MODELLING OF BENZO(A)PYRENE CONCENTRATIONS IN NORTH SEA COASTAL AREAS: CONTRIBUTION OF SHIP EMISSIONS

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Abstract: The effect of benzo(a)pyrene (BaP) ship emissions in the greater North Sea region is investigated in this study. The carcinogenic BaP which belongs to the group of polycyclic aromatic hydrocarbons (PAHs) occurs mainly particle bound at temperatures prevailing in the mid-latitudes. The BaP concentration and deposition distribution is investigated by means of the Community Multiscale Air Quality modelling system (CMAQ). CMAQ is a chemistry transport model developed by the US EPA that is here set up on a 54x54 km^2 grid for Europe. Two different model runs, one excluding and one including ship emissions were performed for January and July 2000. For a sensitivity study three additional model runs considering also ship emissions of NO_x, SO_2, and PM_{10} were performed for January 2000. It is shown that the contribution of BaP ship emissions to the total BaP emissions is generally small but shows a noticeable seasonal variation. Furthermore, the sensitivity study shows indirect effects of other ship emissions on BaP concentration and deposition over land that are larger than those by the added BaP ship emissions alone.

Key words: *CMAQ, chemical transport modelling, benzo(a)pyrene, ship emissions.*

1. INTRODUCTION

Ship emissions can have considerable impact on atmospheric concentrations of several important pollutants especially in coastal areas (Endresen et al., 2003, Tsyro and Berge, 1997). The most important ones are CO_2, NO_x, SO_2, CO, hydrocarbons, and particulates because of their role as e. g. greenhouse gas (CO_2), their contribution to acid rain (NO_x, SO_2), and/or their impact on human health (particulates) (Lloyd´s Register Engineering Services, 1995). Corbett et al. (2007) have recently shown that ship emissions lead to an increase in PM2.5 ambient air concentration and therewith are responsible for an increase of cardiopulmonary and lung cancer deaths. Micropollutants affecting the human health as e. g. a variety of polycyclic aromatic hydrocarbons (PAHs) with their carcinogenic potential to humans and animals (ATSDR, 1995) have to be considered as well. PAHs mainly originate from incomplete combustion of organic matter like fuel oil. Benzo(a)pyrene (BaP) belongs to the group of PAHs and it is often used as their representative substance. BaP is a low-volatile, persistent organic pollutant (POP) which occurs at temperatures prevailing in middle Europe mainly bound to particles. Therefore, their atmospheric transport is closely linked to aerosols. Bound to particles the chemical degradation of PAHs is very slow (Esteve et al., 2006).

This study focuses on the contribution BaP emitted by ships on the BaP distribution in North Sea coastal areas. Ship emissions of other pollutants that influence aerosol formation and depletion like NO_x, SO_2 and PM_{10} are also taken into account and their effect on the BaP distribution is investigated. For the estimation of the ship emissions in this study a bottom-up approach on the basis of ship movement data together with average engine loads and emission factors available in literature (Cooper and Gustafsson, 2004) is used to generate a ship emission inventory.

The ship emission inventory served as input for the Models-3 Community Multiscale Air Quality modelling system (CMAQ) (Byun and Ching, 1999) that is set up on a 54x54 km^2 grid for Europe. The model is driven by meteorological fields that were derived from MM5 (Grell et al., 1995). CMAQ has been extended at GKSS to model the transport of PAHs, in particular of BaP (Aulinger et al., 2007). Matthias et al. (2008) have shown that the model is applicable to North Sea coastal regions by comparing model results to measured air concentrations and depositions.

2. INPUT DATA

Meteorological fields

The MM5 model runs were driven by ERA40 6 hourly global reanalysis data on a 1x1degree grid. We used four dimensional data assimilation of the ERA40 fields and applied 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.

Initial and boundary conditions for CMAQ

The boundary conditions for the simulations presented here were taken from MOZART (Horowitz et al., 2003) model results for the year 2000. The data has a resolution of 1x1 and one day. It includes several gas phase species (e.g. O_3, CO, NO_x, SO_4, OH, HNO_3), but no BaP. The boundary conditions for BaP were zero everywhere except at the eastern edge of the model domain, where monthly average BaP values of a previous model run were assumed.

Land based 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 database used for land-based BaP emissions was derived from TNO (Denier van der Gon et al., 2005). The data were provided as annual bulk

emissions on the 50x50 km^2 EMEP grid. They were interpolated to the 54x54 km^2 CMAQ grid. A temporal variation of the data was achieved by linearly correlating emissions from residential combustion, the dominant source of BaP emissions, to the ambient air temperature. This leads to a pronounced seasonal dependence of the emissions.

Ship emissions

Ship data base

The vessel database was purchased from Lloyds Marine Intelligent Unit (LMIU). It consists of a vessel characteristic database and a vessel movement database and it includes all commercial vessels equal to or greater than 100 gross tonnages (GT). The vessel characteristic database comprises information on e.g. vessel type, engine type, numbers of engines, engine speed at the crankshaft, fuel type, power and maximum speed. The ship movement database provides information on ship movements for the year 2000 in parts of Europe (riparian states of the North and Baltic Sea, Atlantic coast of France, Spain and Portugal). This is covered by 15625 ships, which perform 651825 movements on 58324 different routes. The ship movement database consists of previous departure, arrival, departure and next arrival places and dates with a daily time resolution.

Ship emission factors

Emission factors (power-based in $gk^{-1}Wh^{-1}$) used in this study are obtained from Cooper and Gustafsson (2004) who compiled these emission factors for Sweden´s international reporting duties. The emissions from ships are affected by several characteristics of the ships as well as the fuel used (see Whall et al. (2002) for details). The engine type determines the combustion conditions and therefore the emissions of some pollutants. Due to a very limited dataset for determining the emission factor for BaP, separate engine and fuel specific factors are not provided. Thus, the BaP emission factor has to be considered as a possibly large error source. Most likely the emission factor of Cooper and Gustafsson (2004) is at the low end of the possible values because it is similar to BaP heavy-duty diesel vehicle emission factors (Doel et al., 2005), although the PAH content of the fuel influences the BaP emissions and the majority of vessels use residual oil with extreme poor quality.

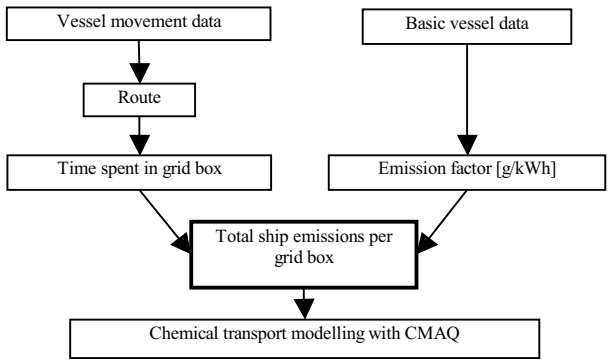

Figure 1. Outline of the procedure to generate the ship emission dataset.

Ship emission data set

The procedure how to obtain the ship emission dataset is displayed in Figure 1. The vessel movement database provides the basis for calculating the routes of the vessels. It is assumed that all vessels take the shortest routes between two ports at sea. For the required temporal resolution of the ship movements it is assumed that all vessels arrive and depart at 6 a.m. for more than one day travelling time. If they leave the same day they leave the port at 6 p.m. or even earlier if they call another port the same day. The travelling time is distributed equally to all passed grid boxes on their route. The ship emissions per grid box and time step are calculated for the different pollutants by means of the corresponding emission factors and the engine power of the particular vessel. Figure 2 presents monthly averaged land-based (a) and marine (b) BaP emissions for January 2000. The ship emissions account for approximately 0.1% of the total emissions in coastal areas.

3. METHODOLOGY

The land-based and marine emission datasets serve as input into the Eulerian air quality modelling system CMAQ which computes the concentration and deposition distribution over Europe. To investigate the contribution of BaP ship emissions to the BaP air pollution in coastal areas two different model runs were performed with CMAQ, one model run including all land-based emissions and the BaP ship emissions (model run: s_0, see Tab. 1) and the reference model run just including the land-based emissions (model run: lb, see Tab. 1). The seasonal impact is investigated by comparing January and July monthly average BaP concentrations as representatives for winter and summer. For the sensitivity study three additional CMAQ model runs were performed to investigate the influence of NO_x, SO_2 and PM_{10} ship emissions on the BaP concentration and deposition distribution over Europe. This sensitivity study is only performed for January because aerosol concentrations are typically much higher in winter than in summer. Table 1 illustrates the setup of the different model runs.

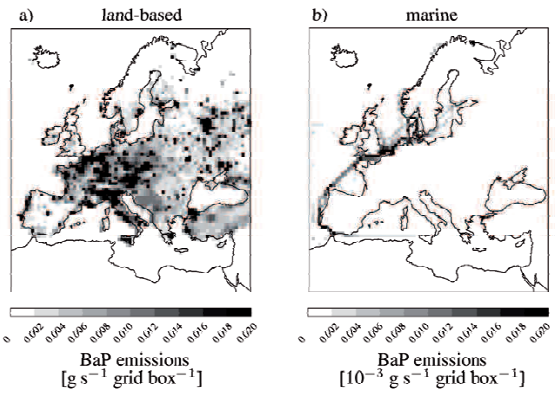

Figure 2. Average land-based (a) and marine (b) BaP emissions for the 54x54 km^2 grid for January 2000

Each model run includes the land-based emissions and different additional marine emissions. The reference model run (lb) contains only land-based emissions. The impact of the ship emissions on the BaP concentration and deposition distribution was calculated by the difference between the s_0-, s_{SO2}-, s_{NOx}-, s_{PM}-model run results (Table 1) and the lb-model run results.

Table 1: Description of the different model runs

Input data	Model run				
	lb	s_0	s_{SO2}	s_{NOx}	s_{PM}
Land-based emissions	+	+	+	+	+
Marine emissions	-	BaP	BaP + NO_x	BaP + SO_2	BaP + PM_{10}

4. RESULTS

Reference model run

Figure 3a) shows the monthly averaged BaP concentration in the lowest model layer, Figure 3b) the monthly cumulated dry deposition and Figure 3c) the monthly cumulated wet deposition over Europe of the reference model run (lb) for January (1st row) and July (2nd row) 2000. BaP concentration peaks appear close to the emission sources in regions of congested urban and industrial areas. The deposition is dominated by wet deposition which is by a factor of approximately four higher than the dry deposition. High deposition rates are noticed close to the emission sources except for Russia and the Ukraine in January. Especially the Ukraine shows comparably higher dry deposition of BaP. The BaP concentration shows a significant difference between the two months. This represents the strong seasonal dependences of the land-based emissions.

B(a)P ship emissions model run

The impact of the BaP ship emissions is illustrated in Figure 4. In contrast to the results of the lb-model run (Fig. 3) it can be seen that BaP concentration changes due to the ship emissions do not vary significantly between January and July (Fig. 4a). The January and July BaP concentrations differ by a factor of approx. two caused by a lower number of vessel movements during winter. BaP concentrations reach their maximum in the Strait of Dover with average values of 0.6 10^{-3} ngm^{-3} in January and 1.1 10^{-3} ngm^{-3} in July. The increase of the BaP concentrations over the North Sea compared to the reference case is 0.2% in January and 0.8% in July (Fig. 4b). Land-based emissions are significantly higher in winter than in summer. These numbers are considered as a lower estimate of the impact of the BaP ship emissions because of the highly uncertain and probably too low emission factor.

Sensitivity study: impact of NO_x, SO_2 and PM_{10} ship emissions on BaP concentration and deposition

The effect of the additional ship emissions of NO_x, SO_2 and PM_{10} to the BaP concentration (model runs s_{SO2}, s_{NOx}, s_{PM}) was investigated by model runs covering January 2000. BaP ship emissions alone increase the BaP concentration at the Belgian, Dutch and German North Sea coastline by around 0.5 10^{-3} ngm^{-3} with a decreasing gradient towards the open North Sea and on land. The addition of the aerosol precursor gases NO_x and SO_2 (s_{NOx}, s_{SO2}) lead to a pronounced decrease of around 2 10^{-3} ngm^{-3} in the ground level BaP concentration in large parts of central and eastern Europe whereas emissions of PM_{10} (s_{PM}) results in a concentration increase of 2 10^{-3} ngm^{-3} to 4 10^{-3} ngm^{-3} over wide areas of Europe. In comparison to the total BaP concentration (Figure 3a) the change in BaP concentrations caused by ship emissions is small but noticeable Europe-wide. While the increase of the BaP concentration considering only BaP emissions from ships (s_0-model run) amounts to 0.1 to 0.2% over the North Sea the BaP concentration is increased by 0.5% at the North Sea coastline with the s_{PM}-model run and amounts to 0.1 to 0.2% over Spain, France and Eastern Europe. In contrast, the addition of NO_x and SO_2 ship emissions (s_{NOx}, s_{SO2}) decreases the BaP concentration by 0.2 to 0.3%.

The s_{NOx} and s_{SO2} model runs show an increase in the BaP dry deposition and a decrease in the wet deposition. For the s_{PM}-model run the effect is the other way round with higher wet deposition and decreased dry deposition. The net deposition changes reflect the BaP concentration changes quite well and it is likely that increased BaP concentrations result from lower total deposition and vice versa. Our hypothesis is that an increased amount of smaller particles that occurs when secondary aerosols are formed leads to more BaP bound to Aitkan mode particles. These particles are scavenged less efficiently and wet deposition is therefore decreased. Dry deposition, on the other hand, is increased because the deposition velocity is higher for smaller particles. Direct emissions of larger particles that are already in the accumulation mode like in the s_{PM}-case leads to a higher amount of BaP bound to these particles and the opposite effects in dry and wet deposition. The combined effect strongly depends on the amounts of the additional NO_x, SO_2 and PM_{10} emissions and on the prevalent weather conditions.

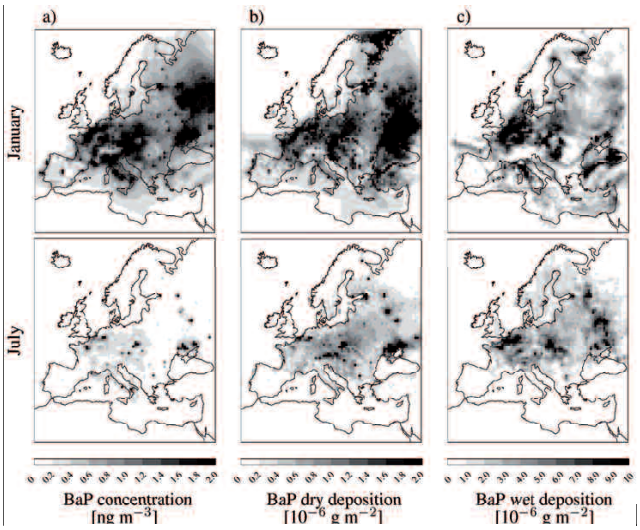

Figure 3: Modelled BaP concentration (a), cumulated dry deposition (b) and cumulated wet deposition (c) with land-based emissions for January (1st row) and July 2000 (2nd row).

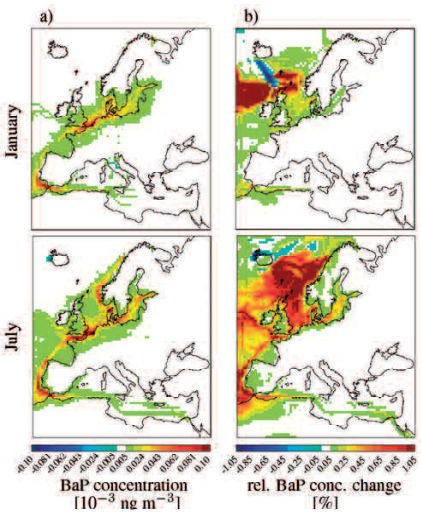

Figure 4: BaP concentration change caused by BaP ship emissions (a) and its relative change compared to the reference case (b) for January (1st row) and July 2000 (2nd row)

5. CONCLUSIONS

The contribution of BaP ship emissions on the BaP concentration in coastal areas was investigated in this study. Secondly, a sensitivity study on the impact of the major ship emissions NO_x, SO_2 and PM_{10} in addition to BaP ship emissions on the BaP concentration and deposition was performed. It was found that the impact of BaP ship emissions is small but it increases from 0.2% in January to more than 0.8% in July because the influence of the strongly seasonal dependent land-based emissions decreases significantly in summer.

The sensitivity study showed that the investigated pollutants have a noticeable impact on the BaP concentration and deposition Europe-wide even though the absolute concentration and deposition change is small. The aerosol precursor gases NO_x and SO_2 which are added with the ship emissions lead to a decrease of 0.1 to 0.3% in concentration and wet deposition and to an increase of 0.5 to 4% of the dry deposition over wide areas of Europe. In contrast, the additional PM_{10} ship emissions result in a BaP concentration and wet deposition increase and in a decrease of the BaP dry deposition. The reason for the different impact of primary and secondary aerosols on the BaP concentration and deposition might be found in the different size of the particles. Furthermore, the added ship-based aerosols affect beside the ship emitted BaP also the land-based emitted BaP. The changes in concentration and deposition are larger than those caused by the additional ship emitted BaP.

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