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Abstract

At GKSS, the chemical transport model CMAQ was expanded to treat the carcinogenic polyaromatic hydrocarbon (PAH) benzo(a)pyrene (B(a)P) and other persistent organic pollutants. B(a)P is mainly particle bound and can be transported over long distances. Therefore, it can be deposited in areas far from the main source regions. We simulated the B(a)P distribution over Europe for the years 2000 and 2001. Significant differences exist between different regions in Europe and between winter and summer concentrations. The latter is not only caused by the higher emissions in winter, also the meteorological conditions and, connected to them, the main transport pathways of B(a)P from the source regions into remote areas play an important role. The model is able to represent the temporal evolution and the regional distribution of B(a)P, however simulated concentrations and depositions are significantly higher than measurements at selected sites of the EMEP network and of the German Federal Environmental Agencies. Modelled wet deposition of B(a)P into the North and Baltic Seas was found to be much higher than modelled air concentrations close to ground would suggest. This indicates that long range transport of persistent pollutants is efficient and that deposition patterns cannot easily be derived from the few existing measurement stations.

Key words: benzo(a)pyrene, aerosol, chemistry transport model, deposition

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) 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 (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

UN-ECE Convention on Long-range Transboundary Air Pollution (CLRTAP) on POPs. Benzo(a)Pyrene (B(a)P) is the most studied PAH and it is often taken as representative for the whole group of PAHs. Because of the significant health risks of PAHs, annual limit values of 1 ng m^{-3} for B(a)P will be implemented in the EU by 2013 (EC, 2005). To study the atmospheric transport and deposition of PAHs over Europe 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) has been extended at GKSS to treat also semivolatile POPs, in particular B(a)P. Model runs covering the years 2000 and 2001 giving hourly concentration fields were carried out over Europe in order to assess the ability of the modelling system to allow multi-year simulations of POPs. The model results are compared to measurements of B(a)P concentrations in air and to measured concentrations in rain water as well as bulk wet and dry depositions. In relation to the EMEP simulations of B(a)P and other POPs (Shatalov et al., 2005) these model runs are regarded as a new approach to investigate the B(a)P concentration and deposition in Europe by using a different model system and a different emission inventory.

2 Model setup

2.1 Chemistry transport model

CMAQ has originally been developed to study air pollution episodes, in particular ozone episodes, in the United States. It has been further developed in recent years and it includes gas phase, aerosol and aqueous chemistry. In this study, the CBM4 mechanism (Gery et al., 1989) is used. The aerosol is represented by 11 different classes and three size modes (Aitken, accumulation and coarse mode). Each of them is assumed to have a lognormal distribution. In the PAH extension of the model (Aulinger et al., 2007), B(a)P is considered as almost completely connected to particles at ambient temperatures. It can occur in each of the three size modes and also in the gas phase, however typically more than 99 % of the B(a)P mass is connected to organic aerosols in the accumulation mode. Only if the available organic aerosol mass is in the accumulation mode is very small, the partitioning of the aerosol bound B(a)P can be shifted to one of the other modes or even to the gas phase. For our multi-annual studies the CMAQ model is setup on a 54 x 54 km^2 grid for Europe. Special emphasis is laid on the representation of the planetary boundary layer (PBL) to capture vertical transport and dispersion of atmospheric air pollution. Therefore, 30 vertical levels up to 100 hPa with 20 levels below approx. 2500 m are used in a terrain following σ-pressure co-ordinate system.

2.2 Emissions

Emission data for the nitrogen, sulfur and volatile organic compounds as well as for aerosol particles was provided by IER Stuttgart based on EMEP area emissions and EPER

point source emissions. The B(a)P emissions are based on annual gridded values from (Denier van der Gon et al., 2005) and not directly on the official EMEP emissions. This is done because there is good reason to assume that the TNO expert emissions are more complete than the EMEP emissions that have to rely as far as possible on official emissions provided by the countries.

The emissions within the 54 km model domain provided by EMEP sum up to about 289 tons in 2000. The TNO emissions for the same year were about 663 tons. When compiling emission files EMEP is obliged to use officially reported country emissions where available. As a consequence the emission ratios sometimes change visibly with the country borders. This may partly be caused by the fact the data are not collected in a consistent way. Also the TNO emissions were created on the base of country emissions, however, completed by TNO experts by means of a bottom up approach and unitarily distributed over Europe. For this reason we regarded the TNO emission files as the more reliable ones.

Because the emissions from residential heating (wood and coal burning) are highly dependent on season, we introduced a temporal cycle that depends on ambient temperature for this sector. Weekly and diurnal cycles of the B(a)P emissions were also considered, they were chosen to follow the NO cycle for traffic emissions and the CO cycle for heating processes.

2.3 Initial and boundary conditions for CMAQ

The boundary conditions for the simulations presented here were taken from MOZART (Horowitz et al., 2003; Niemeier et al., 2006) model results for the years 2000 and 2001. The data has a resolution of $1°$ x $1°$ and one day. It includes several gas phase species (O_3, O, O^1D, CO, NO, NO_2, SO_4, HO_2, OH, PAN, HCOH, isoprene, terpenes and HNO_3), but no B(a)P. The modelled concentrations of these species were interpolated to the boundary of the CMAQ domain, which is one grid cell thick and updated hourly. The boundary conditions for B(a)P were zero at the western, and southern border and at most of the northern border. At the north eastern edge of the model domain, monthly average B(a)P values of a previous model run were assumed to avoid a large gradient in the B(a)P concentrations in the most eastern grid cells. Initial conditions are set once to average winter conditions on 25 December the year before each annual run starts. By this spin-up time of 7 days the influence of the initial conditions is kept very low.

2.4 Meteorological Fields

The meteorological fields are derived from MM5 (Grell et al., 1995) model runs which were driven by ERA40 6 hourly global reanalysis data on a 1 x 1 degree grid. We used four dimensional nudging of the ERA40 fields and the more sophisticated physical parameterisation schemes like Reisner 2 (Reisner et al., 1998) for cloud microphysics, Kain Fritsch 2 (Kain, 2004) for cumulus representation and the MRF (Hong and Pan, 1996) scheme for the boundary layer to produce meteorological data which is as close as possible to wind, temperature and humidity observations. Additionally, the Noah land surface

module (Chen and Dudhia, 2001) was used to account for varying soil temperature and humidity. The simulations were done month by month with a spin up time of 4 days for each run and the sea surface temperature (SST) was varied accordingly. This procedure kept the influence of the initial conditions on the results of the runs negligible. A detailed description of the results is given in Matthias (2008a).

3 Measurement data

3.1 B(a)P concentration

Concentration measurements of B(a)P in air for the years 2000 and 2001 that can be used for comparison purposes are available at five stations of the EMEP measurement network (Aas and Hjellbrekke, 2003). Two of them are in Sweden, Rörvik (ROE) and Aspvreten (ASP), one in Finland, Pallas (PAL), one in Lithuania, Preila (PRE), and one in the Czeck Republic, Kosetice (KOS). To get additional information about the B(a)P distribution in central Europe and in the greater North Sea area, data from three measurement stations that are operated by the German Federal Environmental Agencies (GFEA), Bornhöved (BOR), Radebeul (RAD), and Zarrentin (ZAR) were also taken into account. They were all officially classified as rural background stations. The geographical data of the stations can be seen together with the new introduced station codes and some information about the data gathering in Table 1.

The sampling strategy varies among the stations. At ASP, PAL, and PRE monthly concentration values are available. At ASP and PAL these monthly values rely on one week in each month. At PRE the sampling was done for the entire month. The same sampling as in ASP and PAL was also followed in ROE in the year 2000, for 2001 the measurements are available on a weekly basis. Weekly values are also provided at KOS, but they rely on one day per week. Twentyfour hours sampling is done at BOR, ZAR and RAD but the measurements are not available for all days. At BOR 49 values in 2000 and 60 in 2001, at ZAR 89 values in 2001 and at RAD 179 values per year are available. The samples are usually taken with high volume samplers and the analysis method is Gas Chromatography with Mass Spectrometry (GC/MS). At Preila Thin Layer Chromatography (TLC) is used. Some of the EMEP laboratories took part in a POP intercomparison study that was performed between 2000 and 2002 (Manø and Schaug, 2003). The goal of this study was to test the reliability of the laboratory procedures to determine the concentration of B(a)P (and other PAHs as well as organochlorine compounds). It was found that the laboratory part for the determination of B(a)P concentrations in air is connected with a typical error of about 30 %. The given standard probe was on average underestimated by 20 %. The results of very few laboratories including that from Lithuania showed much larger deviations from the expected result. The results from Lithuania showed systematic overestimations ranging from 38 % to 136 %. Therefore the measurements at Preila have to be taken with care and they are likely too high by a factor of 1.5 to 2.5. Further, the measurements at Preila might be influenced by close permanent sources and different occasional sources, as stated by Shatalov et al. (2005).

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The EMEP measurement program comprises five stations where B(a)P wet deposition, bulk deposition or concentration in rain water in 2000 and 2001 was measured. Additionally to ASP, ROE and PRE two German stations at Westerland (WES) and Zingst (ZIN) provide freely accessible data. The stations are included in Table 1. The data is provided as one value for each month in the unit of ng m^{-2} d^{-1} for wet only and bulk deposition and in ng/l for concentrations in rain water. At all of the stations also the precipitation was measured but at ASP these measurements were very sparse. As it can be seen in Table 1 at WES, ZIN, and PRE, the measurement integration time was one month, where at ROE and ASP it was one week. Irrespective of the different integration time each value was treated as an average daily deposition rate representative for the month it is provided for. These values were multiplied with the days per month and summed up to yield total monthly and yearly depositions. At WES and ZIN where only values of concentrations in rain water were measured the wet deposition was calculated by means of the measured monthly precipitation.

4   Model evaluation and discussion

4.1   *B(a)P concentrations*

The annual mean B(a)P concentration patterns over Europe given by the CMAQ model results for 2000 and 2001 can be seen in Figure 1. Highest concentrations are found close to the main source regions like the Rhine Ruhr area, southern Poland and the Ukraine, as well as in the vicinity of large cities like Moscow, Paris and in the Po valley. However, also in regions which are far from the main source areas like in parts of south Finland high B(a)P concentrations can be seen in the model results. The results for the years 2000 and 2001 are very similar in the annual average. They are based on an emission inventory that contains the same amount of total B(a)P emissions for both years but with a different temporal allocation. Larger differences appear only locally in coastal areas like the Adriatic Sea and the northern coast of the Black Sea.

Comparisons to measurements of B(a)P in ambient air were carried out for the five EMEP sites and for the three additional sites in Germany (see Table 1). An overview of the annual statistics of the measurements and the model results is displayed for both years in Table 2. The mean values of measurements and model, the relative standard deviation (rstd) and the skewness of the distribution function are given. Timeseries of the measurements are displayed together with the respective modelled values in Fig. 2.

Averaged over both years the highest concentrations are observed in RAD (0.68 ng m^{-3}) and PRE (0.63 ng m^{-3}) followed by ZAR (only 2001, 0.35 ng m^{-3}), KOS (0.20 ng m^{-3}) and BOR (0.18 ng m^{-3}). Except PRE these stations are located in the polluted regions of central Europe. In Sweden and Finland significantly lower concentrations below 0.1 ng m^{-3} are observed (ROE: 0.09 ng m^{-3}, ASP: 0.04 ng m^{-3}, PAL: 0.02 ng m^{-3}). The observations show large differences between the two years (more than 30 % at 5 out of 7

stations), but no clear trend (higher values at 4 stations in 2001, lower values at 3 stations, on average lower values in 2001). This indicates that also the emissions undergo significant variations from year to year and from site to site.

The modelled annual mean concentrations are highest at RAD (0.81 ng/m^3), KOS (0.66 ng/m^3), BOR (0.64 ng/m^3) and ASP (0.61 ng/m^3). Fairly high B(a)P concentrations are also modelled for ZAR (0.52 ng/m^3), lower values are found at PRE (0.33 ng/m^3) and the more remote stations ROE (0.27 ng/m^3) and PAL (0.08 ng/m^3). The modelled inter-annual variability is much lower than that of the observations, typically it is below 20 %. Averaged over all stations the modelled values are 80 % higher than the observations in 2000 and 85 % higher in 2001. At individual stations the modelled annual averages can be a factor of 3 - 12 higher than the observations. High B(a)P concentrations are modelled in those regions where the observations also show high concentrations except for two stations: measurements at PRE are much higher than the modelled values while they are much lower at ASP. The measurement station ASP is close to Stockholm the capital of Sweden. The B(a)P emissions inventory shows high B(a)P emissions for this grid cell and consequently the modelled B(a)P concentrations are quite high around Stockholm. Either the grid resolution of the model is too coarse to resolve the effect that ASP 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). At PRE the high measured B(a)P values might result from high emissions in St. Petersburg or Helsinki that could be underestimated in the emission inventory or they might be influenced by local emission sources but it seems most likely from the results of the EMEP POP laboratory comparison that the measurements indicate too high B(a)P values. PRE is the only station where the modelled values are lower than the measured ones.

The measurements show higher intra-annual fluctuations than the model results. This is reflected in the relative standard deviations (rstd) given in Table 1. Except for PRE and PAL in 2000 rstd is always much larger in the measurements than in the model. The modelled rstd values are mostly below 0.9 while the measured values are above 0.85 (excluding PRE). The measurements show more very high values than the model does, this is reflected in the higher skewness of the observations. These results indicate that the observations are influenced by strongly varying emissions that are not reflected in the emission inventory. An earlier study that compared measured and modelled PM10 values for the same years (Matthias, 2008b) showed that rstd values for daily means were typically about 0.6 in both measurements and model results. The large differences in the measured annual averages in both years might underline the hypothesis that the B(a)P emissions are of higher variability than the emission inventory suggests.

Caused by the relatively large positive bias of the modelled B(a)P values (see Table 3) the comparative statistics between model and observations doesn't exhibit a convincing model performance. Here we use normalized mean bias (NMB), normalized mean error (NME) and the correlation coefficient (r) to describe the relation between model results and observations. These error measures are defined as follows:

$$NMB = \frac{\sum_{i=1}^{N}(M_i - O_i)}{\sum_{i=1}^{N} O_i} \tag{1}$$

$$NME = \frac{\sum_{i=1}^{N}|M_i - O_i|}{\sum_{i=1}^{N} O_i} \tag{2}$$

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$$r = \frac{\sum_{i=1}^{N}(M_i - \overline{M})(O_i - \overline{O})}{\sum_{i=1}^{N}(M_i - \overline{M})^2 \sum_{i=1}^{N}(O_i - \overline{O})^2} \qquad (3)$$

where M_i and O_i denote individual model results and observations and $\overline{M}$ and $\overline{O}$ are the respective means.

Excluding those stations with very low measured B(a)P concentrations (below 0.1 ng/m^3 mean value), the NMB is between -0.56 (at PRE in 2000) and 5.55 (at BOR in 2000) with a typical value around 2. Because of the model values being constantly higher than the measured ones, the NME is in most cases the same as the NMB, it varies between 0.41 (at PRE in 2001) and 5.55 (at BOR in 2000). Despite the significant overestimation of the total amount of B(a)P in the atmosphere the temporal development of the concentrations during the two years is captured well by the model. The correlation coefficients are typically between 0.6 and 0.8 with the exception of KOS and ASP (in 2000). The model represents the concentrations in winter better than those in summer. At most of the stations the measured B(a)P values are close to zero in summer while they are still well above zero in the model. One possible reason for this discrepancy could be that the emission estimates for summer are too high, another one might be that chemical and photochemical degradation of B(a)P is more important im summer. These processes are not yet included in the B(a)P module developed at GKSS because laboratory data suggests that particle bound B(a)P doesn't undergo severe degradation processes even at high OH levels and under UV radiation (Esteve et al., 2006). However, if they were of importance they could also explain the very low observed concentrations even at sites with high winter values like RAD and KOS.

The here presented model results show higher B(a)P concentrations and a different spatial distribution over Europe than the EMEP POP model developed by the Meteorological Synthesizing Center - East (MSC-E) (Gusev et al., 2005). This can be attributed to two main differences between the model simulations performed with the EMEP model and with our B(a)P version of CMAQ. One is the different emission inventory giving the annual amount and the spatial distribution of the emissions (see section 2.2). The second major difference arises from the temporal allocation of the emissions over the year. Based on investigations by Bewersdorff et al. (2008) and Aulinger et al. (2008) the B(a)P emissions from residential heating were distributed over the year following a linear dependence on the air temperature. This caused total B(a)P winter emissions to be approx. a factor of 10 higher than the emissions in summer. Connected with less favourable mixing conditions and low PBL heights in winter compared to summer, increased emissions in this season lead to higher annual averages than it would result from emissions that are equally distributed over the year. The high correlation coefficients between model and observations indicate that this approach is reasonable and leads to better results for the B(a)P distribution particularly for monthly and daily values. Nevertheless, it must be stated that the high positive bias of the modelled B(a)P concentrations indicates that either the total B(a)P emissions in the TNO inventory are too high or that a significant loss mechanism is missing in the model. The large overestimation that can be observed during the summer months could be related to chemical or photochemical losses that occur mainly in summer. More research of these processes in laboratories and smog chambers might help to resolve this uncertainty.

255 The spatial distribution of the B(a)P wet deposition (Fig. 3), which contributes more
256 than 90 % to the total B(a)P deposition, is different compared to the concentrations (see
257 Fig. 1). Significant deposition can be observed over sea, where B(a)P concentrations are
258 usually quite low. In 2000, large parts of the North Sea, the Baltic Sea and the southern
259 Black Sea show high B(a)P wet deposition, the values are comparable to those in polluted
260 regions like eastern Germany and in the Balkans. Over the North Sea and the Baltic Sea,
261 lower B(a)P deposition is simulated for 2001, but the Adriatic Sea and the Black Sea
262 show higher amounts of wet deposited B(a)P than in the year before. Here the influence
263 of the specific meteorological situation, namely transport and precipitation, becomes
264 visible.
265 Comparisons to measurements could be done for five EMEP stations, see Table 1. The
266 model output was condensed to monthly and yearly totals, the values of the yearly totals
267 were then directly compared and to the monthly totals some statistics was applied for
268 evaluation purposes. The measured values were compared to modeled depositions in
269 those grid cells where the stations lied in. Because wet deposition accounts for more
270 than 90 % of the bulk deposition one of the most important prerequisites to simulate the
271 deposition correctly is that the precipitation used in the model meets the real precipitation
272 well. As shown in Table 5 this is overall the case even if the simulated precipitation tends
273 to overestimate the measured one a little. The most severe overestimation was found for
274 WES - about 40%. This is not surprising because WES is located on a rather small island
275 and gets on average lower precipitation than locations at land that are, however, in the
276 same model grid cell as WES. In general, precipitation is well represented in the model.
277 The absolute amount of precipitation is of course not the only prerequisite for reliable
278 deposition simulations. Also the precipitation regime, i.e. duration and type of precipi-
279 tation is important as well as the concentration of B(a)P in air. It was already explained
280 that B(a)P concentrations were generally overestimated. As also the precipitation is
281 slightly overestimated it is not surprising that the deposition of B(a)P is systematically
282 overestimated, too. The modelled values are in range of 24 to 73 μgm^{-2} while the
283 measurements are between 0.8 and 16.4 μgm^{-2}. The largest deviation is observed at
284 Westerland and Zingst in 2001 where the measurements were about a factor of 50 higher
285 than the measurements. At Preila and Aspvreten the modelled values were about a factor
286 of 2.5 to 5 higher than the observations.
287 All in all, the deposition are stronger overestimated than the concentrations. On the one
288 hand this could be due to the fact that the rain pattern was not modeled really exactly,
289 e.g. it could have been raining in the grid cell but not necessarily at the measurement site.
290 However, this should not lead to a systematic deviation. On the other hand the model
291 does not tell scavenging of organic aerosols from inorganic aerosols. Because organic
292 aerosols are often less hygroscopic than the inorganic components sulfate, nitrate and
293 ammonium, they will not be so heavily involved in cloud formation. The assumption that
294 all aerosol components are washed out by rain likely overestimates the wet deposition of
295 hydrophobic aerosols (Poster and Baker, 1996).
296

5 Conclusions

Benzo(a)pyrene concentrations in ambient air have been modeled for two years, 2000 and 2001, using an expanded version of the Community Multiscale Air Quality Modelling system (CMAQ). The modeled concentrations are significantly higher than measurements at eight measurement stations in background areas suggest. Nevertheless the temporal evolution over the two years was captured quite well by the model. Also the B(a)P deposition is significantly higher in the model compared to concentration measurements in rain water and to bulk deposition measurements.

The reason of the discrepancies in the total amount of B(a)P in air is not yet clear. Uncertainties in the emission data base might play an important role. For example the variability of the measurements indicates that the emissions undergo large fluctuations on short timescales of about one day as expressed in large short term peaks in the higher resolved measurements. These peaks are not included, and likely cannot be included, in the emission inventory. Chemical degradation of B(a)P and reactions connected with UV radiation are not considered in the current model version because it is assumed that they should be of minor influence for particle bound B(a)P. However if such reactions would exist they might be of importance in the summer months and could help to explain the very low measured concentrations in summer. Wet deposition of B(a)P is treated in the model in the same way as all other, more hygroscopic aerosol components but the measurements indicate that the washout of B(a)P is less efficient. Thus, these findings suggest that the model has to be reworked in order to better account for wet scavenging and degradation of particle bound B(a)P.

Despite the discrepancies in the total amount, the model gives reliable regional distributions of B(a)P in air and its deposition and it can be used to identify the main transport pathways of persistent organic pollutants into remote regions. Particularly the North and Baltic Seas suffer from higher deposition of B(a)P into water than concentration patterns would suggest.

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Table 1: Geographical information about the B(a)P concentration and deposition measurement stations operated by EMEP and the German Federal Environmental Agencies together with the sampling strategies at the individual stations.

Code	Country	Station	Network	Lat. N	Lon. W	Alt.	conc. sampling	depos. sampling
ASP	Sweden	Aspvreten	EMEP	58.80	17.38	20	1 wk. p. month	1 wk. p. month bulk depos.
KOS	Czeck Rep.	Kosetice	EMEP	49.58	15.08	534	1 day p. week	-
PAL	Finland	Pallas	EMEP	67.97	7.12	566	entire month	-
PRE	Lithuania	Preila	EMEP	55.35	21.07	5	1 wk. p. month	monthly wet depos.
ROE	Sweden	Rörvik	EMEP	57.42	11.93	10	1 wk. p. month (2000) weekly (2001)	1 wk. p. month bulk depos.
WES	Germany	Westerland	EMEP				-	monthly conc. in rain
ZIN	Germany	Zingst	EMEP				-	monthly conc. in rain
BOR	Germany	Bornhöved	GFEA	53.88	10.17	45	1-2 days per week	-
RAD	Germany	Radebeul	GFEA	53.10	13.65	246	every second day	-
ZAR	Germany	Zarrentin	GFEA	53.53	10.92	40	1-2 days per week	-

	obs		model		rstd(obs)		rstd(mod)		skew(obs)		skew(mod)	
station	2000	2001	2000	2001	2000	2001	2000	2001	2000	2001	2000	2001
ASP	0.048	0.037	0.592	0.637	1.512	0.922	0.412	0.470	2.126	0.716	0.082	0.452
KOS	0.169	0.223	0.666	0.655	1.676	1.583	0.739	0.757	3.718	4.141	1.648	1.600
PAL	0.006	0.031	0.063	0.088	0.850	1.445	0.890	1.180	1.286	1.928	1.346	1.520
PRE	0.808	0.455	0.355	0.301	0.460	0.670	0.579	0.605	0.760	0.466	0.435	0.732
ROE	0.078	0.105	0.284	0.264	0.992	1.356	0.362	0.632	1.113	1.978	-0.130	1.096
BOR	0.100	0.268	0.655	0.622	0.949	2.611	0.569	0.713	1.388	5.282	1.296	1.792
RAD	0.722	0.639	0.819	0.802	1.449	1.507	0.744	0.807	2.350	3.038	1.730	2.242
ZAR		0.347		0.522		2.997		0.816		5.406		2.069

Table 2: Statistics of the measured and modelled B(a)P time series in 2000 and 2001.

station	bias 2000	bias 2001	NMB 2000	NMB 2001	NME 2000	NME 2001	corr 2000	corr 2001
ASP	0.544	0.600	11.33	16.22	11.33	16.22	0.304	0.674
KOS	0.497	0.432	2.94	1.94	2.97	2.28	0.553	0.265
PAL	0.058	0.057	9.67	1.84	9.67	1.84	0.869	0.976
PRE	-0.453	-0.153	-0.56	-0.34	0.56	0.41	0.715	0.710
ROE	0.206	0.158	2.64	1.50	2.64	1.61	0.710	0.782
BOR	0.555	0.353	5.55	1.32	5.55	1.89	0.681	0.647
RAD	0.097	0.162	0.13	0.25	0.64	0.79	0.739	0.638
ZAR		0.175		0.50		1.33		0.725

Table 3: Comparison between the measured and modelled B(a)P concentrations in 2000 and 2001.

| | B(a)P deposition | | | | Precipitation | | | |
| | obs | | model | | obs | | model | |
station	2000	2001	2000	2001	2000	2001	2000	2001
ASP	7.1	5.25	33.2	24.2			532	417
PRE	8.9	16.4	47.9	42.7	352	599	584	804
ROE	6.0	2.5	73.1	59.1	886	610	1031	973
ZIN		1.0		51.0		669		820
WES	1.4	0.8	50.8	39.2	641	641	1034	967

Table 4: Annual totals of measured and modelled precipitation (in mm) and B(a)P depositions for 2000 and 2001.
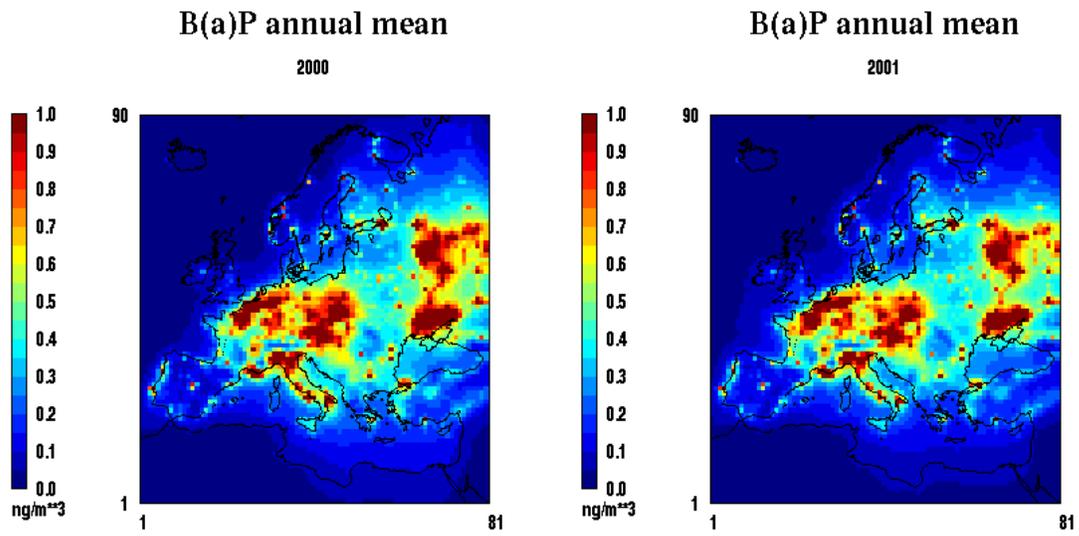
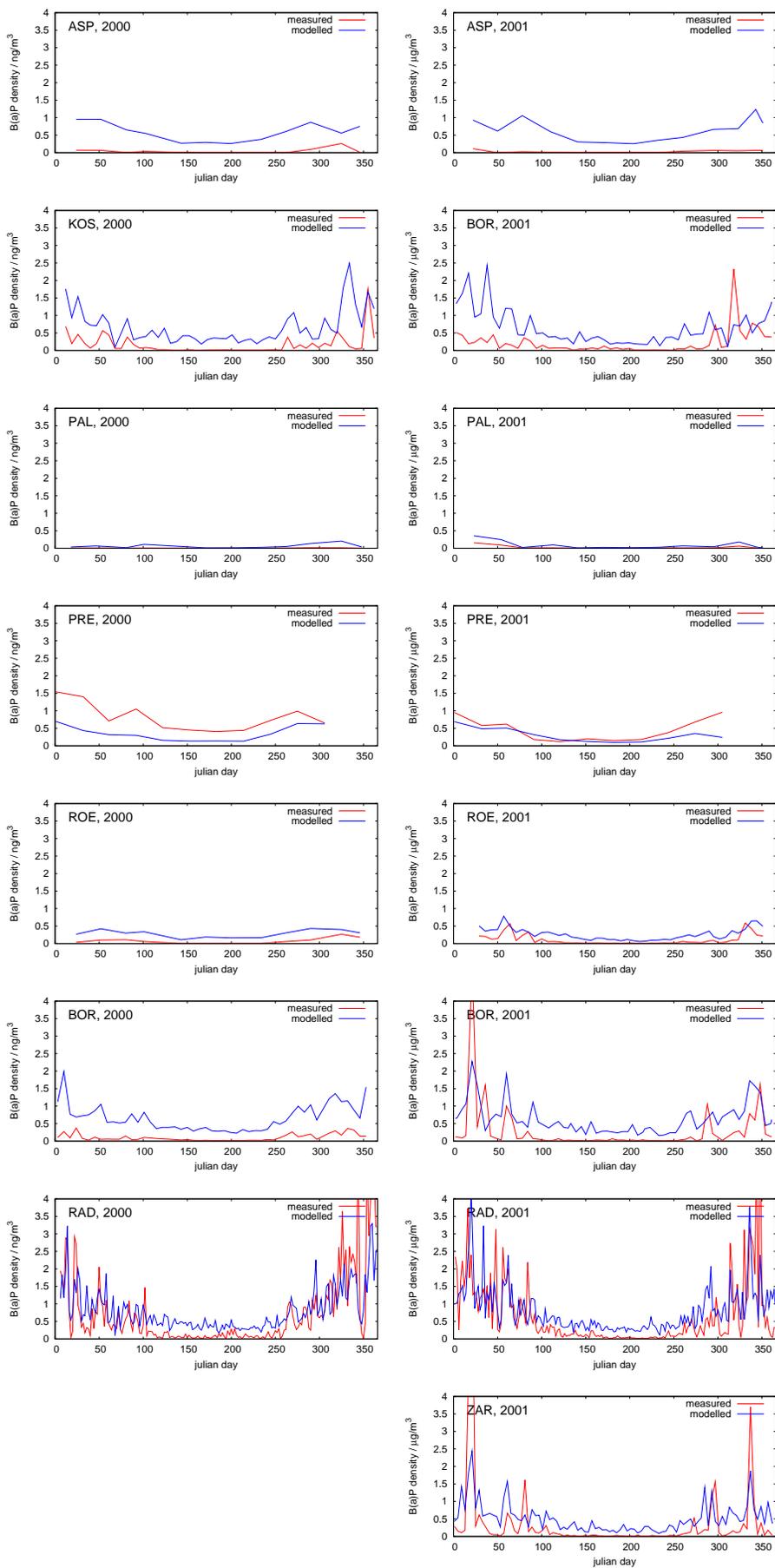Fig. 1. Annual mean B(a)P concentrations for 2000 and 2001 simulated with CMAQ and a PAH extension.

Fig. 2. Timeseries of the B(a)P concentrations at the measurement stations together with the modelled values in 2000 (left column) and 2001 (right column).
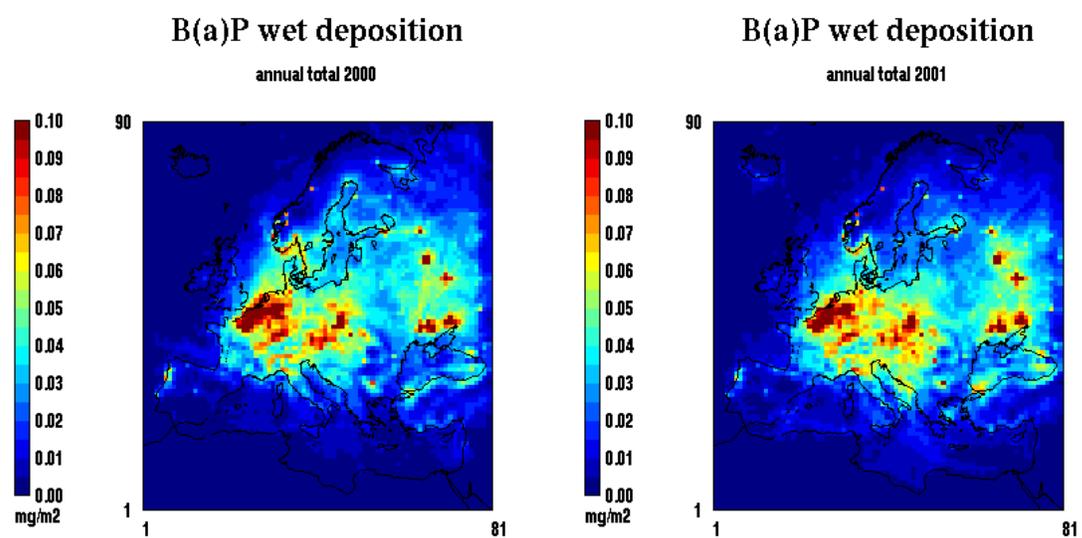
Fig. 3. Annual totals of B(a)P wet deposition in 2000 and 2001 simulated with CMAQ and a PAH extension.