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Assessment of PAH pollution levels, key sources and trends: contribution to analysis of the effectiveness of the POPs Protocol

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Assessment of PAH pollution levels, key sources and trends: contribution to analysis of the effectiveness of the POPs Protocol

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SUMMARY

This technical report is prepared by MSC-E in accordance with the bi-annual workplan of the Convention for 2020-2021 [ECE/EB.AIR/144/Add.2]. The report presents information on contemporary pollution levels of Polycyclic Aromatic Hydrocarbons (PAHs) in the EMEP countries, their long-term trends, and exceedances of air quality guidelines. This work can be regarded as the contribution to the activities of the Task Force on Techno-Economical Issues and the Task Force on Health, aimed at the analysis of the effectiveness of the POPs Protocol with regard to the reduction of unintentional releases of PAHs and their adverse effects on human health.

PAHs comprise a large group of semi-volatile, hydrophobic organic compounds ubiquitous in the environment. Many of PAHs are known or suspected to have carcinogenic, mutagenic, and teratogenic properties that pose risk to human health and ecosystems. High levels of pollution and lack of decrease of PAH air concentrations in the EMEP countries during two recent decades have been indicated as an important issue in the Long-term Strategy of the Convention [ECE/EB.AIR/2018/1/Rev.1]. The Strategy highlights importance of continued scientific research that can support additional efforts for the reduction of unintentional releases of PAHs in the EMEP region and especially for countries of Eastern Europe, the Caucasus and Central Asia.

Taking into account long-range atmospheric transport, accumulation in the environment, and adverse effects on human health, PAHs are considered as priority pollutants in the regulatory activities of many international (WHO, HELCOM, AMAP, OSPAR, EU, etc.) and national (the USA, Canada, China, etc.) organizations. Particular attention is paid to the compilation of inventories of PAH emissions, monitoring of air pollution levels, content in various products, and exceedances of the guideline values as well as the assessment of population exposure and harmful effects. Within EU a new POPs Regulation (EU) 2019/1021[1] has been recently adopted that contains specific control measures for POPs (including PAHs) aimed at protecting human health and the environment. In 2020, the European Commission announced a proposal to revise the EU air quality standards for priority pollutants, including B(a)P, to make them more stringent and closer to the guidelines recommended by WHO.

Many of PAHs are considered to be hazardous to human health and environment due to their carcinogenic, mutagenic, and teratogenic properties, liver and kidney toxicity, hematological effects, pulmonary and respiratory effects, neurotoxicity. In addition, some of the PAHs are classified as very toxic for aquatic environment in accordance to the EU CLP Regulation[2]. Furthermore, chemical transformations of PAHs in the atmosphere can lead to the formation of other groups of toxic pollutants, such as nitrated and oxygenated PAHs, which may induce more significant toxic effects than parent PAHs.

Approaches to the assessment of PAH pollution levels and adverse effects are often based on the use of B(a)P as a marker compound. However, it should be noted that air quality standards for B(a)P concentrations are still not globally defined, and different limit values are established by various

[1] https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32019R1021&rid=3
[2] https://echa.europa.eu/regulations/clp/legislation

organizations and countries to perform assessment of exceedances. Besides, different methodologies and different number of PAHs are used for the evaluation of population exposure to mixture of toxic PAHs. In particular, 4 PAHs are included in LRTAP POP Protocol, 8 PAHs in the EU REACH Regulation, and US EPA Priority list contains 16 PAHs. The use of extended list of PAHs may help to estimate exposure of population to mixture of toxic PAHs more accurately.

PAHs are mostly released to the environment as unintentional by-products of incomplete combustion of biomass and fossil fuels. Main categories of anthropogenic PAH emissions include domestic burning of wood and coal, industrial activities, road transport, and agricultural sources. It should be noted that the residential combustion sector is also among the most significant contributors to PM emissions. Thus, aerosol particles, emitted from the combustion processes, may be enriched by the toxic PAH compounds.

Despite the application of a number of restrictive measures regarding PAHs in recent decades, long-term risks of PAH pollution still exist, and levels of unintentionally released PAHs remain a concern. Available monitoring data and model predictions show that PAH contamination levels in EMEP countries have not changed significantly over the past twenty years. High level of annual mean B(a)P air concentrations, exceeding the EU target value, is still characteristic of some of the countries of Central and Southern Europe as well as of some of the EECCA countries. Furthermore, significant part of the population of EMEP countries lives in areas with exceeded the WHO reference B(a)P air concentration level.

In order to further improve model estimates of PAH pollution, detailed analysis of pollution levels and testing of new national emission inventory was performed in framework of the case study on PAHs for Poland. This activity is aimed at the analysis and reduction of uncertainties in modelling of PAH long-range transport and fate in the EMEP region. Current stage of the case study is focused on the model assessment of pollution by indicator PAH compound B(a)P. Model simulations with the new emission inventory allowed improving agreement between the model and measurements and indicated possible underestimation of national B(a)P emissions in Poland.

Along with the analysis of long-term changes in PAH pollution levels and exceedances of air quality guidelines, the report provides an overview of information on physical-chemical properties of toxic PAHs, reported national inventories and expert estimates of PAH emissions as well as of the approaches to assess population exposure to PAH pollution. In addition, importance of consideration of wider list of toxic PAHs is emphasized and experimental model simulations are carried out to estimate population exposure to mixture of 16 toxic PAHs. Particular attention is also given to the content of toxic PAHs in chemical composition of PM, emitted from various combustion sources, and their contribution to the adverse effects of aerosol particles. Impact of particulate matter on human health may be more significant due to the presence of toxic constituents, including PAHs, in their chemical composition.

An overview of information, comprised in this technical report, was presented and discussed at the twenty-fourth meeting of the Task Force on Health, held in May 2021. Discussions at the meeting highlighted the importance of further cooperation and data exchange between MSC-E and the Task

Force in the field of evaluation of PAH pollution levels and trends as well as exceedances of target values, required for risk assessment of population exposure to PAHs.

At the further stages of this work detailed assessment of PAH pollution levels in the EMEP countries will be continued with focus on the analysis of population exposure to PAH and atmospheric aerosol from the combustion sources. In particular, MSC-E will contribute to a multi-model analysis of B(a)P pollution levels as a part of the EuroDelta-Carb intercomparison exercise, carried out by the Task Force on Measurements and Modelling. Besides, country scale case studies on B(a)P/PAH pollution for particular EMEP countries will be continued. Furthermore, global/regional scale multi-model evaluation of source-receptor relationships for combustion-related POPs, emitted by anthropogenic and natural emission sources (e.g. wildfires) is planned to be carried out in framework of the Task Force on Hemispheric Transport of Air Pollution activities.

CONTENT

INTRODUCTION

This technical report comprises the outcome of the MSC-E work on the model assessment and analysis of PAH pollution levels in the EMEP countries, carried out in accordance with the bi-annual workplan of the Convention for 2020-2021 [ECE/EB.AIR/144/Add.2]. It represents the final version of the previously published technical progress report of MSC-E [*Gusev and Batrakova*, 2020]. The content of the report includes six chapters. It provides updated information on the ongoing international and national regulatory activities on PAHs (Chapter 1). Chapter 2 presents the summary of information on physical-chemical properties and behavior of PAHs in the environment. Updated information on PAH emissions to the atmosphere in the EMEP region and their long-term changes is given in Chapter 3. In Chapter 4 refined analysis of long-term trends in B(a)P pollution levels and of exceedances of air quality guidelines is presented. Results of country scale case study of PAH pollution in Poland are overviewed in Chapter 5. Information on toxicological properties of PAHs and approaches for the assessment of the toxicity of PAH mixtures is presented in Chapter 6. The Annex to the report provides a compilation of information on physical-chemical properties of 16 PAHs required for model assessment of PAH pollution levels.

1. INTERNATIONAL AND NATIONAL REGULATORY ACTIVITIES ON PAHs

Polycyclic aromatic hydrocarbons (PAHs) comprise a large group of semi-volatile hydrophobic organic compounds ubiquitous in the environment. Many of the PAHs are known or suspected to have carcinogenic, mutagenic, teratogenic properties as well as other health effects. Taking into account long-range atmospheric transport, accumulation in the environment, and adverse effects on human health, PAHs are considered as priority pollutants in the regulatory activities of many international and national organizations including the World Health Organization (WHO), the International Agency for Research on Cancer (IARC), the UNECE Convention on Long-range Transboundary Air Pollution (LRTAP), the Stockholm Convention, the Helsinki Commission (HELCOM), the OSPAR Commission, etc. This section provides a brief overview of current global, regional, and national regulatory activities on PAHs with a focus on air quality objectives.

1.1. The Protocol on POPs under UN ECE LRTAP Convention

Under the Convention on Long-range Transboundary Air Pollution (CLRTAP), the Protocol on POPs (in the Article 3.5) requires the Parties to reduce total annual emissions of PAHs from the level of the emission in the reference year 1990 (or alternative year from 1985 to 1995) by taking appropriate effective measures (Annex V of the Protocol). The list of PAHs considered in the Protocol includes 4 indicator compounds, namely, benzo(a)pyrene (B(a)P), benzo(b)fluoranthene (B(b)F), benzo(k)fluoranthene(B(k)F), and indeno(1,2,3-cd)pyrene (IcdP) (Annex III of the Protocol).

Developed measures and control options, recommended for the reduction of PAH emissions from industrial processes as well as residential combustion and wood preservation installations, are listed in the guidance document on best available techniques to control emissions of persistent organic pollutants from major stationary sources [*ECE/EB.AIR/2009/14*, 2009].

Besides, important activity regarding further development of measures to reduce PAH emissions is the preparation of the Code of good practice for wood-burning and small combustion installations carried out by TF TEI [*ECE/EB.AIR/2019/5*, 2019]. This document is aimed to provide recommendations on good practices and best available techniques for domestic wood heating installations.

Under the LRTAP Convention the Task Force on the Health Aspects of Air Pollution pays significant attention to various aspects related to the exposure and adverse effects of PAHs for population (workplan of the Convention for 2020-2021 [*ECE/EB.AIR/144/Add.2*]). In particular, the Working Group on PAHs of the Task Force is carrying out assessment of the knowledge on harmful effects of airborne PAHs for human health, including evaluation of carcinogenic and non-carcinogenic effects, as well as identification of critical gaps. This activity is coordinated by the WHO European Centre for Environment and Health.

1.2. World Health Organization

The World Health Organization (WHO) identifies PAHs as carcinogenic air pollutants. To evaluate exposure and health effects of PAHs, the WHO methodology is applied that considers B(a)P as a marker of PAH mixture. In particular, unit risk for lung cancer of carcinogenic fraction of PAHs was estimated to be 8.7×10^{-5} per ng m^{-3} of B(a)P [*WHO*, 2017]. In accordance with this approach, corresponding B(a)P concentrations for lifetime exposure, producing excess lifetime cancer risks of 10^{-4}, 10^{-5}, and 10^{-6}, were estimated to 1.2, 0.12, and 0.012 ng m^{-3}, respectively. The level of 0.12 ng m^{-3} of B(a)P was defined as a reference level of air concentrations that corresponded to the excess lifetime cancer risk level of 10^{-5}.

The WHO expert meeting on the future update of the WHO Air Quality Guidelines noted that along with carcinogenic effects, the evidence of non-cancer endpoints (e.g. cardiovascular system, neurodevelopment or effects on birth weight) was also recently recognized for B(a)P. Thus, taking into account non-cancer health effects as well as exceedances of EU target value 1 ng m^{-3} in some European countries, health evidence for B(a)P and other toxic PAHs should be re-evaluated [*WHO*, 2016].

A number of recent WHO studies were devoted to investigation of the health risks from particular matter (PM) in correlation with chemical composition of PM [*WHO*, 2013a,b]. Currently used WHO air quality guidelines for PM are set without taking into account the presence of hazardous substances in their composition. However, the carcinogenic effects of PM, originated from combustion sources, could be related to the carcinogenicity of the compounds, presented in PM chemical composition (e.g. PAHs and their nitro- and oxy- derivatives) [*WHO*, 2016].

Along with evaluation of toxicity of atmospheric PAH concentrations, B(a)P is also used as an indicator for estimation of PAH toxicity for drinking water. Based on carcinogenic properties of B(a)P, WHO sets out guideline value for B(a)P water concentrations equal to 0.7 µg L^{-1}, which corresponds to lifetime cancer risk of 10^{-5} [*WHO*, 2011].

1.3. International Agency for Research on Cancer

International Agency for Research on Cancer (IARC) evaluated the carcinogenic risk for human health due to PAH exposure based on existing experimental data. About 60 PAHs were included in the IARC Monographs Programme [*IARC*, 2010]. Among the studied PAHs, benzo(a)pyrene was classified as carcinogenic to humans (Group 1). Dibenz(a,h)anthracene and benz(a)anthracene were classified as probably carcinogenic to humans (Group 2A), while benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, chrysene, and indeno(1,2,3-cd)pyrene were classified as possibly carcinogenic to humans (Group 2B). Other considered PAHs were evaluated to be not classifiable with regard to their carcinogenicity to humans (Group 3), because of limited or inadequate experimental evidence [*IARC*, 2010] (Table 1).

It was also mentioned that epidemiological studies of human exposure to individual PAHs were complicated by that these compounds never occurred in isolation in the environment rather being components of complex chemical mixtures [*IARC*, 2019].

Table 1. *IARC classification of PAHs [IARC, 2010; IARC 2012]*

PAH	Group	PAH	Group
Benzo(a)pyrene	1	Benzo[e]pyrene	3
Benz(a)anthracene	2A	Chrysene[3]	3
Dibenz(a,h)anthracene	2A	Fluoranthene	3
Benzo(b)fluoranthene	2B	Pyrene	3
Benzo(j)fluoranthene	2B	Fluorene	3
Benzo(k)fluoranthene	2B	Benzo(ghi)perylene	3
Indeno(1,2,3-cd)pyrene	2B	Anthracene	3
Naphthalene	2B	Phenanthrene	3

1.4. The Stockholm Convention on POPs

PAHs are not currently listed among the POPs considered in the annexes of the Stockholm Convention. Nevertheless, a number of Parties to the Convention (e.g. Germany, Poland) includes PAHs in their national implementation plans (NIPs) as the substances of high concern, pointing out the need of monitoring of their content in environmental media. These NIPs are developed in accordance with the Article 7 of the Convention by each party and describe national obligations under the Convention. PAHs were proposed to be considered as new POP candidates to the Stockholm Convention by the World Wildlife Fund [*WWF*, 2005].

1.5. EU Regulation

Within EU a target value for PAHs in air has been established in the Directive 2004/107/EC. This value is defined in terms of concentration of B(a)P, which is used as a marker substance for PAHs. EU target value for B(a)P annual mean air concentrations was set to be equal 1 ng m^{-3}. Similar threshold level of B(a)P air concentrations was also established as an air quality standard in a number of other countries in the EMEP domain (e.g. in the EECCA[4] countries). Along with B(a)P, the Article 4 of the Directive 2004/107/EC requires that each Member State shall monitor other PAHs (benzo(a)anthracene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene, and dibenz(a,h)anthracene) at the same monitoring sites to assess the contribution of benzo(a)pyrene in contamination of ambient air.

[3] *IARC updated classification of Chysene to 2B (https://monographs.iarc.who.int/list-of-classifications)*
[4] *EECCA – Eastern Europe, Caucasus and Central Asia*

Some of the Member States have set their own air quality standards for B(a)P that are not mandatory (Table 2).

Table 2. *Non-mandatory ambient air quality standards for the B(a)P [Ravindra et al., 2008]*

Country	Limit value [5] ($ng\ m^{-3}$)	Guide value[6] (annual average) ($ng\ m^{-3}$)
Belgium	1.0	0.5
Croatia	2.0	0.1
Germany		10.0
Netherlands	1.0	0.5
France	0.7	0.1
Italy	1.0	
Sweden		0.1
UK		0.25

Besides, PAHs are identified as priority substances by EU Water Framework Directive (2000/60/EC). PAHs are listed in Annex X, which contains pollutants to be reduced in waste water discharge. In accordance with the EU Directive 2008/105/EC, environmental quality standards in the field of water policy are established for some PAHs (Table 3). It should be noted that most of limit values are established for B[a]P as a marker for other PAHs, however fluoranthene is considered separately.

Table 3. *EU environmental quality standards for PAHs*

Emission medium	Maximum allowable concentration	Annual average value
Inland surface waters[7]		
Benzo(a)pyrene	0.27 $\mu g\ L^{-1}$	$1.7x10^{-4}$ $\mu g\ L^{-1}$
Benzo(b)fluoranthene	0.017 $\mu g\ L^{-1}$	
Benzo(k)fluoranthene	0.017 $\mu g\ L^{-1}$	
Benzo(ghi)perylene	$8.2x10^{-3}$ $\mu g\ L^{-1}$	
Fluoranthene	0.12 $\mu g\ L^{-1}$	0.0063 $\mu g\ L^{-1}$
Other surface waters		
Benzo(a)pyrene	0.027 $\mu g\ L^{-1}$	$1.7x10^{-4}$ $\mu g\ L^{-1}$
Benzo(b)fluoranthene	0.017 $\mu g\ L^{-1}$	
Benzo(k)fluoranthene	0.017 $\mu g\ L^{-1}$	
Benzo(ghi)perylene	$8.2x10^{-4}$ $\mu g\ L^{-1}$	
Fluoranthene	0.12 $\mu g\ L^{-1}$	0.0063 $\mu g\ L^{-1}$
Biota		
Benzo(a)pyrene	5.0 $\mu g\ kg^{-1}$ wet weight	
Fluoranthene	30 $\mu g\ kg^{-1}$ wet weight	

[5] Limit value may not be exceeded

[6] Exceeding the guide value should be avoided

[7] Inland surface waters encompass rivers and lakes and related artificial or heavily modified water bodies (https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A02008L0105-20130913#E0030)

The EU Commission in 2013 proposed a Clean Air Programme for Europe, which sets out new air quality objectives for the period up to 2030 [*EC*, 2013]. The main regulative instrument for this purpose is the EU Directive 2016/2284 on the reduction of national emissions of certain atmospheric pollutants entered into force in 2016. PAHs are included in Tables A, C and D of the Annex I of the Directive. Member States shall prepare and update on a timely basis national emission inventories and projections for PAHs, including preparation of informative inventory reports.

In 2019 a new EU Regulation on POPs (2019/1021) was published in the EU Official Journal [*ECHA*, 2019]. Under revised POPs Regulation the European Chemicals Agency (ECHA) is responsible for administrative, technical and scientific aspects of its implementation and for the exchange of information. One of the main new tasks of ECHA is to support an identification of new POP substances for listing in the Stockholm Convention and Protocol to the Convention on Long-Range Transboundary Air Pollution on Persistent Organic Pollutants.

ECHA takes into consideration 4 PAHs under POPs Regulation and 8 PAHs under REACH Regulation (see Table 4). All of these PAHs are classified as carcinogens of Category 1B and as very toxic for aquatic organisms [*EC*, 2008].

Table 4. *Classification of 8 PAHs according to the EU CLP Regulation.*

Name	Carcinoge-nicity	Mutagenicity	Toxicity for reproduction	Aquatic acute toxicity	Aquatic chronic toxicity
Benzo(a)pyrene	Cat. 1B	Cat. 1B	Cat. 1B	Cat. 1	Cat. 1
Benzo(e)pyrene	Cat. 1B			Cat. 1	Cat. 1
Benzo(a)anthracene	Cat. 1B			Cat. 1	Cat. 1
Dibenzo(a,h)anthracene	Cat. 1B			Cat. 1	Cat. 1
Benzo(b)fluoranthene	Cat. 1B			Cat. 1	Cat. 1
Benzo(j)fluoranthene	Cat. 1B			Cat. 1	Cat. 1
Benzo(k)fluoranthene	Cat. 1B			Cat. 1	Cat. 1
Chrysene	Cat. 1B			Cat. 1	Cat. 1

B(a)P is included in the Candidate List of substances of very high concern for authorization in accordance with the REACH regulation [*EC*, 2006]. Besides, the regulation (Annex XVII) provided restrictions on the content of PAHs in a number of products (e.g. B(a)P content in car tyres or their parts should be below 1 mg kg^{-1} (0,0001 % by weight) and content of the sum of all listed PAHs below 10 mg kg^{-1} (0,001 % by weight); for toys and childcare articles the content of any of the listed PAHs shall not exceed 0.5 mg kg^{-1} (0.00005% by weight)).

The EU Commission Regulation 835/2011 [*EU*, 2011] sets out limit values for B(a)P and the sum of benzo(a)pyrene, benz(a)anthracene, benzo(b)fluoranthene, and chrysene in food stuff [*HBM4EU*, 2018].

The EU Commission adopted a proposal for revised drinking water directive [*EU*, 2017]. Parametric values for PAHs and B(a)P are included in Part B of the Annex I of the directive. This document sets out limit value for B(a)P equal to 0.01 µg L^{-1}, and for the sum of considered PAHs

(benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene, and indeno(1,2,3- cd)pyrene) equal to 0.1 µg L^{-1}. Information on other EU regulations for B(a)P can be found on the ECHA website[8].

In 2020, the European Commission announced revision of the Ambient Air Quality Directives, which is scheduled for 2022[9]. The proposal was initiated taking into account zero pollution ambition of European Green Deal and is aimed to improve existing EU legislation to reduce the negative effects of air pollution on human health and the environment. It is planned to revise the EU air quality standards, including those for B(a)P, to make them closer to the guidelines recommended by WHO.

1.6. Helsinki Commission

PAHs are listed among the hazardous substances selected within the Helsinki Commission (HELCOM) for the integrated assessment of Baltic Sea pollution status. The assessment uses core indicators, for which quantitative threshold values are set up. The core indicators provide the information on the selected substances of high concern to the Baltic Sea in accordance with the HELCOM Baltic Sea Action Plan and HELCOM monitoring programme. In particular, this list includes hazardous substances (or substance groups) that are persistent, toxic, accumulating in biota, and posing hazard to the environment [*HELCOM*, 2013].

The following PAHs were selected for the monitoring and assessment, namely, benzo(a)pyrene, fluoranthene, and anthracene (Table 5). Integrated assessment includes monitoring of the concentration of three PAHs in biota and sediments and comparison to specific threshold values.

Table 5. *HELCOM hazardous substances indicator details and threshold values [HELCOM, 2018a], TOC – total organic carbon, QS – quality standard, EQS – environment quality standard.*

Substance	Assessment	Threshold
Benzo(a)pyrene	Biota (primary)	5 µg kg^{-1} wet weight crustaceans and mollusks (EQS)
Fluoranthene	Biota (secondary)	30 µg kg^{-1} wet weight crustaceans and mollusks (EQS)
Anthracene	Sediment (secondary) (Normalized to 5% TOC)	24 µg kg^{-1} of dry weight sediment (QS from EQS dossier)

In accordance with the HELCOM core indicator report, major sources of PAHs in the Baltic Sea include shipping activities and atmospheric deposition [*HELCOM*, 2018b].

[8] ECHA website https://echa.europa.eu/legislation-obligation/-/obligations/100.000.026
[9] https://ec.europa.eu/environment/air/quality/revision_of_the_aaq_directives.htm

1.7. OSPAR Convention

Under the OSPAR Convention PAHs are included in the list of chemicals for priority action (Part A) [*OSPAR*, 2013] and the list of substances of possible concern[10]. PAHs are among the substances, for which OSPAR continues monitoring of pollution levels and evaluation of necessity for additional measures, including filling the knowledge gaps. Since downward trends of PAHs are not observed in all OSPAR assessment areas, additional actions might be considered, which make it possible to move towards the cessation target. Besides, it is supposed that OSPAR will update the background document on PAH which will present information on environmental and regulatory status [*OSPAR*, 2019].

1.8. Arctic Monitoring and Assessment Programme

Under the Arctic Monitoring and Assessment Programme (AMAP) studies of environment pollution are mostly focused on the 16 USEPA priority PAHs due to adverse effects and accumulation in Arctic fauna. PAH concentrations are monitored for all environmental media including the atmosphere (air, snow), terrestrial compartments (soil, biota), freshwater and seawater compartments (water, sediment, biota). At the same time, it is pointed out that the set of 16 PAHs may not be sufficient for the risk assessment, and other substances like nitro-, oxy-, and hydroxy-PAHs, as well as heterocyclic PAHs (thiophenes, azaarenes), may contribute significantly to total toxicity of PAHs for ecosystems [*AMAP*, 2017].

1.9. PAH regulation in the USA

PAHs are included into the lists of priority pollutants prepared by the US EPA and Agency for Toxic Substances and Disease Registry (ATSDR). The agency considers 17 PAHs, namely, acenaphthene, acenaphthylene, anthracene, benz(a)anthracene, benzo(a)pyrene, benzo(e)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(j)fluoranthene, benzo(k)fluoranthene, chrysene, dibenz(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-c,d)pyrene, phenanthrene, and pyrene. For these pollutants monitoring of their concentrations in air, water, and soil and regulation are required. Selection of the PAHs is based on the information on their harmful properties, probability of exposure to these PAHs, and availability of the monitoring methods [*ATSDR*, 1995].

The US EPA priority list includes 16 PAHs (similar to ATDSR list except of benzo(j)fluoranthene). Despite the fact that in most countries this list is not prescribed by law, EPA priority PAH list is often used for the assessment of exposure to PAH mixtures and estimation of hazard to the environment. The list of 16 USEPA PAHs was issued in 1976, and recent studies suggest that this list should contain more compounds of this group [*Andersson and Achten*, 2015].

[10] https://www.ospar.org/work-areas/hasec/hazardous-substances/possible-concern/list

PAHs are listed as hazardous air pollutants to be regulated under the US Clean Air Act [*US Code*, 2018]. Emissions of hazardous air pollutants, including PAHs, are covered by the Section 112 of the Clean Air Act. PAHs are considered in this regulation as Polycyclic Organic Matter (POM), which contain organic substances with at least two aromatic rings, and which have a boiling point greater than or equal to 100 °C [*US Code*, 2018]. Guidance for locating and estimating air emissions from sources of POM [*EPA*, 1998] recommends the use of 16 PAHs to estimate emissions of POM.

In addition, EPA established the water quality criteria for PAHs is established by USEPA, which contain recommended national limits for PAHs. With regard to drinking water, the Maximum Contaminant Level (MCL)[11] of 0.002 mg L^{-1} for benzo(a)pyrene (as a marker of PAHs) and zero content as the Maximum Contaminant Level Goal (MCLG)[12] is established by the Safe Drinking Water Act [*EPA*, 2009].

1.10. PAH regulation in Canada

Evaluation and regulation of PAH pollution levels in Canada is performed using the Canadian Environmental Protection Act [*CEPA*, 1994]. Selected PAHs, namely, benzo(a)pyrene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, and indeno(1,2,3-cd) pyrene, are considered as the most toxic under CEPA and are included in the list of priority substances for the assessment. The legislative acts of Canada established limit values for B(a)P in ambient air (Table 6). It should be noted, that different air quality criteria are set for different provinces of the country [*Tevlin et al.*, 2021]. Canadian environmental quality guidelines for soil, water and sediment can be found in [*Berthiaume*, 2019].

Table 6. *Canadian ambient air quality objectives for B(a)P.*

Jurisdiction	Limit values	Reference
Alberta Ambient Air Quality Objectives and Guidelines	Benzo(*a*)pyrene: 0.3 ng m^{-3} (annual average concentration)	*Government of Alberta* [2019]
Ontario Ambient Air Quality Criteria	Benzo(*a*)pyrene as a surrogate of total PAHs Annual: 0.01 ng m^{-3} 24-hour: 0.05 ng m^{-3}	*Government of Ontario* [2019]
Quebec Air Quality Guideline	Benzo(a)pyrene 0.9 ng m^{-3}	*MDDEP* [2010]

Information on releases of pollutants, including emissions to air, which is reported by enterprises of Canada, is gathered by the National Pollutant Release Inventory (NPRI). Besides, data on anthropogenic emissions at the national and provincial levels, taking into account emissions from residential and mobile sources, are collected in the Air Pollutant Emissions Inventory (APEI).

[11] *The highest level of a contaminant that is allowed in drinking water. MCLs are set as close to MCLGs as feasible using the best available treatment technology and taking cost into consideration. MCLs are enforceable standards [EPA, 2009].*

[12] *The level of a contaminant in drinking water below which there is no known or expected risk to health. MCLGs allow for a margin of safety and are non-enforceable public health goals [EPA, 2009].*

According to recent studies, forest fires are estimated to be important sources of PAH pollution in Canada, followed by domestic combustion and mobile sources, while the total contribution of industrial sources is insignificant [*Berthiaume et al.*, 2021].

For regulation of B(a)P content in drinking water in Canada the maximum acceptable concentration (MAC) equal to 0.04 μg L^{-1} is established. Ontario Drinking Water Quality Standards[13] provides stricter value of MAC for B(a)P equal to 0.01 μg L^{-1} [*Health Canada*, 2016].

1.11. PAH regulation in China

Air pollution levels in China are regulated using the Ambient Air Quality Standards[14]**.** The limit values for air pollutants are set depending on the Class of the region. In particular, Class 1 is applied to special regions and national parks, whereas Class 2 is applied to all other areas. A number of recent studies China scientists paid special attention to the investigation of adverse effects of PM considering chemical composition of particles (including PAH content) [*Kong et al.*, 2010; *Li et al.*, 2017; *Zhao et al.*, 2020]. So, Table 7 demonstrates limit values, established for B(a)P, $PM_{2.5}$, and PM_{10} by Chinese government.

Table 7. *Ambient air quality standards in China.*

Pollutant	Limit values, μg m^{-3}	
	Class 1	**Class 2**
Benzo(a)pyrene	0.001 (annual) 0.0025 (24 hours)	0.001 (annual) 0.0025 (24 hours)
PM 2.5	15 (annual) 35 (24 hours)	35 (annual) 75 (24 hours)
PM 10	40 (annual) 50 (24 hours)	70 (annual) 150 (24 hours)

It should be noted, that air quality standard in China regulates only B(a)P without consideration of other PAHs. Nevertheless, the most of Chinese studies of air pollution include 16 EPA PAHs for the risk assessment.

Summarizing, significant amount of international and national regulatory efforts is directed to reduce PAH pollution levels in the environment and in specific products. However, different number of toxic PAH compounds are still used in the methodologies for the evaluation of emissions, analysis of pollution levels, and risk assessment by various international organizations and countries. Besides, no globally defined environmental standards for toxic PAHs is available. This points out to the need of further work on harmonization of approaches for the assessment and regulation of PAH releases to the environment and adverse effects.

[13] *Ontario Regulation 169/03; Safe Drinking Water Act, 2002 (https://www.ontario.ca/laws/regulation/030169)*

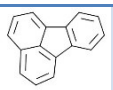
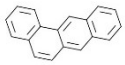
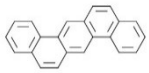
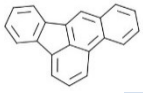
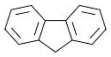
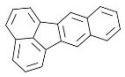
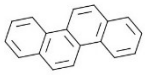
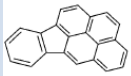
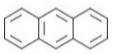
[14] *National Standard GB 3095-2012 (http://english.mee.gov.cn/Resources/standards/Air_Environment/quality_standard1/201605/W020160511506615956495.pdf)*

2. PHYSICAL-CHEMICAL PROPERTIES OF PAHs AND DISTRIBUTION IN THE ENVIRONMENT

2.1. General characteristics

Polycyclic aromatic hydrocarbons include thousands of individual compounds but practically only 16 or less PAHs are usually determined as priority pollutants (Table 8). The considered PAHs can be divided into three groups: low-molecular weight PAHs, containing 2-3 aromatic rings, medium-molecular weight PAHs with 4 rings, and high-molecular weight PAHs (5 rings and more). These PAH groups are characterized by very different physical-chemical properties, which have impact on their long-range transport and partitioning between environmental compartments [*Ma et al*., 2010]. Besides, some of the physical-chemical properties depend on temporal variability of environmental characteristics (e.g. temperature, humidity) that leads to significant seasonal variations of environmental fate of PAHs [*Miura et al*. 2019].

Table 8. *Molecular structure of selected PAHs.*

Substance	Structure	M, g/mol	Substance	Structure	M, g/mol
Benzo(a)pyrene		252.31	Fluoranthene		202.26
Benzo(a)anthracene		228.29	Pyrene		202.25
Dibenzo(a,h)anthracene		278.36	Naphthalene		128.17
Benzo(b)fluoranthene		252.31	Fluorene		166.23
Benzo(k)fluoranthene		252.31	Acenaphthene		154.21
Chrysene		228.29	Benzo(g,h,i)perylene		276.33
Indeno(1,2,3-cd)pyrene		276.33	Anthracene		178.23
Acenaphthylene		152.19	Phenanthrene		178.23

PAHs are solid compounds with relatively high melting and boiling points that increase with increasing of molecular weight. At the same time, the values of subcooled liquid vapor pressure and solubility in water of PAHs decrease with increasing molecular weight (Fig. 1) [*WHO*, 2010; *Achten and Andersson*, 2015]. As seen, the vapour pressure of individual PAHs differs by more than 10 orders of magnitude, which affects their predominant state and partitioning between the gaseous and particulate phases in the atmosphere. PAHs with two and three aromatic rings occur in atmosphere mainly in the gaseous phase, while PAHs with five rings and more are predominantly in the particulate phase. Besides, low-molecular weight PAHs are characterized by lower value of equilibrium partitioning coefficients between octanol and air (K_{OA}, Fig. 1) that also determine their presence in air predominantly in the gaseous phase, as contrasted with high-molecular weight PAHs.

Gas-particle partitioning strongly influences all the other processes (degradation and media exchange).

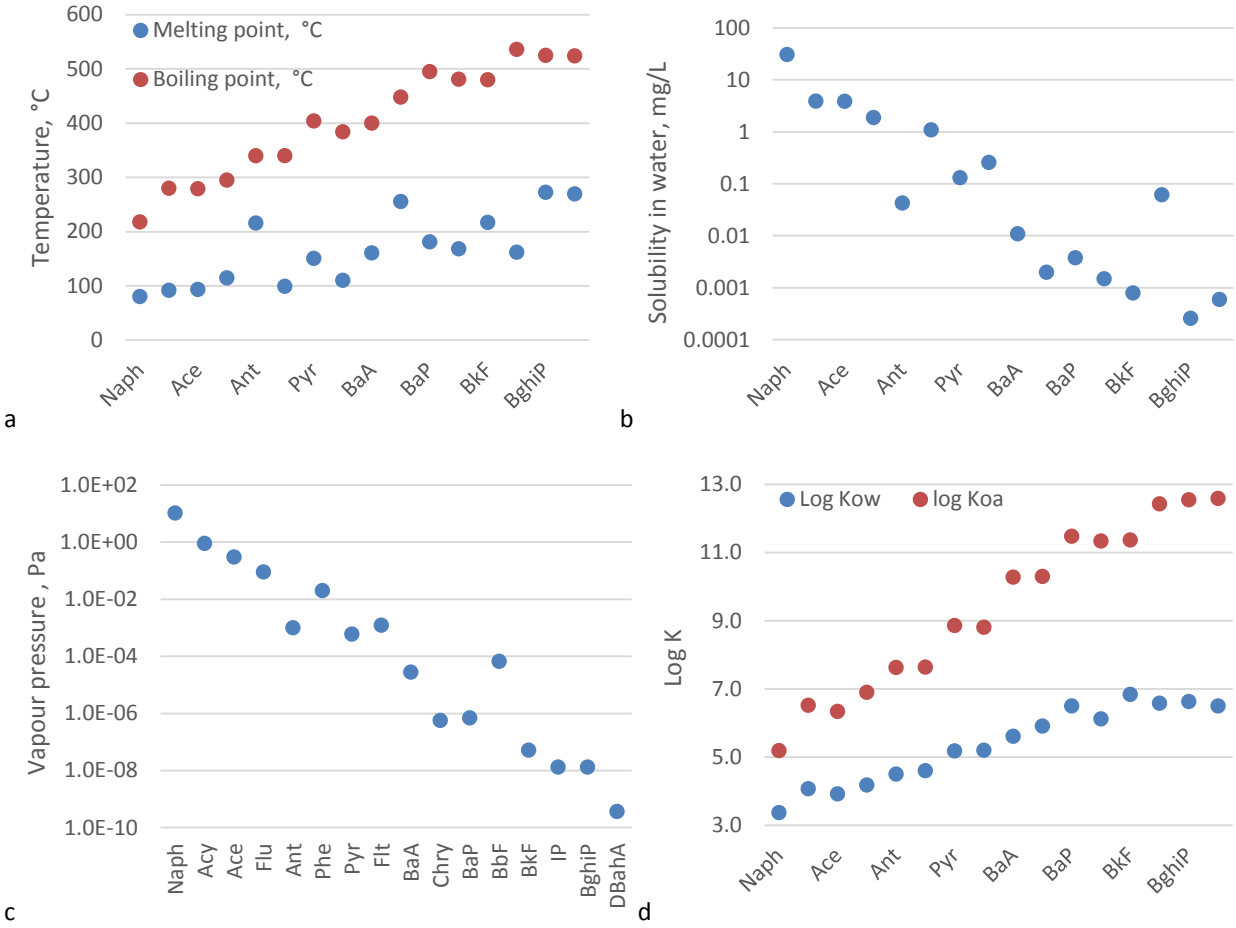


Fig. 1. *Melting and boiling points (a), solubility in water (b), subcooled liquid vapor pressure (c), octanol-air and octanol-water partitioning coefficients (d) of selected PAHs (PAHs are shown in order of increasing molecular weight).*

Other important physical-chemical characteristics of PAHs include equilibrium partitioning coefficients between octanol and water (K_{OW}), as well as between air and water (K_{aw}). The octanol-water partition coefficient of PAHs is relatively high (logK_{OW} value is from 3.37 to 6.84 [*Lammel et al.*, 2015]), so these compounds may be bio-concentrated in living organisms [*ECHA*, 2009], especially for PAHs with logK_{OW} greater than 4.5 (See Table A.6 in the Annex A). The air-water partitioning coefficients of low- and high-molecular weight PAHs can differ by about 3 orders of magnitude (logK_{aw} equal from -1.73 for naphthalene to -4.77 for benzo(g,h,i)perylene) that leads to a greater ability to wet deposition of PAHs with 5 rings or more compared to light PAHs [*Ma et al.*, 2010].

The behaviour of various PAH species in the environment is governed by several processes that include phase partitioning, degradation in, and exchange between the atmosphere and other environmental media. Brief description of these processes is given below, while more comprehensive review can be found in [*Wang et al.*, 2016; *Keyte et al.*, 2013; *Ravindra et al.*, 2008].

2.2. PAHs in ambient air

The most important processes that determine the fate of PAHs in the atmosphere are their partitioning between gaseous and particulate phases and chemical transformations (decomposition) [*Lohmann and Lammel*, 2004; *Keyte et al.,* 2013]. As was mentioned, gas-particle partitioning of various PAHs depends on the amount of fused aromatic rings in their chemical structure. Other factors influencing these processes include variability of environmental conditions as well as the concentration and composition of aerosol particles (for instance, fraction of organic matter and black carbon in aerosol).

Gas-phase PAHs have a short half-life in the atmosphere [*Mackay et al*., 2006]. Degradation of the gas-phase PAHs occurs predominantly by OH radical, while reactions with NO_3 radical and ozone are of minor importance [*Mu et al*., 2018]. Reaction with OH radical in most of the cases leads to a half-life in the air of less than one day [*Vione et al*., 2004]. For that reason, potential for long-range transport in the atmosphere is probably not high for PAHs in gaseous phase. However, when PAHs are included in the composition of aerosol particles, their lifetime in the atmosphere is expected to increase that leads to increasing of long-range transport potential [*Blepp et al*., 2012]. For particulate phase PAHs, degradation occurs mainly through the reactions with ozone.

It should be noted, that specificity of degradation processes affects seasonal variability of PAH fate in ambient air. The degradation rate depends on temperature and concentration of OH radicals which are higher in summer. Hence, concentrations of PAHs in air as well as long-range atmospheric potential are expected to be much higher in winter than in summer [*Beyer et al*., 2003, *Lammel et al*., 2009].

Chemical transformations of PAHs may result in formation of other group of toxic pollutants such as nitrated PAHs (nitro-PAHs) and oxygenated PAHs (oxy-PAHs). PAH derivatives are usually less volatile (in comparison with parent PAHs), respectively, they are more associated with particles [*Vione et al*., 2004].

Nitro-PAHs can be formed as a direct product of incomplete combustion, and also from nitration of PAHs in the atmosphere [*WHO*, 2003a]. Chemical transformations can occur via gas phase reactions with OH and NO_3 radicals or heterogeneous reactions on particles. Nitrated PAHs, are not well-studied, but recently this group of the contaminants has received increasing attention due to their high toxicity [*Nagato and Hayakawa*, 2019]. Levels of nitro-PAH concentrations are lower comparing to the parent PAHs [*Huang et al*., 2014; *Uno et al.,* 2017], however some studies showed their greater toxicity [*Hasei et al.,* 2015; *Gupta et al.,* 1996; *Misaki et al*., 2015; *WHO*, 2003a].

Another group of contaminants which can be derived from parent PAHs is oxygenated PAHs (oxy-PAHs). Oxygenated PAHs can be formed along with other PAHs during incomplete combustion processes [*Lundstedt et al*., 2007]. Some oxy-PAHs are carcinogenic and mutagenic [*Dasgupta et al.,* 2014; *Idowu et al*., 2019].

Despite availability of data on the toxicity of PAH derivatives, it is difficult to ensure systematic monitoring of their levels in ambient air. Main problem is a great variability of these substances, their

low concentrations, and the need for highly sensitive analytical methods. In addition, their formation significantly depends on environmental conditions and concentrations of other contaminants, especially ozone, nitrogen oxides, and photooxidants [*Lee*, 2010]. Currently, modelling approaches to evaluate formation of PAH derivatives are associated with high degree of uncertainty, reduction of which requires further research.

2.3. PAHs in water, sediments and soil

PAHs are widespread in all environmental media. As a rule, the half-life of PAHs in water, soil and sediments is significantly longer than in the atmosphere. Therefore, these media can accumulate significant amounts of PAHs. In addition, PAHs can undergo re-evaporation and gas exchange with water surfaces, soil and vegetation [*Keyte et al.*, 2013]. Exchange between other environmental media also can occur.

The main source of PAHs in water is atmospheric deposition. It is estimated that up to 80% of PAHs enter water bodies through atmospheric deposition [*Srogi*, 2007]. Along with deposition to water surfaces, PAHs can enter water environment with surface runoff from the polluted areas. Other sources of PAHs in water include sewage treatment plants, diffuse sources, oil spillage and leakage, industrial effluents [*Srogi*, 2007; *Manoli and Samara*, 1999].

PAHs are relatively persistent in aquatic environments. Degradation of PAHs in surface water occurs due to direct sunlight photolysis. In the deep layers biodegradation processes are more important. Half-lives of considered PAHs in surface water and groundwater are presented in the Table 9.

Table 9. *Half-lives of PAHs in the environmental media [Mackay et al., 2006; ChemSpider database]*

Substance	Surface water, hour	Groundwater, day	Sediments (estimated values), day	Soil, day
Benzo(a)pyrene	2-900	110 -1060	340	50-3180
Benzo(a)anthracene	3-1440	200-1400	540	50 - 6250
Dibenzo(a,h)anthracene	6-1440	720-1880	540	361-940
Benzo(b)fluoranthene	8.7-1440	720-1220	540	210-3285
Benzo(k)fluoranthene	3.8-1440	1770-4280	540	50-3180
Chrysene	4.4-1440	740-2000	540	50-1000
Indeno(1,2,3-cd)pyrene	900	>1000	340	75
Acenaphthylene	1020-1440	85-120	135	42-60
Fluoranthene	1440	280-880	540	40-2850
Pyrene	0.68-1440	420-3800	540	48-3100
Naphthalene	7-13200	1-258	340	2-770
Fluorene	768-1440	64-120	135	32-60
Acenaphthene	3-900	24-204	340	12-102
Benzo(g,h,i)perylene	1440-15600	1180-1300	540	50-3320
Anthracene	108-1440	100-920	540	3.3-2890
Phenanthrene	8.4-1440	32-400	540	2.5-2080

Sediments can be regarded as important sink for PAHs, but exchange processes between sediments and water can also occur. These processes depend on the number of aromatic rings of considered PAHs. The sediments act as a secondary source of emissions for PAHs with three and four rings, while PAHs with five rings and more are deposited and accumulated in sediments [*Cui et al.*, 2016].

Soil is another significant sink of atmospheric PAHs. Soil is regarded as a steady indicator of environmental pollution since low soil mobility of PAHs (log K_{oc} value is from 2.5 to 8.0). Soil may be possible source of PAHs pollution of groundwater. In addition, the contamination of soil can lead to accumulation of PAHs in vegetation and food chains [*Mueller and Shann*, 2006].

2.4. Basic physical-chemical characteristics of PAHs required for modelling

Physical-chemical properties are basic characteristics required for modelling of PAH fate in the environment. In order to predict long-range transport and distribution of different PAHs in the environment, multi-media modelling approach is usually applied. Model assessment of PAH pollution levels, presented in this report, is performed using the multi-media GLEMOS model (http://en.msceast.org/index.php/j-stuff/glemos). Key processes, considered by the model, include the transport, phase partitioning, and degradation of PAHs in the atmosphere and other environmental compartments. The following main physical-chemical characteristics are used in GLEMOS model parameterization for PAHs:

- subcooled liquid vapour pressure (P^{O}_{L});
- octanol-water (K_{OW}), octanol-air (K_{OA}), organic carbon-water (K_{OC}) partition coefficients;
- degradation rate constants for different environmental compartments;
- air-water Henry's law constant (K_H);
- washout ratio for the particulate (W_p) and gaseous phase (W_g).

Compilation of available data on the physical-chemical properties of 16 PAHs, used for model parametrization of key processes, is included in Annex A. Among the considered PAHs, B(a)P is the most studied one with regard to the processes of gas-particle partitioning and degradation in the atmosphere. Taking this into account more complex model parameterizations of these processes are currently applied for B(a)P comparing to other PAHs. In addition, there is ongoing activity on testing and application of newly developed process parameterizations in the GLEMOS model [*Travnikov et al.*, 2020]. It should be noted also, that parametrization of sorption of PAHs by organic and inorganic components of aerosol particles, as well as heterogeneous reactions of PAHs, are subject to considerable uncertainty [*Shrivastava et al.*, 2017]. For instance, degradation rate constants in air reported in literature may differ by 2-3 orders of magnitude. Other uncertainties concern temperature dependences of subcooled liquid-vapour pressure, coefficients of partitioning between different media, and degradation rates in other environment compartments.

2.5. PAHs and PM chemical composition

Evaluation of content of toxic substances in the chemical composition of particulate matter can be important for improving assessment of adverse effects of PM on human health and the environment, as well as for identifying the sources of PM [*Longhin*, 2012; *Rogula-Kozłowska et al*., 2016; *Kong et al*., 2010; *Murillo et al.,* 2016; *Zhao et al.,* 2020]. Adverse effects of PM include asthma, respiratory diseases, cardiovascular and cardiopulmonary diseases, heart attack, cancer of the trachea, bronchus, and lung, reproductive toxicity [*WHO*, 2013]. According to WHO reports, hazard properties of particles may be caused by presence of hazardous constituents, including PAHs as substances which are characterized by high toxic potency [*WHO*, 2003b, 2013, *Elzein et al.*, 2020].

Aerosol particles exist in a wide range of sizes, and content of PAHs varies with particle size. According to a number of studies, most of particle-bound PAHs (up to 90%) are associated with $PM_{2.5}$ [*Rogula-Kozłowska et al., 2013; Teixeira et al., 2012; Singh et al., 2011; Zhang et al., 2019*]. For instance, the comparison of PAH content in PM_{10} and $PM_{2.5}$ for urban areas (Zagreb, Croatia) indicated, that in winter more than 80% of PAHs were associated with $PM_{2.5}$ [Jakovljević et al., 2018]. Furthermore, a comparison of PAH content in PM_1 and $PM_{2.5}$ demonstrated that most of PAHs were bound to PM_1 particle fraction (more than 90% in winter) [*Jakovljević et al.*, 2018]. PAHs bound to PM_1 should be given particular attention due to their larger specific area and, accordingly, greater adsorption capacity, and smaller size, which leads to their transport into the deeper respiratory tract and to greater impact on human health [*Agudelo-Castaneda et al*., 2015; *Zhang et al.*, 2019]. Therefore, knowledge on the concentrations and speciation of PAHs in PM_1 and $PM_{2.5}$ is of great importance. However, at present in the EU only PAHs associated with the PM_{10} fraction are considered for routine measurements and for air quality standards.

It should be noted, that the emission sources of $PM_{2.5}$ and PAHs to the atmosphere significantly coincide. The most significant contribution to annual PAH emissions (about 70%) is made by the stationary combustion sector (major part of which belongs to Residential Combustion sources). Similarly, in case of $PM_{2.5}$ this emission category contributes up to 40% to annual emissions (Fig. 2). This also applies to natural sources, such as forest fires [*Wentworth et al., 2018*]. Thus, aerosol particles from solid fuels combustion may be enriched by the toxic PAH compounds. In some cases, PAH concentration in PM can exceed the established EU and WHO target levels even if the guideline levels for PM are not exceeded [*Siskos et al.,* 2006*; Szatyłowicz and Skoczko*, 2019].

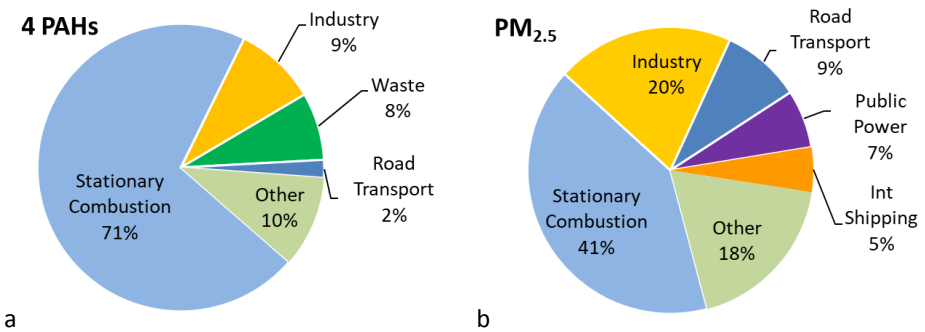


Fig. 2. *Sector distribution of annual emission of 4 PAHs (a) and PM 2.5 (b) for 2018 (based on the officially submitted emission data in 2020).*

PAHs can be contained in the condensable PM that is formed from the hot gaseous phase substances during the contact with cooler ambient air [*Feng et al*., 2018]. Among these PAHs in the condensable PM the compounds with 3 and 4 rings are assumed to dominate. In addition, positive correlation is observed between the mass concentrations of PAHs, contained in particles, and concentrations of condensable PM [*Li et al*., 2017].

Thus, the impact of particulate matter (PM_{10}, $PM_{2.5,}$ and PM_1) on human health may be more significant due to the presence of toxic constituents, including PAHs. Besides, special attention should be paid to the content of PAHs in fine particles. Simultaneous measurements of PM and PAHs may be important for more precise risk assessment. The influence of chemical composition of PM on the hazard of the particles is the subject of future research.

3. PAH EMISSIONS TO THE ENVIRONMENT

PAHs can be released to the environment by pyrogenic or petrogenic sources depending on the condition of their formation [*Manzetti*, 2013]. Pyrogenic PAHs are mainly unintentional by-products of incomplete combustion of biomass and fossil fuels [*Keyte et al.*, 2013]. Main source categories of pyrogenic PAHs include domestic burning of wood and coal, industrial activities, road transport, and agricultural sources as well as forest fires and volcanic activities [*Balmer et al.*, 2019; *Manzetti*, 2013]. Sources of petrogenic PAHs in the atmosphere can include oil production and refining, as well as industrial spills and oil accidents [*Ravindra et al.*, 2008].

Inventories of PAH emission sources are important for understanding of environmental problems due to PAHs. In particular, they provide information on main sources of PAH releases along with spatial and temporal changes of emissions, and thus may help to assess the effectiveness of measures to reduce harmful effects of pollution. To monitor dynamics of unintentional releases of PAHs within the EMEP region, official inventories of PAH emissions are regularly compiled and reported by the EMEP countries. Along with this a number of research-driven emission inventories are available for the evaluation of temporal and spatial trends of PAH pollution.

3.1. PAH emissions in the EMEP region

PAH emission inventories, developed by EMEP countries, provide speciated sector-specific data on atmospheric emissions of 4 PAHs, including their long-term changes from reference year 1990 to the present time [*Travnikov et al.*, 2020]. Officially reported data on PAH emissions in the period 1990-2018 are available for about 65% of the EMEP countries. For other countries reported data cover only part of this period or even not available. In particular, this is characteristic of the countries in Caucasus and Central Asia as well as of some countries in Southern and Eastern Europe. Thus, to characterize temporal changes of B(a)P emissions, expert estimates are used to fill the gaps in the emission time-series following the methodology developed by CEIP [*Tista et al.*, 2019].

A number of sub-regions is defined to compare emission fluxes in different parts of the EMEP domain (Fig. 3). Temporal variations of annual B(a)P emissions in different sub-regions of the EMEP domain for the period 1990-2018 are shown in Fig. 4. The most significant decline is indicated for the countries of Western and Central Europe (74% and 65% respectively).

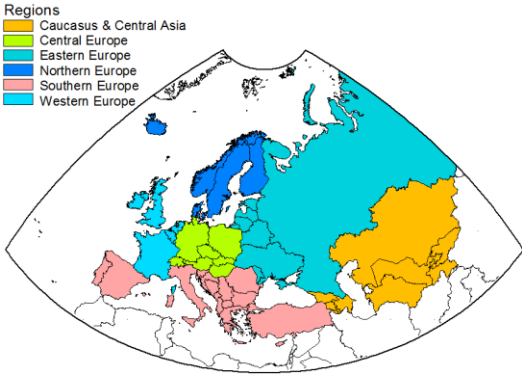


Fig. 3. *Definition of sub-regions of the EMEP region used in the report.*

Less significant decrease is seen in the countries of Northern, Southern, and Eastern Europe (45%, 20%, and 5% respectively), whereas B(a)P emissions in the countries of Caucasus and Central Asia show increasing tendency (64%). At the same time, it should be noted that emission data for this sub-region still incorporate relatively higher uncertainties comparing to other sub-regions due to the gaps in the emission time-series and sector information.

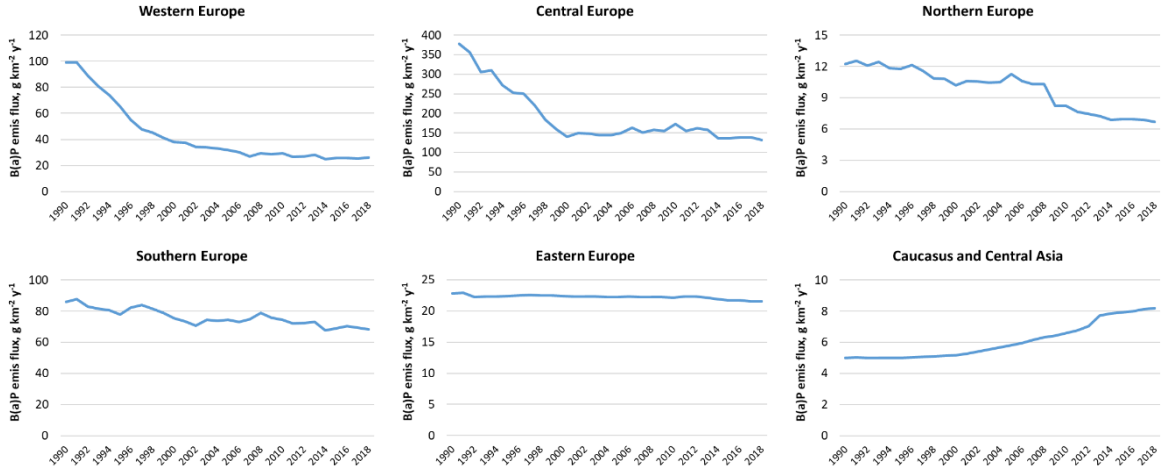


Fig. 4. *Long-term changes of annual B(a)P emissions in six sub-regions of the EMEP domain from 1990 to 2018.*

Officially reported inventories of PAH emissions of individual countries generally show decline of B(a)P releases below the level of 1990 in the period 1990-2018. The exception are inventories of Finland, Romania, Monaco, and Lichtenstein indicating higher level of emissions in 2018 comparing to 1990. At the same time, comparison of B(a)P emissions in the first decade of the period 1990-2018 with emissions in subsequent years shows noticeable decrease of reduction rates after 2000 and even increase of B(a)P emissions in 11 EMEP countries.

Sector-specific B(a)P emissions and their long-term changes in period 1990-2018 are shown in Fig. 5 on the example of Western, Central, and Southern Europe. In all of the sub-region the main contributor to total B(a)P emissions is *Residential Combustion* sector, which share amounts to more than 50% and increases during this period. Following officially reported information, in the majority of countries dominating source of PAH emissions in this sector is wood combustion for domestic

heating. At the same time, some of the countries are characterized by substantial contribution of coal combustion sources (e.g. Poland, Ireland).

Other important contributors include emissions from *Industry*, *Fugitive*, and *Agriculture* sectors. It is seen that B(a)P emissions from *Industry* and *Fugitive* sectors considerably decreased in the beginning of the period 1990-2018. At the same time, reduction of B(a)P emissions from *Residential Combustion* and Agriculture is noticeably smaller and is almost leveled off after 2000.

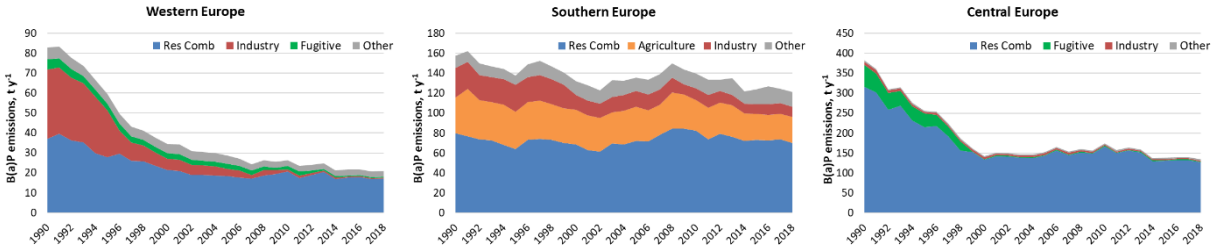


Fig. 5. *Long-term changes of sector-specific B(a)P emissions in the EMEP countries of Western, Southern, and Central Europe from 1990 to 2018.*

Spatial variations of PAH emissions in the EMEP region in 2018 are shown in Fig. 6. Officially reported data show elevated levels of 4 PAHs emissions (0.25-1 kg/km^2/y and higher) in the countries of Central and Southern Europe (e.g. Poland, Czechia, Italy, Greece) (Fig. 6a). Besides, significant emission fluxes (0.025-0.25 kg/km^2/y) are estimated for some of Western European and the EECCA counties. Lower levels of emissions (<0.025 kg/km^2/y) are reported for the countries of Northern Europe. In general, higher emissions are indicated for urban and densely populated areas.

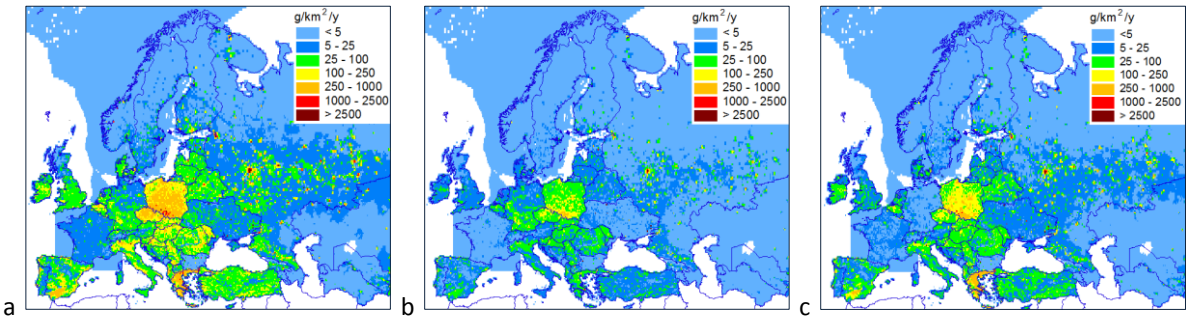


Fig. 6. *Spatial distribution of 4 PAHs (a), B(a)P (b), and B(b)F (c) emissions in the EMEP region for 2018.*

B(a)P, B(b)F, B(k)F, and IcdP have different contributions to total emissions of 4 PAHs. According to the reported emission data, their average fractions in total PAH emissions equal to 30%, 36%, 17%, and 17%, respectively. At the same time, contributions of individual PAHs to the total national PAH emissions vary among the countries. Along with this, there are differences in the spatial distribution of individual PAH emissions. In particular, it can be seen that spatial distributions of B(a)P and B(b)F emissions noticeably differ in some of the EMEP countries as shown in Fig. 6b and c (e.g. for some of the countries in Central and Southern Europe).

Completeness and accuracy of PAH emission inventories developed by the EMEP countries are of particular importance for monitoring of emissions reduction and model assessment of pollution levels in the EMEP region. Officially reported information on PAH emissions is available for 42 EMEP countries (82%), while for the other EMEP countries expert estimates of emissions are generated by CEIP based on various available data [*Travnikov et al.*, 2020]. To improve evaluation of PAH pollution in the EMEP countries, further work on the refinement of sector-specific PAH emissions as well as their speciation is required in cooperation with national expert and CEIP.

3.2. Research-oriented inventories of 16 PAH emissions

Along with the official EMEP emission data a number of research-driven PAH emission inventories were developed using different methodologies. In particular, they include national scale inventory for China [*Xu et al.,* 2006], regional scale inventories for Europe [*Van der Gon et al*., 2007] and for North America [*Galarneau et al*., 2007], and global scale inventories [*Zhang et al*., 2009; *Shen et al*., 2013].

Some of these inventories provide information on spatial distribution as well as temporal variation of PAH emissions and thus can be applied for studies of long-term trends of pollution and exposure analysis. In particular, the global scale inventory of atmospheric emissions for 16 PAHs has been developed by the research group of Peking University [*Shen et al*., 2013]. The inventory is based on top-down approach with application of the newly developed fuel consumption database PKU-FUEL-2007 [*Wang et al.,* 2013] and an updated database of PAH emission factors. The inventory covers 16 PAHs, namely, naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLO), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benzo(a)anthracene (B(a)A), chrysene (CHR), benzo(b)fluoranthene (B(b)F), benzo(k)fluoranthene (B(k)F), benzo(a)pyrene (B(a)P), dibenzo(a,h)anthracene (D(ah)A), indeno(l,2,3-cd)pyrene (I(cd)P), and benzo(g,h,i)perylene (B(g,h,i)P).

Estimates of PAH emissions were disaggregated into 0.1°× 0.1° resolution global grid. Spatial distribution of 16 PAH annual emissions is given in Fig. 7a.

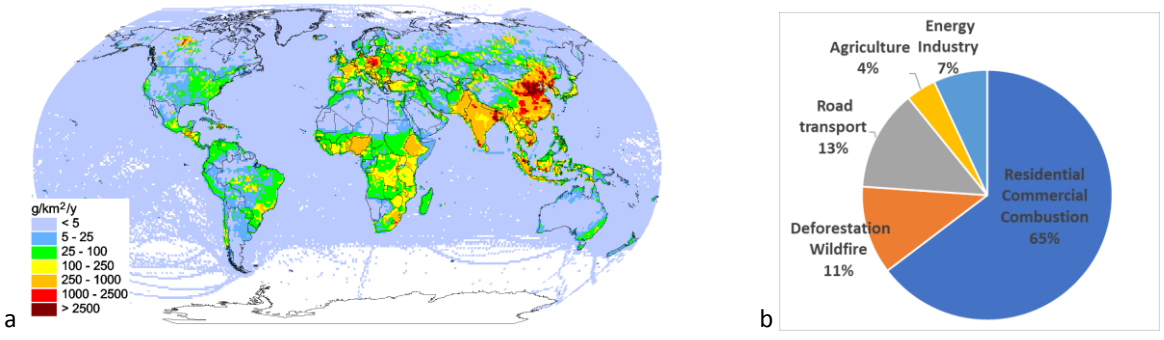


Fig. 7. *Spatial distribution of global annual emissions of 16 PAHs for 2014 (a) and contribution of major source categories to total PAH emission (b).*

According to these data highest level of PAH emissions took place in the countries of Eastern and Southern Asia. PAH emissions were split into six sectors (energy production, industry, transportation, commercial/residential sources, agriculture, and deforestation/wildfire). In Fig. 7b distribution of global PAH emissions by major source categories is given. The largest contribution to total PAH emissions is made up by Residential and Commercial combustion (65%), followed by Road Transport (13%) as well as Deforestation and Wildfires (11%). This inventory is applied to study intercontinental transport, spatial and temporal trends and population exposure to mixture of carcinogenic PAHs.

4. PAH POLLUTION LEVELS AND EXCEEDANCES IN THE EMEP REGION

Analysis on long-term trends in PAH pollution levels can support evaluation of effectiveness of the measures aimed to reduce unintentional PAH emissions and population exposure. In accordance with the Long-term Strategy of the LRTAP Convention, MSC-E performs research activities to assess PAH pollution levels in the EMEP region and their temporal changes. In this chapter, results of model assessment of long-term trends in B(a)P air concentrations and analysis of contributions of major emission sectors to B(a)P pollution as well as exceedances of air quality guidelines are presented.

4.1. Long-term changes of PAH pollution levels

Evaluation of B(a)P pollution long-term changes over time was carried out based on the results of model assessment and measurements. Model simulations were performed using scenario of B(a)P emissions for the period 1990-2018. The scenario was constructed on the basis of official emission inventories, submitted by the EMEP countries in 2020, and expert estimates described in the EMEP Status Report [*Travnikov et al.*, 2020]. Time-series of annual PAH emissions for the whole period 1990-2018 were submitted by 32 EMEP countries (63%). For other EMEP countries that provided data for the part of the period (22% of the countries) or did not submit their emission data (15% of the countries) expert estimates of emissions were used elaborated on the basis of methodology developed by CEIP [*Tista et al.*, 2019]. Spatial distribution of B(a)P emissions in the EMEP domain was constructed by CEIP for the latest year of the considered period 1990-2018. For other years (1990-2017) the distribution of emissions of the year 2018 was applied in the model simulations.

Time-series of modelled B(a)P air concentrations in different sub-regions of the EMEP domain for the period 1990-2018 are shown in Fig. 8. PAH pollution levels in the EMEP countries substantially decreased since 1990. Results of model simulations generally show decreasing levels of annual mean B(a)P air concentrations in most of the sub-regions with the exception of Caucasus and Central Asia.

Modelled concentrations indicate the most significant decrease in Western, Central, and Northern Europe (by 65%, 60%, and 40%, respectively). Relatively lower decrease is estimated for Southern and Eastern Europe (by 20% and 5%), whereas for Caucasus and Central Asia model estimates demonstrate increasing levels of B(a)P pollution (by 65%). It should be noted however that modelling

results for this sub-region incorporate relatively higher uncertainties compared to other sub-regions due to the gaps in the emission time-series and sector information.

The analysis of long-term trends of B(a)P air concentrations in the EMEP region for 1990-2018 was performed using the methodology based on fitting exponential decays [*Shatalov et al.*, 2015]. Bi-exponential approximations of B(a)P concentrations changes over the period 1990-2018 in different sub-regions of the EMEP region are shown in Fig. 8.

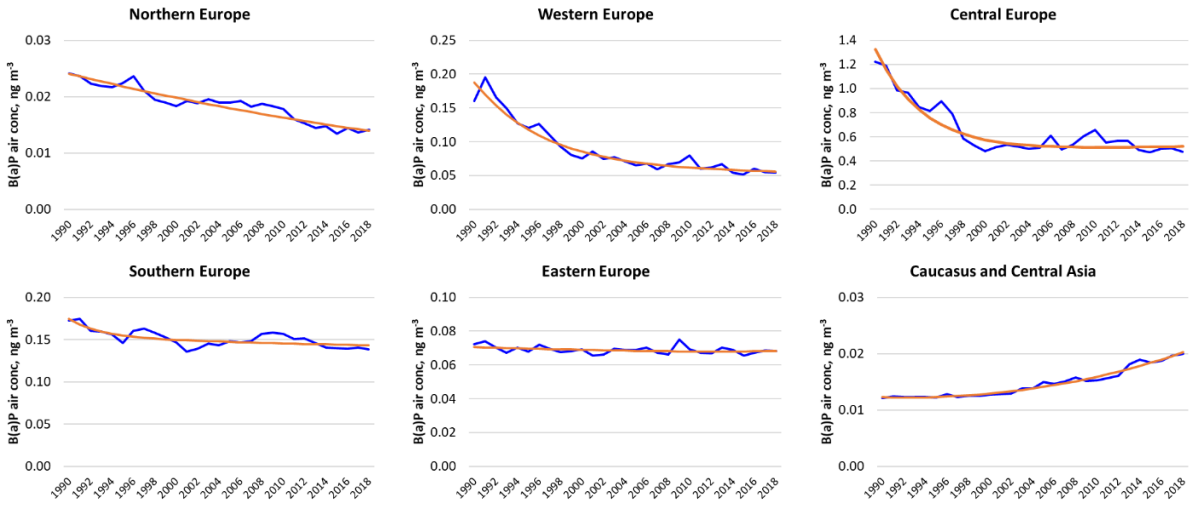


Fig. 8. *Long-term variations of annual mean modelled B(a)P air concentrations over the period 1990-2018, averaged across 6 sub-regions of the EMEP domain (Northern Europe, Western Europe, Central Europe, Eastern Europe, Southern Europe, and Caucasus and Central Asia) and bi-exponential approximation of temporal variations of B(a)P concentrations.*

The trend in B(a)P concentrations can be expressed in terms of reduction rates that are assumed to be positive for a downward trend and negative for an upward trend. Average values of annual reduction rates for each of the considered sub-regions during this period are presented in Fig. 9a. The highest reduction rate (about 4% per year on average) is estimated for Western Europe followed by Central and Northern Europe (3% and 2% per year, respectively). Noticeably lower reduction rates were in Southern and Eastern Europe (less than 1% per year), while increasing rate (about 2% per year) was obtained for Caucasus and Central Asia.

Considered period of time 1990-2018 is characterized by inhomogeneous changes of B(a)P pollution. The most significant decline took place in the beginning of the 1990s, while during the two recent decades the rate of temporal changes in some areas of the EMEP region significantly declined or even levelled off (e.g. in Central and Southern Europe). In Fig. 9b estimates of annual mean reduction rates over the period 2000-2018 are shown. It is seen that reduction of pollution after 2000 is noticeably slower, which is connected with less significant changes of emissions in this period. In particular, mean annual reduction rates in Central, Southern, and Eastern Europe are almost close to zero. Besides, model simulations show that after 2000 some of the countries in the European sub-

regions were characterized by increasing annual mean B(a)P concentrations (e.g. Finland, Romania, Hungary, Italy).

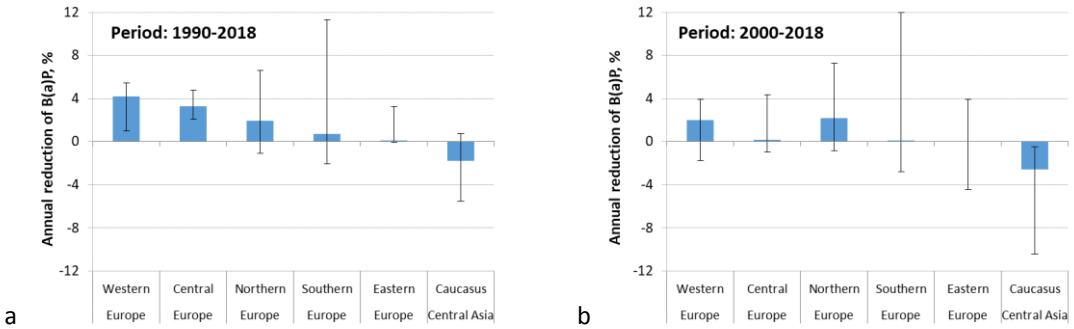


Fig. 9. *Annual mean reduction rates of B(a)P air concentrations for 6 sub-regions of the EMEP domain over the period 1990-2018 (a) and 2000-2018 (b). Positive values represent decrease of concentrations, negative values represent increase of concentrations. Whiskers show the range of annual mean reduction rates among the countries of particular sub-region.*

Additional model simulations were also performed to estimate the contributions of major emission sectors to B(a)P air concentrations and their variations over selected years of the period 1990-2018 (Fig. 10). It is seen that the *Residential Combustion* sector contributed the most to annual mean B(a)P air concentrations in all the sub-regions.

Noticeable contribution was also made by the *Industry* sector in the beginning of the 1990s in Northern, Western and Southern Europe. However, in subsequent period of time the share of this sector decreased significantly. Besides, some of the countries of Southern Europe reported considerable contribution of the *Agriculture* sector.

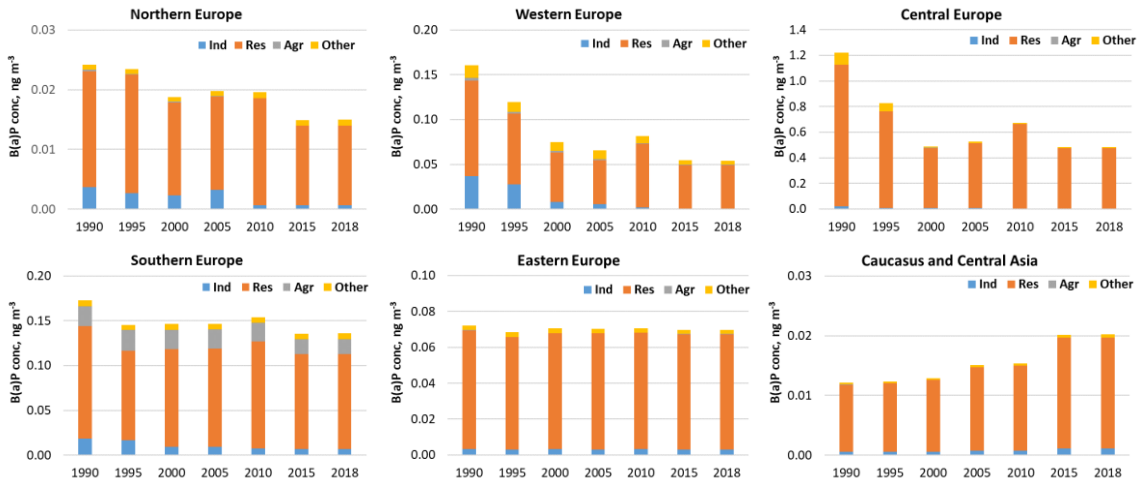


Fig. 10. *Long-term changes of modelled B(a)P annual mean air concentrations for the period 1990-2018, averaged across 6 sub-regions of the EMEP domain with contribution of major emission sectors (Ind – Industry, Res – Residential combustion, Agr – Agriculture, and Other – other GNFR sector).*

Comparison of annual mean modelled B(a)P concentrations for the period 1990-2018 with data of EMEP long-term measurements is shown in Fig.11. Observed concentrations in the selected sub-regions of the EMEP domain were averaged across the monitoring stations and compared with the averaged model estimates.

It is seen that variations of modelled B(a)P concentrations generally correspond to the observed ones in Northern and Western Europe. In case of Central and Eastern Europe measured concentrations have higher interannual variability comparing to that of modelling results. The latter can be explained by lower amount of monitoring stations in these sub-regions as well as shorter periods of monitoring.

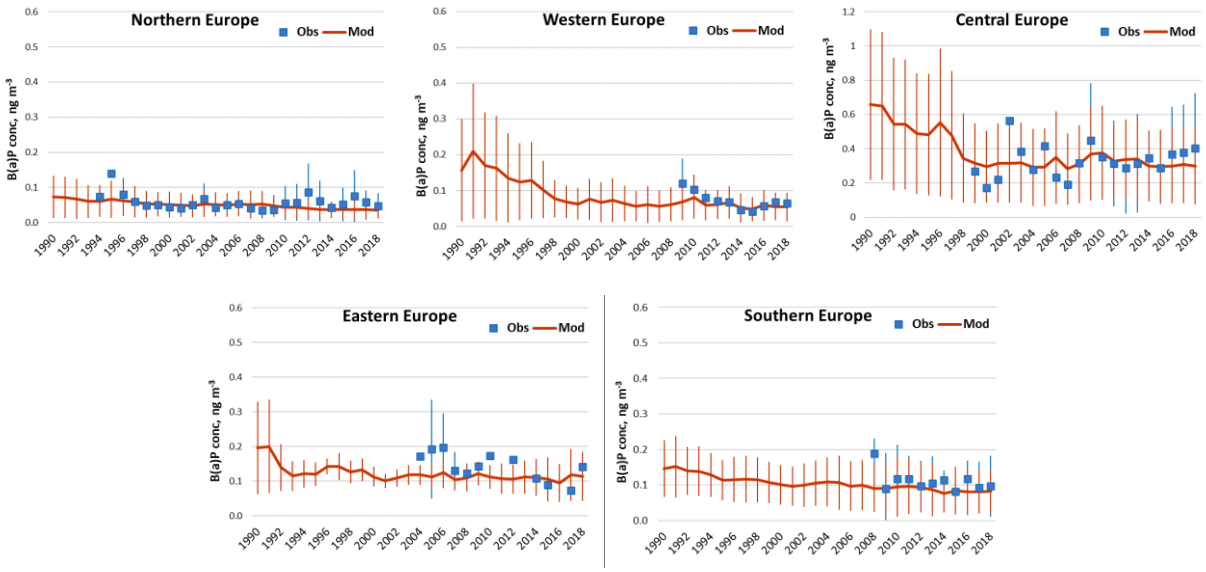


Fig. 11. *Modelled and observed B(a)P annual mean air concentrations for the period 1990-2018, averaged across 5 sub-regions of the EMEP domain, namely, Northern Europe (11 stations), Western Europe (12 stations), Central Europe (7 stations), Eastern Europe (5 stations), and Southern Europe (5 stations). Whiskers indicate standard deviation of modelled and observed annual mean B(a)P air concentrations at individual stations.*

Comparison of long-term annual mean modelled and observed B(a)P concentrations for particular EMEP monitoring stations is presented in the Fig. 12. Measurements of stations SE0002R, SE0014R, BE0013R, SI0008R indicate gradual decrease of B(a)P pollution within the two recent decades. At the same time B(a)P concentrations measured at CZ0003R, SE0012R, and GB0014R stations show almost the same level of pollution during this period. Model estimates correspond in general to the observed annual mean B(a)P concentrations. However, model predictions underestimate measured B(a)P pollution levels at the CZ0003R and some of the peak values, measured at Swedish stations.

Data of national monitoring networks, collected in the EEA Air Quality e-Reporting database, provide more detailed information on B(a)P pollution in the EMEP countries. Variability of annual mean B(a)P concentrations observed at rural and background urban monitoring sites in Poland and Italy in period 2007-2018 is shown in Fig. 13a and b, respectively.

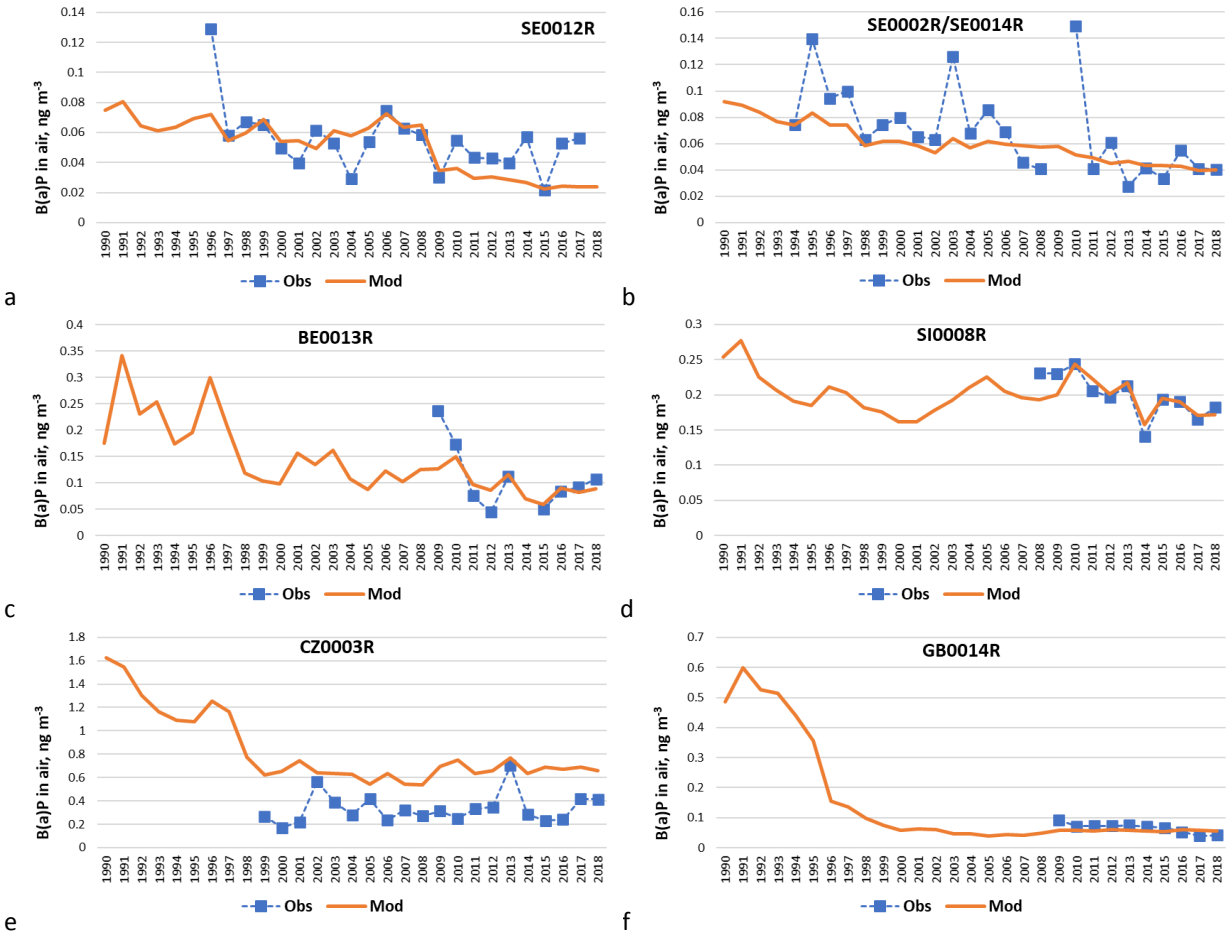


Fig. 12. *Comparison of long-term annual mean modelled and observed B(a)P concentrations for the EMEP monitoring sites in Sweden (a,b), Belgium (c), Slovenia (d), Czechia (e), and the UK (f).*

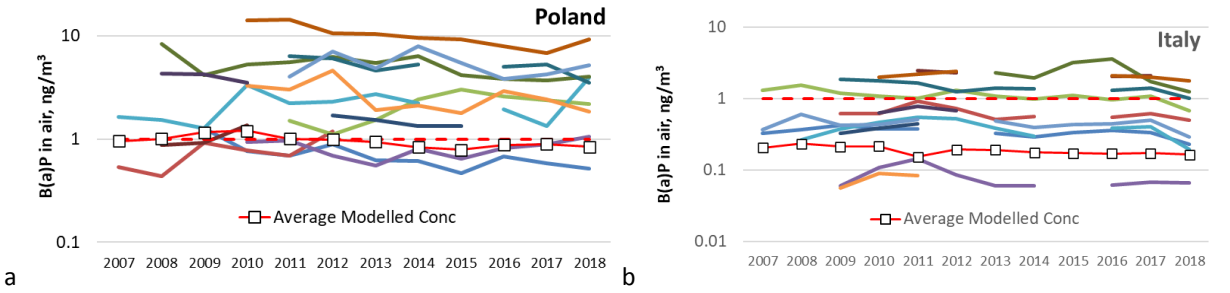


Fig. 13. *Comparison of average annual mean modelled B(a)P concentrations in Poland (a) and in Italy (b) with B(a)P measurements of rural and background urban monitoring stations. Colored solid lines indicate observed B(a)P concentrations. Red dashed line indicates the EU target level 1 ng m^{-3} for B(a)P. Red solid line with squares shows average modelled B(a)P concentrations in the country.*

Along with measurements, averaged modelled B(a)P concentrations for the selected countries are presented. It can be seen that model predictions and measured concentrations similarly indicate the absence of noticeable decreasing trends in the B(a)P pollution levels in these countries. Some of the monitoring sites show increasing concentrations of B(a)P. Additionally, significant part of monitoring stations in both countries indicated exceedances of the EU target level for B(a)P (1 ng m^{-3}) by the observed concentrations.

4.2. Exceedances of air quality guidelines

The information on exceedances of the EU and WHO air quality guidelines for B(a)P is of importance for the analysis of population exposure to toxic substances and adverse health effects. Annual mean B(a)P air concentrations continue to exceed air quality guidelines in some of the areas of the EMEP region. Model predictions for 2018 (Fig. 14a) indicate high levels of B(a)P concentrations for the countries of Central and Eastern Europe, e.g. in Poland, Czechia, Bulgaria, northern Italy, Greece, Romania, as well as in some areas of Spain and Turkey. In some of these countries estimates of B(a)P air concentrations exceed the EU air quality guideline. Areas of concentrations above the EU target value are also noted for some of the EECCA countries. However, these estimates are subject of higher uncertainties due to incomplete information on emissions for this part of EMEP region.

According to the modelling results, about 7% of total population of the EMEP countries in 2018 (Fig. 14b) were exposed to B(a)P annual mean air concentrations above the EU target level. Besides, the upper assessment thresholds (UAT) and lower assessment thresholds (LAT) values were exceeded in the areas with 17% and 25% of population, respectively. It can be seen that most of these exceedances took place for the population of urban areas.

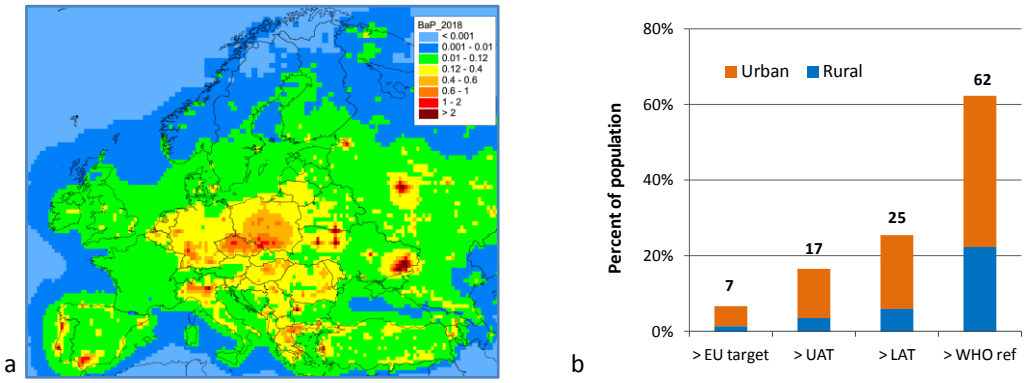


Fig. 14. *Map of annual mean modelled B(a)P air concentrations for 2018, ng m^{-3} (a) and percentage of urban and rural population of the EMEP countries in the areas with annual mean B(a)P air concentrations above the EU limit values (EU target value for B(a)P – 1.0 ng m^{-3}, UAT – 0.6 ng m^{-3}, LAT – 0.4 ng m^{-3}), and WHO reference level 0.12 ng m^{-3} (b)*

With respect to the WHO reference level, it was estimated for 2018 that more than 60% of population in the EMEP countries lived in the areas with annual mean B(a)P air concentrations above this limit, while only for less than 40% of population B(a)P concentrations were below the reference level.

Detailed observational data on B(a)P pollution levels are available from national monitoring in the EU countries (EEA Air Quality e-Reporting database). Spatial distribution of observed annual mean B(a)P air concentrations in 2018 is presented in the Fig. 15a. Similar to the modelling results, the highest average B(a)P air concentrations in 2018 were observed at the monitoring stations in Central, Eastern, and Southern Europe.

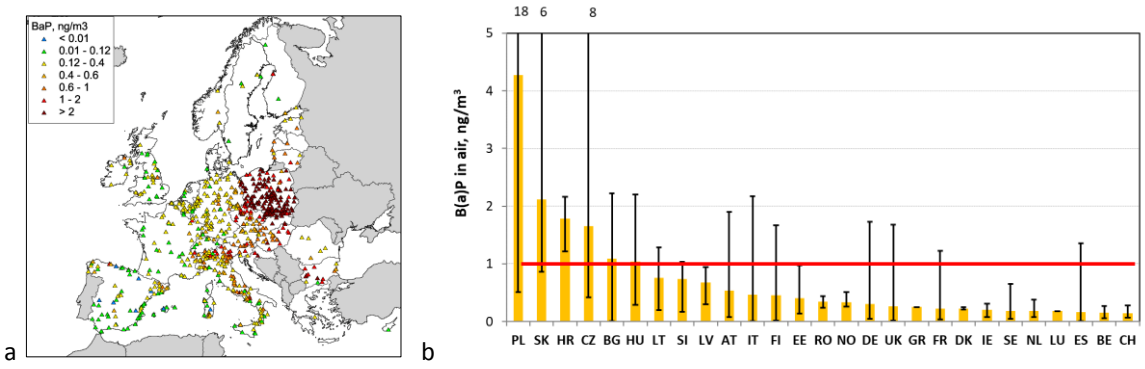


Fig. 15. *Spatial distribution of B(a)P air concentrations observed at EEA Air Quality e-Reporting monitoring sites in 2018 (a) and average values of measured annual mean B(a)P air concentrations in the EU countries in 2018 (b). Whiskers denote the range from minimum to maximum of measured concentrations.*

Annual mean B(a)P air concentrations observed in 2018 in the selected European countries are illustrated in Fig. 15b. According to these data B(a)P air concentrations, averaged over the monitoring sites of particular country, were above the EU target value in 6 EU countries, namely, Poland, Slovakia, Croatia, Czechia, Bulgaria, and Hungary.

In addition, maximum measured B(a)P concentrations above the EU target value were also reported by some of the monitoring stations in Lithuania, Slovenia, Austria, Italy, Finland, Germany, France, Spain, and the UK. The highest concentrations were measured in the southern part of Poland (more than 10 ng/m^3). Most of exceedances of the EU target value were observed at the urban background stations.

Exceedances of WHO reference level in 2018 took place in most of the countries performing regular monitoring of B(a)P pollution levels. In particular, annual mean B(a)P concentrations were higher than 0.12 ng/m^3 in 27 European countries. Thus, further measures are required to reduce elevated levels of B(a)P concentrations and their adverse effects on population.

5. CASE STUDY OF PAH POLLUTION FOR POLAND

Case study oh PAH pollution for Poland continued a series of national scale case studies on PAHs for Spain and France [*Gusev et al.*, 2017; 2018; 2019] that followed the recommendation of the 2nd joint session of the Working Group on Effects and the Steering Body to EMEP (held in 2017). This activity is aimed at the analysis and reduction of uncertainties in the assessment of PAH pollution levels in the EMEP region.

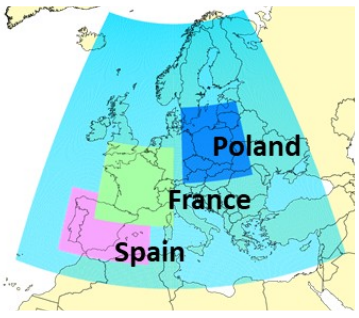


Fig. 16. *Spatial configuration of modelling domains used in the ongoing case studies for Poland and previous studies for Spain and France.*

Current stage of the case study is focused on the model assessment of PAH pollution in Poland (Fig. 16). It was initiated in 2020 after the meeting of EMEP and national

experts in modelling and emissions of B(a)P, held in November 2019 in Warsaw (Poland). Multi-model simulations for 2018 were planned to analyze levels of B(a)P/PAH air concentrations in Poland based on the new and previous national PAH emission inventories in co-operation with national experts. The study includes evaluation of modelling results against EMEP and other national measurements as well as evaluation of exceedances of the EU and WHO air quality guidelines in the country. This chapter presents results of model simulations carried out using the EMEP GLEMOS model.

5.1. Emission data for modelling

Polish inventory of national PAH emissions was substantially updated in 2019-2020 [*Bebkiewicz et al.*, 2020] following the review recommendations. Most of 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. Example of time-series of annual B(a)P emissions for 1990-2018 is shown in Fig. 17a. Besides, sector distribution of PAH emissions in Poland was changed. In particular, contribution of stationary combustion sources to annual B(a)P emissions noticeably increased, whereas contribution of fugitive sources decreased (Fig. 17b).

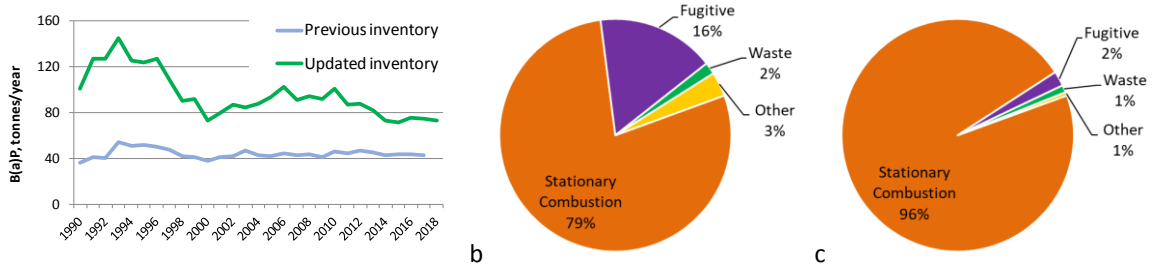


Fig. 17. *Comparison of B(a)P emission inventories submitted in 2019 (Previous inventory) and in 2020 (Updated inventory). Time-series of B(a)P annual total emission of Poland (a), sector distributions of annual total B(a)P emissions based on the previous inventory for 2017 (b), and updated inventory for 2018 (c).*

To explore the effect of B(a)P emission updates, three datasets of gridded anthropogenic emissions for 2018 were prepared for the model simulations. The first one (Previous Inventory) was constructed using the previous national emission inventory of Poland (year of submission 2019) and emissions of other EMEP countries for 2018 provided by CEIP (year of submission 2020). In the second and third datasets emissions of Poland were substituted by the new inventory (Updated Inventory) and by the scenario emissions (Scenario Emissions), respectively.

The scenario emissions were prepared using the uncertainty range for the Residential Combustion sector (equal to 76%) defined in the inventory information report of Poland [*Bebkiewicz et al.*, 2020].

Constructed emission scenario represents possible maximum level of B(a)P emissions in the country. Spatial distributions of annual B(a)P emissions in the modelling domain, including data of the previous and new inventory of Poland, are presented in Fig. 18a and b, respectively. In Fig. 18c comparison of annual total B(a)P emissions in Poland according to the previous and new inventory, and constructed scenario is shown.

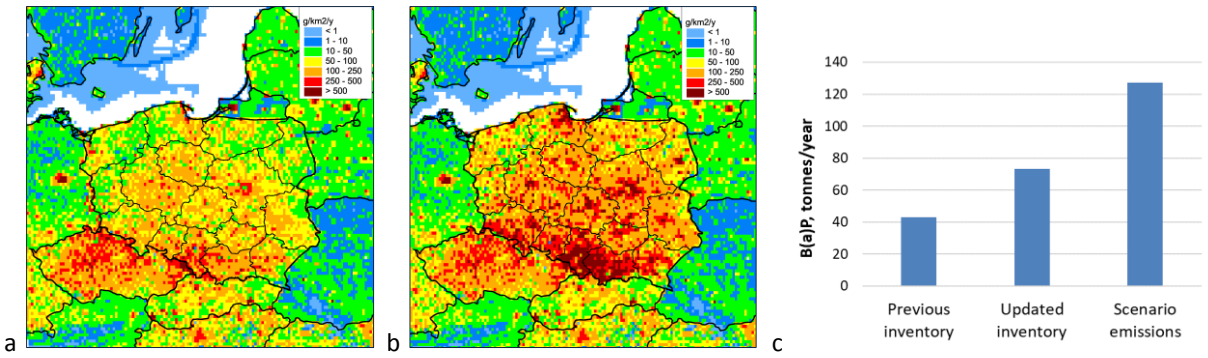


Fig. 18. *Spatial distribution of annual B(a)P emission fluxes in 2018 (g km^{-2}y^{-1}) according to previous (a) and updated (b) B(a)P emission inventory for 2018 (spatial resolution 0.1°x0.1°), and comparison of total annual B(a)P emission of Poland according to previous and updated emission inventories and scenario of B(a)P emissions.*

5.2. Modelling results and their analysis

Modelling of B(a)P pollution levels was carried out with spatial resolution 0.1°x0.1° for the domain shown in Fig. 16. The year 2018 was selected as a reference year for the model simulations. Annual mean modelled B(a)P air concentrations, obtained in the model simulations with the three emission datasets are given in Fig. 19.

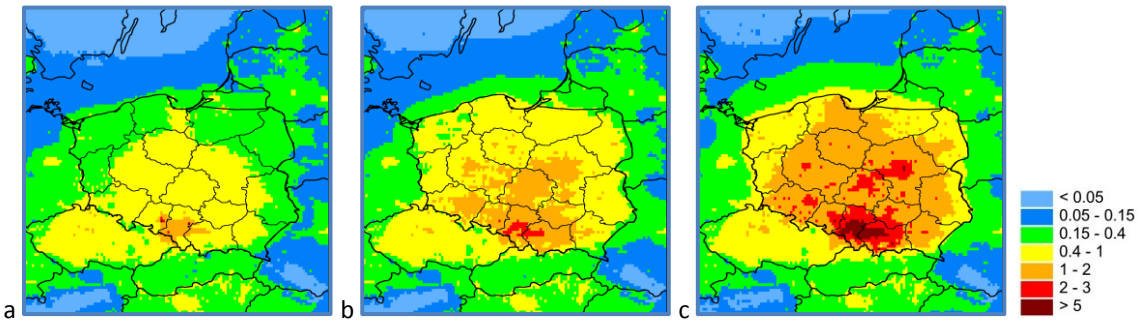


Fig. 19. *Annual mean modelled B(a)P air concentrations (ng m^{-3}) in 2018 simulated using the B(a)P emissions including previous version of B(a)P emission inventory of Poland (a), the new B(a)P emission inventory (b), and scenario of B(a)P emission (c) (spatial resolution 0.1°x0.1°)*

The largest differences between the three sets of simulated air concentrations can be seen over the territory of Poland. In particular, modelling results based on the new inventory show that B(a)P concentrations in most parts of the country are higher than 0.4 ng m^{-3}, and exceed the WHO

reference level (0.12 ng m^{-3}). Area of B(a)P air concentrations above the EU target value (ng m^{-3}) is also significantly wider comparing to the results based on the previous inventory. In case of the scenario emissions the area of concentrations above the EU target value covers the most of the country with highest concentrations (over 2 ng m^{-3}) in its southern part.

Model estimates were compared with B(a)P air concentrations observed in 2018 at the EMEP and EEA Air Quality e-Reporting monitoring stations (Fig. 20). In particular, rural, remote, and sub-urban stations in Poland and surrounding countries were selected for the comparison.

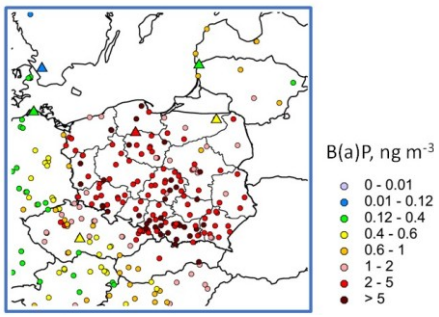


Fig. 20. *Annual mean B(a)P air concentrations in 2018, measured at the EMEP (triangles) and EEA Air Quality e-Reporting (circles) monitoring stations.*

Relative mean bias between the model estimates and measurements of rural and remote stations is shown in Fig. 21a for the three groups of monitoring stations, namely, all stations in the modelling domain, stations in Poland, and stations in other countries. The use of updated national emission inventory leads to significant decrease of the model bias from approximately -55% to -42% for all the stations of this type in the modelling domain. More significant decrease of the bias was obtained for the Polish stations (from almost -80% to -60%). Along with this, noticeable improvement of spatial correlation between the modelled and measured values is obtained (Fig. 21b). Model simulations with the scenario emissions showed further improvement of the agreement between the model and measurements indicating possible underestimation of B(a)P emissions. In particular, the bias decreases down to -20% for all the stations, to -35% for Polish stations, and to -1% for the stations outside Poland.

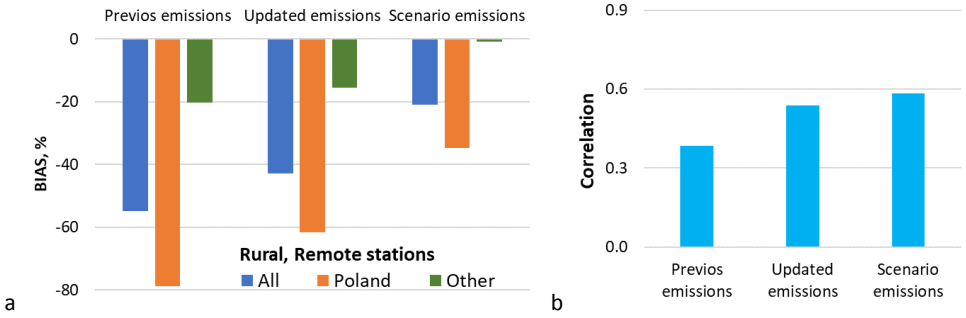


Fig. 21. *Relative mean bias (a) and spatial correlation (b) between the modelled and measured at* ***Rural and Remote stations*** *(24 stations) annual mean B(a)P air concentrations for 2018 simulated based on previous and new B(a)P emission inventory, and scenario emissions. Relative mean bias is calculated for the three groups of monitoring stations: (1) all stations in the modelling domain, (2) stations in Poland, and (3) stations in other countries.*

In Fig. 22a comparison of model estimates with larger set of measurements including rural, remote, and sub-urban stations is presented. Almost similar improvement of agreement between the modelling results for three emission datasets and measured B(a)P concentrations is seen for this

group of stations. Along with this the use of updated national emission inventory and scenario emissions leads to significant increase of correlation between annual mean modelled and observed concentrations (from 0.4 to 0.8) as shown in Fig. 22b.

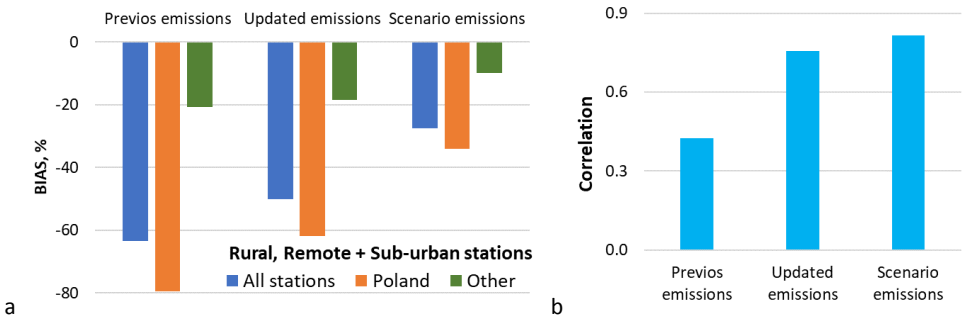


Fig. 22. *Relative mean bias (a) and spatial correlation (b) between the modelled and measured at* ***Rural, Remote, and Sub-urban stations*** *(56 stations) annual mean B(a)P air concentrations for 2018 simulated based on previous and new B(a)P emission inventory, and scenario emissions. Relative mean bias is calculated for the three groups of monitoring stations: (1) all stations in the modelling domain, (2) stations in Poland, and (3) stations in other countries.*

Comparison of modelled and observed seasonal variations of B(a)P air concentrations for 2018 shows in general satisfactory agreement between the model results and measurements. In Fig. 23 examples of model predictions and measurements for Polish monitoring stations PL0005R and PL0009R are presented. In general, model simulations with scenario emissions better capture seasonal variations of observed B(a)P air concentrations comparing to the simulations using the new and previous inventories of emissions. However, in some of the episodes, especially winter months in the beginning of the year, the model underpredicts measured B(a)P concentrations. Differences between the modelled and measured intra-annual variations of B(a)P concentrations may be explained by uncertainties of temporal disaggregation of B(a)P emissions which is currently based on the TNO estimates.

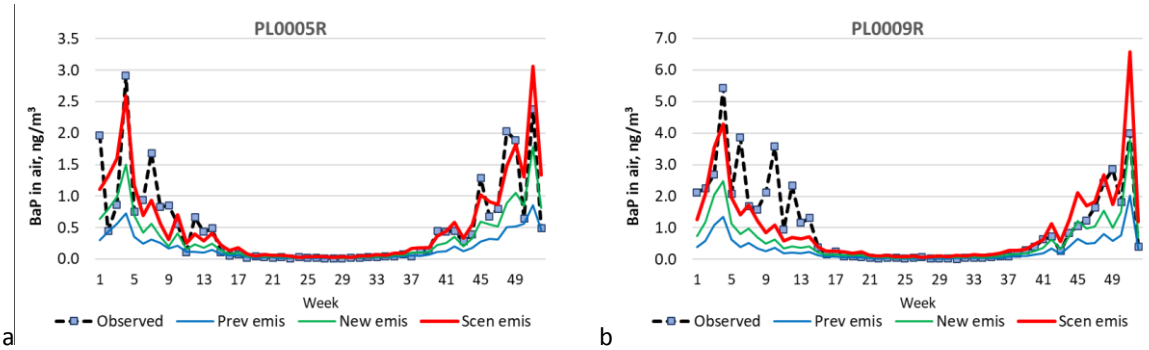


Fig. 23. *Seasonal variations of modelled B(a)P air concentrations (ng m^{-3}) for 2018, calculated on the basis of the previous and new national B(a)P emission inventories and scenario emissions, against measurements of EMEP monitoring stations.*

Results of model simulations for 2018, based on the new national B(a)P emission inventory, showed better agreement with measurements comparing to the previous inventory. At the same time, the model still tends to underpredict observed B(a)P air concentrations. Model simulations with the scenario emissions on the basis of emissions uncertainty range allow to further improve the agreement between the model and measurements indicating possible underestimation of national B(a)P emissions in Poland. At the same time, additional contribution to the model-measurement differences can be made by the uncertainties in currently applied model parameterizations of B(a)P degradation in the atmosphere and measurements of its concentrations. Model results and measurements indicate high level of annual mean B(a)P air concentrations, exceeding the EU target value (1 ng m^{-3}) and the WHO reference level (0.12 ng m^{-3}), in many areas of Poland.

Further steps of the study can include multi-model simulations, application of more detailed temporal and spatial disaggregation of B(a)P emissions, and more detailed analysis of exceedances of the EU and WHO air quality guidelines for B(a)P. In addition, model assessment of pollution by other three PAHs of the CLRTAP POP Protocol (B(b)F, B(k)F, and IcdP) can be performed for Poland and surrounding countries.

6. TOXICITY AND HUMAN EXPOSURE TO PAHs

PAHs are highly hazardous for human health as well as for environment [*Theakston*, 2000]. Effects for human health include carcinogenicity and mutagenicity, reproductive toxicity, liver and kidney toxicity, hematological effects, pulmonary and respiratory effects, neurotoxicity, and skin irritation in case of direct contact [*Danish EPA*, 2013]. PAHs in ambient air may cause asthma [*Karimi et al.* 2015, *Liu et al*., 2016]. Some PAHs are endocrine disrupters and may affect the immune system [*WWF*, 2005]. In addition, the presence of UV light may induce more toxic effects of PAHs, and their effects may be underestimated [*MAFF,* 2000].

6.1. Routes of exposure

The main routes of exposure to PAHs for the general population include inhalation and ingestion [*EFSA*, 2008]. Some studies suppose that dermal contact also might have significant impact comparable with inhalation exposure [*Strandberg et al*., 2018; *Van Rooij et al*., 1993a,b].

The important route of human exposure to PAHs is through the lungs and respiratory tract after inhalation of aerosols and particles containing PAHs, due to the high carcinogenic potency of PAHs. Estimated intake of benzo(a)pyrene by inhalation route is about 20 ng/day per person (for general population) [*EC*, 2002].

Ingestion of PAHs can occur through food and drinking water. Contamination of food by PAHs may be due to presence of these substances in air, water, soil, and plants. The major source of PAHs for plants is atmospheric deposition [*Knoche et al*., 1995; *Wilcke*, 2000]. Besides, plants can absorb PAHs through the root system from soil. Other important source of PAHs in food may be specific processes

which are used for cooking (especially heating, smoking, grilling and roasting processes). European Food Safety Authority estimated that the overall average dietary exposure in EU is ranged from 185 to 255 ng/day for benzo(a)pyrene, and from 1415 to 2136 ng/day for the sum of 8 PAHs. PAH intake from drinking-water is usually less significant comparing to the intake from food. However, these values could be equal, if water is contaminated by coal tar coatings of drinking-water distribution pipes [*WHO*, 2011].

Dermal exposure is possible during contact with contaminated soil or in cases of skin contact with materials containing PAHs. Among these materials soot, tar, petroleum products could be mentioned [*EPA*, 2017].

6.2. Toxicity and adverse effects

The main toxicological endpoints of PAHs include acute toxicity, short-term toxicity, carcinogenicity, mutagenicity, reproductive and developmental toxicity and other effects.

Studies on the acute toxicity of PAHs are limited. The LD50[15] values show that acute toxicities of PAHs are low to moderate [*SCF*, 2002a; *ATSDR*, 1995]. Among the 16 PAHs, only naphthalene is classified as harmful (if swallowed) in accordance with the EU CLP Regulation [*ECHA,* 2018].

A number of studies of the short-term effects have shown that PAHs can affect various tissues of experimental animals after oral administration. Some of the endpoints (e.g., for benzo(a)pyrene, acenaphthene, fluoranthene, fluorene) are associated with effects on the liver, indicating varied degrees of hepatotoxicity. Other significant effects are related to immune response [*Silkworth et al*. 1995*; SCF,* 2002b; *CCME*, 2010]. In addition, exposure to benzo(a)pyrene may induce adverse hematologic effects in animals [*Larsen*, 2013; *EPA*, 2017].

The most of international and national regulations consider carcinogenic potential as the main reason for setting limit values for PAHs (see Section 1). Development of cancer can be associated with the route of exposure, for instance, ingestion causes tumors of the stomach, inhalation and direct instillation to respiratory tract led to lung tumors. However, this dependence is not always observed [*IPCS*, 1998].

Literature data demonstrate that the most of PAHs have evidence of mutagenicity/genotoxicity in vivo or in vitro (Table 10). For number of PAHs only in vitro data are available, so further investigations are required. Anthracene, naphthalene and pyrene have negative results in the most of (or in all) short term tests.

[15] Median lethal dose

Table 10. *Evaluation of genotoxicity of considered 16 PAHs [SCF, 2002b]*

Substance	Genotoxicity
Benzo(a)pyrene	Genotoxic
Benzo(a)anthracene	Genotoxic
Dibenzo(a,h)anthracene	Genotoxic
Benzo(b)fluoranthene	Genotoxic
Benzo(k)fluoranthene	Genotoxic
Chrysene	Genotoxic
Indeno(1,2,3-cd)pyrene	Genotoxic
Acenaphthylene	Inappropriate data
Fluoranthene	Limited evidence of genotoxicity
Pyrene	Not genotoxic
Naphthalene	Probably not genotoxic
9H-Fluorene	Inappropriate data
Acenaphthene	Inappropriate data
Benzo(g,h,i)perylene	Genotoxic
Anthracene	Not genotoxic
Phenanthrene	Limited evidence of genotoxicity

Reproductive and developmental toxicity of some of the PAHs (e.g. Benzo(a)pyrene and dibenzo(a,h)anthracene) was observed in several studies [*IARC*, 1983; *EPA*, 2017; *SCF,* 2002b]. It should be noted, that in most cases impact of B(a)P on reproduction and development is observed at relatively high doses in comparison with doses corresponded to carcinogenic effects.

Some PAHs have been identified as endocrine disrupting substances [*Clemons et al.,* 1998; *Safe et al.,* 1997]. Studies on the relationship between the effects of PAHs and the endpoints of endocrine toxicity are limited. The capability of PAHs to bind to endogenous receptors which act as the pathways of the endocrine response are the main evidence for the role of PAHs as endocrine disruptors [*CCME*, 2010].

The cardiovascular effects of PAHs consist in the potential for the development of atherosclerosis due to endothelial damage and changes in smooth muscle cells, which leads to their clonal expansion in the walls of arteries [*SCF*, 2002b].

6.3. Toxicity of PAH mixtures

Human health toxicity of a PAH mixture may be estimated through converting of the PAH concentrations in the mixture to an equivalent concentration of benzo(a)pyrene [*EPA*, 2010]. Historically, toxic equivalent factor (TEF) was calculated for 16 PAH, but recent studies include estimates for up to 88 PAHs both in gaseous and particle phases for more accurate estimation of carcinogenic potency of PAH mixtures [*Samburova et al*., 2017]. For PAH derivatives (nitro-PAH, oxy-PAH) TEF also could be generated to estimate impact of these groups of contaminants [*Wei et al*.,

2015]. Total toxic equivalent concentration of PAH mixture can be calculated using the following formula:

$$TEQ_{total} = \sum c_n \cdot TEF_n,$$

where: TEQ_{total} - total toxic equivalent concentration of PAH mixture for assessment of carcinogenic potency; c_n - concentration of the individual PAH in the mixture; TEF_n - toxic equivalent factor for the individual PAH in the mixture (relative to the carcinogenic potency of B(a)P).

The TEF for B(a)P is defined equal to 1. The TEF values of the other PAHs represent a ratio of their toxicity to that of B(a)P. These TEFs can be applied to characterize the carcinogenic potency of each considered PAH and calculate B(a)P equivalent concentration of total PAH mixture (Table 11). This method does not take into account possible synergistic effects of PAH in mixtures, but it is significantly more cost-effective in comparison with testing in laboratories. The toxicity equivalent concentration is widely used to evaluate carcinogenic risk of PAH mixtures and may be applied for any environmental media.

Table 11. *TEF for individual PAHs from literature*

Substance	TEF [*Samburova*, 2017]	TEF [*Bari*, 2010]	TEF [*Liu*, 2009]
Benzo(a)pyrene	1	1	1
Benzo(e)pyrene	1	0.01	
Benzo(a)anthracene	0.1	0.1	0.005
Dibenzo(a,h)anthracene	5	1	1.1
Benzo(b)fluoranthene	0.1	0.1	0.1
Benzo(j)fluoranthene	0.1	0.1	
Benzo(k)fluoranthene	0.1	0.1	0.05
Chrysene	0.01	0.01	0.03
Indeno(1,2,3-cd)pyrene	0.1	0.1	0.1
Acenaphthylene	0.001	0.001	
Fluoranthene	0.001	0.001	0.05
Pyrene	0.001	0.001	0.001
Naphthalene	0.001	0.001	
9H-Fluorene	0.001	0.001	
Acenaphthene	0.001	0.001	
Benzo(g,h,i)perylene	0.01	0.01	0.02
Anthracene	0.01	0.01	0.0005
Phenanthrene	0.001	0.001	0.0005

Similarly, the mutagenic equivalent concentration (MEQ) can be estimated for assessment of joint mutagenic potency of PAH mixtures.

$$MEQ_{total} = \sum c_n \cdot MEF_n,$$

where MEQ_{total} - total toxic equivalent concentration of PAH mixture for assessment of mutagenic potency; c_n - concentration of the individual PAH in the mixture; MEF_n - toxic equivalent factor for the individual PAH in the mixture (relative to the mutagenic potency of B(a)P).

Available estimates of MEF values for individual PAHs are listed in the Table 12 below.

Table 12. *Estimates of MEF values for individual PAHs*

Substance	MEF [*Durant*, 1996]
Benzo(a)pyrene	1
Benzo[e]pyrene	0.0017
Benzo(a)anthracene	0.082
Dibenzo(a,h)anthracene	0.29
Benzo(b)fluoranthene	0.25
Benzo(j)fluoranthene	0.26
Benzo(k)fluoranthene	0.11
Chrysene	0.017
Indeno(1,2,3-cd)pyrene	0.31
Acenaphthylene	5.6E-04
Benzo(g,h,i)perylene	0.19

Assessment of the inhalation cancer risk of PAH mixtures

The inhalation cancer risk (ICR) from exposure of PAH mixtures can be estimated by using of formula [*Bootdee et al*., 2016; *Jung et al*., 2010; *Jia et al*., 2011; *Sarkar and Khillare*, 2012; *Wiriya et al*., 2013]:

$$ICR = TEQ \cdot IUR_{BaP}$$

$$Risk = ICR \cdot 10^6$$

where ICR – inhalation cancer risk; TEQ – total toxic equivalent concentration of PAH mixture for assessment of carcinogenic potency; IUR_{BaP} – the inhalation unit risk; Risk - societal inhalation cancer risk (number of cancer cases per million people). Values of IUR_{BaP} which can be used for assessment of inhalation cancer risk are listed in the Table 13.

Table 13. *Values of inhalation unit risk* IUR_{BaP}

	IUR_{BaP}	Reference
World Health Organization (WHO)	8.7×10^{-5} m^3/µg	*WHO*, 2000
Office of Environmental Health Hazard Assessment (OEHHA) of California Environmental Protection Agency (CEPA)	1.1×10^{-6} m^3/µg for lifetime (70 years) PAH exposure	*Collins et al.,* 1998, *OEHHA*, 2003

Some studies use WHO and CEPA IUR values as upper and lower estimates of potential cancer risk [*Sarkar and Khillare*, 2012]. ICR value between 10^{-6} and 10^{-4} corresponds to medium cancer risk. If ICR value exceeds 10^{-4} it may indicate high cancer risk [*Bootdee et al.,* 2016].

Thus, many PAHs pose a serious risk to human health. At the same time, data for number of toxicological endpoints are limited and additional investigations are required. To assess the toxicity of PAH mixtures, approach of calculation of total toxic equivalent concentrations may be used. Besides, modelling results can be used to estimate the spatial and temporal distribution of indicators of the total population exposure, especially for urban areas.

6.4. Evaluation of exposure to mixture of 16 PAHs

Evaluation of population exposure to elevated B(a)P air concentrations can be extended by the analysis of other toxic PAH substances in the PM chemical composition and estimation of cumulative human health risk [*Liu et al.*, 2019; *Delgado-Saborit et al.*, 2011]. In particular, atmospheric aerosol particles can be enriched by a mixture of various toxic compounds including other PAHs as well as other POPs (e.g. PCDD/Fs, HCB) and heavy metals.

To evaluate population exposure to mixture of toxic PAH compounds, experimental modelling of 16 EPA PAHs was performed. The set of physical-chemical properties of selected PAHs, necessary to run the GLEMOS model, was prepared on the basis of literature data (Chapter 2). According to collected data on the properties, 8 heavier PAHs present in the atmosphere at ambient temperatures mainly in particulate phase, whereas for other of selected PAHs more significant fraction of gaseous phase can take place. Emission data for model simulations were based on the global gridded emission inventory of PKU (Chapter 4). Model simulations of transboundary pollution and fate of 16 PAHs within the EMEP domain have been carried using nested modelling approach. Boundary conditions for the regional scale simulations were obtained from the GLEMOS model run on a global scale.

Exposure to mixture of toxic PAHs can be estimated using the WHO toxicity equivalency factors defined for individual PAH compounds (TEFs) [*ALS*, 2013]. These TEFs can be applied to characterize the carcinogenic potency of each considered PAH and calculate B(a)P equivalent concentration of total PAH mixture. B(a)P equivalent concentration of PAH mixture can be calculated as the sum of the products of individual PAH compounds concentrations and their toxic equivalency factors:

$$B(a)P_{eq} = \sum (C_{PAHi} * TEF_i)$$

Thus, B(a)P equivalent concentrations depends both on the TEF values and the emissions.

Based on the modelling results for the selected 16 PAHs, B(a)P equivalent concentrations were calculated. The spatial distribution of B(a)P equivalent concentrations of 16 PAHs in comparison to distribution of single B(a)P concentrations are presented in Fig. 24. It can be seen that areas with the exceedances of air quality guidelines in case of B(a)P equivalent concentrations are more significant comparing to the B(a)P concentrations only.

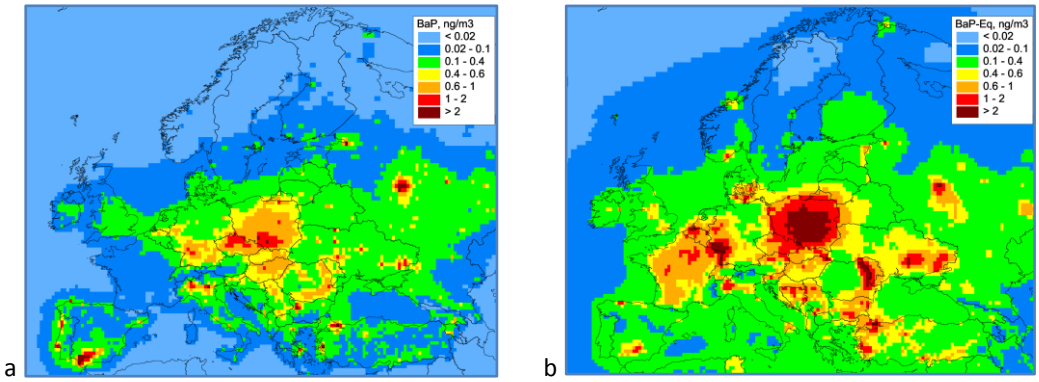


***Fig. 24**. Annual mean modelled B(a)P air concentrations (a) and B(a)P-equivalent air concentrations of 16 PAHs (b) estimated for 2018.*

Modelling results make it possible to estimate the contributions of individual 16 compounds to the sum of B(a)P equivalent concentrations (Fig. 25). The contribution of particular compounds depends both on the toxic equivalent factor and the magnitude of emissions. The largest contribution to total B(a)P equivalent concentration is made by dibenzo(a,h)anthracene, followed by B(b)F and B(a)P. It can be noted that in spite of relatively high level of toxicity and significant concentrations dibenzo(a,h)anthracene is not currently included in the list of PAHs considered in the POPs Protocol. Thus, inclusion of additional compounds may help to characterize population exposure to toxic PAHs more accurately.

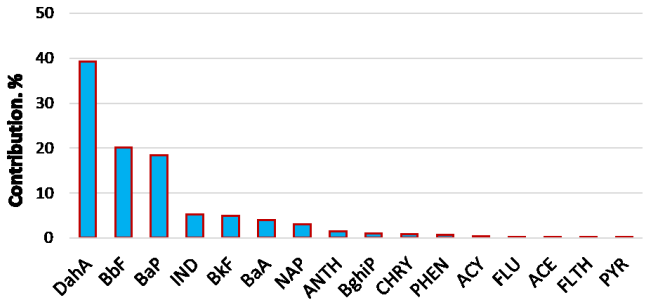


***Fig. 25**. Contributions of individual 16 PAH compounds to the sum of B(a)P equivalent annual mean concentrations*

The information on exceedances of the EU and WHO air quality guidelines for B(a)P as well as data on B(a)P equivalent air concentrations of PAHs are expected to support activities of the Task Force on Health and Working Group on Effects with regard to the analysis of population exposure to toxic substances and their impacts on human health and ecosystems.

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Annex A

PHYSICAL-CHEMICAL PROPERTIES OF SELECTED PAHs

The Annex contains information on physical-chemical properties, substance-specific parameters and degradation rates of PAHs in the environmental media, which were used in model parameterization. Description of parameters including forms of temperature dependences were taken out from EMEP/MSC-E Technical Report 5/2005 [*Gusev et al.*, 2005].

Subcooled liquid-vapour pressure

According to the Junge-Pankow adsorption model, the value of subcooled liquid-vapour pressure (p_{OL}, Pa) is one of the basic parameters in the modelling of PAH partitioning between its particulate and gaseous phase in air [*Junge*, 1977; *Pankow*, 1987]. In addition, the p_{OL} value have impact on subsequent important processes such as dry and wet deposition and atmospheric degradation [*Gusev et al*., 2005].

The value of subcooled liquid-vapour pressure (p_{OL}, Pa) depends on the ambient temperature and is included in the model as follows:

$$p_{OL} = p_{OL}^0 \exp\left[-a_p\left(\frac{1}{T}-\frac{1}{T_0}\right)\right],$$

where T is the ambient temperature, K; T_0 is the reference temperature, K; p_{OL}^0 is the value of p_{OL} at the reference temperature T_0; a_p is the coefficient of the vapour pressure temperature dependence, K.

This formula is obtained from the standard form of the temperature dependence by recalculating the coefficients of the exponential equation:

$$\log p_{OL}\,(Pa) = -A/T(K) + B$$

using the following formulas:

$$a_p = A \cdot ln(10)$$
$$p_{OL}^0 = 10^{-A/T_0+B}$$

The coefficients of p_{OL} temperature dependence and base values given at the temperature 283.15 K (T_0) for the selected PAHs are listed in Table A.1.

Table A.1. *Coefficients of p_{OL} temperature dependence used in model parameterization*

Substance	Value					Log p_{OL} (298 K)	Reference
	T_0	A	B	p_{OL}^0	a_p		
Benzo(a)pyrene	283.15	6060	14.864	2.8968E-07	13953.6657	-5.461	*Allen et al.*, 1999
Benzo(a)anthracene	283.15	3731	8.864	4.8667E-05	8590.94498	-3.648	*Allen et al.*, 1999
Dibenzo(a,h)anthracene	283.15	7009	16.378	4.2105E-09	16138.8189	-7.129	*Allen et al.*, 1999
Benzo(b)fluoranthene	283.15	4578	9.48	2.0506E-07	10541.2346	-5.875	*Paasivirta et al.*, 1999
Benzo(k)fluoranthene	283.15	4427	9.48	7.0013E-07	10193.5442	-5.368	*Paasivirta et al.*, 1999
Chrysene	283.15	5676	14.663	4.1408E-06	13069.473	-4.374	*Allen et al.*, 1999
Indeno(1,2,3-cd)pyrene	283.15	4839	9.60	3.2368E-08	11142.2093	-6.630	*Paasivirta et al.*, 1999
Acenaphthylene	283.15	2751	9.53	0.0012495	8445.882	-2.252	*Paasivirta et al.*, 1999
Fluoranthene	283.15	3668	10.051	0.0012495	8445.88212	-2.252	*Allen et al.*, 1999
Pyrene	283.15	4067	11.260	0.00078811	9364.61357	-2.382	*Allen et al.*, 1999
Naphthalene	283.15	3075	11.835	9.44129973	7080.44916	1.518	*Allen et al.*, 1999
Fluorene	283.15	3779	12.330	0.09632014	8701.46907	-0.347	*Allen et al.*, 1999
Acenaphthene	283.15	3561	12.073	0.3137813	8199.50552	0.129	*Allen et al.*, 1999
Benzo(g,h,i)perylene	283.15	6707	10.487	6.3082E-14	15443.4382	-12.010	*Allen et al.*, 1999
Anthracene	283.15	3667	11.015	0.0115949	8443.57954	-1.285	*Allen et al.*, 1999
Phenanthrene	283.15	4297	13.177	0.01002993	9894.20814	-1.237	*Allen et al.*, 1999

Henry's law constant and air/water partition coefficient

The value of the Henry's law constant and the air/water partition coefficient are used to describe the process of gas exchange between the atmosphere and soil, the atmosphere and seawater, as well as wet deposition of gaseous phase of PAHs [*Gusev et al.,* 2005]. The ratio between the Henry's law constant, K_H, Pa·m^3/mol) and the air/water partition coefficient K_{aw}, dimensionless) is as follows:

$$K_{aw} = K_H^{'} = \frac{K_H}{RT},$$

where T - temperature, K; R = 8.314 J/(mol·K) - universal gas constant.

The temperature dependence of the Henry's law constant $K_H^{'}$ (dimensionless) is used in the model parameterization, as follows:

$$K_H^{'} = \frac{K_{H0}}{RT} exp\left[-a_H\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$$

where T is the ambient air temperature, K; T_0 is the reference temperature; R is the universal gas constant, J/(mol·K), a_H is the coefficient of Henry's law constant temperature dependence, K; K_{H0} is the value of Henry's law constant at reference temperature, Pa·m^3/mol.

This formula is obtained from the standard form of the temperature dependence by recalculating the coefficients of the exponential equation

$$\log K_H\,(Pa \cdot m^3/mol) = -A/T(K) + B$$

using the following formulas:

$$a_H = A \cdot ln(10)$$

$$K_{HO} = 10^{-A/T_0+B}$$

Coefficients of the temperature dependence of the Henry's law constant for the selected POPs are presented in Table A.2.

Table A.2. *Coefficients of temperature dependence of Henry`s law constant used in model parameterization*

Substance	Value					$logK_H$ (298.15 K)	Ref
	T_0	A	B	K_{H0}	a_H		
Benzo(a)pyrene	283.15	3373.71	10.5985	0.048259	7768.254	-0.71698	*Parnis et al.,* 2015
Benzo(a)anthracene	283.15	3222.02	10.4494	0.117544	7418.975	-0.35731	*Parnis et al.,* 2015
Dibenzo(a,h)anthracene	283.15	3804.62	11.3258	0.007745	8760.461	-1.43496	*Parnis et al.,* 2015
Benzo(b)fluoranthene	283.15	3438.16	10.7422	0.03978	7916.656	-0.78945	*Parnis et al.,* 2015
Benzo(k)fluoranthene	283.15	3457.54	10.8171	0.040375	7961.28	-0.77955	*Parnis et al.,* 2015
Chrysene	283.15	3204.84	10.3614	0.110376	7379.417	-0.38769	*Parnis et al.,* 2015
Indeno(1,2,3-cd)pyrene	283.15	3613.54	10.9810	0.01656	8320.483	-1.13887	*Parnis et al.,* 2015
Acenaphthylene	283.15	2271.52	8.8156	6.21269	5230.368	1.196885	*Parnis et al.,* 2015
Fluoranthene	283.15	2850.20	9.7903	0.529977	6562.828	0.230682	*Parnis et al.,* 2015
Pyrene	283.15	2780.21	9.6440	0.668561	6401.67	0.31913	*Parnis et al.,* 2015
Naphthalene	283.15	2004.90	8.4590	23.89465	4616.453	1.734532	*Parnis et al.,* 2015
Fluorene	283.15	2482.51	9.3181	3.55326	5716.191	0.991721	*Parnis et al.,* 2015
Acenaphthene	283.15	2250.90	9.0081	11.44467	5182.889	1.458544	*Parnis et al.,* 2015
Benzo(g,h,i)perylene	283.15	3525.61	10.7566	0.020194	8118.017	-1.06835	*Parnis et al.,* 2015
Anthracene	283.15	2620.30	9.4938	1.736578	6033.464	0.705271	*Parnis et al.,* 2015
Phenanthrene	283.15	2606.56	9.4130	1.612204	6001.826	0.670555	*Parnis et al.,* 2015

Washout ratio

The model separately considers the wet deposition of gaseous and particulate phases of PAHs.

In regard to the leaching of the gaseous phase of PAHs with precipitation, it is assumed in the model that the equilibrium between the vapor phase and the dissolved phase in the raindrop is reached rapidly, and the washout ratios for the gaseous phase (W_g dimensionless) of PAHs is determined as inverse values to dimensionless Henry's law constant:

$$W_g = \frac{1}{K_H^{'}}$$

where $K_H^{'}$ is the dimensionless Henry's law constant.

It should be noted, that the values of the washout ratios for the gaseous phase of PAHs can also be determined experimentally based on the relationship of a compound concentration in the dissolved phase in wet depositions and in the gaseous phase in

In regard to the leaching of the particle bound phase of PAHs with precipitation (W_p, dimensionless), the values of the washout ratio which are determined experimentally or obtained theoretically can be used. Wet deposition of particulate phase of PAHs is the prevailing mechanism of removing of pollutants that occur in the air predominantly associated with the particles.

Table A.3 gives washout ratio values of the considered PAHs used in the model parameterization.

Table A.3. *Washout ratio, used in the model parameterization*

Substance	W_p, dimensionless	References
Benzo(a)pyrene	$3.0 \cdot 10^3$ (Range 7.2 - $1.4 \cdot 10^6$)	*Skrdlíková et al,* 2011
Benzo(a)anthracene	$4.3 \cdot 10^3$ (Range 47-$9.1 \cdot 10^5$)	*Skrdlíková et al,* 2011
Dibenzo(a,h)anthracene	$2.2 \cdot 10^3$ (Range 290-$5.1 \cdot 10^6$)	*Skrdlíková et al,* 2011
Benzo(b)fluoranthene	$1.5 \cdot 10^4$(Range 8.8-$9.4 \cdot 10^5$)	*Skrdlíková et al,* 2011
Benzo(k)fluoranthene	$2.0 \cdot 10^4$ (Range 24-$8.1 \cdot 10^5$)	*Skrdlíková et al,* 2011
Chrysene	$1.5 \cdot 10^4$ (Range 94-$8.0 \cdot 10^5$)	*Skrdlíková et al,* 2011
Indeno(1,2,3-cd)pyrene	$6.2 \cdot 10^3$ (Range 28-$1.6 \cdot 10^7$)	*Skrdlíková et al,* 2011
Acenaphthylene	$2.1 \cdot 10^3$ (Range 61-$1.7 \cdot 10^5$)	*Skrdlíková et al,* 2011
Fluoranthene	$2.0 \cdot 10^4$(Range 3000-$4.7 \cdot 10^5$)	*Skrdlíková et al,* 2011
Pyrene	$1.3 \cdot 10^4$ (Range 50-$3.8 \cdot 10^5$)	*Skrdlíková et al,* 2011
Naphthalene	$2.7 \cdot 10^7$	*He & Balasubramanian*, 2009 *Zhang et al,* 2015
Fluorene	$1.6 \cdot 10^4$ (Range 34-$4.3 \cdot 10^5$)	*Skrdlíková et al,* 2011
Acenaphthene	$5.5 \cdot 10^3$ (Range 32-$4.7 \cdot 10^5$)	*Skrdlíková et al,* 2011
Benzo(g,h,i)perylene	$1.8 \cdot 10^5$	*He & Balasubramanian*, 2009
Anthracene	$6.3 \cdot 10^3$ (Range 62-$1.7 \cdot 10^6$)	*Skrdlíková et al,* 2011
Phenanthrene	$1.8 \cdot 10^4$ (Range 550-$4.2 \cdot 10^5$)	*Skrdlíková et al,* 2011

Degradation rate constants in environmental media

Degradation process of PAHs in the atmosphere includes the gas-phase reactions and degradation of PAHs associated with particles with hydroxyl radicals, ozone and NO_3 radicals. These reactions are described by the equation:

$$\frac{dC}{dt} = -k_{air} \cdot C \cdot [reactant],$$

where C is the pollutant concentration in air, ng/m^3; $[reactant]$ is concentration of considered reactant, molec/cm^3.

Values of second order degradation rate constants in air (k_{air}), used in model parameterization are presented in Table A.4.

Table A.4. *Degradation rate constants in air k_{air}, used in model parameterization*

Substance	Gaseous			Particles		
	$k_{g\ OH}$, $cm^3\ molec^{-1}\ s^{-1}$	$k_{g\ O3}$, $cm^3\ molec^{-1}\ s^{-1}$	$k_{g\ NO3}$, $cm^{-3}molec^{-1}\ s^{-1}$	k_{OH}, $cm^3\ molec^{-1}\ s^{-1}$	k_{O3}, $cm^3\ molec^{-1}\ s^{-}$	k_{NO3}, $cm^3\ molec^{-1}\ s^{-}$
Benzo(a)pyrene	$3.5 \cdot 10^{-12}$ *Lammel et al.*, 2015		$5.4 \cdot 10^{-11}$ *Lammel et al.*, 2009	$4.1 \cdot 10^{-12}$ *Lammel et al.*, 2015	$5.3 \cdot 10^{-17}$ *Keyte et al.*, 2013	$2.6 \cdot 10^{-17}$ *Lammel et al.*, 2009
Benzo(a)anthracene	$50 \cdot 10^{-12}$*			$5.6 \cdot 10^{-12}$ *Lammel et al.*, 2015	$2.8 \cdot 10^{-17}$ *Keyte et al.*, 2013	
Dibenzo(a,h)anthracene	$50 \cdot 10^{-12}$ *Keyte et al.*, 2013			$1.6 \cdot 10^{-14}$ *Keyte et al.*, 2013		
Benzo(b)fluoranthene	$16 \cdot 10^{-12}$ *Keyte et al.*, 2013			$1.2 \cdot 10^{-14}$ *Keyte et al.*, 2013		
Benzo(k)fluoranthene	$54 \cdot 10^{-12}$ *Keyte et al.*, 2013			$3.5 \cdot 10^{-12}$ *Lammel et al.*, 2015	$1.9 \cdot 10^{-17}$ *Keyte et al.*, 2013	
Chrysene	$50 \cdot 10^{-12}$ *Keyte et al.*, 2013			$5.0 \cdot 10^{-12}$ *Lammel et al.*, 2015	$1.5 \cdot 10^{-17}$ *Keyte et al.*, 2013	$4.0 \cdot 10^{-12}$ *Keyte et al.*, 2013
Indeno(1,2,3-cd)pyrene	$64 \cdot 10^{-12}$ *Lammel et al.*, 2015			$3.5 \cdot 10^{-13}$ *Keyte et al.*, 2013	$1.9 \cdot 10^{-17}$ *Keyte et al.*, 2013	
Acenaphthylene	$110 \cdot 10^{-12}$ *Lammel et al.*, 2015	$5.5 \cdot 10^{-16}$ *Keyte et al.*, 2013	$7.96 \cdot 10^{-24}$ Keyte et al., 2013			
Fluoranthene	$50 \cdot 10^{-12}$ *Lammel et al.*,2015		$5.1 \cdot 10^{-28}$ *Keyte et al.*, 2013	$3.2 \cdot 10^{-12}$ *Keyte et al.*, 2013	$1.9 \cdot 10^{-17}$ *Keyte et al.*, 2013	$4.0 \cdot 10^{-19}$ *Lammel et al.*, 2009
Pyrene	$50 \cdot 10^{-12}$ *Keyte et al.*, 2013		$1.6 \cdot 10^{-27}$ *Keyte et al.*, 2013	$3.1 \cdot 10^{-12}$ *Lammel et al.*, 2015	$2.5 \cdot 10^{-17}$ *Keyte et al.*, 2013	$6.4 \cdot 10^{-12}$ *Keyte et al.*, 2013
Naphthalene	$23 \cdot 10^{-12}$ *Lammel et al.*, 2015	$<0.3 \cdot 10^{-18}$ *Keyte et al.*, 2013	$3.3 \cdot 10^{-28}$ - *Keyte et al.*, 2013	$5 \cdot 10^{-12}$ *Lammel et al.*, 2015	$0.9 \cdot 10^{-18}$ *Keyte et al.*, 2013	
Fluorene	$13 \cdot 10^{-12}$ *Keyte et al.*, 2013		$5.1 \cdot 10^{-26}$ *Keyte et al.*, 2013	$3.1 \cdot 10^{-12}$ *Lammel et al.*, 2015		
Acenaphthene	$100 \cdot 10^{-12}$ *Lammel et al.*, 2015	$<0.5 \cdot 10^{-18}$ *Keyte et al.*, 2013	$1.7 \cdot 10^{-27}$ *Keyte et al.*, 2013			
Benzo(g,h,i)perylene	$87 \cdot 10^{-12}$ *Lammel et al.*, 2015			$5.9 \cdot 10^{-12}$ *Lammel et al.*, 2015		
Anthracene	$17 \cdot 10^{-12}$ *Lammel et al.*, 2015			$4.4 \cdot 10^{-12}$ *Lammel et al.*, 2015	$9.8 \cdot 10^{-17}$ *Keyte et al.*, 2013	$9.0 \cdot 10^{-19}$ *Lammel et al.*, 2009
Phenanthrene	$13 \cdot 10^{-12}$ *Lammel et al.*, 2015	$4.0 \cdot 10^{-19}$ *Keyte et al.*, 2013	$1.74 \cdot 10^{-25}$ *Keyte et al.*, 2013	$5.0 \cdot 10^{-12}$ *Keyte et al.*, 2013	$2.4 \cdot 10^{-17}$ *Keyte et al.*, 2013	

The degradation process of PAHs in soil is described in the model as a first-order process as follows:

$$\frac{dC}{dt} = -k_{soil}C,$$

where C is the concentration of substance in soil, ng/m^3; k_{soil} is the degradation rate constant for soil, s^{-1}.

For seawater, the degradation process of PAHs can be described also as a first-order process by following equation:

$$\frac{dC}{dt} = -k_{sea}C,$$

where C is the concentration of substance in seawater, pg/L; k_{sea} is the degradation rate constant for seawater, s^{-1}.

Values of the degradation rate constants in soil and seawater for the considered PAHs are presented in Table A.5.

Table A.5. *Degradation rate constants in environmental media k_{soil} and k_{sea} used in model parameterization*

Substance	k_{soil}, s^{-1}	k_{sea}, s^{-1}	References
Benzo(a)pyrene	$1.13 \cdot 10^{-8}$	$1.13 \cdot 10^{-7}$	*Mackay et al.*, 2006
Benzo(a)anthracene	$1.13 \cdot 10^{-8}$	$1.13 \cdot 10^{-7}$	*Mackay et al.*, 2006
Dibenzo(a,h)anthracene	$1.13 \cdot 10^{-8}$	$1.13 \cdot 10^{-7}$	*Mackay et al.*, 2006
Benzo(b)fluoranthene	$1.13 \cdot 10^{-8}$	$1.13 \cdot 10^{-7}$	*Mackay et al.*, 2006
Benzo(k)fluoranthene	$1.13 \cdot 10^{-8}$	$1.13 \cdot 10^{-7}$	*Mackay et al.*, 2006
Chrysene	$1.13 \cdot 10^{-8}$	$1.13 \cdot 10^{-7}$	*Mackay et al.*, 2006
Indeno(1,2,3-cd)pyrene	$1.13 \cdot 10^{-8}$	$1.13 \cdot 10^{-7}$	*Mackay et al.*, 2006
Acenaphthylene	$1.34 \cdot 10^{-7}$	$1.34 \cdot 10^{-7}$	*Mackay et al.*, 2006
Fluoranthene	$1.13 \cdot 10^{-8}$	$1.13 \cdot 10^{-7}$	*Mackay et al.*, 2006
Pyrene	$1.13 \cdot 10^{-8}$	$1.13 \cdot 10^{-7}$	*Mackay et al.*, 2006
Naphthalene	$1.13 \cdot 10^{-7}$	$1.13 \cdot 10^{-6}$	*Mackay et al.*, 2006
Fluorene	$3.5 \cdot 10^{-8}$	$3.5 \cdot 10^{-7}$	*Mackay et al.*, 2006
Acenaphthene	$3.5 \cdot 10^{-8}$	$3.5 \cdot 10^{-7}$	*Mackay et al.*, 2006
Benzo(g,h,i)perylene	$1.36 \cdot 10^{-8}$	$1.36 \cdot 10^{-8}$	*Mackay et al.*, 2006
Anthracene	$3.5 \cdot 10^{-8}$	$3.5 \cdot 10^{-7}$	*Mackay et al.*, 2006
Phenanthrene	$3.5 \cdot 10^{-8}$	$3.5 \cdot 10^{-7}$	*Mackay et al.*, 2006

Octanol-water partition coefficient

The octanol-water partition coefficient (K_{OW}, dimensionless) a characteristic of the hydrophobicity of a substance. It describes distribution of the compound between water and the lipid medium. K_{OW} can be used also for the estimation of the partition coefficient in the organic carbon-water system (K_{OC}), and for the calculation of the bioconcentration factor (BCF).

For the considered PAHs partition coefficients in the "octanol-water" system selected for modelling are given in Table A.6.

Table A.6. *Octanol-water partition coefficient (K_{OW}), dimensionless used in the model parameterization*

Substance	logK_{OW}	K_{OW}	References
Benzo(a)pyrene	6.50	3.16E+06	*Lammel et al.,* 2015
Benzo(a)anthracene	5.61	4.07E+05	*Lammel et al.,* 2015
Dibenzo(a,h)anthracene	6.5	$3.16 \cdot 10^6$	*Lammel et al.,* 2015
Benzo(b)fluoranthene	6.12	1.32E+06	*Lammel et al.,* 2015
Benzo(k)fluoranthene	6.84	6.92E+06	*Lammel et al.,* 2015
Chrysene	5.91	8.13E+05	*Lammel et al.,* 2015
Indeno(1,2,3-cd)pyrene	6.58	3.80E+06	*Lammel et al.,* 2015
Acenaphthylene	4.07	1.17E+04	*Lammel et al.,* 2015
Fluoranthene	5.20	$0.16 \cdot 10^6$	LOG KOW Databank, compiled by Dr. James Sangster, Canada
Pyrene	5.18	1.51E+05	*Lammel et al.,* 2015
Naphthalene	3.37	2344	*Lammel et al.,* 2015
Fluorene	4.18	15136	*Lammel et al.,* 2015
Acenaphthene	3.92	8317	*Lammel et al.,* 2015
Benzo(g,h,i)perylene	6.63	$4.27 \cdot 10^6$	*Lammel et al.,* 2015
Anthracene	4.50	31623	*Lammel et al.,* 2015
Phenanthrene	4.60	39811	*Lammel et al.,* 2015

Octanol-air partition coefficient

The octanol-air partition coefficient (K_{OA}, dimensionless) is used to describe the distribution of the substance between air and the cuticle of plants, between the gaseous phase and the organic film of atmospheric aerosol particles, etc. K_{OA} can be defined experimentally (by the ratio of equilibrium concentrations of a substance in octanol and air) or through using of coefficients "octanol-water" (K_{OW}) and "air-water" (K_{AW}).

Octanol-air partition coefficient (K_{OA}) depends on temperature of ambient air. The temperature dependence of partition coefficient in the "octanol-air" system is expressed in the following form:

$$K_{OA} = K_{OA}^0 \exp\left[a_k \left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$$

where T_0 = 283.15 K is the reference temperature; K_{OA}^0 is the K_{OA} value at the reference temperature; T_0, *K;* a_K is the coefficient of K_{OA} temperature dependence, K.

Coefficients for K_{OA} temperature dependence of the considered PAHs used for modelling are presented in Table A.7.

Table A.7. *Octanol-air partition coefficient (K_{OA}), dimensionless used in the model parameterization*

Substance	Value					Reference
	T_0	A	B	a_k	K^0_{OA}	
Benzo(a)pyrene	283.15	5382	-6.5	12392	3.22·1012	*Odabasi et al.,* 2006
Benzo(a)anthracene	283.15	4746	-5.64	10928	1.32·1011	*Odabasi et al.,* 2006
Dibenzo(a,h)anthracene	283.15	5887	-7.17	13555	4.18·1013	*Odabasi et al.,* 2006
Benzo(b)fluoranthene	283.15	5285	-6.40	12169	1.84·1012	*Odabasi et al.,* 2006
Benzo(k)fluoranthene	283.15	5301	-6.42	12206	2.0·1012	*Odabasi et al.,* 2006
Chrysene	283.15	4754	-5.65	10946	1.38·1011	*Odabasi et al.,* 2006
Indeno(1,2,3-cd)pyrene	283.15	5791	-7.00	13334	2.83·1013	*Odabasi et al.,* 2006
Acenaphthylene	283.15	2476	-1.97	5701	5.94·106	*Odabasi et al.,* 2006
Fluoranthene	283.15	3904	-4.34	8989	2.80·109	*Odabasi et al*., 2006
Pyrene	283.15	3985	-4.56	9175	3.26·109	*Chen et al.,* 2018
Naphthalene	283.15					
Fluorene	283.15	2833	-2.61	6523	2.48·107	*Odabasi et al.,* 2006
Acenaphthene	283.15	2597	-2.20	5970	9.37·106	*Odabasi et al.,* 2006
Benzo(g,h,i)perylene	283.15	5834	-7.03	13433	3.75·1013	*Odabasi et al.,* 2006
Anthracene	283.15	3316	-3.41	7635	2·108	*Odabasi et al.,* 2006
Phenanthrene	283.15	3293	-3.37	7582	1.81·108	*Odabasi et al.,* 2006

Molecular diffusion coefficients in air and water

Molecular diffusion coefficients (D_A, D_W, m^2/s) are used in the description of the PAH air-soil exchange process. The molecular diffusion coefficient of an organic compound in air (D_A, m^2/s) can be estimated by the formula [*Schwarzenbach et al.,* 1993]:

$$D_A = 10^{-7} \cdot \frac{T^{1.75} * \left[\frac{1}{M_{air}} + \frac{1}{M}\right]^{0.5}}{p \cdot [\bar{V}_{air}^{1/3} + \bar{V}_m^{1/3}]^2}$$

where T is the absolute temperature, 298 K; M_{air} is the mean molecular air weight, ~29 g/mol; M is the molecular weight of an organic substance, g/mol; p is the pressure, 1 atm; $\bar{V}_{air}$ is the mean molar gas volume in the air, ~20.1 cm^3/mol; $\bar{V}_m$ is the molar volume of an organic substance, cm^3/mol.

For the determination of molecular diffusion coefficients for organic substances in water (D_W, m^2/s), the following ratio [*Schwarzenbach et al.,* 1993] can be used:

$$D_W = \frac{13.26 \cdot 10^{-9}}{\mu^{1.14} \cdot \bar{V}_m^{0.589}}$$

where μ is the solution viscosity in centipoise at a certain temperature, taken to be equal to water viscosity, 0.894 cps at 298K; $\bar{V}_m$ is the mean molar volume of a substance, cm^3/mol.

Table A.8 contains values of molecular diffusion coefficients for air and water as well as molar volume and molar masses of considered PAHs.

Table A.8. *Molecular diffusion coefficients in air and water, m^2/s used in the model parameterization*

Substance	M, g/mol	V_m, cm^3/mol	D_a, m^2/s	D_w m^2/s	References
Benzo(a)pyrene	252.31	263	5.032×10^{-6}	5.658×10^{-10}	*Mackay et al.,* 2006
Benzo(a)anthracene	228.29	212.9	5.579×10^{-6}	6.408×10^{-10}	*Mackay et al.,* 2006
Dibenzo(a,h)anthracene	278.36	300.0	4.707×10^{-6}	5.236×10^{-10}	*Mackay et al.,* 2006
Benzo(b)fluoranthene	252.31	268.9	4.980×10^{-6}	5.585×10^{-10}	*Mackay et al.,* 2006
Benzo(k)fluoranthene	252.31	268.9	4.980×10^{-6}	5.585×10^{-10}	*Mackay et al.,* 2006
Chrysene	228.29	251.0	5.171×10^{-6}	5.816×10^{-10}	*Mackay et al.,* 2006
Indeno(1,2,3-cd)pyrene	276.33	233.8	5.292×10^{-6}	6.064×10^{-10}	*Mackay et al.,* 2006
Acenaphthylene	152.19	141.2	6.893×10^{-6}	8.161×10^{-10}	*Mackay et al.,* 2006
Fluoranthene	202.26	217.0	5.571×10^{-6}	6.336×10^{-10}	*Mackay et al.,* 2006
Pyrene	202.25	214.0	5.607×10^{-6}	6.389×10^{-10}	*Mackay et al.,* 2006
Naphthalene	128.17	147.6	6.861×10^{-6}	7.951×10^{-10}	*Mackay et al.,* 2006
Fluorene	166.23	188.0	6.027×10^{-6}	6.895×10^{-10}	*Mackay et al.,* 2006
Acenaphthene	154.21	173.0	6.293×10^{-6}	7.241×10^{-10}	*Mackay et al.,* 2006
Benzo(g,h,i)perylene	276.33	277.0	4.889×10^{-6}	5.488×10^{-10}	*Mackay et al.,* 2006
Anthracene	178.23	197.0	5.871×10^{-6}	6.708×10^{-10}	*Mackay et al.,* 2006
Phenanthrene	178.23	199.0	5.845×10^{-6}	6.668×10^{-10}	*Mackay et al.,* 2006