Bieser, J.; Aulinger, A.; Matthias, V.; Quante, M.:
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In: Water, Air, and Soil Pollution (2012) Springer

DOI: 10.1007/s11270-011-0953-z

Impact of emission reductions between 1980 and 2020 on atmospheric benzo[a]pyrene concentrations.

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To be submitted to Water, Air & Soil Pollution

Abstract

Benzo[a]pyrene (BaP) has been proven to be toxic and carcinogenic. Since 2010 the European Union officially established target values for BaP concentrations in ambient air. In this study BaP concentrations over Europe have been modelled using a modified version of the Chemistry Transport Model CMAQ which includes the relevant reactions of BaP. CMAQ has been run using different emission datasets for the years 1980, 2000, and 2020 as input data. In this study the changes in BaP concentrations between 1980 and 2020 are evaluated and regions which exceed the European annual target value of 1 ng/m³ are identified, i.e. the Po-Valley, the Paris metropolitan area, the Rhine-Ruhr area, Vienna, Madrid, and Moscow. Additionally the impact of emission reductions on atmospheric concentrations of BaP is investigated. Between 1980 and 2000 half of the BaP emission reductions are due to lower emissions from industrial sources. These emission reductions, however, only contribute to one third of the total ground level BaP concentration reduction. Further findings are that between 2000 and 2020 a large part (40%) of the BaP concentration reduction is not due to changes in BaP emissions but caused by changes in emissions of criteria pollutants which have an impact on the formation of ozone.

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1. Introduction

Benzo[a]pyrene (BaP) is a polycyclic aromatic hydrocarbon (PAH). For a variety of PAHs, including BaP, toxic and carcinogenic effects on animals and humans have been recognised in epidemiological and experimental studies (Redmond, 1976; EPA, 1984; Armstrong et al., 1994; ATSDR, 1995, Pedersen et al, 2004; Pedersen et al., 2005). In the group of non-volatile, carcinogenic PAHs (e.g. benzo[b]fluoranthene, benzo[k]fluoranthene, indeno(1,2,3-cd)pyrene) BaP is the best investigated species (WHO, 2000). Thus, BaP is often used as an indicator for the total burden of carcinogenic PAHs (WHO, 1987). Non-volatile PAHs originate almost solely as unintentional by-product from incomplete combustion of organic matter. BaP emission factors found in the literature are largest for the combustion of wood and coal while oil and gas have much lower emission factors (Berdowski et al., 1995, Parma et al. 1995). These emission factors, however, can vary depending on fuel type (e.g. wood type, hard coal, bituminous coal) and combustion process (e.g. temperature, pressure, oxygen concentration) and therefore are subject to large uncertainties (Khalfi et al., 2000). In their literature review about PAHs Ravindra et al. (2008a) compiled a list of emission factors for different PAHs.

The few existing emission inventories show that the total BaP emissions in Europe generally have been decreasing since 1970 (Breivik et al., 2004; Pacyna et al., 2003; Denier van der Gon et al., 2005; Denier van der Gon et al., 2006). A large fraction of the emission decrease can be attributed to better abatement technologies in the industry and production decreases in eastern European countries after 1990. The main source for BaP are residential combustion (mainly wood combustion) followed by industrial sources.

Only about 5% of the total BaP emissions are emitted from other sources. In 1980 residential BaP emissions were responsible for roughly 50% of the total (Pacyna et al., 2003). Until 2020 the relative contribution to the total emissions is estimated to rise to up to 80% (Denier van der Gon et al., 2007). Because industrial emissions are emitted at higher altitudes than residential emissions changes in industrial BaP emissions are expected to have a lower impact on ground level concentrations as changes in non-industrial sources.

In the year 2000 the European Union established a target value for the annual mean ambient air concentration of BaP of 1 ng/m³ (EC, 2005). The Directive came into effect in January 2010. There are some countries which recommend a lower target value of 0.5 ng/m³ in Belgium and the Netherlands (RVIM, 1999), 0.25 ng/m³ in the UK (DETR, 1999; EPAQS, 1999), and 0.1 ng/m³ in Croatia, France, and Sweden (Ravindra et al., 2008a). Besides the target value of 1 ng/m³ the European Union also defined an upper and a lower *assessment threshold* of 0.6 and 0.4 ng/m³ per annum. If BaP concentrations exceed an *assessment threshold* national authorities are obliged to monitor the atmospheric concentration of BaP. For areas with BaP concentrations between the lower and the upper *assessment threshold* the directive allows to determine the atmospheric burden with the help of models instead of observations.

In the last decade there have been several studies on modelling the behaviour of BaP in the environment. Most studies focused on the long range transport (LRT) and the distribution of BaP between different compartments. The first models treating BaP were zero to two dimensional multi media mass balance models (Klöpffer, 1994; Scheringer et al., 2001). The first three dimensional Eulerian model including BaP was the persistent organic pollutants (POP) model developed by the Meteorological Synthesizing Centre – East (MSC-E). The MSCE-POP model is a multi compartment hemispheric model with a resolution of 2.5°x2.5° which is also used on a 50x50km² nested domain over Europe (Gusev et al., 2005). The degradation of BaP in different compartments is included in the model. However, no degradation of particulate BaP in the atmosphere is taken into account. Sehili and Lammel (2007) determined the global distribution of BaP emitted in Europe and Russia between different compartments using the general circulation model (GCM) ECHAM5 with a 2.8°x2.8° resolution. In the study the impact of different gas-particle partitioning mechanisms on the LRT of BaP were investigated. Also it was the first model to include degradation of particulate BaP. A study on the sensitivity of modelled BaP concentrations on different input parameters has been performed by Hauck et al. (2008). Prevedouros et al. (2008) developed a multi media model to determine the influence of sorption to black carbon on the fate of different PAHs in Sweden. The first mesoscale model to include a complete in-line representation of all relevant chemical species was a modified version of the Community Multiscale Air Quality (CMAQ) modelling system (Aulinger et al., 2007). Recently the MSC-E developed a POP module for the Global EMEP multimedia Modelling System (GLEMOS) (Tarrason and Gusev, 2008; Jonson and Travnikov, 2010).

So far there have only been few modelling studies aiming at the reconstruction of atmospheric BaP concentrations over Europe. The MSC-E has calculated atmospheric BaP concentrations over Europe with a 50x50km² resolution for the years 1990 to 2003 (Mantseva et al., 2004). The near surface BaP concentrations calculated with the MSCE-POP model were compared with observations from 13 rural measurement stations (Shatalov et al., 2005). It was found that the model is able to reproduce annual mean concentrations within a factor of 3 for 80% and within a factor of 2 for 60% of the observations. The model underestimates the stong annual variations of BaP concentrations. Another study utilized the CMAQ-BaP model to determine the influence of heterogeneous degradation reactions of particulate BaP on atmospheric concentrations over Europe for the years 2000 and 2001 (Matthias et al., 2009). The study showed that degradation of BaP by heterogeneous reaction with ozone leads to a decrease in modelled ground level BaP concentrations by a factor of 3 to 5. Recently, the MSC-E has published BaP concentrations modelled with GLEMOS for 2008 (Shatalov et al., 2010).

The purpose of this study is the evaluation of the effect of emission reductions between 1980 and 2020 on atmospheric concentrations of BaP. The atmospheric concentrations of BaP are directly controlled by the primary emissions (Lohmann and Lammel, 2004; Lohmann et al., 2007). A large part of

the emission reductions of BaP in Europe can be attributed to decreasing industrial emissions in accordance with the UN-ECE POP protocol (UNECE, 1998). The industrial emissions have been regulated with the purpose to reduce human exposure to BaP. Thus, it is of major interest how emission reductions of elevated sources affect the near surface concentrations. Also, changes of exposure due to changes in population distribution are of interest, since ever more people are living in urban and thus higher polluted areas. Finally, the reduction of criteria pollutants (e.g. nitrogen oxide (NO_X), volatile organic compounds (VOCs), and carbon monoxide (CO)) lead to changes in concentrations of ozone, which is the main chemical degradation agent for BaP in the atmosphere (WG-PAH, 2001).

2. Methodology

To investigate the development of atmospheric BaP concentrations over Europe different emission datasets are used as input to the Community Multiscale Air Quality (CMAQ) modelling system which was developed under the leadership of the U.S. Environmental Protection Agency (EPA) (Byun and Ching, 1999; Byun and Schere, 2006). For this study three different years have been chosen, 1980, 2000, and 2020. The year 1980 represents one of the years with the highest total BaP emissions in Europe (Pacyna et. al, 2003). The year 2000 has been selected for the evaluation of the model because it is a year for which many data on BaP emissions and observations are available. (Denier van der Gon et al., 2007, Aas and Hjellbrekke, 2003). The year 2020 represents a future scenario, because different emission estimates for this year are given in a study on POP emissions (Denier van der Gon et al., 2005; Denier van der Gon et al., 2006).

2.1 Emission Inventories

Gridded hourly emission data are created from national annual total emission estimates with the SMOKE for Europe (SMOKE-EU) emission model (Bieser et al., 2011a). Annual emissions of criteria pollutants for the years 1980, 2000, and 2020 were taken from the European Monitoring and Evaluation Program (EMEP). Additionally, point source emissions from the European Point-source Emission Register (EPER) were used. A detailed description of the creation of gridded hourly emission data by SMOKE-EU can be found in Bieser et. al (2011a).

For BaP, however, a consistent emission inventory from 1980-2020 does not exist because there is only little information on historic BaP emissions and their development in the future (Pacyna et al., 2003). Before 2000 mostly total PAH emissions have been reported (Berdowski et al., 1997, Breivik et al., 2006). Because a large part of total PAH emissions concern volatile PAHs (e.g. naphthalene, antracene, phenantrene), which are emitted by different sources than the non-volatile PAHs, estimating BaP emissions from total PAH emissions is highly uncertain. Additionally, the emission factors for BaP from various sources found in the literature are not consistent (Ravindra et al., 2008). This can be explained by variations in the chemical composition of substances (e.g. wood, coal) and different conditions in the combustion process.

For this study it was decided to use the most recent expert estimates of annual BaP emissions. Pacyna et al. (2003) published an emission inventory covering the time span from 1970 to 1995. A BaP emission inventory for the year 2000 as well as future emission scenarios for 2020 were published by TNO (Denier van der Gon et al., 2005, 2006, 2007). For the year 2020 a baseline scenario and a reduction scenario is available. To assure that the emission inventories for 1980 and 2000 are consistent we adjusted the 1980 emissions. This was done by comparing BaP emissions for the year 1990 as published by Pacyna et al. with emissions from TNO (Berdowski et al., 2001). The main difference between the two emission inventories is the amount of BaP emitted by combustion of wood. In some countries (e.g. Austria) the TNO emission inventory features much larger BaP emissions from wood combustion. In a first step we increased the amount of BaP from wood combustion in the inventory of Pacyna et al. for 1990 to meet with the emissions estimated by TNO. In a second step we added the increased emissions from wood combustion to the 1980 emission inventory. Since the Pacyna et al. emission inventory does not cover all countries in our model domain (e.g. Cyprus, Turkey), we interpolated emissions from the TNO inventory for the year 2000 according to the development of emissions between 1980 and 2000 in comparable countries. Figure 1 illustrates the resulting sectoral BaP emissions for 1980, 2000, and 2020.

Between the three emission years investigated in this study a large shift in BaP sources has occurred.

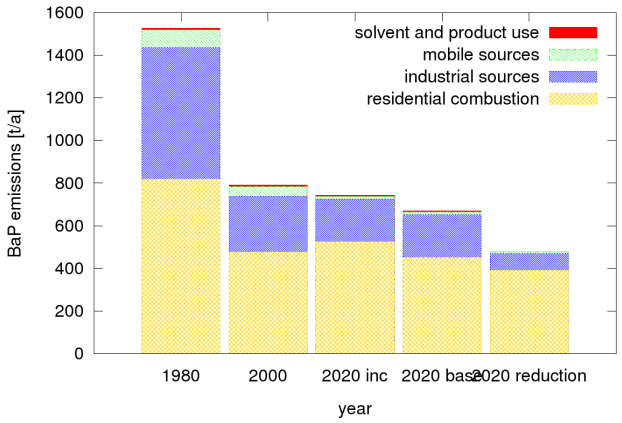

Figure 1: Annual total emissions for the three years modelled in this study. For the year 2020 three different emission scenarios are used. All emission scenarios are described in Table 1.

In 1980 44% of the BaP emissions originated from industrial sources, 49% from non-industrial combustion processes, and 6% from mobile sources. In the year 2000 already 60% of the BaP emissions originated from residential combustion and only 33% from industrial sources. In the 2020 baseline scenario 30% of the BaP emissions originate from industrial sources, 67% from non-industrial combustion processes and in the 2020 reduction scenario residential combustion is responsible for 82% of the emissions while industrial sources only contribute 16% to the total BaP emissions. The amount of BaP emitted by solvent and product use is below 1% for all scenario years. The remaining BaP emissions originate from mobile sources. Generally, the total amount of BaP emitted in the model domain is constantly decreasing. The development of BaP emissions, however, differs strongly between countries.

2.2 Spatial and temporal disaggregation of BaP emissions

Currently only two databases with gridded BaP emissions for Europe exist, one created by TNO and one by EMEP. Figure 2 depicts gridded annual emissions for the year 2000 as published by EMEP and the gridded emissions used in this study, which rely on a dataset from TNO (Denier van der Gon et al., 2005). The TNO emission data is based on expert estimates for each country. The EMEP dataset is compiled from BaP emissions which are officially reported by the parties under the Convention on Long-Range Transport (CLRTAP). This can lead to large differences in data quality for different countries. Thus very large differences in annual total BaP emissions for several countries are seen when comparing the two datasets (e.g. Austria, Bulgaria, France). Generally BaP emissions in the EMEP database are much lower than those published by TNO. The uncertainties of emission inventories for PAHs in general were estimated to be within a factor of 2 to 5 (Berdowski et al., 1997). Most countries also report the spatial distribution of BaP emissions. Here large differences between the two datasets can be observed for several countries (e.g. Poland, Spain) (Fig. 2).

In this study the spatial distribution of BaP emissions for the years 2000 and 2020 as published by TNO, was interpolated to our model grid. For the year 1980 no gridded BaP emissions are available. To spatially disaggregate BaP emissions for 1980 a similar approach as the one followed by TNO is used. For emissions from residential combustion the population density has been chosen as a proxy, accounting for differences in fuel use between urban and rural areas. Furthermore the wood availability is taken into account, leading to lower BaP emissions in areas with sparse forest coverage. Industrial sources are disaggregated using information on individual point sources. Because point source information for the year 1980 is not available the distribution published by TNO for the year 2000 is taken. Mobile sources are disaggregated using data on roads, railways, and airports. Finally the emissions from solvent and product use are disaggregated using the population density.

For the temporal disaggregation of BaP emissions from residential combustion heating degree days are used as a proxy (Aulinger et al., 2007). The daily heating degree days for each grid cell are calculated using the 2m temperature from reconstructed meteorological fields. The main industrial sources of BaP are coke ovens, aluminium production, iron and steel electric arc furnaces, oil refineries, industrial combustion processes, solid fuel production, and waste incineration. Most of these sources involve production processes which are constant throughout the year (e.g. coke ovens) or only subject to small annual variations (e.g. refineries). For these annual variations European statistics from EUROSTAT are used as a proxy. This leads to slightly lower emissions during holiday times. Finally, plume rise calculations are used to determine the effective emission heights of industrial sources using source specific stack data (Bieser et al., 2011b).

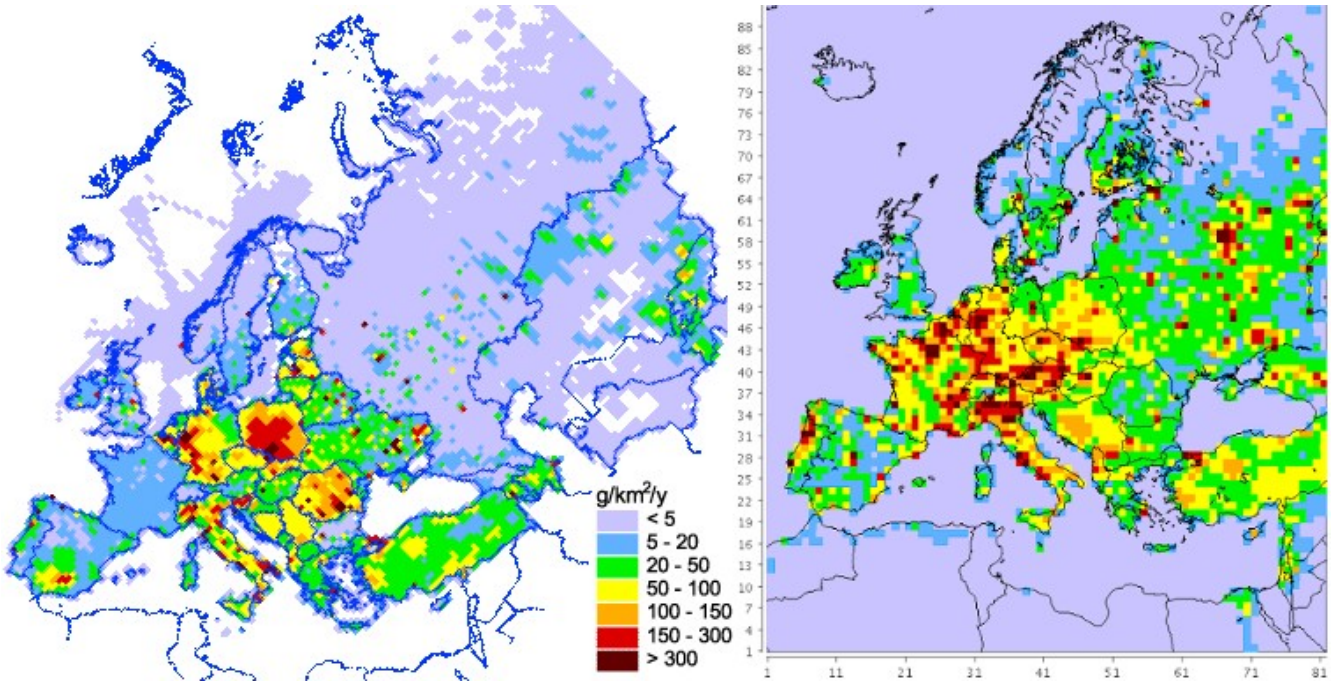

Figure 2: Gridded annual total BaP emissions. On the left gridded emissions as published by EMEP are depicted (Mantseva et al., 2004). On the right emissions for the year 2000 from this study, which are based on data from TNO (Denier van der Gon et al., 2006), are shown. Additionally on the right side the model domain with 54x54km² resolution as used in this study is depicted.

2.3 Emission scenarios

To determine the changes in BaP concentrations between 1980 and 2000 the BaP emission estimates as described in section 2.1 are used. These emission datasets are called *1980base* and *2000base*. For the year 2020 three different emission scenarios were chosen. In addition to the baseline scenario *(2020base)* TNO published a reduction scenario *(2020red)* where a full implementation of the UNECE POP Protocol in all countries is assumed. Because the protocol is already in effect in the European Union (EU) emissions from industrial sources do not differ substantially between the reduction and the baseline scenario in the EU. Additionally a scenario with increased BaP emissions (2020inc) was created. In the 2020inc scenario it is assumed that in the future wood becomes more important as a regenerative energy source for residential heat production. Because there are no estimates for increasing wood combustion in the literature we assume a 10% increase for this scenario.

Additionally several emission scenarios were created to determine the effect of emission reductions on BaP concentrations. First of all the impact of changes in emissions of criteria pollutants is evaluated. Therefore two emission scenarios with criteria pollutant emissions for the year 2000 and BaP emissions for the year 1980 and 2020 respectively have been created. These emission scenarios are called 1980crit and 2020crit. Furthermore, the impact of reductions of BaP emissions from different source sectors on ground level concentrations of BaP is investigated. For this an additional emission scenario (1980alt) was created. This emission scenario differs from the year 2000 baseline scenario only concerning non-industrial BaP emissions, which are taken from the 1980 emission inventory. All emission scenarios are listed in Table 1.

Table 1
Different SMOKE-EU emission scenarios used as input to the CTM CMAQ. Criteria pollutant emissions are taken from EMEP (CEIP, 2010). Emission invetories used for annual BaP emissions are described in section 2.1.

Scenario name	Criteria pollutant emissions	Elevated BaP emissions	Surface BaP emissions
1980 base	1980	1980	1980
1980 crit	2000	1980	1980
1980 alt	2000	2000	1980
2000 base	2000	2000	2000
2020 crit	2000	2020 baseline	2020 baseline
2020 base	2020	2020 baseline	2020 baseline
2020 red	2020	2020 reduction	2020 reduction
2020 inc	2020	2020 baseline	2020 baseline +10% increase in wood combustion
2020 inc crit	2000	2020 baseline	(see 2020 inc)

2.4 Chemistry transport modelling

The CMAQ modelling system used for this study is a state-of-the-art CTM which includes gas phase, aerosol and aqueous chemistry (Byun and Ching, 1999; Byun and Schere, 2006). Unlike other CTMs used to model BaP CMAQ does not include re-emissions from soil, vegetation, and the ocean. Because of its strong affinity to bind to particles BaP acts as a so called *single hopper* (Lohmann et al., 2007). Sehili and Lammel (2007) found that in Europe on average 1.5% of the deposited BaP is re-emitted from the soil. Compared to the primary emissions of more than 600 t/a it can be assumed that, in our model domain, re-emissions of BaP play only a minor role compared to primary emissions (Shatalov et al., 2010). Therefore it is justified to neglect re-emissions of BaP.
Atmospheric concentrations of BaP have been calculated using a modified version of CMAQ (Aulinger et. al, 2008). This CMAQ version includes gaseous and particulate BaP and its degradation by ozone, OH, and photolysis. The heterogeneous degradation by ozone is assumed to follow a Langmuir-Hinshelwood type reaction where the ozone first needs to adsorb to the aerosol before it reacts with BaP (Kwamena et. al, 2004). The main degradation path for gaseous BaP is the reaction with OH radicals. For particulate BaP the reaction rate with ozone is one order of magnitude higher than other degradation processes. Because 99% of the total BaP is bound to particles the reaction with ozone can be considered the only effective degradation path of BaP in the atmosphere (WG-PAH, 2001). In CMAQ particles are implemented as three modes representing log normal size distributions. BaP is mainly bound to particles with a mean diameter of 0.2 µm and a maximum diameter of 2.5 µm. For particles of that size wet deposition is a major sink.
For each emission scenario CMAQ has been run for a whole year using meteorological fields for the year 2000 from the state-of-the-art mesoscale meteorological model COSMO-CLM (Rockel et al., 2008; Rockel and Geyer, 2008). Because this study focuses on the influence of emissions on BaP concentrations the same meteorological fields were used for all CMAQ runs. The evaluation of climatological impacts on modelled BaP concentrations is beyond the scope of this study. However, it was tested if CMAQ results using meteorological fields for the year 2000 are representative. A Comparison of BaP concentrations modelled with CMAQ for the years 2000 and 2001 showed that the inter annual variability of modelled BaP concentrations is small (Matthias et al., 2009). Also the same boundary conditions were used for each CMAQ run. For BaP daily average concentrations from a previous model run were used as boundary conditions. For all other substances daily average values for the year 2000 were taken from the global CTM TM4 (van Velthoven, 1996). For this study CMAQ was run on a 54x54km² grid covering the European continent and the north of Africa (Fig. 2). The vertical resolution is 30 layers up to 10 hPa. The four lowest layers each have a height of 42m.

3. Evaluation of model results

3.1 Benzo[a]pyrene

To evaluate the atmospheric concentrations calculated with CMAQ, modelled values are compaerd to observations. Only few measurement stations in Europe observe BaP. There are only six EMEP stations, four of which are in the Scandinavian region, with observations for the year 2000 (Aas and Hjellbrekke, 2003). Additional observations are available at six sites in Germany and the UK. No BaP observations are available for the whole Mediterranean area and most countries in eastern Europe, making an evaluation of the model difficult for those areas. In addition BaP measurements are only available at low temporal resolutions. At the EMEP stations BaP measurements are available as weekly or monthly averages. Only at the station Radebeul, which is run by the German federal environmental agencies (GFEA), two-day averages are available (Table 2). Generally CMAQ is able to reproduce the annual variation of BaP concentrations which is influenced by the ozone concentrations, the primary emissions and the mixing layer height. The annual variation of BaP is very strong because all these factors lead to higher concentrations in winter and lower concentrations in summer. At some stations modelled BaP concentrations show good agreement with observations (Fig. 3b,c,d). At other stations CMAQ is underestimating BaP concentrations (Fig. 3a,e,f). This can have several reasons like missing emissions or too high ozone concentrations which lead to an overestimated degradation. The largest differences between modelled and observed concentrations is found during winter. During winter the measurements often show large peaks which can be up to ten times higher than the annual average. These peaks are likely to be caused by local sources in the vicinity of the measurement station which are not covered by the emissions data. The station Radebeul (Fig. 3b) for example is influenced by the suburbs of a major German city (Dresden). Due to the small number of measurements per year and the irregular sampling intervals these peaks have a large influence (20% to 70%) on the observed annual mean concentrations. The results from this study agree with findings from Matthias et al. (2009).

Table 2

Description of measurement stations with data of atmospheric BaP concentrations in 2000. The stations are operated by the European Monitoring and Evaluation Program (EMEP) or the German Federal Environmental Agencies (GFEA).

Code	Country	Station	Network	Lat. N	Lon. W	Altitude	Sampling
BOHV	Germany	Bornhöved	GFEA	53.88	10.17	45m	weekly
CZ03	Czech Rep.	Kosetice	EMEP	49.58	15.08	534m	1 day per week
FI96	Finland	Pallas	EMEP	67.97	7.12	566m	1 week per month
RADE	Germany	Radebeul	GFEA	53.10	13.65	246m	every second day
SE02	Sweden	Rörvik	EMEP	57.42	11.93	10m	1 week per month
SE12	Sweden	Aspvreten	EMEP	58.80	17.38	20m	1 week per month

3.2 Ozone

For criteria pollutants the EMEP measurement network provides good spatial and temporal coverage for most European countries (www.ceip.at). For the year 2000, for example, hourly ozone observations are available at 48 stations all over Europe. A detailed comparison of modelled concentrations of criteria pollutants_(SO_2, SO_4^{2-}, NO_2, NO_3^-, NH_4^+, O_3) for the year 2000 has already been carried out (Bieser et al., 2011a). Here, ozone concentrations are evaluated in more depth because they have a large impact on BaP concentrations. For the year 2000 the comparison revealed that 79% of the modelled hourly ozone concentrations are within a factor of 2 of the observations (Table 3). Because of a lack of measurement data no evaluation of ozone concentrations for the year 1980 could be performed.

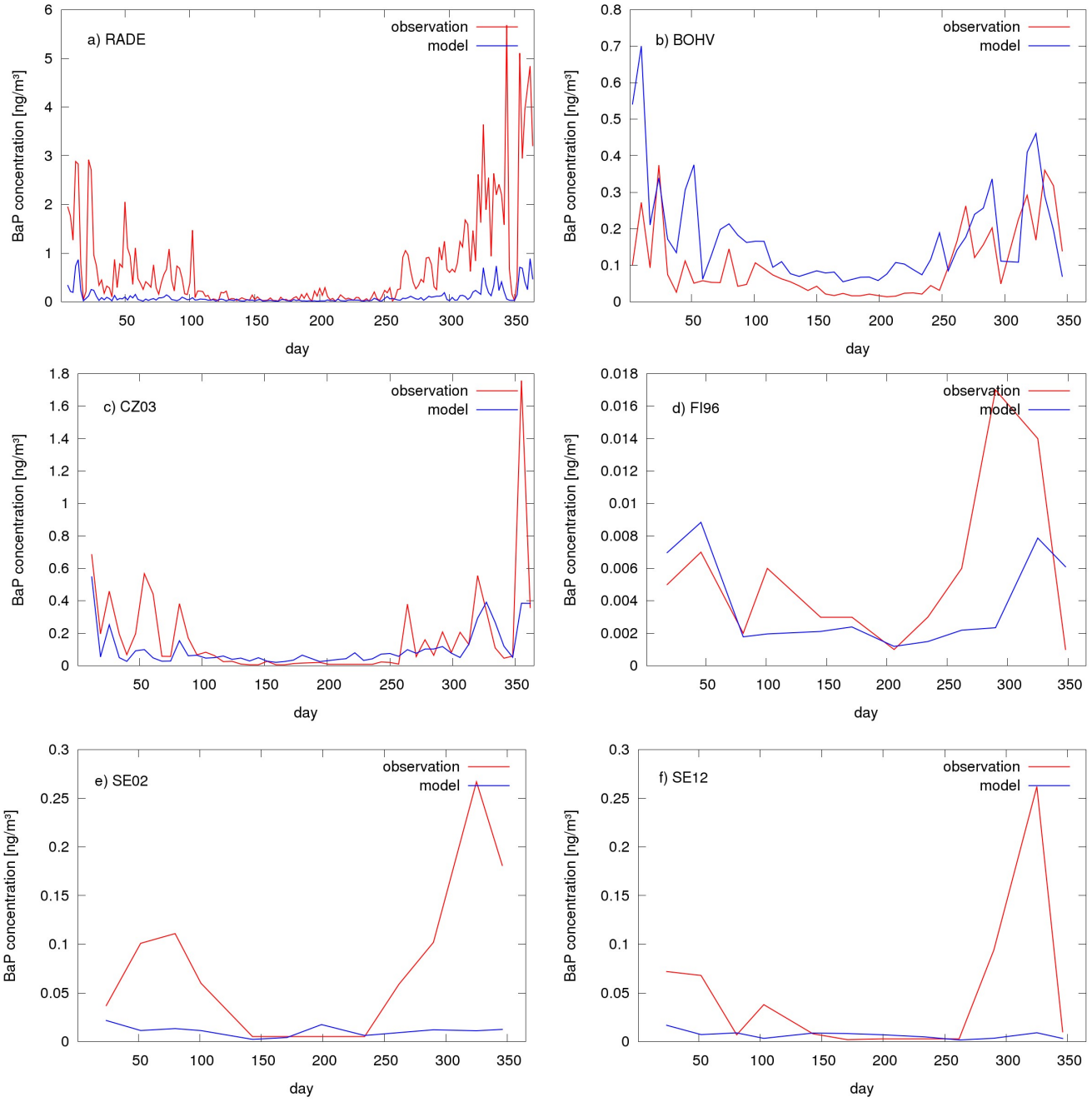

Figure 3: Comparison of modelled BaP concentrations for the year 2000 with observations. Observations (red) are compared to CMAQ model results (blue). The measurement stations are listed in Table 2,

Table 3

Comparison of modelled hourly Ozone concentrations for the year 2000 with hourly observations from 40 EMEP stations (N = 329 197). Statistical measures are fractional bias (FB), normalized mean error (NME), percentage of values within a factor of 2 (FAC2), correlation (CORR), index of agreement (IOA), annual mean concentration in µg/m³ (MEAN), and observed values in µg/m³ (OBS).

Station	FB	NME	FAC2	CORR	IOA	MEAN	OBS
42 EMEP stations	0.29 ± 0.13	0.36 ± 0.19	0.79	0.62 ± 0.08	0.45 ± 0.28	77.43 ± 6.05	
CZ03	0.13	0.14	0.9	0.76	0.84	74.35	65.15
SE02	0.33	0.4	0.8	0.64	0.41	83.13	59.48
SE12	0.38	0.47	0.77	0.56	0.19	85.71	58.16

Generally CMAQ is able to reproduce daily maximum 8-hour ozone concentrations (Fig. 4). At many measurement stations, however, modelled values show a lower diurnal variability than the observations because of an underestimation of night time ozone degradation. This can be partly explained by the fact that the measurement stations represent local near surface ozone concentrations, while the modelled concentrations are average values for 54x54 km² grid cells with a height of 42m. Figure 4a illustrates a case where the model shows high agreement with observations. This ia a rural measurement stations which is located in central Europe (Czech Republic), where the emission data is assumed to have low uncertainties, the surrounding terrain is mostly flat, and the influence of the boundary conditions is low. Figure 4b,c shows two remote Swedish stations where the model is only able to reproduce the maximum ozone concentrations. The reason for this could be missing local emissions or the boundary conditions. Ozone from the domain boundaries is transported effectively over the Atlantic Ocean to the Scandinavian countries. Since we are using daily average concentrations as boundary conditions, low diurnal variations can be an indication of an influence of the boundary conditions. Figure 4 depicts only three out of 42 evaluated EMEP measurement stations because at these stations ozone and BaP observations are available for the year 2000.

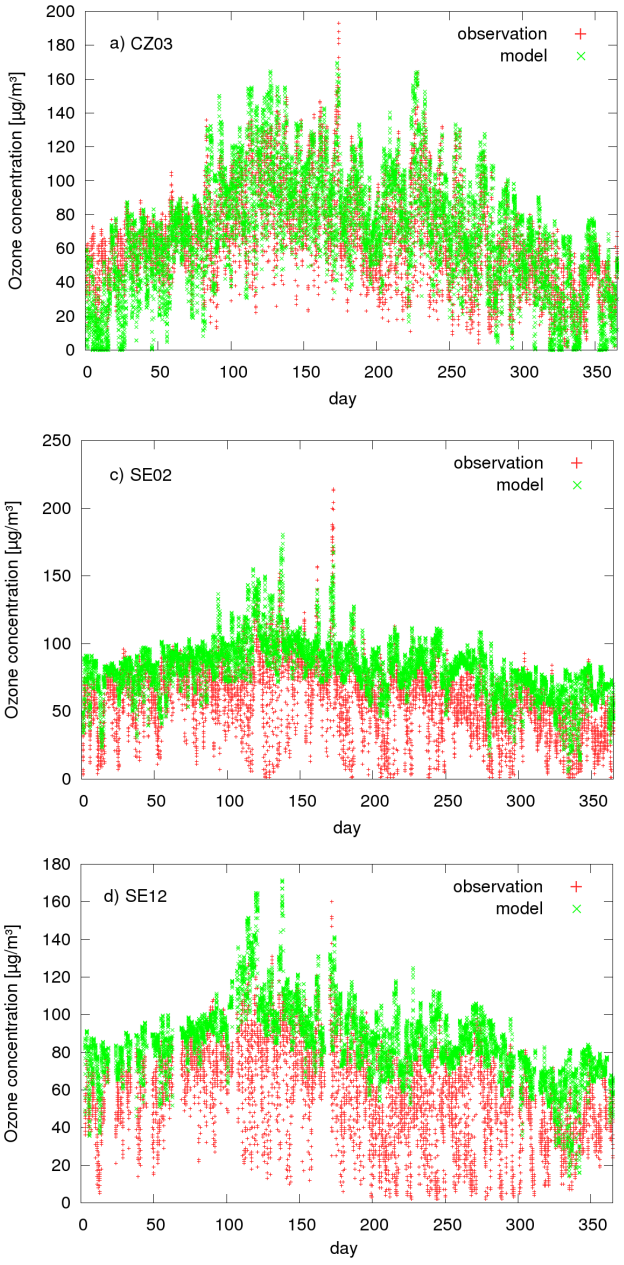

Figure 4: Comparison of modelled ozone concentrations for the year 2000 with observations. Hourly ozone concentrations from observations (red) are compared to hourly CMAQ model results (green).

4. Results and Discussion

4.1 Development of BaP concentrations between 1980 and 2020

The comparison of modelled annual average BaP concentrations in ambient air indicate that near surface BaP concentrations in general have been decreasing since 1980 (Fig. 5). Only in five countries (i.e. Cyprus, Finland, Greece, Portugal, and Russia) the annual BaP concentrations are increasing between 1980 and 2020 (Appendix A). From 1980 to 2000 average surface BaP concentrations over Europe decrease from 0.1 ng/m³ to 0.06 ng/m³ (-40%). Depending on the emission scenario ground level BaP concentrations between 2000 and 2020 are predicted to decrease by 5% *(2020inc)*, 12% *(2020base)*, or 30% *(2020red)* compared to the year 2000. Without the effect of changes in criteria pollutant emissions BaP concentrations are even increasing (+5%) in the scenario with increasing emissions from wood combustion (*2020inc)* although the total BaP emissions in this scenario are 6% lower than in the year 2000. While in most western European countries there are no significant differences between the baseline and the reduction scenario for 2020, in the eastern European countries there is a large reduction potential. In western Europe the largest differences are found for Spain. To give an impression of the changes in exposure to BaP figure 5 also illustrates population weighted annual average concentrations (C_W). The C_W of BaP is 0.28 ng/m³ in 1980 and decreased by 44% to 0.16 ng/m³ in 2000. Depending on the emission scenario for 2020 the value lies between 0.11 and 0.17 ng/m³. This shows that, on average, the relative reduction of BaP in populated areas is higher than in remote areas. Due to changes in population distribution between 1980 and 2020 the population weighted annual average concentration increased by 4%. All statistical values can be found in Table 4. The development of annual average concentrations for different countries is given in Appendix A.

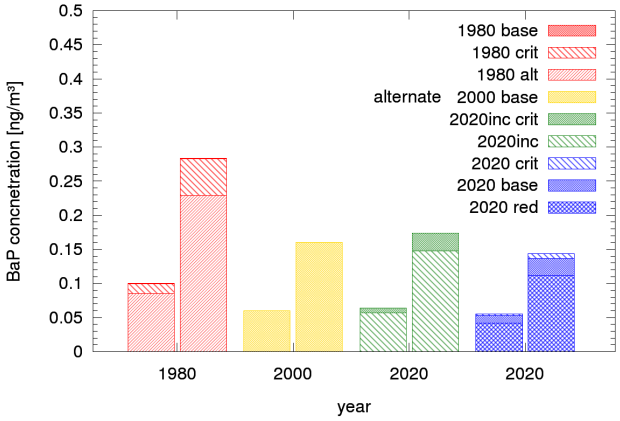

Figure 5: Annual average concentration (left) and population weighted average concentration (right) of BaP for different emission scenarios. In the case of increased wood combustion the concentration is increasing when using the same criteria emissions as in the 2000 base case. The concentrations for the 1980base and 1980crit case differ only by 1%. All emission scenarios are described in Table 1.

Table 4

Annual average BaP concentration, population weighted annual average BaP concentration, number of persons exposed to more than 1 ng/m³ annual average BaP concentration, and annual BaP emissions. The emission values in brackets indicate the amount of BaP emitted in the surface layer.

Scenario	concentration ng/m³	Pop. weighted conc. ng/a	inhabitants exposed to > 1ng/m³	Emissions t/a
1980 base	0.100	0.284	43 200 000	1526(910)
1980 crit	0.099	0.283	43 200 000	1526(910)
1980 alt	0.085	0.229	33 800 000	1172(910)
2000 base	0.060	0.160	25 400 000	792(530)
2000 deg	0.360	0.474	96 900 00	792(530)
2020 crit	0.055	0.144	25 000 000	617(417)
2020 base	0.053	0.137	23 100 000	617(417)
2020 red	0.042	0.111	21 800 000	478(400)
2020 inc	0.057	0.148	27 000 000	744(544)
2020 inc crit	0.064.	0.174.	27 000 000	744(544)

4.2 Regional distribution and exceedance of BaP target values

Generally modelled annual average BaP concentrations in remote areas mostly lie between 0.01 ng/m³ and 0.1 ng/m³ (Fig. 6). In the Scandinavian region and parts of the British Islands annual average BaP concentrations are as low as 0.001 ng/m³ to 0.01 ng/m³. For the UK this can be explained by the domination of westerly winds advecting unpolluted air and transporting BaP towards the east. In central Europe from France to Poland and from Denmark to Italy there is a large area where BaP concentrations lie between 0.1 ng/m³ and 0.4 ng/m³. Similar concentrations are found for the area around and south of Moscow. In 1980 large parts of west Germany had BaP concentrations above the upper assessment threshold of 0.4 ng/m³.

A total of six regions with higher BaP concentrations than the EU target value of 1 ng/m³ have been identified (Fig. 6). These are The Po valley in northern Italy, the Rhine-Ruhr area, and the metropolitan regions around Paris, Vienna, Madrid, and Moscow. Although BaP concentrations are decreasing, even in the 2020 reduction scenario the target value is still exceeded in the Po valley, eastern Austria, and Moscow. In 1980 annual average BaP concentrations of more than 1 ng/m³ were found in 19 model grid cells (Table 5) (55 404 km²), affecting a total of 43 million persons (Fig. 6a). In 2000 only 7 model grid cells (20 412 km²) with 25 million inhabitants show values exceeding the European target value (Fig. 6b). In the year 2020 6 grid cells are predicted to exceed 1 ng/m³ for the base case and 5 grid cells for the reduction case (Fig 6c-f).

Table 5

Number of grid 54x54 km² grid cells exceeding certain target values for different emission scenarios.

	> 1 ng/m³	> 0.6 ng/m³	> 0.4 ng/m³	> 0.25 ng/m³
1980 base	19	67	128	290
1980 crit	19	66	127	288
1980 alt	15	45	92	212
2000 base	7	24	43	106
2000 deg	83	573	1273	2030
2020 crit	7	22	45	100
2020 base	6	21	42	94
2020 red	5	14	27	69
2020 inc	9	21	46	104

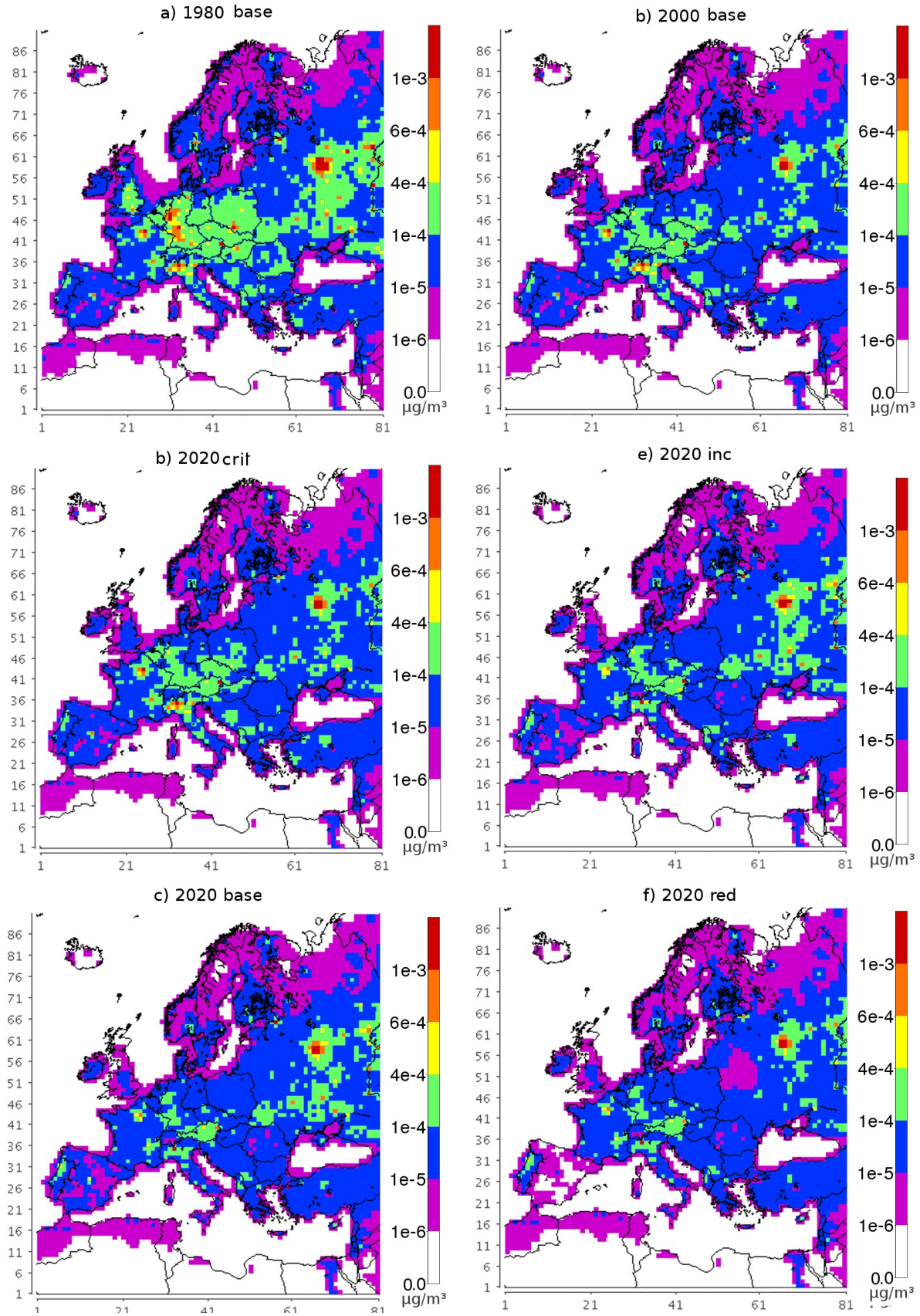

Figure 6: Annual average BaP concentrations for different emission scenarios (Table 1). Different colors indicate the level of BaP concentration: i.e. (red) above European target value of 1 ng/m³, (orange) above upper assessment threshold of 0.6 ng/m³, (yellow) above lower assessment threshold of 0.4 ng/m³, (green) above the lowest national European target value of 0.1 ng/m³.

4.3 Influence of primary emissions on BaP concentrations

To examine the effect of decreasing BaP emissions from different primary sources on ground level concentrations four different emission datasets were used as input for CMAQ: (1) *1980base case:* BaP and criteria pollutant emissions for the year 1980. (2) *1980crit case:* BaP emissions for the year 1980 and criteria pollutant emissions for the year 2000. (3) *2000alt case:* Non-industrial BaP emissions for the year 1980, industrial BaP emissions and emissions from criteria pollutants for the year 2000. (4) *2000base* case: BaP and criteria pollutant emissions for the year 2000 (Table 1).

Generally emissions of BaP and criteria pollutants are decreasing between 1980 and 2020. From 1980 to 2000 the BaP emissions are reduced by 740 t/a (48%). In the observed area (all model grid cells over Europe which are less than 80% covered by water) 48.5% of the emission reduction is due to industrial sources and 51.5% due to non-industrial sources (Fig. 1). In this time span the average surface BaP concentrations over Europe decrease by 40%. Of this reduction 32% can be attributed to reduced BaP emissions from industrial sources and 67% to reduced emissions from non-industrial BaP sources (Fig. 7). This shows that the impact of reductions of elevated BaP emissions on surface concentrations is by a factor of 1.97 lower than the impact of near surface BaP emission reductions. During winter, where the highest BaP concentrations are found, the factor is 2.6. Changes in emissions from criteria pollutants have only a minor (1%) impact on BaP concentration changes between 1980 and 2000. In the future emission scenarios for the year 2020, however, the impact of criteria pollutants is much larger. In the baseline scenario only 63% of the BaP ground level concentration reduction is caused by reduction of BaP emissions. This can be explained by the fact that changes in ozone concentrations between 2000 and 2020 are larger than between 1980 and 2000.

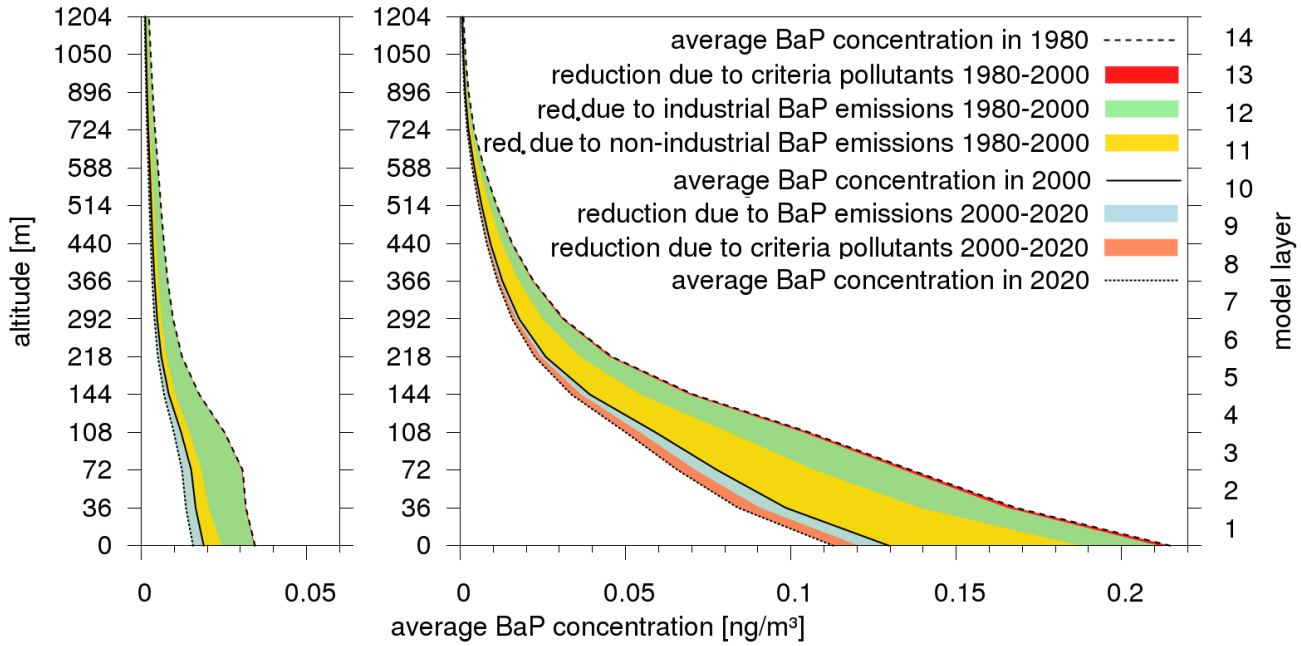

Figure 7: Depicted are vertical profiles of the BaP concentrations over the European continent for 1980 (dashed line), 2000 (solid line), and the year 2020 baseline scenario (dotted line). Two profiles, one summer profile (left) and one winter profile (right) are given. From 1980 to 2020 BaP concentrations have been decreasing at all altitudes. The colored areas between the lines indicate the cause for the emission reduction between two years. 1980 to 2000: changes in criteria pollutants (red), reduction of elevated BaP emissions (green), and reduction of near surface BaP emissions (yellow). 2000 to 2020: reduction due to total BaP emission reduction (blue) and reduction due to changes in criteria emissions (pink).

4.4 Influence of ozone on BaP concentrations

The reaction of ozone with particulate BaP is a non-linear process. Assuming a Langmuir-Hinshelwood type reaction the life time of particulate BaP depends on the ability of ozone to bind to the particle substrate (Kawamena, 2004). The reaction is mainly driven by the ozone concentration and the chemical composition of the particle BaP is bound to. Comparison of concentrations of ozone and BaP showed that BaP concentrations increase significantly when ozone concentrations drop below approximately 40 µg/m³ to 60 µg/m³ (Fig 8). This supports the assumption that the underestimation of BaP concentrations at the measurement stations SE02 and SE12 (Fig. 9e,f) can be explained by missing night time degradation of modelled ozone concentrations (Fig. 4b,c). While the observations indicate ozone concentrations are mainly in the range of 1 µg/m³ to 120 µg/m³, modelled concentrations range mainly between 60 µg/m³ and 120 µg/m³.

To assess the influence of modelled ozone concentrations on BaP an additional CMAQ run with an reduced reaction rate of BaP with ozone has been performed. In this case the ozone concentration used to determine the degradation of BaP is multiplied by 0.5. In the alternative degradation case the modelled ozone concentration is mostly below 60 µg/m³ at the two Swedish measurement stations. In figure 9 modelled BaP concentrations from the default CMAQ run are plotted together with results from the alternate degradation case, and observed concentrations. It can be seen that the underestimation of BaP concentrations in the default run can be explained by missing night time degradation of ozone in the model. At the measurement site CZ03, where modelled ozone concentrations in the default run show good agreement with observations the reduced degradation by ozone leads to an over prediction of BaP concentrations (Fig. 4a and 9a). On average modelled BaP concentrations in Europe are higher by a factor of 2.8 than in the default run.

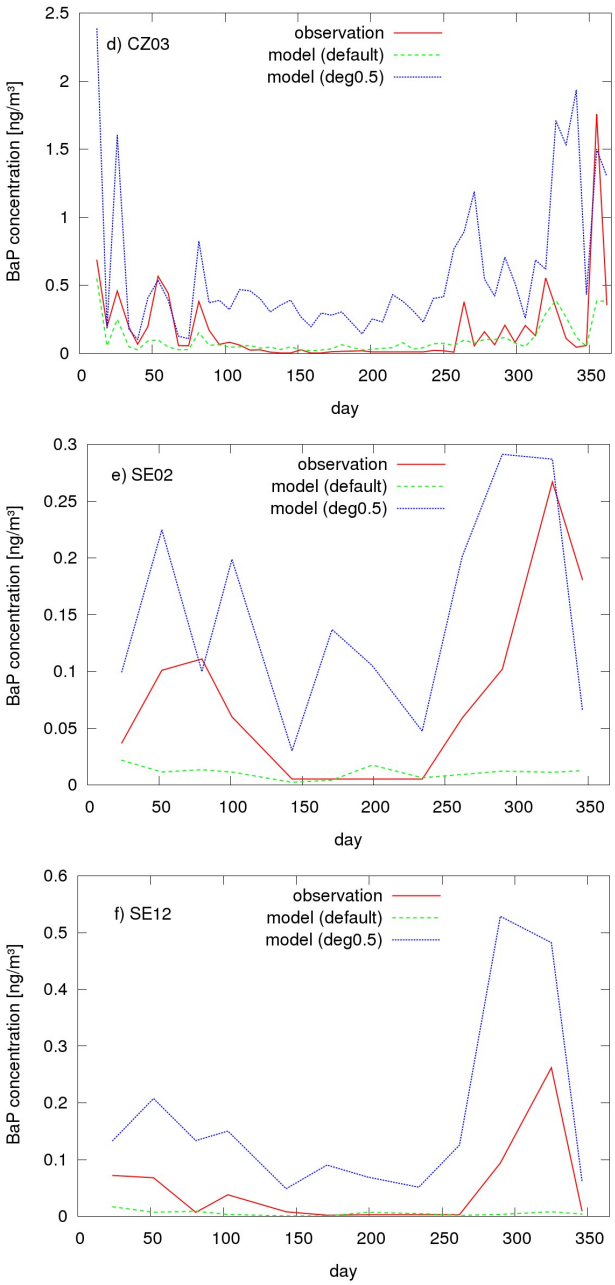

Figure 9: Comparison of observed BaP concentrations (red) with modelled values from the default CMAQ run (green) and the reduced degradation CMAQ run (blue).

To show the relation of BaP and ozone the development of ozone concentrations between 1980 and 2020, the frequency distribution of ozone concentrations for different scenario years has been investigated (Fig. 8). For this purpose ozone concentrations in grid cells which showed good agreement with observations for the year 2000 have been evaluated (Fig. 4). It is assumed that in these model grid cells also for the years 1980 and 2020 the diurnal variation is captured by the model. The diurnal variation of ozone concentrations is slightly decreasing. This leads to lower peak ozone concentrations during midday. Generally, ozone concentrations are increasing during winter where

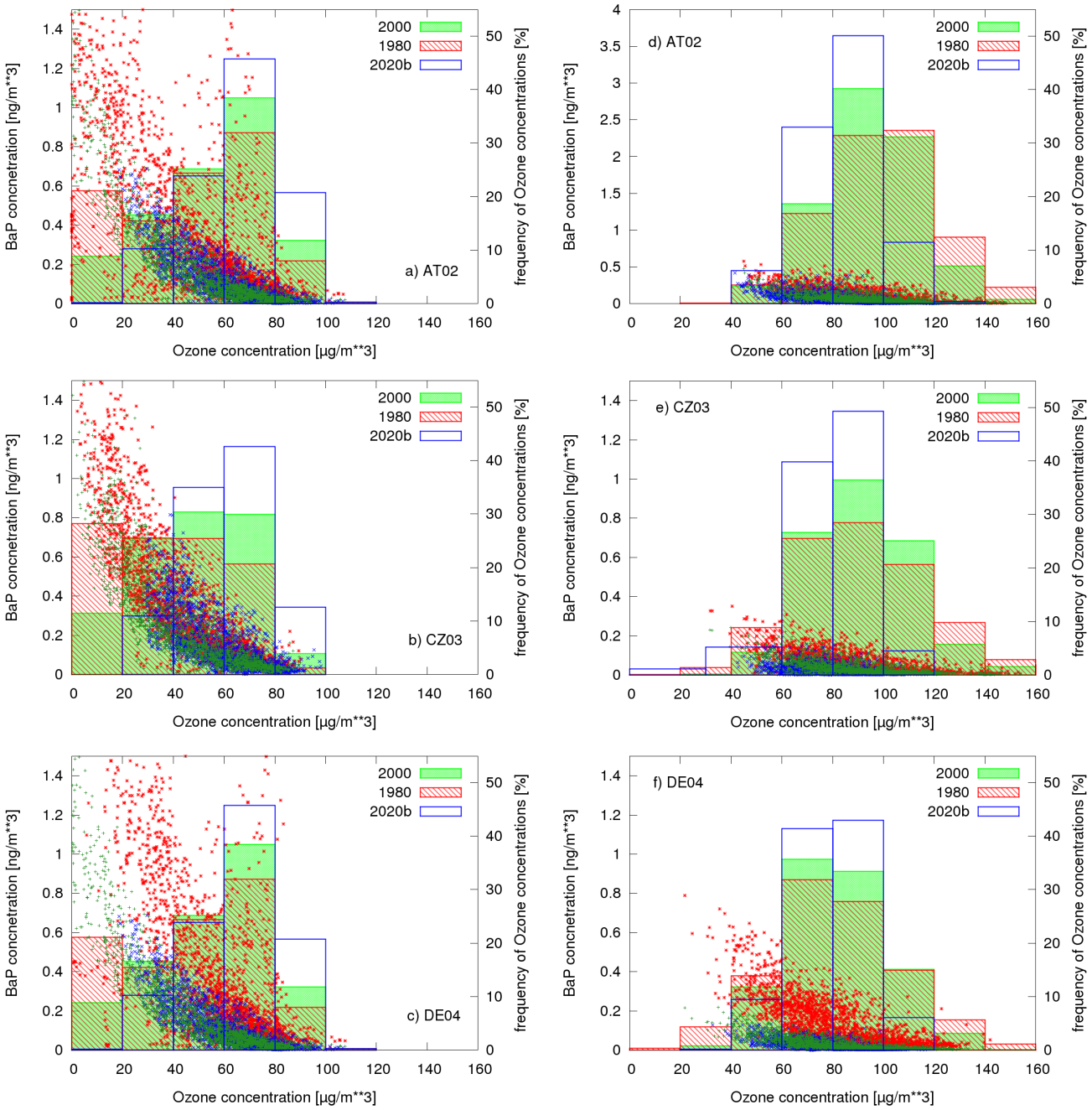

Figure 8: Correlation of ozone concentrations (x axis [µg/m³]) and BaP concentrations (left y axis [ng/m³]). For ozone concentrations below 40 µg/m³ to 60 µg/m³ the BaP concentrations grow exponentially. The boxes indicate the frequency distribution (x axis [µg/m³] step size 20 µg/m³) of daily average ozone concentrations (right y axis frequency [%]) due to different criteria pollutant emissions between 1980 and 2020. Data for winter (left) and summer (right) are illustrated separately. It can be seen that during winter Ozone concentrations are growing over the years, while for summer ozone concentrations are decreasing.

concentrations are often low. In the evaluated grid cells the frequency of ozone concentrations below 60 µg/m³ during winter, on average, decrease by 30% between 1980 and 2020. This leads to an increase in BaP degradation during winter. On the other hand ozone concentrations in summer are decreasing. This decrease, however, has only a minor effect on degradation of BaP because the ozone concentrations are mostly above 60 µg/m³.

5. Conclusions

A modified version of the CTM CMAQ which includes heterogeneous degradation reactions of particulate benzo[a]pyrene (BaP) with ozone as well as degradation of gaseous BaP by photolysis and reduction with OH was used to model atmospheric concentrations of BaP over Europe. CMAQ was run using a total of 10 different emission datasets for the years 1980, 2000, and 2020 (Table 1). To investigate the influence of the emissions on BaP concentrations the same meteorological fields and boundary conditions were used for all CMAQ runs.

In Europe between 1980 and 2000 BaP emissions decreased by 48%. The modelled annual average concentration of BaP was reduced by 40%. Future emission scenarios for the year 2020 showed that for further reduction of near surface BaP concentrations emissions from residential wood combustion need to be reduced. Different estimates for BaP emissions in 2020 lead to a change of ground level concentrations of -25% to +5% compared to the year 2000. Changes of criteria pollutant emissions are predicted to lead to a decrease of BaP concentrations of about 10%. Between 1980 and 2000 criteria pollutants had only a minor (1%) impact on BaP concentrations. Differences in population distribution between 2000 and 2020 will lead to an increase of population weighted average concentrations by 4%.

Generally the model predicts annual average BaP concentrations below the *lower assessment* value of 0.4 ng/m³ for most of Europe. However, several regions where the European target value of 1 ng/m³ is exceeded have been identified. These polluted areas are densely populated urban regions. For the year 2020 CMAQ predicts annual mean BaP concentrations above 1 ng/m³ for the Po-Valley in Italy, the eastern part of Austria, and around Moscow. BaP concentrations between 0.6 ng/m³ and 1 ng/m³ are found in the Rhine-Ruhr area, Madrid, and around Paris. Depending on the emission scenario in Europe a total of 4.6 to 6.6 million people life in areas with BaP concentrations above 1 ng/m³.

An assessment of BaP reductions from different sources showed that the influence of industrial BaP emissions on ground level concentrations of BaP is two times lower than the influence of non-industrial emissions. This is due to the fact that the effective emission heights of industrial emissions are much higher than those of non-industrial sources. Thus, there is more time for degradation of BaP by reaction with ozone before it reaches the surface layer. Also ozone concentrations in higher altitudes are often higher than on ground level.

Comparisons with observations revealed that CMAQ often underestimates BaP concentrations. It could be shown that too low night time degradation of ozone in the model leads to an overestimation of BaP degradation. A CMAQ run with a decreased reaction rate of BaP with ozone lead to 2.8 times higher BaP concentrations over Europe.

In order to better evaluate modelled atmospheric BaP concentrations a higher spatial and temporal coverage of observations in Europe is necessary. Further, we emphasize that it is important to also evaluate ozone concentrations at stations measuring BaP.

Acknowledgements

US EPA is gratefully acknowledged for the use of SMOKE and CMAQ. We are thankful to Beate Geyer for providing the CLM meteorological fields and to Hugo Denier van der Gon and Joseph Pacyna for the emission data. EMEP gratefully acknowledged for providing data on emissions and observations.

Appendix A: Annual average concentrations and number of inhabitants in regions exceeding annual average BaP concentrations of 1 ng/m³

ISO norm country abbreviations are used. (FFR = former federal republic of Germany, FGD = former German democratic republic).

country	annual average concentration [ng/m³]					million inhabitants exposed to more than 1 ng/m³ per annum				
	1980	2000	2020base	2020red	2020inc	1980	2000	2020base	2020red	2020inc
EU	0.102	0.059	0.052	0.042	0.055	23.4	10.7	4.6	4.6	6.6
total domain	0.048	0.029	0.026	0.021	0.028	43.2	25.4	23.1	21.8	27.0
AL	0.098	0.085	0.078	0.073	0.085	0	0	0	0	0
AT	0.262	0.237	0.205	0.206	0.226	1.9	1.9	0	0	1.9
BE	0.236	0.146	0.064	0.062	0.070	0	0	0	0	0
BG	0.063	0.056	0.032	0.031	0.035	0	0	0	0	0
DK	0.025	0.018	0.015	0.015	0.017	0	0	0	0	0
FI	0.027	0.026	0.029	0.029	0.032	0	0	0	0	0
FR	0.111	0.098	0.064	0.064	0.070	4.0	4.1	0	0	0
FGD	0.147	0.071	0.037	0.037	0.041	0	0	0	0	0
FFR	0.429	0.140	0.100	0.101	0.110	9.9	0	0	0	0
GR	0.034	0.028	0.033	0.032	0.036	0	0	0	0	0
HU	0.182	0.096	0.038	0.037	0.042	0	0	0	0	0
IS	0.001	0.001	0.001	0.001	0.001	0	0	0	0	0
IE	0.022	0.012	0.012	0.011	0.013	0	0	0	0	0
IT	0.168	0.169	0.067	0.065	0.074	4.7	4.7	4.6	4.6	4.6
LU	0.219	0.134	0.074	0.075	0.081	0	0	0	0	0
NL	0.258	0.103	0.040	0.039	0.042	7.7	0	0	0	0
NO	0.048	0.022	0.018	0.018	0.019	0	0	0	0	0
PL	0.212	0.093	0.034	0.029	0.036	3.0	0	0	0	0
PT	0.026	0.027	0.035	0.033	0.039	0	0	0	0	0
RO	0.105	0.043	0.022	0.020	0.024	0	0	0	0	0
ES	0.029	0.028	0.017	0.002	0.019	0	0	0	0	0
SE	0.016	0.013	0.010	0.010	0.011	0	0	0	0	0
CH	0.127	0.091	0.044	0.043	0.048	0	0	0	0	0
TR	0.062	0.054	0.040	0.036	0.044	0	0	0	0	0
GB	0.107	0.011	0.006	0.006	0.006	0	0	0	0	0
BY	0.045	0.042	0.038	0.005	0.041	0	0	0	0	0
UA	0.128	0.101	0.115	0.047	0.120	0	0	0	0	0
MD	0.066	0.039	0.036	0.020	0.038	0	0	0	0	0
EE	0.032	0.029	0.016	0.016	0.018	0	0	0	0	0
LV	0.033	0.023	0.017	0.015	0.018	0	0	0	0	0
LT	0.054	0.036	0.027	0.020	0.029	0	0	0	0	0
CZ	0.246	0.157	0.093	0.093	0.102	3.0	1.9	0	0	1.9
SK	0.192	0.096	0.045	0.043	0.049	1.9	0	0	0	0
SI	0.113	0.098	0.051	0.049	0.055	0	0	0	0	0
HR	0.063	0.049	0.026	0.025	0.029	0	0	0	0	0
BA	0.105	0.091	0.039	0.037	0.043	0	0	0	0	0
CS	0.098	0.077	0.055	0.052	0.060	0	0	0	0	0
MK	0.085	0.073	0.070	0.067	0.076	0	0	0	0	0
CY	0.022	0.019	0.079	0.078	0.086	0	0	0	0	0
MT	0.006	0.003	0.003	0.003	0.004	0	0	0	0	0
DE	0.344	0.120	0.081	0.082	0.089	9.9	0	0	0	0
UA	0.128	0.101	0.115	0.047	0.120	0	0	0	0	0
RU	0.128	0.070	0.088	0.070	0.095	19.8	14.7	18.5	17.2	20.4

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