

Contaminants of emerging concern

Contaminants of emerging concern (CECs) comprise a wide range of substances having potential to adversely affect wildlife and human health. Many of CECs are being used in consumer and personal care products and in building materials. CECs include new POPs recently started to be regulated and characterized by limited data on their pollution levels, fate and effects, and substances which are currently unregulated due to the properties falling partly outside existed criteria to be considered as POPs. In spite of limited knowledge, significant attention is paid to the CECs in recent and ongoing research activities including monitoring and assessment of their distribution in the environment and potential risks.

Some of the CECs are included in the annexes of the Stockholm Convention and are listed by AMAP, HELCOM, OSPAR for the analysis of their pollution levels, exposure assessment, and regulatory activities. Selected CECs were added to the CLRTAP POP Protocol for regulation of their production and use, namely, hexachlorobutadiene (HCBd), octabromodiphenyl ether (octa-BDE), pentachlorobenzene (PeCB), pentabromodiphenyl ethers (PBDEs), perfluorooctane sulfonates (PFOS), polychlorinated naphthalenes (PCN) and short-chain chlorinated paraffins (SCCPs). Ambient concentrations of CECs (e.g. of PBDEs, SCCPs, and per- and polyfluoroalkyl substances (PFAS)) are being monitored at EMEP monitoring stations in Northern Europe in accordance with the new EMEP monitoring strategy [ECE/EB.AIR/144/Add.1]. Besides, national monitoring networks carry out measurements of selected CECs in mosses in framework of ICP-Vegetation Programme activities. Furthermore, preparatory work for evaluation of CEC pollution levels, transport and fate in the environment is performed in accordance with the EMEP work plan for 2022-2023. As a part of this activity, a workshop on CEC monitoring and model assessment is planned to be organized in 2023 in co-operation with TFMM, TF HTAP and CCC.

In framework of co-operation with HELCOM, MSC-E carried out compilation of information on some of the CECs (e.g. SCCPs, PFOS, (hexabromocyclododecanes (HBCDDs), PBDEs) with the focus on the Baltic Sea area. In this section an overview of information on these substances including regulatory activities, their production, usage and emissions, as well as results of monitoring and model assessment of their transport and fate in the environment are presented. More detailed information can be found in the Joint reports of the EMEP Centres for HELCOM [Gauss *et al.*, 2021].

Short-chain chlorinated paraffins (SCCPs)

Chlorinated paraffins (alkanes) are a group of saturated hydrocarbons with different chlorine content and different length of carbon chain. Short-chain chlorinated paraffines comprise a complex mixture, which are characterized by a carbon chain-length from 10 to 13 carbon atoms and the degree of chlorination of more than 48% by weight. Assuming that SCCPs do not contain dechlorinated carbon atoms and branched chains, there can be 7820 SCCP isomers and 46 congener groups [Diefenbacher *et al.*, 2015, Krogseth *et al.*, 2013].

SCCPs are considered as substances posing risk both for human health and the environment. International Agency for Research on Cancer (IARC) has classified SCCPs with average carbon chain length 12 (C12) and average chlorination 60% as possible carcinogens for humans (group 2B) [IARC, 1990]. In accordance with the EU REACH (1907/2006/EC) and CLP Regulation (1272/2008/EC), SCCPs are

classified as carcinogens (Category 2), as very toxic to aquatic life with long lasting effects (Category 1), and as persistent, bioaccumulative, and toxic substances (PBT).

Regulation

Taking into account hazardous properties, SCCPs are included in the work programs of various national and international activities, aimed to collect the information on their environmental levels and trends as well as to develop measures for the restriction of their usage and reduction of emissions. SCCPs are recognized as contaminants of concern by the CLRTAP (since 2009) and Stockholm Convention (since 2017). Besides, SCCPs are considered as pollutants of priority action and specific concern in the regulatory activities of OSPAR and HELCOM. In the European Union, the manufacturing, placing on the market and use of SCCPs shall be restricted in accordance with the Article 3 of the EU Regulation (EU) 2019/1021 on POPs.

Production, use, and emissions

Technical mixtures of SCCPs have been widely used in Europe, America, Asia, Australia, and South Africa. The major areas of chlorinated paraffins usage include application in metal working fluids or lubricants, water repelling agents, flame retardants, and plasticizers. SCCPs were used in the production of polyvinyl chloride and consumer goods on its basis, for filling of expansion and movement joints in building and general engineering, filling of joints for protection from spillages, and in other areas where resistance to water, chemicals, alkalis, solvents and biological agents was required. Besides, SCCPs were used in sealants, rubbers, textiles, paints and coatings [Fiedler *et al.*, 2010; Lassen *et al.*, 2014].

Large-scale commercial production of chlorinated paraffins (CPs) was initiated in USA in 1930s. Since 1977 they started to be produced also in Europe and Japan. The highest volume of production was reached after 2006, when China increased sharply manufacturing of CPs. SCCP releases to the environment can occur at all stages of their life cycle including production, formulation, use, and disposal [Breivik *et al.*, 2012]. However, it is widely believed that production and application of SCCPs for manufacturing of other products take place in the closed systems, thus main releases of SCCPs to the environment can take place at the use and disposal stages.

Although SCCPs are included in the Protocol on POPs to LRTAP Convention, no officially reported information on their emissions to the atmosphere is currently available, since SCCPs are not considered to be subject to emission reporting obligations under the Convention in accordance with the Guidelines for Reporting Emissions and Projections Data under the Convention [UNECE, 2014]. As an exception, the inventory of SCCP emissions in Finland [Finland, 2021] can be noted. The European Pollutant Release and Transfer Register (E-PRTR) contains specifications for the reporting of SCCP releases to the environmental compartments. However, SCCP emissions to the atmosphere are not currently submitted by the EU countries. At the same time, it can be noted that under the Stockholm Convention, development of the guidance on preparing inventories of SCCP releases was initiated. Developed methodology for the inventory of SCCP emissions was made available at the end of 2020 [UNEP, 2021].

Monitoring

In accordance with the EMEP monitoring strategy for the period 2020-2029 [ECE/EB.AIR/144/Add.1], it is recommended to monitor SCCPs at the research-based stations (Level 3). Chlorinated paraffins were included in the monitoring campaigns of several countries in Northern Hemisphere [Šebková *et al.*, 2021; Harner *et al.*, 2021]. In Norway, measurements of SCCPs are carried out at the Zeppelin and Birkenes stations. In the period 2017-2019, measured concentrations varied from 60 to 900 pg m^{-3} . Over these three years, some decrease of pollution levels by 30% - 40% was indicated at these two stations. In Sweden, concentrations of SCCPs in air have been regularly monitored at the stations Råö and Aspvreten since 2009. In 2009-2017, SCCP pollution levels ranged from 7 to 220 pg m^{-3} at Råö, and from 6 to 2100 pg m^{-3} at Aspvreten. No clear temporal trend in airborne SCCP concentrations was observed at these stations. However, for the past two years a slight decrease of SCCPs in air can be noted [Swedish EPA, 2020].

Data on SCCP content in atmospheric deposition have been reported by Swedish stations since 2009 [Swedish EPA, 2020]. Sampling was carried out at two stations Råö and Aspvreten 4 times a year. Average annual deposition of SCCPs varied over a wide range from 4.3 to 840 $\text{ng m}^{-2} \text{day}^{-1}$ at Råö and from 1.6 to 190 $\text{ng m}^{-2} \text{day}^{-1}$ at Aspvreten [Fredricsson *et al.*, 2018]. The maximum SCCP deposition flux was observed at Råö in December 2015, while in subsequent years deposition fluxes at this station decreased significantly.

Modelling

Distribution, transport and fate of SCCPs in the environment was investigated using several multi-media models [Vulykh *et al.*, 2007; Glüge *et al.*, 2013; Gawor and Wania, 2013; Krogseth *et al.*, 2013; Chen *et al.*, 2019]. A number of aspects related to environmental pollution by SCCPs was studied including physical-chemical properties, emissions, and approaches to describe their fate. It should be noted that model assessment of chlorinated paraffins represents a challenging task due to the complexity of composition of their mixtures [Chen *et al.*, 2019] and wide range of variations of isomers properties that leads to remarkable variability of their behaviour in the environment [Gawor and Wania, 2013].

Estimates of long-range transport potential and persistence in the environment for selected SCCPs were obtained using numerical multi-media model MSCE-POP [Vulykh *et al.*, 2007]. The model predictions using conventional point emission source in Europe showed atmospheric half-lives of the selected three isomers in the range from 2 to 4 days, and transport distance in the atmosphere from 1700 up to 2600 km.

Systematic investigation of the SCCP physico-chemical properties was carried out in the study [Glüge *et al.*, 2013]. The study of [Gawor and Wania, 2013] describes an approach to analyze variability of physical-chemical properties of individual isomers within the complex mixtures (e.g. SCCPs), determined using quantitative structure–property relationships methods.

Investigation of environmental fate of SCCPs in the western part of the Baltic Sea region was carried out using the combination of environmental fate model CoZMoPOP and bioaccumulation model ACC-HUMAN [Krogseth *et al.*, 2013]. The study indicated the large variability of environmental fates of individual isomers within the group of SCCPs that needs to be taken into account in the assessment of SCCP pollution. The global environmental fate of SCCPs was studied using a mechanistic fugacity-based multimedia fate model BETR-Global [Chen *et al.*, 2019]. The obtained results showed that the effect of

usage of single and multiple sets of SCCP physical-chemical properties was less remarkable in areas with substantial emissions comparing to the areas with negligible emissions.

Perfluorooctane sulfonic acid and its derivatives (PFOS)

Perfluorooctane sulfonic acid and its derivatives (perfluorooctane sulfonates) comprise a group of fully fluorinated chemicals with eight carbons chain length, belonging to the larger group of chemicals, known as per- and poly-fluoroalkyl substances (PFAS).

PFOS are substances of anthropogenic origin. They are widely distributed in the environment both in the vicinity of emission sources and in the remote regions. PFOS can occur in the ionic form as a fully fluorinated anion or as a part of PFOS-related substances, which can degrade and form PFOS [Brooke *et al.*, 2004]. For example, the precursors of PFOS are volatile PFAS.

Although PFOS are related to POPs, their physical-chemical properties differ markedly from those of traditional POPs. PFOS do not undergo hydrolysis, photolysis or biodegradation in the environment, and, hence, they are extremely persistent [OECD, 2002]. Compared to other POPs, PFOS and their precursors are easier dissolved in water. Because of relatively low vapour pressure and small air-water partition coefficient, PFOS themselves are not expected to volatilize significantly [UNEP, 2006]. Therefore, most likely they present in the atmosphere in particulate phase that was confirmed experimentally by the study [Ahrens *et al.*, 2012] demonstrated that about 90% of PFOS in air of Toronto was bound to aerosol particles. However, a number of PFOS-related substances, e.g., precursors of PFOS, have much higher vapour pressure than PFOS itself. Therefore, the PFOS precursors can volatilize and disperse in the atmosphere over the globe and degrade to PFOS even in remote locations.

Regulation

PFOS are identified as highly persistent [Frömel *et al.*, 2010; Young *et al.*, 2010], potentially bioaccumulative [Conder *et al.*, 2008] and toxic substances [OECD, 2013]. Studies of PFOS in different regions of the world indicated their widespread occurrence in the environment including the presence in biota and humans [Giesy *et al.*, 2001; Vestergren *et al.*, 2009]. Since 2000, PFOS were included in the work programs of various national and international organizations, aimed to collect the information on their environmental levels and trends as well as to develop measures for the restriction of their use (in particular, by CLRTAP, Stockholm Convention, OECD, AMAP, OSPAR and HELCOM). PFOS are identified as priority hazardous substances by the EU Regulation (EU) 2019/1021 on POPs, Water Framework Directive (2000/60/EC), Directive on environmental quality standards in the field of water policy (2008/105/EC), Directive on the quality of water intended for human consumption (2020/2184), and Directive on Industrial Emissions (2010/75/EU).

Production, use, and emissions

PFOS and related substances are used in various industrial applications including metal plating, production of fire-fighting foams, photographic processes, photolithography and semiconductors, hydraulic fluids for aviation, treatment of metal, glass, leather and fabrics, etc. [OSPAR, 2006]. Manufacturing and disposal of PFOS causes their release to the environment. In order to evaluate levels

and trends of PFOS content in the environment, biota, and humans several inventories of their production, application, disposal, and emissions were elaborated.

Although PFOS is included in the Protocol on POPs to CLRTAP, no official emission data are collected currently. Nevertheless, there is a number of research activities describing emission expert estimates of PFOS and their precursors. According to [Paul *et al.*, 2009] total global emissions of PFOS to air and water for the period from 1970 to 2002 ranged from 450 to 2700 tonnes. Similar magnitude of emissions (353 – 3252 tonnes) in the period 1957-2010 was estimated by Armitage *et al.*, [2009].

The most recent global PFOS emission inventory [Wang *et al.*, 2017] is based on new methodology, the information and knowledge published in the literature as well as data reported to the UNEP Stockholm Convention after 2009. PFOS emissions were estimated for the period 1958-2015 and projections of emissions up to 2030. According to this inventory total direct and indirect emissions of PFOS are estimated as 1228–4930 tonnes, and emissions of PFOS precursors as 1230–8738 tonnes. The largest part of these emissions took place between 1958 and 2002. The subsequent period of time is characterised by substantial decrease of emissions due to reduction of production of PFOS and POSF-based products. At the same time, they are still produced in different countries and thus can be released into the environment.

Monitoring

In accordance with the EMEP monitoring strategy for the period 2020-2029 [ECE/EB.AIR/144/Add.1], per- and polyfluoroorganic compounds (PFAS) are classified as organic pollutants of growing concern. It is recommended to monitor these compounds at the research-based stations (Level 3).

Information on concentrations of PFAS in air, observed at the EMEP stations, is available since 2013. Measurements have been carried out at three Norwegian stations Birkenes, Zeppelin and Andøya, at Finnish station Pallas/Matarova and at Swedish station Råö. Observed annual mean concentrations at Pallas were lower than the detection limit value [Aas and Bohlin-Nizetto, 2019, 2020]. In case of Råö, the measured values are substantially higher (0.36 – 1.46 $\mu\text{g m}^{-3}$) compared to those at other stations.

Observed annual mean concentrations of PFOS, including measured monthly mean concentrations, are available from the results of Norwegian national monitoring programme for the period from 2013 to 2019 [Nizetto and Aas, 2014, 2016; Nizetto *et al.*, 2015, 2017, 2018, 2019, 2020]. Measured concentrations range from 0.02 to 0.16 $\mu\text{g m}^{-3}$. Similar to the EMEP data, a large fraction of the observed values is below the detection limit.

Measurements of PFOS at national monitoring network of Sweden have been carried out since 2009. For the period from 2009 to 2015 PFOS air concentrations ranged from 0.35 to 1.4 $\mu\text{g m}^{-3}$, and concentrations in precipitation varied from 0.58 to 3.7 ng L^{-1} at station Råö [Fredricsson *et al.*, 2021]. The highest concentrations in air were observed in 2011 and 2013. Concentrations in precipitation exhibit declining trend for 2009 – 2019 period.

AMAP monitoring network carried out measurements of PFOS in air. Along with the Norwegian Arctic monitoring stations Zeppelin and Andøya, monitoring of PFOS was performed at the station Alert [Wong *et al.*, 2018]. It was shown that as much as 96% of measurements collected at Alert station from 2006 to 2014 were above the detection limit, and median concentrations were 0.07 $\mu\text{g m}^{-3}$.

Modelling

Several attempts have been made to model environmental levels of PFOS or its precursors. Most of the works are focused on evaluation of the pollution levels in water bodies, and some take into account atmospheric processes involving PFOS. Modified BETR model was applied to simulate fate and transport of PFOS in the Bohai coastal region (Northeastern China) [Lui *et al.*, 2015]. It was shown that soil and coastal waters are the most important sinks of PFOS in the considered region, storing more than 90% of PFOS at steady-state conditions.

Zhang *et al.* [2017] investigated processes of transport, accumulation and temporal evolution of PFOS in waters of Northern Atlantic using simulations of ocean circulation model MITgcm. Time-dependent inventory of PFOS inputs from wastewaters was prepared for the period from 1958 to 2010. It was assumed that generation of PFOS from degradation of its precursors in the atmosphere is insignificant. Evaluation of modelling results against measurement data showed general underestimation (~75%) of the observed levels. Temporal long-term variability of PFOS levels demonstrated increase until 2000s and further decline.

An effort to predict the long-term fate and concentrations of PFOS in water, sediment and fish of San-Francisco Bay was made by Sánchez-Soberón *et al.* [2020], using the multi-box model originally developed by Mackay [1994], which was adopted for simulations of PFOS. It was predicted that PFOS concentrations exhibited exponential decline from 2009 to 2059, and about 500 years would be required to reach stable concentrations of PFOS in sediments and fish.

In order to simulate long-term fate of PFOS and transport of volatile precursors to remote locations (e.g. Arctic) global CliMoChem model was applied by Armitage *et al.* [2009]. It was shown that air and water concentrations of the pollutants increased from 1970 to 2000. Although concentrations of the precursors in air and water dropped after 2000, concentrations of PFOS in the Arctic waters continued to increase. Model assessment revealed the ability of PFOS to disperse over the global scale reaching even remote regions of the Northern hemisphere.

Most of researches consider transport and dispersion of PFOS and related species taking into account anthropogenic emissions or releases to water or air. A Norwegian Earth System Model (NorESM) was used to simulate global-scale suspension of PFOS to the atmosphere via sea spray aerosols and consequent atmospheric transport to land [Johansson *et al.*, 2019]. Modelling of wind suspension of sea spray aerosols from water surface allowed estimating emissions of PFOS in the range from about 40 to 800 tonnes per year which represented significant source comparing to anthropogenic emissions.

General peculiarity of the available modelling studies for PFOS was the consideration of water bodies as the main environmental compartment for their dispersion, while other compartments including the atmosphere played less important role.

Hexabromocyclododecanes (HBCDDs)

HBCDDs are the most often used brominated flame retardants throughout the world. Technical HBCDD mixture consists of a number of stereoisomers. Main stereoisomers, namely α -HBCDD, β -HBCDD and γ -HBCDD have different physical-chemical properties which lead to the different character of their behavior in the environment. The most complete information on physical-chemical properties of HBCDD stereoisomers is available for γ -HBCDD. Technical HBCDD products contain about 10% of α -HBCDD, 5% of β -HBCDD and 80% - 85% of γ -HBCDD. However, in biological samples α -HBCDD is a predominant stereoisomer [Covaci *et al.*, 2006; DEFRA, 2010].

Regulation

Toxicological and ecotoxicological properties of HBCDDs were intensively investigated beginning from early 2000s. The EU CLP Regulation 1272/2008 marks them as reproductive toxicants. In other notified classifications, submitted by industry enterprises, HBCDDs are considered also as toxic compounds for aquatic wildlife. In 2013, HBCDDs were included into the Stockholm Convention for elimination without specific exemptions. In May 2019 HBCDDs were included into Annex III (List of Banned or Restricted Chemicals) of Rotterdam Convention. The latter document classifies HBCDDs as substances of very high hazard for aquatic toxicity (both acute and chronic), high persistence and very high bioaccumulation potential. HBCDDs is a candidate for the inclusion into the Protocol on POPs to the CLRTAP. HBCDDs are included as part of the brominated flame retardants group in the List of Substances for Priority Action of the OSPAR Convention. Additional information on HBCDD regulation can be found in [WHO, 2013].

Production, use, and emissions

HBCDD technical mixtures were mainly applied as additive-type brominated flame retardants (BFR) for extruded and expanded polystyrene foams. Other applications include their use in crystal and high-impact polystyrene, resins, textile, adhesives, and coatings. HBCDDs can enter the environment at all stages of their life-cycle. Main pathways of emissions include production of BFRs or the manufacture of flame-retarded products, leaching from consumer products, or following disposal as wastes [Covaci *et al.*, 2006; ECHA, 2009].

Monitoring

First data on the presence of HBCDD in the environment were obtained in the beginning of 1990s [De Wit, 2002; Lee *et al.*, 2016]. Most widely the presence of HBCDD in the atmosphere in Sweden and Finland in 2000 – 2001 was investigated by [Remberger *et al.*, 2004]. An urban site had concentrations between 76 pg m^{-3} and 610 pg m^{-3} whereas the remote sites showed the concentrations between less than 1 pg m^{-3} and 280 pg m^{-3} .

During the recent decade measurements of HBCDD in Sweden and Finland were performed at two EMEP sites Pallas and Råö in 2015–2018. Observed values of HBCDD concentrations ranged from less than 0.1 pg m^{-3} up to 10 pg m^{-3} .

Modelling

A number of studies were recently performed to evaluate levels of HBCDD concentrations in the environment using available modelling approaches. In particular, BETR-Global model [MacLeod *et al.*, 2011] with emissions estimates obtained using dynamic substance flow model CIP-CAFÉ [Li and Wania, 2016; Li and Wania, 2017; Li *et al.*, 2017] was used. As stated in Li and Wania [2017], BETR-Global models succeeded in reproducing concentrations of sum of three main HBCDD isomers observed at GAPS monitoring stations [Lee *et al.*, 2016]. Besides, long-range atmospheric transport potential and persistence of HBCDDs were evaluated using the MSCE-POP multicompartiment hemispheric transport model [Vulykh *et al.*, 2009]. The model predicted that the residence time of HBCDD mixture in the atmosphere was about 3 days and the transport distance was about 1800 km.

Concluding remarks and further activities

CECs comprise a large group of pollutants that are characterized by a wide range of physical-chemical properties and different behavior in the environment. These substances are receiving increasing attention in many international and national environmental organizations due to potential risk for wildlife and human health. However, literature overview demonstrates, that information on physical-chemical properties of CECs, on concentrations in environmental compartments, and on levels of emission is not sufficient or lacking.

Model assessment of pollution by CECs requires more detailed monitoring data on their content in the environment and temporal trends as well as elaboration of emission inventories. Besides, further improvement of understanding of processes governing their fate is of importance for the assessment of pollution levels (e.g. of gas-partide partitioning in the atmosphere, air-surface exchange, degradation in media). Furthermore, improvements of existing modelling approaches are needed to apply them for some of the new POPs and CECs (e.g. polar, ionizable compounds), which have different behavior in the environment comparing to traditional POPs.