PAH pollution: A case study for Poland

The case study for Poland continues a series of national scale case studies on PAHs [*Gusev et al.,* 2017; 2018; 2019] that were performed following the recommendation of the 2^{nd} joint session of the Working Group on Effects and the Steering Body to EMEP held in 2017. The study was initiated in 2020 after the meeting of EMEP and national experts in modelling and emissions of PAHs (November, 2019). Main objectives of the study include:

1. Evaluation of the updated national PAH emission inventory reported to EMEP [*Bebkiewicz et al.*, 2020];
2. Analysis of PAH pollution levels and exceedances of air quality guidelines in Poland using modelling results and detailed measurements.

Polish inventory of national PAH emissions was substantially updated in 2019-2020 following the review recommendations of Task Force on Emission Inventories and Projections (TFEIP). Most of the updates were associated with the refinement of emission factors in the NFR category 1A4 related to the emissions from stationary combustion sources. Besides, time-series of total annual PAH emissions for the period 1990-2018 were updated on the basis of the EUROSTAT statistical data. These changes led to substantial increase of PAH emission estimates in the inventory submitted in 2020 comparing to the previous PAH emission estimates.

The first phase of the study was focused on the model assessment of B(a)P pollution in the country using three different emission data sets, based on national inventories and emission scenarios. The model simulations with the scenario emissions allowed improving agreement between the model and measurements and indicated possible underestimation of national B(a)P emissions in Poland. The results were described in the EMEP Status Report on HMs and POPs [*Ilyin et al.*, 2021].

In the second phase of the study other 3 PAHs of the Protocol, namely, B(b)F, B(k)F, and I(cd)P, were considered. In particular, analysis and update of GLEMOS model parameterization for these 3 compounds was carried out. The GLEMOS model was used to evaluate previous and updated national emission inventories of 3 PAHs. Besides, exceedances of air quality guidelines for PAHs were estimated. Below in this section the outcome of the second phase of the study is briefly presented.

Refinement of GLEMOS model parameterization

As the initial step of the second phase, it was planned to analyze and update GLEMOS model parameterization for B(b)F, B(k)F, and I(cd)P. Similar to B(a)P these PAHs are semi-volatile compounds presenting in the atmosphere both in gaseous and particulate forms and undergo reactions with atmospheric reactants. The most significant processes influencing their transport and fate in the atmosphere include gas-particle partitioning and degradation.

In contrast to B(a)P, simplified parameterization of B(b)F, B(k)F, and I(cd)P gas-particle partitioning (GPP) and degradation was implemented in the GLEMOS model. In particular, it was based on the adsorption Junge-Pankow GPP scheme [*Junge*, 1977; *Pankow*, 1987]. The degradation was assumed to take place only in the gaseous form of PAHs due to reaction with OH radical. These simplifications led to an overestimation of observed air concentrations, especially for the warm period of the year.

To improve performance of the model, the GPP parameterization was changed to the dual scheme that includes absorption into organic matter and adsorption to black carbon [*Dachs and Eisenreich*, 2000; *Lohmann and Lammel*, 2004]. Besides, parameterization of PAH degradation in particulate form was added based on the results of experimental studies [*Kahan and Donaldson*, 2006; *Kwamena et al.*, 2004, 2007]. Results of sensitivity model simulations showed noticeable improvement of model performance for B(b)F, B(k)F, and I(cd)P (Fig.4.11).

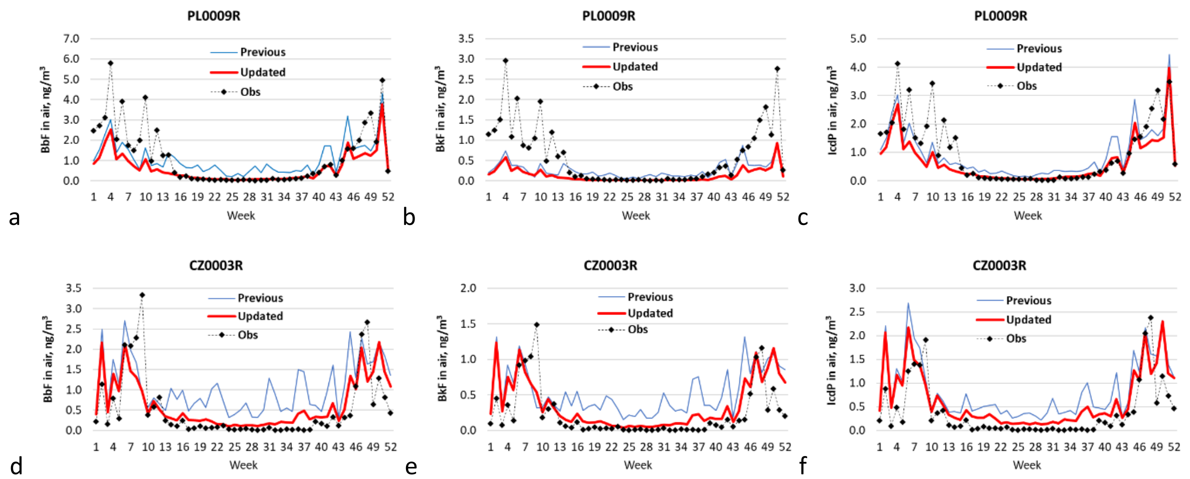

Fig. 4.11. *Seasonal variations of B(b)F (a,d), B(k)F (b,e), I(cd)P (c,f) air concentrations for 2018, simulated by the GLEMOS model on the basis of the previous and new model parameterizations, in comparison with observed concentrations at stations PL0009R (upper row) and CZ0003R (lower row).*

Model setup and input data

Model simulations for the PAH case study for Poland were carried out for the year 2018. Two datasets of gridded anthropogenic emissions for each of three considered PAHs (B(b)F, B(k)F, I(cd)P) were prepared for model simulations. The first dataset (*PL_OLD*) was constructed using the previous national emission inventory of Poland for EMEP (submission 2019). In the second dataset emissions of Poland were substituted by the new inventory (*PL_NEW*). For other EMEP countries emission data for 2018 provided by CEIP (submission 2020) was used. Spatial distributions of annual emissions of B(b)F, B(k)F, and I(cd)P used in model simulations are presented in Fig. 4.12.

It is seen that B(b)F and B(k)F emission estimates of PL_NEW inventory are higher comparing to PL_OLD inventory. On the contrary, PL_NEW inventory provided lower I(cd)P emissions in comparison to PL_OLD inventory.

Seasonal variations of PAH anthropogenic emissions for the GLEMOS model were generated for each emission source sector using monthly temporal factors, based on the TNO estimates of the MACC project [*Denier van der Gon et al.*, 2011].

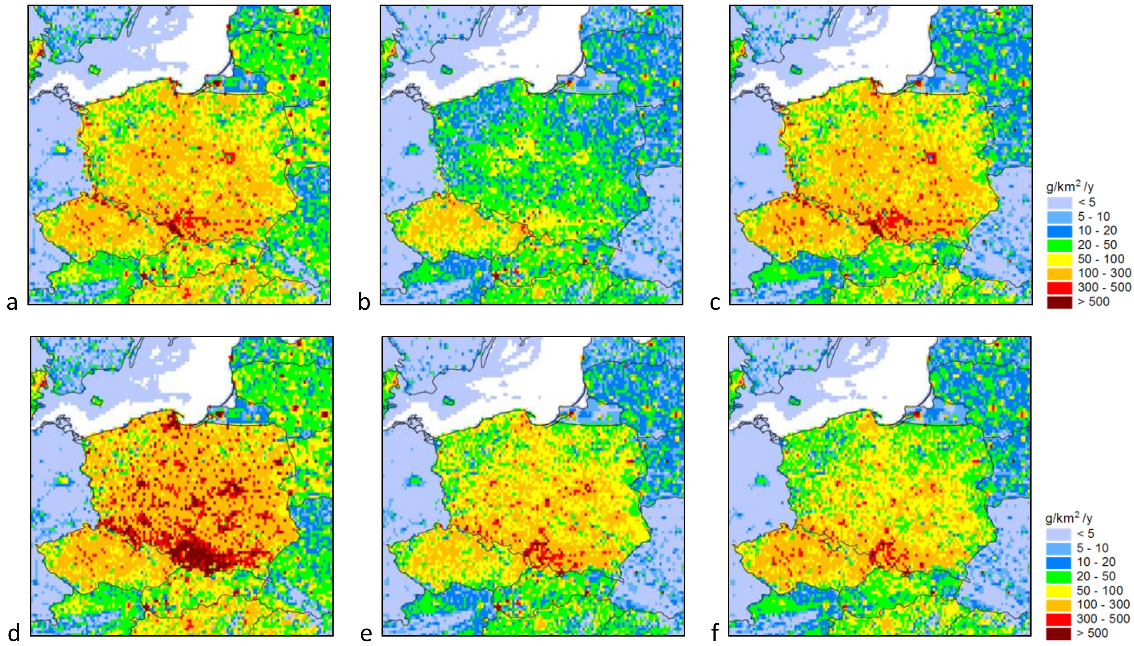

Fig. 4.12. *Spatial distribution of annual emission fluxes in 2018 according to PL_OLD inventory (a,b,c) and PL_NEW inventory (d,e,f) of B(b)F, B(k)F, and I(cd)P, respectively (spatial resolution 0.1°x0.1°).*

Modelling results and analysis

Results of model simulation were evaluated using measurement data of EMEP monitoring network and of EEA AQ e-reporting database. Annual mean modelled air concentrations of B(b)F, B(k)F, and I(cd)P for 2018, simulated using PL_OLD and PL_NEW emission datasets are shown in Fig. 4.13. The largest differences between the simulated air concentrations can be seen over the territory of Poland. Model simulations of B(b)F and B(k)F with PL_NEW emissions provided increased air concentrations whereas simulations for I(cd)P resulted in lower air concentrations compared to simulations with PL_OLD emissions.

Modelled air concentrations were compared with measurements of EMEP monitoring network and background rural, remote, and suburban stations of EEA AQ e-Reporting made in 2018. Statistical indicators of GLEMOS model performance in case of the use PL_OLD and PL_NEW emissions are illustrated in Fig. 4.14. The use of the updated national emission inventory leads to noticeable decrease of the model bias for B(b)F and B(k)F. Along with this, significant improvement of spatial correlation between the modelled and measured values is obtained. At the same time, model simulations of I(cd)P with updated emissions showed increase of model bias and decrease of spatial correlation compared to the simulations with the previous emissions.

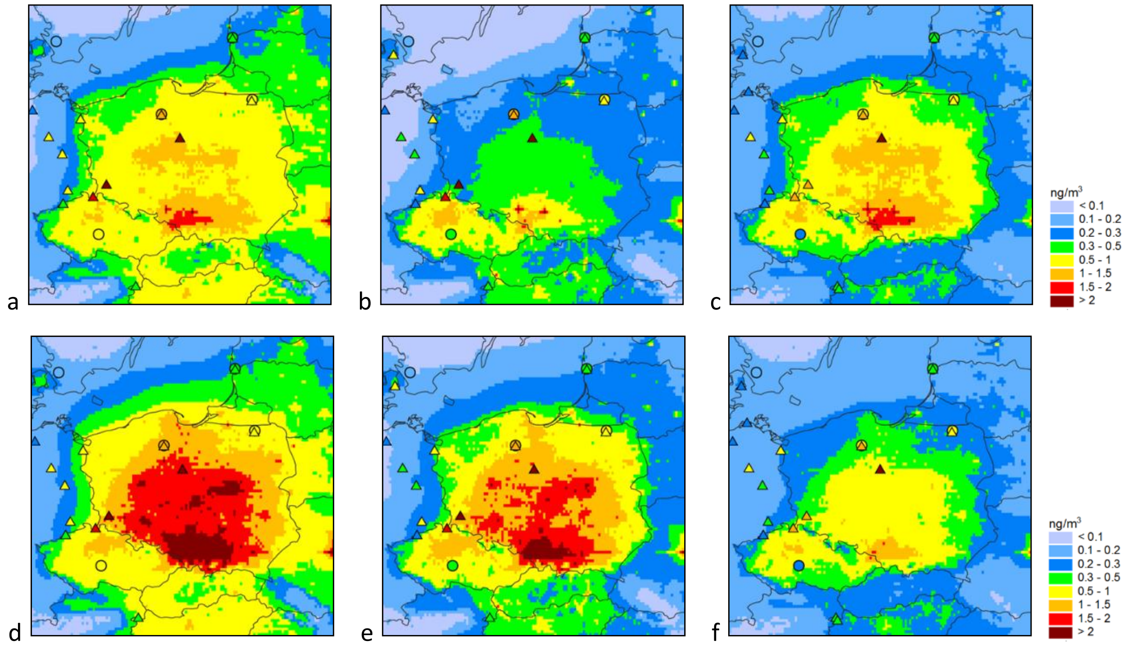

Fig. 4.13. Annual mean modelled air concentrations of B(b)F, B(k)F, and I(cd)P in 2018 simulated using PL_OLD emissions (a,b,c) and PL_NEW emissions (d,e,f), respectively (spatial resolution 0.1°x0.1°). Maps of air concentrations are overlayed with annual mean observed concentrations of B(b)F, B(k)F, and I(cd)P for 2018 in the same scale as the modelling results (circles indicate EMEP stations, triangles – AQ e-reporting stations).

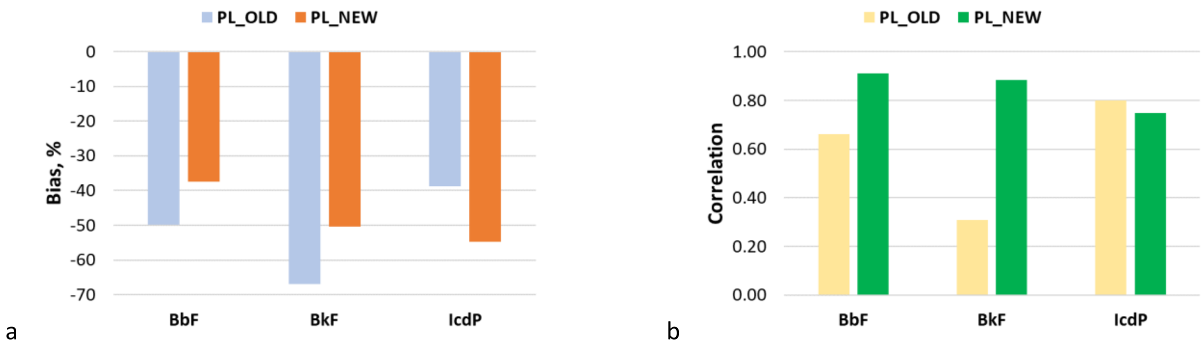

Fig. 4.14. Mean relative bias (a) and spatial correlation (b) between the measured and modelled annual mean air concentrations of B(b)F, B(k)F, and I(cd)P for 2018 simulated using PL_OLD emissions and PL_NEW emissions.

Results of model simulations with the new national emission inventory of 4PAHs for EMEP show that it allows to achieve better agreement with measurements for B(a)P, B(b)F, and B(k)F and improvement of accuracy of pollution assessment. At the same time, application of the new emissions for I(cd)P did not lead to improvement of model estimates. Furthermore, the study showed that modelling results still tend to underpredict observed air concentrations of the 4PAHs. Thus, further activities to reduce uncertainties of the model assessment of PAH pollution are required. They include refinement of emission estimates and model parameterizations of processes affecting PAH fate in the atmosphere. Possible future steps of the case study can include multi-model simulations, application of more detailed temporal and spatial disaggregation of PAH emissions, and co-operation with national experts in monitoring, modelling, and emissions.