



Article Atmospheric Deposition of Benzo[a]pyrene: Developing a Spatial Pattern at a National Scale

Iva Hůnová *🗅, Pavel Kurfürst, Leona Vlasáková, Markéta Schreiberová 🕒 and Hana Škáchová

Czech Hydrometeorological Institute, Na Šabatce 17, 143 06 Praha, Czech Republic; pavel.kurfurst@chmi.cz (P.K.); leona.vlasakova@chmi.cz (L.V.); marketa.schreiberova@chmi.cz (M.S.); hana.skachova@chmi.cz (H.Š.) * Correspondence: iva.hunova@chmi.cz

Abstract: Benzo[a]pyrene (BaP), an indicator of polycyclic aromatic hydrocarbons (PAHs) in the atmosphere, is an important ambient air pollutant with significant human health and environmental effects. In the Czech Republic (CR), BaP, together with aerosol and ambient ozone, ranks (with respect to limit value exceedances and resulting population exposure) among the most problematic air pollutants. The aim of this study is to develop atmospheric deposition patterns of BaP in three years, namely 2012, 2015 and 2019, reflecting different BaP ambient levels. With respect to the available measurements, we accounted for dry deposition fluxes, neglecting wet contribution. We assumed, nevertheless, that the real atmospheric deposition is dominated by dry pathways in our conditions, which is supported by measurements from the rural site of Košetice. The dry deposition spatial pattern was constructed using an inferential approach, with two input layers, i.e., annual mean ambient air BaP concentrations, and deposition velocity of 0.89 cm·s⁻¹. Though our results show an overall decrease in BaP loads over the years, the BaP deposition fluxes, in particular in the broader Ostrava region, remain very high. The presented maps can be considered an acceptable approximation of total BaP deposition and are useful for further detailed analysis of airborne BaP impacts on the environment.

Keywords: benzo[a]pyrene; Czech Republic; dry deposition

1. Introduction

Benzo[a]pyrene (BaP), $C_{20}H_{12}$, belongs among the group of polycyclic aromatic hydrocarbons (PAHs), hydrophobic organic pollutants with a complex chemical structure consisting of several aromatic nuclei [1]. Due to their partial volatility, PAHs in the air may be present both in vapour form and bound to particles facilitating their long-range transport, and their environmental fate is partly dependent on their partitioning between the gas and particle phases [2,3]. Though PAHs' water solubility is low, recent studies suggest that the condensed phase in fog and clouds should not be neglected as a PAH sink, specifically at low temperatures [4].

BaP is a by-product originating from incomplete combustion of organic substances in temperatures ranging between 300 and 600 °C. Its major emission sources are local heating systems, cars, thermal power plants burning fossil fuels, and industrial processes. Hence, it is ubiquitous in the environment, predominantly close to emission sources in impacted regions, including urban and industrialised areas [5]. With respect to regulations, it should be noted, however, that efforts to reduce BaP emissions may be hampered by the climate penalty due to natural climatic variability [6]

BaP is considered one of the most chemically reactive PaHs [7]. Numerous experiments indicate that PAHs are prone to photochemical and/or chemical oxidations [8], though in real conditions, PAH degradation depends strongly on its substrate. BaP, however, can be transported over long distances [9]. In the atmosphere, due to low volatility, it is mostly related to suspended particles (ca 90%), specifically to fine particles PM_{2.5}. A total of 10%



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). of atmospheric BaP at most is assumed to be in gas form [10]. The phase distribution is ambient temperature-dependent [11].

BaP is considered an indicator of PAH loading, as it is stable and exhibits a relatively constant contribution to the carcinogenic activity of PAHs mixture bound to suspended particles [12]. PAHs are dangerous substances with respect both to human health and the environment. They are toxic, mutagenic and carcinogenic, belong among the endogenic disruptors (i.e., substances affecting the endocrine glands) and are immunosuppressive [13,14]. Furthermore, PAHs are harmful with respect to their ability for bioaccumulation in the environment and accumulation in food chains [15]. BaP itself exhibits profound negative effects both on human health and the environment and it belongs among human carcinogens [11]. With respect to the above, the fate, behaviour, transport and removal mechanisms of PAHs, including BaP, in and from the atmosphere have been widely studied [16–18].

In Europe, BaP was reported to exceed the target value of 1 ng m⁻³ [12] at 31% of the measuring sites reporting BaP concentrations to the European ambient air quality database AIRBASE in 2017 [15]. In the CR, with respect to limit value exceedances and population exposure, BaP belongs, along with aerosol and ground-level ozone, among the most problematic ambient air pollutants [19–21]. The aim of this paper was to construct spatial patterns of BaP deposition fluxes for the Czech Republic, as an important input to broader environmental analysis. To address this issue, we used an inferential approach, building on a spatial data-driven model of ambient air BaP levels in detailed spatial resolution of 1×1 km, and an average BaP deposition velocity modelled by EMEP.

2. Materials and Methods

2.1. Monitoring Network

BaP has been monitored in the CR since 1997. The number of monitoring sites has evolved over time (Figure 1) to the current 52 monitoring stations. The stations are situated predominantly in BaP impacted areas (Figure 2). The majority of the stations are located in cities (28 urban and suburban stations). Transport and industrial contributions to BaP are monitored at six traffic and seven industrial stations, whereas background BaP levels are observed at 11 rural monitoring stations. The stations are operated by different owners; most of them, however, are operated by the CHMI.



Figure 1. Changing number of BaP monitoring stations covering the CR in 1997–2019.

BaP is measured in PM_{10} sampled by low- or high-volume samplers on a quartz filter and collected at a three-day frequency at minimum. The samples are processed in a certified chemical laboratory using high-pressure liquid chromatography (HPCL) or gas chromatography with mass detection (GC/MS). The lower detection limit is 0.04 ng·m⁻³ for GC/MS and 0.10 ng·m⁻³ for HPLC. The measurement uncertainty of BaP is up to 25%. BaP concentrations are stored as daily averaged values in the nation-wide Air Quality Information System (AQIS) database [21].



Figure 2. BaP monitoring network, stations selected for time trend analysis are indicated in orange.

2.2. BaP Trends and Seasonal Changes

For the analysis of BaP concentration trends, 18 monitoring stations were selected. Based on the data availability and adequate data coverage, the trends were assessed for 2009–2019. The monitoring stations were classified according to their type, i.e., regional, background suburban, background urban and industrial stations. The set of stations for the time trend assessment was selected based on their data coverage and to represent each zone or agglomeration specified for the ambient air quality evaluation by the Czech legislation (Act 201/2012 Coll., on Clean Air Protection, as amended) by at least one urban/suburban station. This was not possible only for the Moravian-Silesian zone. Industrial stations were evaluated only for the problematic area of the Ostrava/Karviná/Frýdek-Místek agglomeration. With respect to regional sites, only one site, the Košetice station, had a complete time series suitable for the trend analysis.

The input data for the time trend analysis were the annual mean BaP concentrations calculated for sites adhering to sufficient data coverage required by EC directive [12]. The minimum data capture for the annual BaP mean concentrations was 90%, and the minimum data coverage was 33%, accordingly. Furthermore, the measurements had to be distributed over the year to be representative of various conditions for climate and anthropogenic activities. The same principal was adhered to for BaP concentration mapping (Section 2.3).

Temporal trends, i.e., annual averages of BaP concentrations, were analysed using the non-parametric Mann–Kendall trend test with a level of significance of 0.05 [22,23]. This test is among the most widely used statistical methods for this kind of data [24–27] and is particularly useful since it tolerates missing values, and the data need not to conform to any particular distribution. Moreover, as only relative rather than absolute magnitudes of the data are used, this test is less sensitive towards incomplete data capture and special meteorological conditions leading to extreme values that often affect air quality data [28]. If a linear trend is significant, the slope and severity of the trend are estimated by Sen's test [29]. We used R-Studio software (R version 4.0.3; R Foundation for Statistical Computing, Vienna, Austria) for statistical analyses of trends [30]. With respect to the main emission source of BaP, i.e., local heating [21], we assessed concentration trends not only for the calendar year as a whole, but also specified for the winter (October–March) and summer (April–September) periods.

2.3. Ambient BaP Concentration Maps

Maps of annual mean BaP concentrations for three selected years (2012, 2015 and 2019) were used as the main input for preparing spatial patterns of BaP dry deposition fluxes. Air pollution maps of BaP were created using an approach of Regression–Interpolation–Merging Mapping (RIMM [31]) and were prepared by the CHMI during the regular annual ambient air quality assessment [32–34]. A linear regression model followed by an interpolation of its residuals is used for the preparation of concentration maps. Rural and urban maps are prepared separately. The resulting map is created by merging rural and urban maps by population density.

The estimate of concentrations is calculated using the following equation:

$$\hat{Z}(s_0) = c + a_1 \cdot X_1(s_0) + a_2 \cdot X_2(s_0) + \ldots + a_p \cdot X_p(s_0) + \hat{R}(s_0), \tag{1}$$

where \hat{Z} is the estimated concentration value at point s_0 , X_i denotes the various supplementary data, c and a_i are the parameters of the linear regression model and \hat{R} is the spatial interpolation of the residuals of the linear regression model at point s_0 , calculated on the basis of the residuals at the points of measurement. Interpolation of the residuals of the linear regression model at measuring points is performed using ordinary kriging and the inverse distance weighting (IDW) methods [35].

The basic data used for the creation of the BaP concentration maps are the BaP annual mean concentrations measured at 52 individual monitoring stations. Furthermore, additional data used, supplementing the measured BaP concentrations, provide comprehensive information on the entire territory of the CR and indicate a regression dependence on the measured data.

The main secondary supplementary sources of information are outputs of dispersion models, i.e., BaP concentrations, and maps of annual mean PM_{10} or $PM_{2.5}$ concentrations. Dispersion models combine data from emission inventories and meteorological data. For the BaP air pollution maps, annual mean concentrations of BaP provided by EMEP/MSC-E [36–38], the Czech Gaussian model SYMOS [39], and CAMx (Comprehensive Air Quality Model with Extensions, Ramboll, Copenhagen, Denmark) [40], were the secondary data used. Namely, for the 2012 BaP map the SYMOS, for the 2015 BaP map both EMEP and SYMOS, and for the 2019 BaP map both CAMx and SYMOS outputs were used. As BaP in the atmosphere occurs predominantly bound to suspended particles, PM, namely PM_{10} or $PM_{2.5}$, ambient air concentration maps can be utilized as valuable additional data for BaP spatial patterns creation.

The calculated urban and rural map layers are subsequently merged by a layer of population density α :

$$\hat{Z}(s_0) = \begin{cases} \hat{Z}_r(s_0), \text{ for } \alpha(s_0) \le \alpha_1 \\ \frac{\alpha_2 - \alpha(s_0)}{\alpha_2 - \alpha_1} \cdot \hat{Z}_r(s_0) + \frac{\alpha(s_0) - \alpha_1}{\alpha_2 - \alpha_1} \cdot \hat{Z}_u(s_0), \text{ for } \alpha_1 < \alpha(s_0) < \alpha_2 \\ \hat{Z}_u(s_0), \text{ for } \alpha(s_0) \ge \alpha_2 \end{cases}$$
(2)

where \hat{Z} is the final estimate of the concentration at point s_0 , \hat{Z}_r and \hat{Z}_u are the concentration for the rural or urban map layer and α_1 and α_2 are the classification intervals corresponding to the population density. For the BaP concentration maps, α_1 was set to 200 inhabitants per km² and α_2 was set to 1000 inhabitants per km².

The entire concept of separate mapping of rural and urban pollution is based on the assumption that $\hat{Z}_r(s_0) \leq \hat{Z}_u(s_0)$ for BaP. For areas where this assumption is not fulfilled, a third layer created in a similar way to the urban and rural layers is used; this third layer is created using all the background stations without distinguishing between urban and rural stations.

The uncertainty of the map was assessed using the cross-validation method: concentration at the location of a measuring site is always estimated from other station data only, thus providing an objective estimate of the map quality away from measurement site locations. In this study, the uncertainty of the maps is expressed by the relative root-mean-square error (RRMSE):

$$\text{RRMSE} = \frac{\sqrt{\frac{1}{N}\sum_{i=1}^{N} (\hat{Z}(s_i) - Z(s_i))^2}}{\frac{1}{N}\sum_{i=1}^{N} Z(s_i)} \cdot 100$$
(3)

where *Z* is the measured value of the concentration at point Zs_i , \hat{Z} is its estimate using cross-validation and *N* is the number of measuring stations. The spatial distribution of the uncertainty was not estimated. It should be noted that the cross-validation is applied only during the interpolation of residuals; the parameters of linear regression are always estimated using all the stations. Therefore, the overall uncertainty of the maps is somewhat underestimated. The uncertainties (RRMSE) were calculated for each map layer separately and were up to 30% for urban and over 60% for rural areas.

The maps are prepared with a spatial resolution of 1×1 km. The described methodology of map creating is used in the Czech Republic and elsewhere in Europe [10,21,41].

2.4. BaP Deposition Flux Maps

For preparing a spatial pattern of BaP dry deposition flux, we used an inferential approach [1] accounting for a spatial pattern of annual mean BaP concentrations in ambient air (as described in Section 2.3) and annual mean deposition velocity of 0.89 cm·s⁻¹. The deposition velocity value we used was based on an EMEP model [37], a three-dimensional Eulerian chemical transport model working in the geographical domain of the EMEP region, originally in a spatial resolution of 50×50 km. Current air pollution maps are provided in finer resolution, however, namely for 0.1×0.1 geographic degrees, which represents a grid of ca 8×10 km for central Europe. With respect to vertical span, the EMEP model covers practically the entire troposphere, including the upper soil layer to 20 cm of depth and ocean water. Model runs carried out specifically for the CR for 2018 by EMEP modellers [42] demonstrated that monthly means of deposition velocity ranged between 0.18-2.22 cm·s⁻¹, with 0.89 cm·s⁻¹, on average. Dry deposition velocity was highest in summer, with 2.22 cm·s⁻¹ as the monthly mean in June. The terrain roughness, including vegetation presence, contributed to higher deposition velocity.

2.5. Wet-Only BaP Deposition at the Košetice Site

The only station measuring BaP concentrations in precipitation is the National Atmospheric Observatory Košetice (NAOK) run by the CHMI [43]. The NAOK (49°35′ N, 15°05′ E, 534 m above sea level) is situated in the Czech–Moravian Uplands, some 70 km southeast of the capital, Prague, within 20 km of two towns with up to 20,000 inhabitants, with several small villages nearby, and 6 km from a major motorway. The station is classified as a rural background of the CR, reflecting a typical agricultural area. NAOK is affected by local sources of PAHs, as well as regional and long-range transport; high PAH concentrations are related to local heating [44].

BaP has been collected since 1997 at one-day intervals by a wet-only sampler, a device exposed only during a precipitation event, preventing dry deposition from entering. In the beginning, metal pots with lids were employed for manual sampling before being replaced in 2008 by an automated sampler, Baghirra 1 m². The sampled precipitation was analysed by gas chromatography with mass spectroscopy detection (GCH-MS) during the entire measuring period. The annual BaP wet deposition fluxes were estimated as BaP annual volume weighted averages multiplied by annual precipitation amounts.

3. Results

3.1. Ambient BaP Concentration Trends and Seasonal Changes

Annual average BaP concentrations at particular types of stations decreased for the period of 2009–2019, with several fluctuations due to the meteorological and dispersion situations. The highest concentrations were measured at industrial stations in the Ostrava/Karviná/Frýdek–Místek agglomeration. Slightly higher BaP concentrations were



measured at suburban background stations than in urban background stations (Figure 3). This probably indicates the stronger influence of local heating boilers in suburban areas.

Figure 3. Annual average concentrations of BaP at particular types of stations (**a**), at particular types of stations without industrial stations (**b**) and averages from all stations and from all stations without industrial stations (**c**).

On average for all stations, the annual average BaP concentrations for 2009–2019 ranged between 1.6 ng·m⁻³ in 2019 and 2.3 ng·m⁻³ in 2012 (Table 1, Figure 3). The value of 1.6 ng·m⁻³ in 2019 was about 20% lower in comparison with the ten-year average 2009–2018 value of 2 ng·m⁻³ (average of annual average concentrations from all selected stations for 2009–2018). On average, for all stations excluding the industrial ones, the annual average BaP concentrations for 2009–2019 were within a range of 1.0 in 2019 and 1.5 ng·m⁻³ in 2010; the ten-year average 2009–2018 value was 1.3 ng·m⁻³.

Type of Station	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	Mann– Kendall (Tau)	Sen's Slope [ng∙m ⁻³ year ⁻¹]	<i>p-</i> Value
Annual Average BaP Concentration [ng·m ⁻³]														
regional	0.5	0.6	0.4	0.6	0.7	0.4	0.4	0.4	0.5	0.4	0.3	-0.43		0.0983
suburban	1.6	1.7	1.5	1.7	1.6	1.4	1.4	1.3	1.4	1.3	1.1	-0.73	-0.05	0.0025
urban	1.4	1.5	1.4	1.4	1.4	1.3	1.3	1.2	1.3	1.1	1.0	-0.84	-0.04	0.0009
industrial	6.5	5.7	6.1	6.7	5.6	5.7	4.5	4.6	4.8	4.8	4.3	-0.61	-0.22	0.0122
all	2.3	2.2	2.2	2.3	2.1	2.0	1.8	1.8	1.9	1.7	1.6	-0.82	-0.07	0.0007
Winter (October-March) Average BaP Concentration[ng·m ⁻³]														
regional	0.8	1.0	0.7	1.1	1.2	0.7	0.6	0.8	0.9	0.8	0.4	-0.25		0.3433
suburban	2.8	3.2	2.8	3.3	2.9	2.6	2.5	2.3	2.6	2.3	1.9	-0.67	-0.10	0.0060
urban	2.9	2.9	2.8	2.9	2.8	2.5	2.2	2.2	2.4	2.0	1.8	-0.84	-0.11	0.0007
industrial	10.5	10.2	9.7	10.6	8.5	8.7	7.1	7.1	7.5	8.0	6.6	-0.66	-0.39	0.0063
all	3.7	3.8	3.6	3.9	3.4	3.2	3.0	2.9	3.3	3.0	2.5	-0.70	-0.13	0.0039
Summer (April-September) Average BaP Concentration[ng·m ⁻³]														
regional	0.1	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	-0.09		0.8744
suburban	0.3	0.3	0.2	0.3	0.5	0.3	0.3	0.3	0.3	0.2	0.3	-0.11		0.7626
urban	0.2	0.3	0.2	0.3	0.4	0.3	0.2	0.3	0.2	0.2	0.2	-0.23		0.4263
industrial	2.1	1.4	1.7	1.6	1.9	2.0	1.8	2.1	2.2	1.7	2.0	0.30		0.2386
all	0.5	0.4	0.4	0.5	0.6	0.5	0.5	0.6	0.6	0.4	0.5	0.24		0.3997

Table 1. Concentrations of BaP $[ng \cdot m^{-3}]$ at particular types of stations in 2009–2019.

Note: regional—presented by the Košetice station; suburban—presented by the Praha 4-Libuš, Č.Budějovice-Antala Staška, Ostrava-Poruba/CHMI, Ústí n.L.-Kočkov, Zlín stations; urban—presented by the Praha 10-Šrobárova, Brno-Masná, Brno-Líšeň, Pardubice Dukla, Ždár nad Sázavou, Kladno-Švermov, Teplice, Olomouc-Hejčín and Plzeň-Roudná stations; industrial—presented by the Ostrava-Mariánské Hory, Ostrava-Přívoz and Ostrava-Radvanice ZÚ stations; *p*-values < 0.05 are highlighted.

On average for the type of station, the annual average concentrations of BaP exceeded the target value of $1 \text{ ng} \cdot \text{m}^{-3}$ set by a European directive (EC 2004) at industrial, suburban and urban stations. At industrial stations, the annual average concentrations for 2009–2019 ranged from 4.3 to 6.7 ng·m⁻³, on urban stations from 1.0 to 1.5 ng·m⁻³ and at suburban sites from 1.1 to 1.7 ng·m⁻³. At the Košetice regional station, the annual average concentrations were below the target value, ranging from 0.3 to 0.7 ng·m⁻³.

The average annual concentrations for industrial, suburban backgrounds and urban backgrounds, for all stations and overall, exhibited a significant decreasing trend. At the Košetice regional site, however, no significant trend was found. The approximate decrease in the annual average concentration was $-0.07 \text{ ng} \cdot \text{m}^{-3} \cdot \text{year}^{-1}$ (Sen's slope) on average for all stations.

Similarly, statistically significant decreases in average winter concentrations were found for all types of stations except the Košetice regional station. For the winter period, the average decrease for all stations overall was $-0.13 \text{ ng} \cdot \text{m}^{-3} \cdot \text{year}^{-1}$ (Sen's slope). In contrast, no significant trend was found for summer BaP concentrations.

From the above information, it can be concluded that the levels and development of BaP concentrations were significantly affected by the winter period, i.e., the length and temperature of the winter season and the consequent intensity of heating. BaP concentrations can reach high values during the winter period and are measured in a much wider range as compared to the summer concentrations. Based on the measured data, it can be indicated that approximately 90% of the values of daily summer concentrations from all stations for the period 2009–2019 were equal to or less than the target value. In winter, only about 35% of the concentration values from all stations for the period 2009–2019 equalled or were less than the target value (i.e., $1 \text{ ng} \cdot \text{m}^{-3}$).

3.2. BaP Deposition Flux Maps

The spatial distribution of BaP dry deposition fluxes over the CR in 2012, 2015 and 2019 are presented in Figures 4–6. As there are no limit or threshold values for BaP deposition, the deposition flux classes are chosen purely arbitrarily to make presented maps user-friendly and easily comparable among themselves. Our results show the steadily highest BaP loads in the broader Ostrava region in North Moravia, adjacent to the highly industrialised Lower Silesia in Poland.



Figure 4. BaP dry deposition flux over Czech Republic, 2012.



Figure 5. BaP dry deposition flux over Czech Republic, 2015.



Figure 6. BaP dry deposition flux over Czech Republic, 2019.

BaP deposition fluxes have obviously decreased over the years, reflecting the decreasing ambient BaP levels, documented by Table 2 showing the percentages of the CR area under BaP concentrations within defined ambient level classes. While the percentage in the lowest concentration class, i.e., less than $0.4 \text{ ng} \cdot \text{m}^{-3}$ increased over the years, the two highest concentration classes, i.e., above $2 \text{ ng} \cdot \text{m}^{-3}$, and between 1 and $2 \text{ ng} \cdot \text{m}^{-3}$ showed a steady decrease.

	(ng⋅m ⁻³)										
Years	≤0.4	0.4–0.6>	0.6–1.0>	1.0-2.0>	>2.0						
			(%)								
2012	25.5	18.8	29.2	23.8	2.7						
2013	12.1	26.3	44.3	15.2	2.1						
2014	29.8	29.0	30.5	9.0	1.7						
2015	28.3	24.9	26.4	17.5	2.9						
2016	25.0	19.0	30.1	23.1	2.8						
2017	25.8	20.3	27.9	23.0	3.0						
2018	41.2	15.7	30.5	9.9	2.7						
2019	50.6	17.5	23.5	7.1	1.3						

The differences between the recent and past BaP loads can be seen from a spatial pattern in Figure 7, showing the differences between BaP dry deposition fluxes between 2012 and 2019. The dark green colour marks the biggest improvement in BaP deposition between 2012 and 2019, measured in the Ostrava region, Drahanská Vysočina and Chřiby (the areas east of Brno), the vicinity of the town of Most, and the north-western vicinity of the capital, Prague. The most pronounced decreases in BaP deposition (more than $0.5 \text{ mg} \cdot \text{m}^{-2} \cdot \text{year}^{-1}$) were observed in Kladno and Slaný near the capital of Prague, and the relatively largest region with the best improvement is situated north-west of Ostrava, i.e., Havířov, Bohumín and the areas between these towns. The maximum decrease was measured north-east of Bohumín, at the border with Poland. In contrast, slight increases

in BaP deposition fluxes, $0.2 \text{ mg} \cdot \text{m}^{-2}$ at most, were observed in the surroundings of the towns of Železný Brod, Trutnov, Náchod and Broumov in Northern Bohemia, and České Budějovice in Southern Bohemia. About 45% of the CR showed a steady state in BaP deposition fluxes.



Figure 7. Map showing the differences in BaP dry deposition flux between 2012 and 2019.

3.3. Comparison of Wet-Only and Dry BaP Deposition at the Košetice Site

According to our results, dry deposition dominates over the wet-only deposition pathway for BaP for NAOK. The annual wet-only deposition flux, ranging between 0.4 and $1.9 \,\mu\text{g}\cdot\text{m}^{-2}\cdot\text{year}^{-1}$, was on average about 1% in 2005–2020 (Figure 8). The highest wet-only deposition ($1.9 \,\mu\text{g}\cdot\text{m}^{-2}\cdot\text{year}^{-1}$) was recorded in 2010, the lowest ($0.4 \,\mu\text{g}\cdot\text{m}^{-2}\cdot\text{year}^{-1}$) in 2015. The lowest proportion of wet deposition (0.3% equal to $0.6 \,\mu\text{g}\cdot\text{m}^{-2}\cdot\text{year}^{-1}$) was recorded in 2006; the highest proportion, in contrast, was in 2019 (2%, $1.6 \,\mu\text{g}\cdot\text{m}^{-2}\cdot\text{year}^{-1}$).



Figure 8. BaP dry and wet-only deposition fluxes at the NAOK, 2005–2020.

The total BaP deposition at NAOK in 2005–2020 ranged between 74 and 242 μ g·m⁻²· year⁻¹, with the highest value (241.6 μ g·m⁻²·year⁻¹) measured in 2006, and the lowest (74.3 μ g·m⁻²·year⁻¹) in 2020.

4. Discussion

4.1. Ambient BaP Exposure in the CR in Spatial and Temporal Context

The major emission sources of BaP are generally biomass and coal burning in residential heating systems, in particular in old-fashioned and incorrectly operated boilers [45]. In the CR, the major problems with airborne BaP over a long-term basis have been reported in the broader Ostrava region, where the target value of $1 \text{ ng} \cdot \text{m}^{-3}$ is often violated, as many as 7–9 times at some sites [34]. Among the emission sources contributing substantially to this unsatisfactory situation in the broader Ostrava region—in addition to old-fashioned residential boilers—are local steel factories, coking plants and regional air pollution transport from highly industrialised Poland with old-fashioned industries [46–50].

Our results indicated decreasing BaP depositions in 2012–2019, reflecting decreasing ambient BaP levels over the CR. A decrease in concentrations has been especially noticeable since 2014 in accordance with the milder winter seasons of 2014 and 2018, prevailing good dispersion conditions in 2015–2019, and decreasing coal consumption in recent years [21]. Moreover, the significant decrease at two particular stations, i.e., Ostrava-Poruba/CHMI and Kladno-Švermov, belonging among those with the highest, above-target value concentrations in the CR recorded, also point out the effect of improvements in residential heating [20]. In spite of the reported improvement, the broader Ostrava region in Northern Moravia, adjacent to the industrial and highly air-polluted Polish Silesia [51], remains the most BaP-loaded region of the CR [52].

Similar to other studies, e.g., [25,53–55], the typical seasonal behaviour of the BaP concentrations has been recorded. The reasons are generally known, i.e., seasonal BaP emission sources such as residential heating, higher emissions from motor vehicles, and less mixing in the atmosphere due to the thermal inversions [25,55,56]. During warmer seasons, on the other hand, concentrations are less dependent on anthropogenic emission sources. Summer concentrations are mainly determined by atmospheric conditions favourable for ambient air pollutant dispersion, increased chemical and photochemical decomposition of PAHs due to higher levels of solar radiation and high air temperatures [57–59]; hence, the trends in summer concentrations found were not significant.

Our finding of a decrease in BaP deposition fluxes corresponds with decreasing BaP emissions [20], though a decrease in emissions may not be the only cause of this favourable development. Interestingly, Bieser et al. [17], in their study modelling ambient BaP levels over Europe within different emission scenarios, reported that between 2000 and 2020, a large part (ca. 40%) of the ambient BaP concentration decrease was related to reductions in criteria emissions resulting in changed ambient ozone (O_3) formation rather than to a direct BaP emission decrease. O_3 , as the principal chemical degradation agent for BaP, actually affects its ambient levels via photolytic degradation of particulate BaP [11,60]. Indeed, in the CR, a decrease in peak ambient O_3 concentrations has been reported over time [61], though mean O_3 concentrations have been on the increase since 2014 [62].

4.2. Relevance of BaP Dry Deposition for the Estimation of Total BaP Deposition Flux

In our BaP deposition spatial pattern, only dry deposition is considered. The wet contribution to BaP deposition could not be accounted for as there is only one site measuring BaP concentration in precipitation over the country, i.e., Košetice. However, for temperate climates (which is the climate in Central Europe), dry deposition of PAHs may dominate over wet deposition [60,63] and particle deposition seems to be the major pathway for all PAHs [64].

Nevertheless, it must be remarked that deposition fluxes of PAHs are site-dependent and that various authors have reported different predominant mechanisms. For example, Kiss et al. [65] reported comparable wet and dry deposition fluxes for PAHs in Hungary. We can speculate that if the BaP concentrations in the CR were measured in precipitation at several rural sites rather than only one, in particular at sites situated in relatively clean mountain areas, with lower ambient BaP concentrations but higher precipitation amounts, then the relative contribution of wet deposition to BaP deposition on these sites is likely to be higher. We do not expect, however, any radical change in the overall BaP spatial pattern. Meteorology plays a substantial role in deposition patterns, with the highest effect particularly in winter, with respect both to BaP emissions and dispersion conditions. In cold winters, BaP emissions are much higher due to higher demand for residential heating. Additionally the dispersion conditions are frequently deteriorated due to occurrence of the thermal inversions. Furthermore, the transport of air masses plays a crucial role in deposition processes [66,67].

With respect to BaP specifically: BaP bound to particles (aerosol), i.e., BaP as measured by the CHMI, is assumed to form the predominant part of atmospheric BaP due to its low volatility. Guerreiro et al. [10] reported, for Europe, that 90% of BaP is found in particles and only up to 10% are in the gas phase. When applying the TREND model over the European domain, even 100% BaP was assumed to exist in the solid phase with respect to temperatures being closer to 10 °C rather than 20 °C, i.e., the temperature when BaP partitions to the gas phase [68].

4.3. Strength and Limitations of the BaP Concentration and Deposition Maps

4.3.1. Strength of Final BaP Deposition Maps

We have developed BaP deposition maps at the national level in spatial resolution of 1×1 km, using the methodological approach of Regression–Interpolation–Merging Mapping, consisting of merging direct measurements of BaP concentrations in ambient air, models and auxiliary data, and a uniform annual mean deposition velocity of 0.89 cm·s⁻¹ for the entire CR domain. Hence, the final BaP deposition flux spatial patterns are primarily influenced by ambient BaP levels. The maps clearly show the spatial differences in BaP loadings in space and time in detail and indicate regions where human health and environmental effects of BaP can be expected. The maps presented the benefit of long-term regular direct measurements of BaP concentrations in ambient air at different types of sites as classified by EoI [69], reflecting different environments (urban, rural, industrial, traffic), dispersion model outputs and auxiliary data.

4.3.2. Uncertainties in the BaP Concentration Maps

The BaP concentration maps created on the basis of BaP measurements and auxiliary data (i.e., outputs of dispersion models and PM_{10} or $PM_{2.5}$ concentration maps) are burdened by higher uncertainty than air pollution maps for other criteria pollutants, such as SO_2 , NO_x , O_3 , PM_{10} and $PM_{2.5}$. This high uncertainty is due to the inadequate number of direct ambient BaP concentration measurements. At the same time, uncertainty differs for rural and urban maps. The uncertainty estimated by a cross-validation analysis and expressed as the relative RMSE is lower for urban than for rural maps. This consists of a higher number of BaP measurements in urban than in rural areas (e.g., 36 urban and 11 rural stations in 2019). The European directive EC, 2004 [12] requires 60% uncertainty at most for modelling BaP concentrations, and the air pollution maps for urban areas were within this limit, whereas in rural areas, the estimated uncertainty was higher than the required value.

In comparison with European maps of annual mean BaP concentrations, which were prepared by similar methodologies [10,41], the uncertainty of the Czech BaP concentration maps is lower. It is necessary to specify, however, that this 60% includes only the interpolation process itself. Additionally, the quality of BaP concentration maps is also affected by the quality of the input data, i.e., the output of dispersion models and the quality of emission data, and obviously of the directly measured BaP ambient air concentrations. Air pollution maps of BaP, however, have been prepared on the basis of the best data currently available and the best approach currently available, and the maps—despite their higher uncertainty—present a reasonable estimate of BaP pollution levels in the CR.

4.3.3. Uncertainties Due to Deposition Velocity

Fairly high uncertainty may arise from the selection of a proper deposition velocity. Generally, for all ambient air pollutants, deposition velocity is affected by numerous factors, such as meteorological parameters (wind speed, relative humidity, atmospheric stability), properties of the receptor surface and the physical and chemical properties of the substance examined [70]. Hence, deposition velocity can vary in a wide range, whereas an assumption of one constant value is a very crude approximation, which may result in large uncertainty in estimating the deposition flux [1,71]. In the scientific literature, a wide range of deposition velocities for both PAHs as a group and for individual PAHs is reported [72,73]. For BaP as an individual, however, deposition fluxes rather than dry deposition velocities themselves are frequently presented [74,75]. That was the reason we opted for using the deposition velocity computed by the EMEP model. The value of 0.89 cm·s⁻¹ that we worked with is similar to the 0.76 cm·s⁻¹ reported by Chang et al. [76] as an average for three sites in Taiwan.

4.4. BaP at the Košetice Site

The Košetice observatory is the only site in the CR monitoring PAHs, including BaP in both ambient air and precipitation [77]. The reported results for this station indicated higher PAH loading as compared to other European rural sites participating in the EMEP project, surprisingly equalling one-third of the PAH concentration measured in big US cities such as Chicago and Cleveland, likely explainable by different fuel consumption [78]. According to our estimate, the total BaP deposition at NAOK ranged between 74 and 242 μ g·m⁻² per year, with the highest value (241.6 μ g·m⁻² per year) measured in 2006 and the lowest (74.3 μ g·m⁻² per year) in 2020. These deposition fluxes are much higher than these reported by Settimo et al. [79] for Italy and referenced fluxes for some European sites regardless of their type, ibidem.

According to our estimates, wet-only deposition surprisingly contributed regularly only about 1% to the total annual BaP deposition flux at this site. In another recent two years, i.e., 2019 and 2020, the slightly higher proportion of wet-only BaP deposition (2% in 2019 and 1.8% in 2020) was likely due to meteorological conditions: with respect to meteorology, 2019 had exceptionally high air temperature, distinctly better dispersion conditions and the usual annual precipitation amount, and 2020 had considerably higher air temperature, standard dispersion conditions and a higher annual precipitation amount.

The estimated wet-only BaP deposition flux at the Košetice observatory is much lower than might be expected for a rural site—a station representing rural background ambient air pollution levels for the CR. Such a value, however, might be supported by estimates from other sites, such as Lake Superior, for which the dry aerosol deposition was reported to dominate the wet removal mechanism for PAHs by an average ratio of 9:1 [80].

5. Conclusions

We have developed maps of BaP dry deposition fluxes over the CR for 2012, 2015 and 2019 in a spatial resolution of 1×1 km. These spatial patterns have been constructed on the basis of maps of annual BaP concentrations in ambient air and overall deposition velocity of $0.89 \text{ cm} \cdot \text{s}^{-1}$ uniform for the entire territory and over the entire calendar year. Measurements from the only station in the CR measuring BaP concentrations in precipitation, i.e., Košetice, suggested that the wet-only deposition pathway played a negligible role in total BaP deposition in rural areas in the CR. Hence, the dry deposition map of BaP can be considered an acceptable approximation of total BaP deposition flux in conditions of BaP-polluted Central Europe. We have found an overall decrease in BaP deposition fluxes over 2012–2019, reflecting decreasing ambient BaP levels. These were possibly related to decreases in BaP emissions in the CR and reductions in emissions of criteria pollutants in Europe, likely influencing the formation of O₃, a principal chemical degradation agent for BaP. In spite of the presented decrease in BaP deposition fluxes, the broader Ostrava region, adjacent to the industrial Polish Silesia, remains the most BaP-loaded area in the CR. In spite of

the high uncertainty of the BaP deposition maps, resting in the inherent properties of the selected methodological approach, the limitations of which we indicated in the Discussion section, we believe that the maps provided contribute to our better understanding of different BaP loadings in the CR over time. Furthermore, the BaP deposition maps identify the areas with the highest BaP deposition fluxes where environmental impacts can be expected. The spatial pattern of BaP deposition flux is a valuable tool that might be used for a broader environmental analysis relating the impacts of airborne BaP with its impacts on the environment and ecosystems.

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