactions of surface-bound PAHs. Journal of Physical Chemistry A 111(43):11,050–11,058, DOI 10.1021/jp075300i

Matthias V, Aulinger A, Quante M (2009a) CMAQ simulations of the benzo(a)pyrene distribution over Europe for 2000 and 2001. Atmospheric Environment 43:4078–4086, doi:10.1016/j.atmosenv.2009.04.058

Matthias V, Quante M, Aulinger A (2009b) Determination of the Optimum MM5 Configuration for Long Term CMAQ Simulations of Aerosol Bound Pollutants in Europe. Environmental Fluid Mechanics 9:91–108, DOI 10.1007/s10652-008-9103-6, doi 10.1007/s10652-008-9103-6

Otte TL (1999) Science Algorithms of the EPA Models-3 Community Multiscale Air Quality Modeling System, US Environmental Protection Agency, Office of Research and Development, Washington DC, chap Developing meteorological fields

Shatalov V, Gusev A, Dutchak S, Holoubek I, Mantseva E, Rozovskaya O, Sweetman A, B S, Vulykh N (2005) Modelling of pop contamination in european region: Evaluation of the model performance. Emep/msc-e technical report 7/2005, Meteorological Synthesizing Centre - East, Moscow, Russia