EXECUTIVE SUMMARY

Heavy metals and persistent organic pollutants (POPs) are toxic substances that adversely affect human health and ecosystems. The problem of the environmental pollution by these contaminants is targeted by various international bodies including the UNECE Convention on Long-range Transboundary Air Pollution (hereafter, CLRTAP or the Convention). The priority heavy metals and POPs addressed by the Convention include lead (Pb), cadmium (Cd), mercury (Hg), polychlorinated biphenyls (PCBs), polychlorinated dibenzo(p)dioxins and dibenzofurans (PCDD/Fs), hexachlorobenzene (HCB), and polyaromatic hydrocarbons (PAHs). The priority PAHs are 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 (IP). Scientific support of implementation of the Protocols on Heavy Metals and POPs under the Convention is provided by the Co-operative Programme for Monitoring and Evaluation of Long-range Transmission of Air Pollutants in Europe (EMEP, www.emep.int). Research and operational assessment of heavy metal and POP pollution are carried out by relevant EMEP Centres – the Centre on Emission Inventories and Projections (CEIP), the Chemical Coordinating Centre (CCC), the Meteorological Synthesizing Centre – East (MSC-E).

This Status report presents an overview of activities of the EMEP Centres focused on research and assessment of heavy metal and POPs pollution in 2018 carried out in accordance with the bi-annual workplan of the Convention for 2020-2021 [ECE_EB.AIR_144_Add.2]. The report includes information on emissions, monitoring, and model assessment of heavy metal and POP pollution in 2018; research activities and co-operation with subsidiary bodies to the Convention and international organizations. Detailed technical information aimed to support the Status Report is available in the Supplementary Data Reports on heavy metals [*Ilyin et al.,* 2020] and POPs [*Gusev et al.,* 2020] as well as at the MSC-E website (www.msceast.org).

Emissions

Completeness and consistency of reported data on heavy metal emissions have improved significantly. Forty three countries reported data on the priority heavy metal emissions, and 42 countries - on POP emissions in 2020. The quality of submitted data differs quite significantly among countries. Uncertainty of reported data (national totals and sectoral data) is considered relatively high and affects long-term trends of the emissions in the EMEP domain. Heavy metal emissions in the western part of the EMEP domain show smooth downtrend. Emission trends of heavy metals in the eastern part of the EMEP domain as well as POP trends in the both EMEP parts exhibit strong fluctuations because of incomplete or inconsistent reporting by particular countries. In order to improve reported emission data, re-calculations of national emissions are performed regularly. Due to the re-calculations the emissions data of 25 countries changed by more than 15% for one or several pollutants, and the changes were minor (< 1%) for 8 countries.

The main emission sectors for heavy metals and PCB are ‘Industry’ and ‘Public electricity and heat production’. The most of PAHs are emitted by the sector ‘Other stationary combustion’. This sector and ‘Industry’ are almost equally important for emissions of PCDD/Fs and HCB. Sectoral gridded emissions of heavy metals and POPs in the new resolution were reported by 31 countries. Final emissions maps for modelling were generated by MSC-E based on the reported emissions data collected and gap-filled by CEIP and supplemented by additional information on vertical distribution, seasonal variation and chemical speciation emissions. Global emission maps were also prepared based on data derived from research projects and expert estimates.

Monitoring

Measurements of heavy metal and POP pollution levels are performed in the EMEP monitoring network under methodological guidance of CCC. Measurements of Pb and Cd concentrations in air or in precipitation were carried out in 2019 at 64 stations. Measurements of Hg were performed at 25 stations, and 15 of them were co-located. The highest concentrations of Pb and Cd in air in 2018 were observed at stations in Hungary, Slovakia, the Benelux countries. The highest concentrations in precipitation of Pb were noted for Spain and Slovakia, and for Cd – in Estonia and Spain. The highest concentrations of total gaseous and elemental Hg were measured in Germany, whereas the highest Hg concentrations in precipitation – in the Czech Republic. Besides, concentrations of Pb, Cd and Hg in precipitation were much higher in 2018 compared to the previous year because of extremely dry summer.

In total 32 sites reported data on POPs, whereof 26 sites reported measurements in both air and precipitation. The highest PAH and PCB levels took place at sites located in the central part of Europe, whereas the highest HCB levels are noted for the Arctic stations (Spitsbergen, Greenland). The regional distribution of PAHs for the different seasons clearly shows higher concentrations during winter in Eastern Europe, where the emissions from residential heating are highest. The analysis of intra-annual changes of PAH concentrations shows strong seasonal variability with higher air concentrations in winter for all considered PAHs that can be attributed to a combination of both elevated emissions during winter and/or reduced half-lives during summer. Besides, based on the EMEP measurement data for the selected PAHs, it is suggested that sampling strategies based on filters only (PM10) may represent a poor measure of total concentrations in air for low-molecular PAHs.

Transition to finer spatial resolution makes possible more thorough analysis of heavy metal and POP levels in highly populated and urbanized areas. In order to facilitate evaluation of the model performance MSC-E utilized monitoring data from AIRBASE database collected and processed by European Environmental Agency (EEA). In particular, information on the observed air concentrations of B(a)P in 2018 from more than 700 national monitoring sites was involved into the analysis of pollution levels. Besides, measurement data from about 120 national sites were used in the country-scale study of heavy metal pollution in Germany.

Status of heavy metal and POP pollution in 2018

Assessment of heavy metal and POP pollution of the EMEP region is performed using both modelling results and measurement data and includes evaluation of spatial patterns of pollution levels as well as transboundary transport in 2018. The assessment is based on the gridded emissions data for the previous 2017 year. Besides, changes in pollution levels due to inter-annual meteorological variability are evaluated. Update of the modelling results based on the new emission data for 2018 is available In Annex A.

The performed analysis shows that the highest levels of Pb, Cd, and Hg deposition took place in 2018 in Central Europe (Poland, Germany, the Czech Republic, Slovakia) and Southern Europe (Italy, Bulgaria, the Balkan countries). Considerable deposition of Cd also occurs in the European part of Russia. Elevated Hg deposition fluxes are predicted in the high Arctic as a result of intensive Hg oxidation during springtime. The lowest deposition fluxes are in Northern Europe as well as in the Caucasus and Central Asia.

High levels of PAH air concentrations in 2018 occurred in countries of Central, Eastern, and Southern Europe. Countries of Central and Southern Europe are also characterized by elevated concentrations of PCDD/Fs, whereas relatively high concentrations of PCB-153 are predicted in Western Europe. Model estimates indicate substantial spatial gradients of PCDD/Fs and PCB-153 concentrations in the EMEP region, whereas spatial distribution of HCB concentrations is more homogeneous that can be conditioned by its relatively high persistence in the atmosphere.

The assessment of pollution changes due to the inter-annual meteorological variability indicate considerable increase of Pb (13-17%) and Cd (17-20%) deposition in 2018 compared to the previous year in Western and Southern Europe. Eastern Europe as well as Caucasus and Central Asia were characterized by the largest decline of Pb and Cd deposition (7-14%). Mercury deposition flux increased in Southern Europe (18%) and Western Europe (7%) but decreased in Central Europe (8%). The most significant increase of PAH air concentrations (16 %) took place in Northern Europe followed by Southern and Central Europe. At the same time, decreasing air concentrations were estimated for Western and Eastern Europe. It should be noted that concentration and deposition changes can be larger in particular countries (up to ±50%).

Modelled air concentrations and wet deposition of heavy metals generally agree with the levels observed at the EMEP monitoring network. The mean relative bias between the annual average modelled and observed air concentrations does not exceed -10% and -5% for Pb and Cd, respectively. Deviation between the modelled and observed Hg^0 air concentrations does not exceed ±10%. Simulated wet deposition fluxes of all heavy metals demonstrate satisfactory agreement with measurements with deviations being mostly within a factor of two. However, the model tends to underestimate (by 20-25%) observed wet deposition of Pb and Cd and overestimate Hg wet deposition.

The modelling results on the sum of 4 PAHs agree with EMEP measurements with the mean relative bias about -9% and high spatial correlation (0.8). Validation of individual PAH compounds indicates some underprediction of observed B(a)P and B(k)F air concentrations by the model, and over-prediction of observed B(b)F and IP concentrations. Similarly, the model tends to underpredict AIRBASE measurements of B(a)P at rural and suburban monitoring stations. Modelled air concentrations of PCB-153 and HCB reasonably well agree with measurements with average relative biases -2% and -27%, respectively, and significant spatial correlation (0.6-0.75). Monitoring of PCDD/F air concentration was carried out in 2018 only at two EMEP stations (SE0014R and SE0022R) for the period of four months. Comparison of measured and modelled air concentrations shows systematic underestimation of observed values at both stations by a factor of 2.

Atmospheric deposition of Pb and Cd in the EMEP countries is largely formed by anthropogenic emissions and secondary sources (wind re-suspension). Anthropogenic sources make up the largest contribution in Central Europe (66% for Pb and 80% for Cd), whereas the effect of secondary sources is the most significant in Caucasus and Central Asia. Contribution of non-EMEP sources is relatively small except for the countries located close to the borders of the EMEP region. Regional anthropogenic emissions sources contribute 25% of Hg deposition in the EMEP countries, whereas contribution of intercontinental transport exceeds 75%. However, this large estimate contains implicit contribution of EMEP emissions that flew out through the boundaries and returned back to the region. The contribution of transboundary transport exceeds deposition form national sources in 38, 41 and 38 of 51 EMEP countries for Pb, Cd and Hg, respectively.

Anthropogenic emission sources made up the most significant contribution to PAH pollution levels. Contrary to this, for PCDD/Fs, PCB-153, and HCB significant contribution (about 50-70%) is estimated for secondary

emission sources. Model assessment of POP long-range transport indicates considerable role of transboundary transport between the EMEP countries. In particular, contribution of transboundary transport to PAH deposition exceeds 50% of total deposition in 27 of 51 EMEP countries. The prevalence of transboundary pollution of domestic sources is also characteristics of 20, 30, and 39 countries for PCDD/Fs, PCB-153, and HCB, respectively.

Marine environment is protected on national and international levels by a number of regional conventions such as HELCOM, OSPAR, Barcelona Convention, Bucharest Convention, and Tehran Convention. Information on heavy metal and POP atmospheric input to the marginal seas surrounding the EMEP region is prepared by MSC-E. These are the Baltic, North, Mediterranean, Black, and Caspian Seas. Deposition fluxes of heavy metals and POPs to different marginal seas vary significantly depending on location of anthropogenic and secondary sources, and meteorological conditions. Deposition fluxes of Pb and Cd are higher for the Mediterranean, Caspian and Black seas and are lower the Baltic and North Seas. The highest deposition fluxes of Hg take place to the North Sea. The most significant deposition of most POPs is estimated for the Baltic or Black Sea, whereas the lowest is for the Caspian Sea.

Information of pollution of the Arctic by heavy metals and POPs in 2018 is prepared by MSC-E. The information on the Arctic pollution includes spatial distribution and sources apportionment of heavy metal and POP deposition. Due to remoteness of Arctic from main emission sources of Europe, Asia or North America deposition fluxes of heavy metals and POPs in the Arctic are typically lower compared to those in temperate latitudes. Russian Federation makes up the largest contribution to the Arctic anthropogenic pollution by all considered heavy metals and POPs. The reason for that is location of significant of the country within the Arctic region. Some other EMEP countries also considerably contribute to pollution of the region (e.g. Sweden, Norway, Finland, Kazakhstan, France, Germany).

Contamination of the EMEP countries by heavy metals and POPs is affected by long-range transport of the pollutants from emission sources located in other regions or continents. It is particular relevant for Hg and some POPs (HCB, PCDD/Fs), which are characterized by long residence time in the atmosphere. Therefore, model assessment of pollution levels in the EMEP domain is supported by global scale simulations. It should be noted that the global scale modelling of heavy metal and POP pollution requires reliable and up-to-date global emission inventories. However, no data on contemporary emissions is available for Pb, Cd, HCB and PCDD/Fs. Thus, improvement of the global scale assessment requires additional efforts for development of global emissions inventories for heavy metals and POPs in co-operation with other international bodies (UN Environment, Stockholm Convention, Minamata Convention).

Information for exposure assessment

The ultimate aim of pollution assessment is evaluation of risks for human health and ecosystems associated with adverse effects of the pollution. Therefore, MSC-E continues providing the effect community with information that can be useful for the exposure assessment. In particular, information of ecosystem-specific deposition of heavy metals and POPs is provided for evaluation of the critical loads exceedances. Besides, exceedances of the PAH air quality standards are analyzed along with discussion about heavy metal and POP content in composition of particular matter that can lead to additional toxicity of atmospheric aerosol.

Information on calculated deposition fluxes of heavy metals and POPs is used for evaluation of the effects of the pollutants on human health and biota. In order to support this activity of the Working Group on

Effects, MSC-E regularly calculates deposition fluxes to various types of land cover (forests, shrubs, grasslands, crops, water bodies, etc.) within the EMEP domain. Data on the modelled Pb, Cd and Hg deposition to 17 land-cover types is available at the MSC-E website. However, the most recent estimates of the adverse effects of heavy metals on human health and biota relate to 2010 and can hardly reflect present status of pollution. More efforts of the effects community in the field of evaluation of heavy metal and POP pollution adverse impacts are needed.

Results of model simulations for 2018 and measurements from national monitoring stations, collected in the AIRBASE, indicate high level of annual mean B(a)P air concentrations, exceeding the EU target value, in number of EMEP countries (Poland, Spain, Italy, Germany, the Czech Republic, Portugal, Hungary, Serbia, and Bulgaria). Areas of high concentrations (above the EU target value) are also noted in some of the EECCA countries. Considerable part of total population of the EMEP countries lived on territories, where the air quality guidelines for B(a)P air concentrations were exceeded (5% for the EU target level and 60% for the WHO reference level). Along with B(a)P, modelling results on 4 PAHs were also used to estimate population exposure to mixture of toxic PAHs in the form of B(a)P equivalent air concentrations.

Particular attention is paid to the chemical composition of atmospheric aerosol (PM_{10} and $PM_{2.5}$), which may contain toxic substances such as heavy metals, PAHs and other organic pollutants (e.g. PCB and PCDD/Fs). Current assessments of air pollution by particulate matter (PM) are largely focused on the mass concentration analysis. However, impact of PM on human health may be more significant due to the presence of hazard constituents. For instance, aerosol particles from solid fuels combustion can be enriched with 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. Besides, PAHs can be contained in condensable PM, which is generated from hot gaseous phase during contact with cooler ambient air. Thus, simultaneous measurements of PM and its components may be useful for more precise risk assessment. The influence of chemical composition of on the PM toxicity is the subject of future research.

Research activities

The main directions of the research included evaluation of PAH pollution and population exposure in the EMEP countries, downscaling of heavy metal pollution assessment for Germany, further study of Hg oxidation and reduction in the atmosphere, update of model parameterizations of gas-particle partitioning, degradation and air-surface exchange of POPs.

High levels 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. Specific attention in this respect is paid to the emissions from residential combustion and biomass burning as prevailing source categories of PAHs. In order to contribute to these activities, MSC-E collects and analyses information on physical-chemical properties of toxic PAHs, reported national inventories and expert estimates of PAH emissions as well as approaches to assess population exposure to PAH pollution. Besides, trends in observed and modelled PAH concentrations in air are analyzed and exceedances of air quality guidelines are estimated. Along with this, 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 interaction of PAHs and PM in the atmosphere, and contribution of toxic PAHs to the adverse effects of aerosol particles.

A country-scale study of heavy metal pollution in Germany was performed jointly by EMEP/MSC-E and the German Environment Agency (UBA). The main objective of the study was generation of detailed information on levels and spatial distribution of air concentration and atmospheric deposition of three heavy metals (Pb, Cd, and Hg) for the period 2014-2016. The fine resolution modelling on a country scale provides detailed patterns of heavy metal pollution in the country. Refined national emissions inventory for heavy metals and updates of other input information favour general improvement of the model assessment in comparison with previous EMEP operational modelling. Simulated spatial patterns well agree with background measurements at the EMEP stations. Measurement data from national monitoring networks significantly expand the scope of the analysis. However, more detailed information on the methodology, physical conditions and pollution from local sources in the surrounding of the monitoring stations is needed. Evaluation of the modelling results against national monitoring data reveals discrepancies in some locations or provinces of Germany. Performed analysis showed that the differences between the modelled and measured data can be caused by a number of factors related to uncertainties of emissions data, measurements and modelling approaches. Further in depth analysis of the revealed discrepancies requires assessment on a local scale involving national expertise, collection of more detailed information on emissions and measurements as well as local scale modelling.

Atmospheric chemistry is critical for Hg dispersion in the atmosphere from emission sources and pollution of terrestrial and aquatic ecosystems. It determines the overall Hg residence time in the atmosphere and deposition to the ground. Despite significant improvements in measurements and modelling of Hg cycling in the environment, current knowledge on Hg chemistry in the atmosphere remains incomplete. The GLEMOS model was used for evaluation of the newest suggested mechanisms of Hg oxidation initiated by the reactions with Br and OH as well as photo-reduction of oxidized Hg in the atmosphere. It was shown that inclusion of the mechanisms to the model allows partly reproducing observations but demonstrates insufficient Hg oxidation in the free troposphere. Further analytical studies of Hg redox mechanisms are needed along with the model evaluation to improve model assessment of Hg pollution on both global and regional scales.

The work on the refinement of parameterizations of particle-bound B(a)P degradation and gas-particle partitioning processes in the GLEMOS model was continued. A new parameterization of B(a)P sorption to various components of aerosol particles (water soluble, organic, and inorganic sub-fractions) based on the poly-parameter linear free energy relationships (pp-LFER) was tested. Besides, inclusion of additional species, namely, NO_3 and ozone, into parameterization of gaseous phase B(a)P degradation and alternative degradation constants for particulate phase B(a)P degradation in the atmosphere were considered. Evaluation of currently used and updated parameterizations showed comparable results with somewhat better agreement of modelling results with measurements in case of new pp-LFER approach. Therefore, analysis and testing of this approach will be continued with the aim to include it to the operational model simulations.

Gaseous exchange of POPs between the atmosphere and vegetation is an important process that affects their distribution in the environment. To improve description of the air-vegetation process in the GLEMOS model, an overview of model parameterizations available in the literature was performed. An alternative approach, considering the vegetation and soil as parts of a single compartment (ecosystem) was selected to be implemented in the GLEMOS model after additional testing to describe the cycling of POPs between the environmental compartments (air, vegetation, and soil).

Modelling of atmospheric transport of POPs and Hg requires data on concentrations of various chemical reagents and constituents of aerosol particles. Datasets of the reagents generated by two chemistry transport models (MOZART-4 and GEOS-Chem) were compared and tested with the GLEMOS model for simulation B(a)P. The test simulations showed generally better agreement of the modelling results with measurements in case use of the data from GEOS-Chem. Therefore, the GEOS-Chem model is planned to be preferably used as a chemical preprocessor of reactants concentrations for the GLEMOS model in future.

Cooperation with subsidiary bodies of the Convention and other international bodies

Scientific co-operation is an important part of MSC-E activities aimed at support and improvement of heavy metal and POP pollution assessment within EMEP as well as dissemination of the assessment results to wider international audience. Co-operation with the Working Group on Effects (WGE) included join analysis and interpretation of moss measurement data together with experts from ICP-Vegetation. Results of current research activities and future plans of MSC-E were discussed at the recent meeting of the Task Force on Measurements and Modelling (TFMM). The work on the model retrospective analysis of long-term changes of Hg and POP levels is initialized by the Centre in collaboration with the Task Force on Hemispheric Transport of Air Pollution (TF HTAP). The Centre also contributes to the work of the Task Force on Techno-Economical Issues (TF TEI) aimed at further reduction of PAH pollution levels in the EMEP countries. In co-operation with the Arctic Monitoring and Assessment Programme (AMAP) the Centre takes part in the new AMAP Assessments on the Arctic pollution by Hg. Besides, regular evaluation of airborne pollution load of heavy metals and POPs to the Baltic Sea is carried out in the framework of cooperation with the Helsinki Commission (HELCOM). Finally, MSC-E continues collaboration and data exchange with the Stockholm and Minamata Conventions.

Main challenges and directions of future research

Future directions of the EMEP centre's activities will be aimed at improvement of heavy metal and POP pollution assessment in the EMEP region. Detailed assessment of PAH concentrations trends, contributions of the key emission sources, and evaluation of exceedances of the EU and WHO target levels will be further performed to support activities of WGE, TF Health and TFTEI. Besides, quality of B(a)P modelling will be improved in the framework of the EMEP EuroDelta-Carb intercomparison exercise (TFMM) and a country-scale assessment of PAH pollution in Poland. The newly descovered mechanisms of Hg oxidation and photo-reduction in the atmosphere will be further studied and evaluated along with Hg exchange processes between the atmosphere and other environmental media (water bodies, vegetation etc.). A retrospective analysis of long-term changes of Hg and POP pollution will be performed in co-operation with TF HTAP to identify the key drives of the pollution changes. The emissions, monitoring and modelling issues revealed in the recent country-scale study for Germany will be further examined in co-operation with national experts in order to improve assessment of heavy metal pollution on both national and regional scales. Particular attention of research and development activities will be paid to particle-related processes occurred with heavy metals and POPs in the atmosphere. Finally, MSC-E will continue long-term co-operation with WGE focusing on joint analysis of heavy metal measurements in moss, preparation of information on Hg deposition to various ecosystems, and estimates of B(a)P exceedances of air quality guidelines.