

Atmospheric Supply of Nitrogen, Cadmium, B(a)P, HBCDD, PCNs and PeCB to the Baltic Sea in 2020

Technical Report for HELCOM

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msc-w & msc-e & ccc

EMEP Centres Joint Report for HELCOM
EMEP MSC-W TECHNICAL REPORT 2/2022

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Preface

The Co-operative Program for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe (EMEP) and the Baltic Marine Environment Protection Commission (HELCOM) are both conducting work on air monitoring modelling and compilation of emission inventories. In 1995, HELCOM decided to rationalise its current programs by avoiding duplication of efforts with specialised international organizations.

At the request of HELCOM, the Steering Body of EMEP at its nineteenth session agreed to assume the management of atmospheric monitoring data, the preparation of air emission inventories and the modelling of air pollution in the Baltic region.

Following the coordination meeting held in Potsdam in Germany and the Pollution Load Input meeting held in Klaipeda-Joudkrante in Lithuania, both in 1996, it was agreed that EMEP Centres should be responsible for regular evaluation of the state of the atmosphere in the Baltic Sea region and should produce an annual joint summary report which includes updated emissions of selected air pollutants, modelled deposition fields, allocation budgets and measurement data.

The present web report was prepared for HELCOM, in accordance with the contract between HELCOM and the three EMEP Centres MSC-W, MSC-E and CCC. It is based on model estimates and monitoring results presented to the Eighth Joint session of the Working Group on Effects and the Steering Body to EMEP which took place on 12-16 September 2022.

Acknowledgement

The authors thank HELCOM and the EMEP Trust Fund for their continuous support to conduct this type of studies. The authors also acknowledge great help from colleagues at the EMEP Centres, and in particular CEIP for the provision of anthropogenic emission data.

Table of Contents

Preface.....	ii
Acknowledgement	ii
List of Contents	iii
1. Introduction.....	1
2. Observations at HELCOM Stations in 2020.....	7
3. Information on Hexabromocyclododecane (HBCDD)	11
4. Information on Polychlorinated naphthalenes (PCNs)	18
5. Information on Pentachlorobenzene (PeCB)	25
6. References	32

Fact sheets published as annexes

(available at <https://emep.int/publ/helcom/2022/>)

- A. Baltic Sea Environmental Fact Sheet for Nitrogen Emissions, 1990-2020
- B. Baltic Sea Environmental Fact Sheet for Nitrogen Deposition, 1990-2020
- C. Baltic Sea Environmental Fact Sheet for Cadmium Emissions, 1990-2020
- D. Baltic Sea Environmental Fact Sheet for Cadmium Deposition, 1990-2020
- E. Baltic Sea Environmental Fact Sheet for B(a)P Emissions, 1990-2020
- F. Baltic Sea Environmental Fact Sheet for B(a)P Deposition, 1990-2020

Data tables published as annexes

(available at <https://emep.int/publ/helcom/2022/>)

- G. [Country-to-basin contributions \(2020\) for Nitrogen deposition](#)
- H. [Annual Cadmium emissions for the 1990-2020 period](#)
- I. [Trends \(1990-2020\) and country-to-basin contributions \(2020\) for Cadmium deposition](#)
- J. [Annual B\(a\)P emissions for the 1990-2020 period](#)
- K. [Trends \(1990-2020\) and country-to-basin contributions \(2020\) for B\(a\)P deposition](#)

1. Introduction

The present EMEP Centres Joint Report for HELCOM is focused on the year 2020. It is based on the modelling and monitoring data presented to the Eighth Joint session of the Working Group on Effects and the Steering Body to EMEP, which occurred in September 2022. This introduction gives a brief overview of what is available and which tools and methods have been used.

1.1 Measurements (EMEP CCC)

The HELCOM monitoring stations regularly collect data on nitrogen compounds, heavy metals and persistent organic pollutants (POPs). All the data can be downloaded from the EBAS database hosted by the Norwegian Institute for Air Research (<http://ebas.nilu.no/>). Measurements are done in air and in precipitation to monitor trends in pollution and to evaluate models that calculate air concentrations and deposition of pollutants. More than twenty HELCOM stations have submitted data for 2020. More details about the methods and the data themselves can be found in Chapter 2.

1.2 Nitrogen modelling (EMEP MSC-W)

Nitrogen components are emitted to the air from a large variety of natural and anthropogenic sources and can be transported over large distances (hundreds to thousands of kilometres) in the atmosphere, undergoing physical and chemical transformations on the way until eventually deposited to land and marine surfaces. Calculating concentrations and deposition of nitrogen requires a detailed representation of all important processes involved, as well as reliable input data on emissions, meteorology, land use data, etc.

For all nitrogen computations, the EMEP MSC-W model, a multi-pollutant 3D Eulerian Chemical transport model, has been used. The model takes into account processes of emissions, advection, turbulent diffusion, chemical transformations, wet and dry depositions and inflow of pollutants into the model domain. It was documented in detail in Simpson et al. (2012) and in the annual chapters on model updates in subsequent EMEP status reports (Simpson et al., 2020; 2021; 2022; and references therein). The model is regularly evaluated against measurements from the EMEP network under the LRTAP Convention (e.g. Gauss et al., 2020) and online at the new AeroVal evaluation website (<https://aeroval.met.no/evaluation.php?project=emep>), but also in a large number of international research projects and operational services (e.g. Copernicus Atmosphere Modelling Service <https://regional.atmosphere.copernicus.eu/>). The performance of the EMEP MSC-W model can be considered as state-of-the-art over a large range of both gaseous species and particulate matter. The model code (software) is also available as Open Source (<https://github.com/metno/emep-ctm>) and has been widely used both as a research

tool and for underpinning of air quality legislation.

The EMEP MSC-W model version rv4.45 (EMEP, 2022) has been run on 0.1×0.1 degree resolution to calculate nitrogen deposition to the Baltic Sea during the 31-year period 1990-2020. Source-receptor matrices for nitrogen have been calculated for 2020 on a 0.3° longitude x 0.2° latitude grid. Meteorological data have been taken from ECMWF (cy40r1 for the 1990-2018 period, cy46r1 for 2019 and 2020), emissions are based on officially reported data to CEIP (June 2022), and boundary conditions and forest fires for 2020 are based on observations and the GFED data base, respectively.

Annexes A and B contain fact sheets with emissions and depositions of nitrogen. Source-receptor data for nitrogen deposition are found in Annex G. All annexes are available at <https://emep.int/publ/helcom/2022/>.

1.3 Heavy metals and POPs (EMEP MSC-E)

Atmospheric input, long-term trends and source allocation budgets of cadmium and benzo(a)pyrene (B(a)P) were calculated using the latest version of the GLEMOS model over the EMEP domain (https://www.ceip.at/ms/ceip_home1/ceip_home/new_emep-grid/). The global modelling framework GLEMOS is a multi-scale multi-pollutant simulation platform developed for operational and research applications within the EMEP programme (Tarrason and Gusev, 2008; Travníkov et al., 2009; Jonson and Travníkov, 2010; Travníkov and Jonson, 2011). The framework allows simulations of dispersion and cycling of different classes of pollutants (e.g. heavy metals and persistent organic pollutants) in the environment with a flexible choice of the simulation domain (from global to local scales) and spatial resolution. In the vertical direction, the model domain covers heights up to 10 hPa (about 30 km). The current vertical structure consists of 20 irregular terrain-following sigma layers. Among them 10 layers cover the lowest 5 km of the troposphere and the thickness of the lowest layer is about 75 m. The global-scale configuration of the GLEMOS model was used to simulate boundary concentrations of cadmium and B(a)P for the EMEP domain.

It is assumed that cadmium is transported in the atmosphere in the composition of aerosol particles and its chemical transformations do not affect the properties of carrying particles with regard to removal processes. The model description of removal processes includes dry deposition and wet scavenging. The dry deposition scheme is based on the resistance analogy and takes into account deposition to different types of land cover. The model distinguishes in-cloud and sub-cloud wet scavenging of cadmium. Wind re-suspension of particle-bound cadmium from soil and seawater surface is an important process which considerably affects ambient pollution levels, particularly in areas with low direct anthropogenic emissions. The model includes parameterization of heavy metal re-suspension with dust aerosol particles from soil and generation of sea-salt aerosol and wind

suspension of heavy metals from sea surface.

The modelling approach for B(a)P assumes that it is transported in the atmosphere in the gaseous and particulate phases. Besides, partitioning between gaseous and particulate phases as well as degradation and deposition processes for both phases are considered. Parameterizations of wet and dry deposition of B(a)P in particulate phase are similar to those implemented for heavy metals. Along with this, gaseous exchange of B(a)P between the atmosphere and surface media and B(a)P accumulation in soil, water, vegetation and forest litter are taken into account.

Meteorological data used in model simulations for the period 1990-2020 were generated using the WRF numerical weather prediction model as meteorological data pre-processor (Skamarock et al., 2008). Pre-processing was performed on the basis of meteorological re-analyses data (ERA-Interim) of the European Centre for Medium-Range Weather Forecasts (ECMWF). Atmospheric concentrations of chemical reactants and particulate matter, which are required for POP chemistry, were taken from the MOZART and p-TOMCAT models (Emmons et al., 2010; Yang et al., 2005; 2010). The GLEMOS model results are regularly evaluated against measurements of the EMEP monitoring network under the LRTAP Convention (e.g. Travníkov et al., 2020).

Fact Sheets are provided for cadmium and B(a)P and are available as annexes C to F at <https://emep.int/publ/helcom/2022/>. On the same page, data tables can be downloaded in Excel format (annexes H to K). For HBCDD, PCNs, and PeCB, a literature review of available information is provided in Chapters 3, 4, and 5 of this report, respectively.

1.4 Model geometry, domains and definitions

For most pollutants the EMEP models are run on a regular longitude-latitude grid covering the EMEP domain as depicted in Figure 1.1.

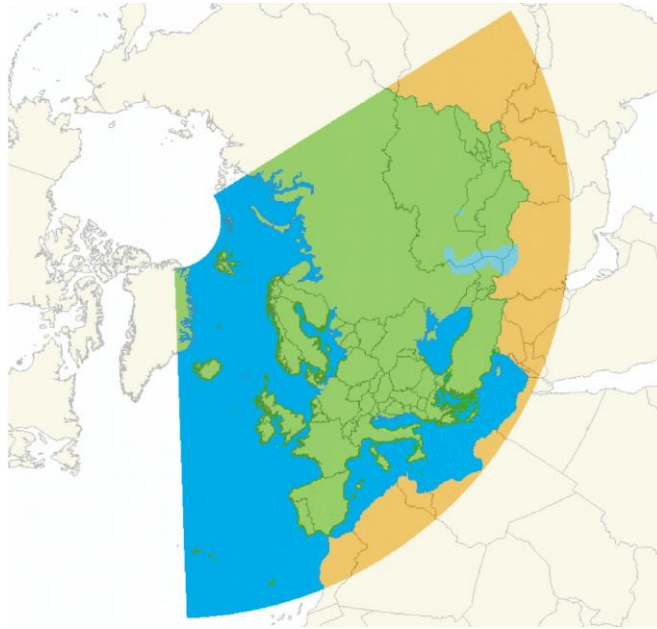


Figure 1.1 Domain used in the EMEP model calculations.

Table 1.1 The nine sub-basins of the Baltic Sea used for computing depositions, with abbreviations used in this report and areas given in km².

Sub-basin	Abbreviation	Area
Archipelago Sea	ARC	13405
Baltic Proper	BAP	209258
Bothnian Bay	BOB	36249
Bothnian Sea	BOS	65397
Gulf of Finland	GUF	29998
Gulf of Riga	GUR	18646
Kattegat	KAT	23659
The Sound	SOU	2328
Western Baltic	WEB	18647
Baltic Sea basin	BAS	417587

The nine sub-basins of the Baltic Sea used in the computations are listed in Table 1.1 and shown in Figure 1.2. There are large differences in the sizes of individual sub-basins. The area of the largest one, Baltic Proper, is almost two orders of magnitude higher than the area of the smallest one, The Sound. The area of the entire Baltic Sea basin, calculated as the sum of sub-basins is 417 587 km².

In this report and accompanying data tables, the names of countries, sources and receptors are often abbreviated. The list of these abbreviations is given in Table 1.2 together with the EMEP identification number.

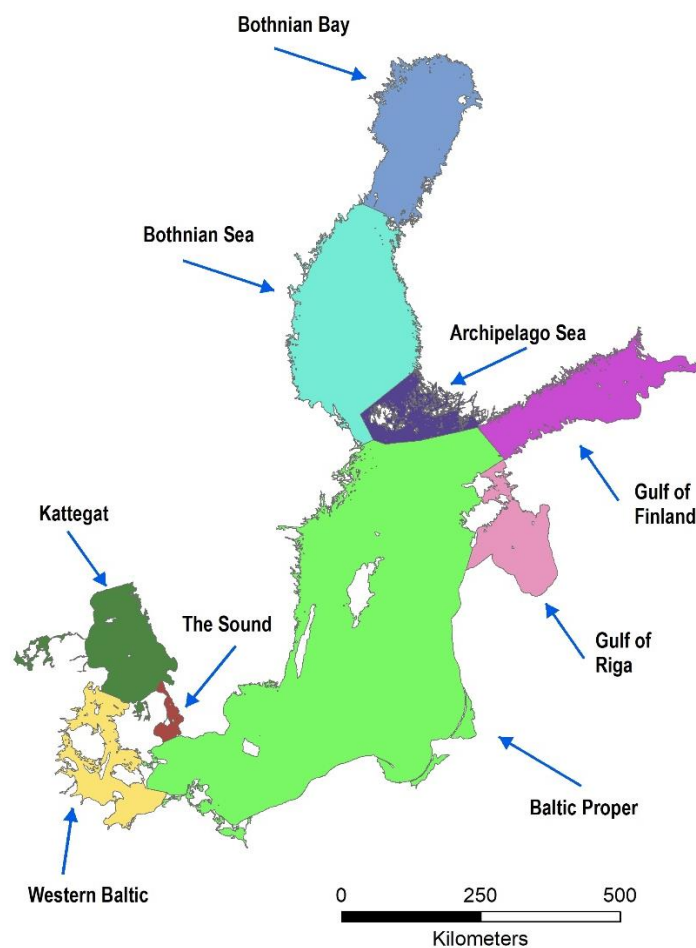


Figure 1.2 Locations of the sub-basins of the Baltic Sea listed in Table 1.1 and used for all nitrogen deposition calculations presented in this report. This figure has been provided by the Baltic Nest Institute (BNI).

Table 1.2 Country and area names and abbreviations used in this report and accompanying tables, along with the EMEP identification number.

CODE	EMEP ID	NAME	CODE	EMEP ID	NAME
AL	1	Albania	EE	43	Estonia
AT	2	Austria	LV	44	Latvia
BE	3	Belgium	LT	45	Lithuania
BG	4	Bulgaria	CZ	46	Czechia
DK	6	Denmark	SK	47	Slovakia
FI	7	Finland	SI	48	Slovenia
FR	8	France	HR	49	Croatia
GR	11	Greece	BA	50	Bosnia and Herzegovina
HU	12	Hungary	MK	52	North Macedonia
IS	13	Iceland	KZ	53	Kazakhstan
IE	14	Ireland	GE	54	Georgia
IT	15	Italy	CY	55	Cyprus
LU	16	Luxembourg	AM	56	Armenia
NL	17	Netherlands	MT	57	Malta
NO	18	Norway	LI	59	Liechtenstein
PL	19	Poland	DE	60	Germany
PT	20	Portugal	RU	61	Russian Federation
RO	21	Romania	MC	62	Monaco
ES	22	Spain	NOA	63	North Africa
SE	23	Sweden	EU	64	European Union (EU-28)
CH	24	Switzerland	BIC	67	Boundary and Initial Conditions
TR	25	Turkey	KG	68	Kyrgyzstan
GB	27	United Kingdom	AZ	69	Azerbaijan
VOL	28	Volcanic emissions	RS	72	Serbia
BAS	30	Baltic Sea	ME	73	Montenegro
NOS	31	North Sea	CAS	80	Caspian Sea
ATL	32	North-East Atlantic Ocean	TJ	81	Tajikistan
MED	33	Mediterranean Sea	UZ	94	Uzbekistan
BLS	34	Black Sea	TM	95	Turkmenistan
BY	39	Belarus	AST	96	Asian areas
UA	40	Ukraine	GL	601	Greenland
MD	41	Moldova			

2. Observations at HELCOM Stations in 2020

Eight countries have submitted data from all together twenty-two HELCOM stations for 2020. In the figure and overview table below (Figure 2.1), the measurements program is indicated. There are not reported any changes in measurement programme or the methodology used in 2020 compared to what was reported last year.

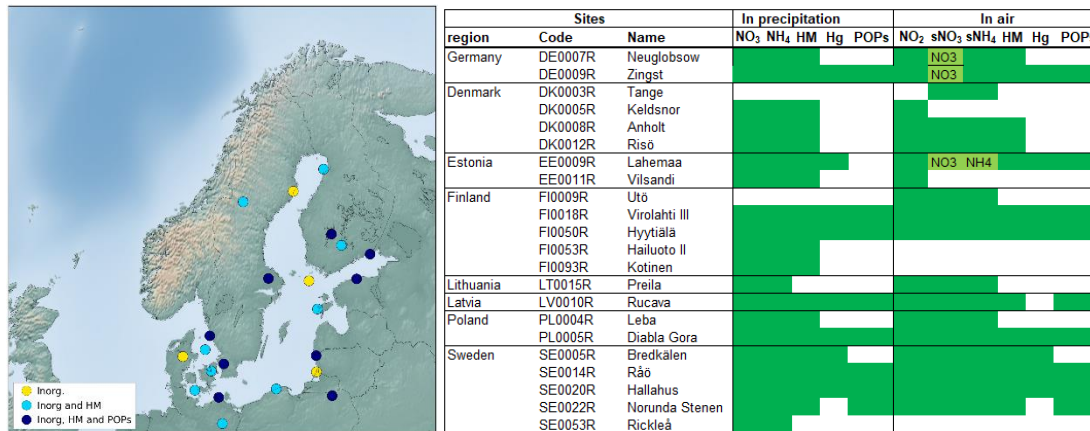


Figure 2.1 HELCOM sites and their measurement programme in 2020.

Table 2.1 Annual average mean concentrations of different nitrogen components in air and precipitation measured at HELCOM sites in 2020 compared with the average of the period 2015-2019. Green shaded area indicates lower concentration than the preceding years. The five-year averages are calculated when there are three years of data or more.

Site	precip. amount (mm)		NH ₄ precip (mg/NL)		NO ₃ precip (mg/NL)		NO ₂ air (ugN/m ³)		NH ₄ +NH ₃ in air (ugN/m ³)		NO ₃ +HNO ₃ in air (ugN/m ³)	
	2020	2015-2019	2020	2015-2019	2020	2015-2019	2020	2015-2019	2020	2015-2019	2020	2015-2019
DE0007R	535	572	0.47	0.56	0.28	0.36	1.02	1.52	1.09	1.52	0.25	0.37
DE0009R	668	518	0.51	0.68	0.31	0.42	1.27	1.55	1.24	1.53	0.32	0.41
DK0003R									1.60	1.77	0.63	0.63
DK0005R	444	500	0.57	0.60	0.31	0.42	1.93	2.34				
DK0008R	489	476	0.37	0.39	0.32	0.38	1.09	1.39	0.75	0.83	0.58	0.60
DK0012R	451	555	0.35	0.54	0.28	0.37	1.64	2.19	1.42	1.64	0.75	0.81
EE0009R	794	756	0.10	0.14	0.13	0.19	0.44	2.04	0.85	0.88	0.10	0.04
EE0011R	627	593	0.22	0.28	0.25	0.31	0.51	1.88				
FI0009R							0.89	1.02	0.30	0.31	0.25	0.28
FI0018R	694	669	0.25	0.26	0.27	0.29	0.93	1.16	0.25	0.30	0.13	0.17
FI0050R	618	-	0.14	-	0.18	-	0.50	-	0.20	-	0.10	-
FI0053R	600	491	0.12	0.19	0.11	0.19						
FI0093R	675	618	0.14	0.14	0.18	0.21						
LT0015R	501	596	0.33	0.39	0.40	0.39	0.82	0.90	0.77	0.88	0.45	0.58
LV0010R	815	729	0.34	0.31	0.26	0.30	0.66	0.70	0.83	0.89	0.37	0.42
PL0004R	560	671	0.36	0.35	0.35	0.36	1.34	1.44	1.12	1.33	0.45	0.52
PL0005R	533	625	0.53	0.45	0.30	0.32	1.15	1.30	1.46	1.78	0.49	0.60
SE0005R	658	538	0.08	0.13	0.07	0.10	0.11	0.12	0.11	0.12	0.03	0.04
SE0022/12R	537	540	0.19	0.27	0.18	0.23	0.37	0.69	0.54	0.31	0.12	0.19
SE0014R	585	587	0.28	0.43	0.29	0.34	0.92	0.88	0.39	0.60	0.40	0.43
SE0020/11R	708	749	0.43	0.41	0.40	0.37	0.92	0.84	0.68	0.79	0.36	0.45
SE0053R	805	509	0.14	0.19	0.17	0.23						

Statistical details and information on measurement methods are found in the EMEP reports (Hjellbrekke, 2022; Aas and Nizzetto, 2022, and all the data are available from the web

database at <http://ebas.nilu.no/>. The annual mean concentrations of nitrogen components and heavy metals in air and precipitation in 2020 are given in Table 2.1 and 2.2. These are compared to the average of the five preceding years. As seen in Table 2.1, most of the sites show lower concentrations in 2020 for both reduced and oxidized nitrogen compared to the average of the preceding five-year period. One should notice for oxidized nitrogen, the concentrations in 2020 is influenced by lower emissions of NO₂ due to the pandemic and the resulting restrictions on activities (EMEP,2022).

Table 2.2 Annual average mean concentrations of Arsenic (As), cadmium (Cd), Lead (Pb), copper (Cu) and mercury (Hg) in air and precipitation measured at HELCOM sites in 2020 compared with the average of the period 2015-2019. Green shaded area indicates lower concentration than the preceding years. The five-year averages are calculated when there are three years of data or more.

Site	As, precip (ug/L)		Cd, precip (ug/L)		Pb, precip (ug/L)		Cu, precip (ug/L)		Hg, precip (ng/L)	
	2020	2015-2019	2020	2015-2019	2020	2015-2019	2020	2015-2019	2020	2015-2019
DE0007R	0.060	0.086	0.015	0.018	0.37	0.55	0.82	1.14		
DE0009R	0.044	0.077	0.011	0.019	0.23	0.50	0.45	1.07	7.1	7.6
DK0005R	0.104	0.091	0.042	0.031	1.51	2.03	4.29	1.29		
DK0008R	0.153	0.163	0.018	0.035	0.43	1.19	0.83	2.24		
DK0012R	0.160	0.068	0.156	0.028	2.93	0.69	9.42	1.50		
EE0009R	0.034	0.065	0.016	0.052	0.18	0.49	1.72	1.94	2.5	5.9
EE0011R			0.015	0.052	0.35	0.69	3.64	2.31		
FI0018R	0.089	0.085	0.025	0.028	0.74	0.74	0.59	0.67		
FI0050R	0.069	0.062	0.014	-	0.32	-	0.49	-		
FI0053R	0.036	0.059	0.008	0.016	0.20	0.34	0.55	0.60		
FI0093R	0.053	0.055	0.018	0.016	0.32	0.37	0.43	0.52		
LV0010R	0.177	0.163	0.022	0.030	0.47	0.84			5.8	11.6
PL0004R			0.012	0.015	0.25	0.29	0.59	0.99		
PL0005R	0.255	0.277	0.027	0.038	0.24	0.51	0.91	1.02	10.2	3.9
SE0005R	0.044	0.048	0.021	0.017	0.42	0.25	5.88	0.41	3.8	5.7
SE0022/12R	0.065	0.167	0.013	0.023	0.24	0.38	3.73	0.67		
SE0014R	0.116	0.101	0.074	0.036	0.45	0.40	4.22	0.84	6.4	7.4
SE0020/11R	0.088	0.093	0.097	0.027	0.37	0.40	3.62	1.14	6.4	8.6

Site	As, aerosol (ng/m ³)		Cd, aerosol (ng/m ³)		Pb, aerosol (ng/m ³)		Cu, aerosol (ng/m ³)		Hg air (ng/m ³)	
	2020	2015-2019	2020	2015-2019	2020	2015-2019	2020	2015-2019	2020	2015-2019
DE0007R	0.068	0.546	0.068	0.094	1.94	3.20	1.26	1.70		
DE0009R	0.058	0.389	0.058	0.073	1.61	2.46	1.22	1.48	1.39	1.52
DK0008R	0.033	0.321	0.033	0.036	0.96	1.22				
DK0012R	0.047	0.389	0.047	0.052	1.31	1.63				
EE0009R	0.045	0.231	0.045	0.085	1.47	2.40			1.40	1.30
FI0018R	0.052	0.226	0.052	0.053	1.68	1.72	0.79	0.77	1.21	1.26
FI0050R	0.043	0.172	0.043	-	1.21	-	0.68	0.52	1.11	1.16
LV0010R	0.050	0.288	0.050	0.071	1.45	1.33				
PL0005R	0.061	0.311	0.061	0.096	1.62	2.64	0.81	1.65	1.61	1.50
SE0005R	0.006	0.052	0.006	0.010	0.22	0.32	0.17	0.16	1.27	1.32
SE0022/12R	0.022	0.207	0.022	0.028	0.64	0.88	0.49	0.60		
SE0014R	0.032	0.236	0.032	0.033	0.79	1.04	0.85	0.82		1.33
SE0020/11R	0.033	0.183	0.033	0.027	0.93	0.95	1.02	0.90	1.27	1.35

From 1995 to 2020 the oxidized nitrogen average concentrations have decreased about 25% for all the components, while for reduced nitrogen the reductions in average

concentration in precipitation has been ca 15% while in air more than 40% (Figure 2.2). The sum($\text{NH}_3 + \text{NH}_4$) in air is dominated by ammonium and this trend is very much linked to the trends in sulfate which has decreased substantially in the same period. See details in EMEP Status Report (EMEP, 2021).

For 2020 the POPs that should be assessed, as defined in the work plan for the centres are benzoapyrene (BaP), hexabromocyclododecane (HBCDD), polychlorinated naphthalenes (PCNs), and Pentachlorobenzene (PeCBz). Of these, it is only BaP data which are reported from HELCOM sites in 2020. At SE0014 there are however data of HBCDD from earlier years. Table 2.3 shows the annual concentration of BaP and some other selected POPs.

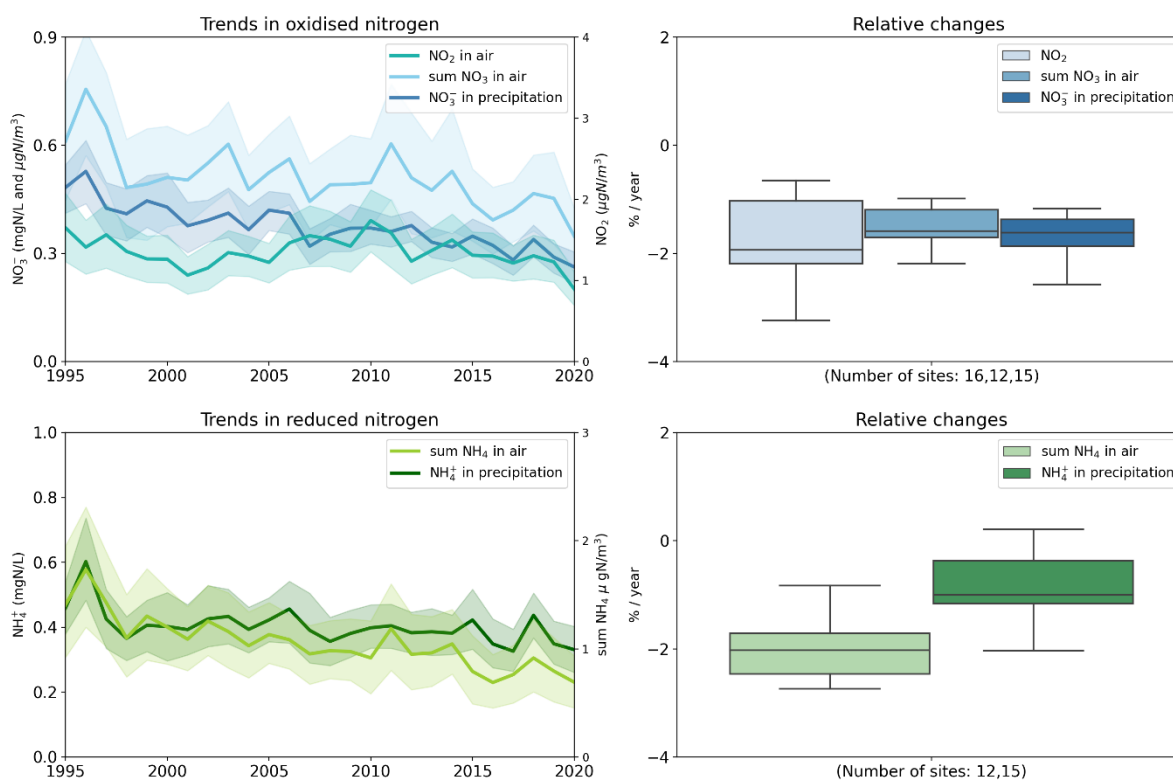


Figure 2.2. Trends in reduced and oxidized nitrogen components at HELCOM sites since 1995. Average of the sites with more than 15 years of observations during the period.

Table 2.3 Annual average mean concentrations of various PAHs and POPs in air and aerosol, and precipitation or deposition at HELCOM sites in 2020.

			In air and aerosols						
Site	Matrix		BaP ng/m ³	pyrene ng/m ³	BaA ¹ ng/m ³	BgP ng/m ³	PCB153 pg/m ³	HCB pg/m ³	γHCH pg/m ³
DE0009R	air+pm10		0.128	0.431	0.143	0.133			
EE0009R	pm10		0.083		0.066	0.112			
FI0018R	pm10		0.098	0.256	0.083	0.088			
FI0050R	pm10		0.081	0.179	0.059	0.022			
LV0010R	pm10		0.214		0.300	0.058			
PL0005R	pm10		0.512		0.425	0.016			
SE0014R	air+aerosol		0.027	0.133	0.030	0.168	0.730	7.90	1.89
SE0020R	air+aerosol		0.045	0.077	0.040	0.263			
SE0022R	air+aerosol		0.013	0.107	0.015	0.020	0.274	9.60	1.57

			In precipitation or total deposition						
Site	Matrix	unit	BaP	pyrene	BaA ¹	BgP	PCB153	HCB	γHCH
DE0009R	precip_tot	ng/l	1.81	5.8	1.54	2.67			
FI0018R	precip+dry_dep	ng/m ² day	12.42	43.2	11.11	20.39			
FI0050R	precip+dry_dep	ng/m ² day	3.24	12.6	2.66	4.54			
LV0010R	precip	ng/l	4.33		4.64				
PL0005R	precip	ng/l	16.20		13.51				
SE0014R	precip+dry_dep	ng/m ² day	4.51	12.2	3.55	5.05	0.085	0.053	0.134
SE0020R	precip+dry_dep	ng/m ² day	10.60	27.0	7.55	12.19			
SE0022R	precip+dry_dep	ng/m ² day	5.01	11.4	3.28	6.43	0.022	0.057	0.058

¹ BaA: Benzo[a]anthracene ² BgP: benzo[ghi]perylene

3. Information on hexabromocyclododecane (HBCDD)

3.1 Introduction

Hexabromocyclododecane (HBCDD¹) is one of the most commonly used brominated flame retardants. It has been primarily applied as a fire protection additive to synthetic materials (e.g. expanded (EPS) and extruded (XPS) polystyrene foams), which have been used in the construction of buildings (e.g. as thermal insulation materials), in furniture, vehicle textiles, packaging materials and electrical and electronic equipment. Releases of HBCDD to the atmosphere and other environmental compartments can take place at all stages of the HBCDD products life cycle including production, transportation, usage and disposal [Schrenk *et al.*, 2021].

HBCDD is a persistent, bioaccumulative, toxic compound that has low solubility in water, high affinity to particulate matter and potential to long-range transport in the environment. HBCDD is known to have adverse effects for terrestrial and aquatic organisms, and to pose risks to human health. The toxicological effects of HBCDD include reproductive and developmental toxicity. In addition, HBCDD is suspected of causing neurobehavioral effects and endocrine disruption [WHO, 2013; European Commission, 2014; Feiteiro *et al.*, 2021].

This chapter provides an overview of available information on HBCDD. It briefly describes regulatory activities, production, use and emissions of HBCDD. In addition, results of monitoring and modelling studies of HBCDD concentrations, transport and fate in the environment are outlined.

3.2 Regulation activities on HBCDD

Due to physical-chemical properties and adverse effects, HBCDD was included in the lists of hazardous pollutants by various national and international organizations for the restriction of production and use. In 2007, HBCDD was included in the HELCOM Baltic Sea Action Plan as one of the substances of specific concern to the Baltic Sea [HELCOM, 2007]. HELCOM Contracting Parties agreed on severe restrictions of the use of hazardous substances, including HBCDD, in the entire catchment area of the Baltic Sea. HBCDD was also included in list of chemicals for priority action of OSPAR Convention [OSPAR, 2009].

¹HBCDD is a standardized abbreviation (in a singular form) of a group of HBCDD stereoisomers commonly used in scientific literature. Other possible abbreviations include HBCD, however HBCDD is preferable to avoid confusion with hexabromocyclododecane [AMAP, 2016]

In 2009, HBCDD was considered as a candidate for the inclusion into the Protocol on POPs to the Convention on Long-Range Transboundary Air Pollution. Two options were identified for possible inclusion of HBCDD to the Protocol, namely, listing in Annex I to the Protocol to eliminate production and use, and in Annex II to the Protocol to restrict certain uses [UNECE, 2010]. In 2013, HBCDD was added to Annex A of the Stockholm Convention on Persistent Organic Pollutants as the chemical which production and use should be eliminated. HBCDD is one of the chemicals of emerging Arctic concern which is considered in AMAP Assessment [AMAP, 2016].

HBCDD is considered as priority substance in the EU Water Framework Directive [EU, 2013]. In particular, it sets the environmental quality standards (EQS) for HBCDD for inland surface waters and other surface waters as annual mean concentrations to 0.0016 and 0.0008 $\mu\text{g L}^{-1}$, and as maximum allowable concentrations to 0.5 and 0.05 $\mu\text{g L}^{-1}$, respectively. The EQS for biota is set to 167 $\mu\text{g kg}^{-1}$ wet weight.

In accordance with the EU REACH² and CLP Regulation³, HBCDD is classified as a chemical suspected to be toxic to reproduction and causing harm to breast-fed children. Besides, this chemical is considered by ECHA also as very toxic to aquatic life with long lasting effects⁴. The European Chemical Agency included HBCDD in the Candidate list of substances of very high concern and in the Authorization List as persistent, bioaccumulative, and toxic substance (PBT). HBCDD is listed in the Annexes I and IV of the EU Regulation 2019/1021 on persistent organic pollutants⁵. In accordance with the Article 3 of the Regulation, manufacturing, placing on the market and use of HBCDD shall be restricted. In accordance with the Article 7, specific waste management provisions are to be applied for HBCDD.

In 2019, HBCDD was listed in Annex III of Rotterdam Convention, where banned or severely restricted chemicals were listed [Rotterdam Convention, 2019]. Following this decision, the export of HBCDD is only possible with the prior consent of the recipient

² Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC

³ Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006

⁴Source: European Chemical Agency, <https://echa.europa.eu/registration-dossier/-/registered-dossier/15003/2/1>

⁵ Regulation (EU) 2019/1021 of the European Parliament and of the Council of 20 June 2019 on persistent organic pollutants. Source: <http://data.europa.eu/eli/reg/2019/1021/oj>

countries, which should be properly informed about the associated health and environmental risks.

3.3 Production, use and emissions

HBCDD is an industrial chemical which belongs to the group of brominated flame retardants. It is used as an additive in polymer applications, providing fire protection during the service life of vehicles, buildings, articles, as well as protection while stored. HBCDD is applied in four principal polymer product types, which are expandable polystyrene (EPS), extruded polystyrene (XPS), high impact polystyrene (HIPS) and in polymer dispersions for textiles.

Examples of HBCDD application in EPS and XPS materials include insulation boards for buildings construction, for protection of transport vehicles, for insulation of coolers as well as for packaging material (excluding food packaging). Content of HBCDD in these products ranged from 0.5 to 2.5%. HIPS end-products were applied in electrical and electronic parts. Further, HBCDD was used as a textile coating agent in polymer dispersion on cotton or cotton-synthetic blends for upholstery fabrics. Other minor applications included HBCDD use in polypropylene, in styrene-acrylonitrile copolymer resins, in polyvinylchloride as well as in unsaturated polyesters, adhesives and coatings [ESWI, 2011].

HBCDD has been produced for the world market since the late 1960s. It was mainly manufactured in China, Europe, Japan and the United States of America [UNEP, 2017]. According to industry information, global consumption of HBCDD in 2001 was 16,700 t y⁻¹ with approximately 57% in Europe, 23% in Asia-Pacific region, 17% in North America and 5% in other regions [Nordic Council of Ministers, 2007]. From 2001 to 2011 the global production of HBCDD increased to 31,000 t y⁻¹ that included about 13,000 t y⁻¹ in the EU and the United States, and 18,000 t y⁻¹ in China [UNEP, 2017].

Commercially produced HBCDD products contained a mixture of several stereoisomers with the most significant fraction of γ -HBCDD (72-90%) followed by α -HBCDD (9-13%) and β -HBCDD (<0.5-12%) [Schrenk *et al.*, 2021]. HBCDD stereoisomers are characterized by unique physical-chemical properties, which lead to different distribution and behavior in the environment, including accumulation in biota. HBCDD stereoisomers are widely dispersed in the environment including biota and humans with predominant concentrations of α -HBCDD [WHO, 2013; Schrenk *et al.*, 2021].

HBCDD stereoisomers are not chemically bound to the produced polymers. Therefore, their releases into the environment may occur at any stage during the life-cycle of products (during production, manufacturing, processing, transportation, use, handling, storage, and disposal) [Schrenk *et al.*, 2021]. The emissions of HBCDD during production and use are estimated to be small compared to the releases from waste [ECHA, 2009]. Due to long lifetime of XPS and EPS once installed in buildings, which is above 30 years, releases of HBCDD from waste disposal are difficult to estimate. Thus, information on the historical use of materials containing HBCDD is of importance. Under the Stockholm Convention, the guidance on preparing inventories of HBCDD production, uses and disposal has been developed to help parties to implement measures on HBCDD elimination [UNEP, 2021].

In the EU the annual HBCDD emissions into air, surface water and waste water in 2006 were estimated to 649, 924 and 1553 kg y⁻¹, respectively [ECHA, 2009]. The releases to water were the largest in the EU, while for Japan the largest releases were estimated to air (571 kg y⁻¹ to air and 41 kg y⁻¹ to water) [Managaki *et al.*, 2009].

3.4 Environmental levels

HBCDD is included in the monitoring campaigns of several countries as a persistent organic pollutant of emerging concern. In particular, measurements of HBCDD air concentrations are available from monitoring sites in Norway, Sweden and Finland. Due to low vapor pressure and affinity to particulate matter HBCDD stereoisomers were mainly found in particulate phase in the atmosphere. In Northern Europe HBCDD levels in air have been measured since 1990s [de Wit, 2002]. In particular, in 1990-1991 observed air concentrations of HBCDD at two monitoring sites in the Baltic Sea (at southern tip of Gotland) were 5.3 and 6.1 pg m⁻³.

At monitoring sites Birkenes and Zeppelin in Norway, measurements of three HBCDD stereoisomers (α -HBCDD, β -HBCDD and γ -HBCDD) in air have been made since 2006. Measured concentrations showed significant decrease of HBCDD levels after 2006, however a lot of observed values (especially in period 2008-2020) were below the detection limit [NILU, 2021].

In 2020, at Zeppelin all HBCDD stereoisomers were detected in >50% of the samples. On the contrary, at Birkenes only α -HBCDD concentrations were above the detection limit [NILU, 2021]. The measurement results for HBCDD stereoisomers at Zeppelin monitoring site obtained in 2019 and 2020 are shown in Figure 3.1. It can be seen that α -HBCDD is

predominant in the atmosphere. In the previous periods of observations at the Norwegian monitoring sites, seasonal fluctuations in HBCDD air concentrations were not detected [NILU 2018, 2019]. However, in March 2019 and March and April 2020 at the Zeppelin, the concentrations of all HBCDD stereoisomers demonstrated maximum values. Besides, annual mean observed HBCDD concentrations (0.418 pg m^{-3}) in 2020 appeared to be higher than that in 2019 (0.16 pg m^{-3}) [NILU, 2021].

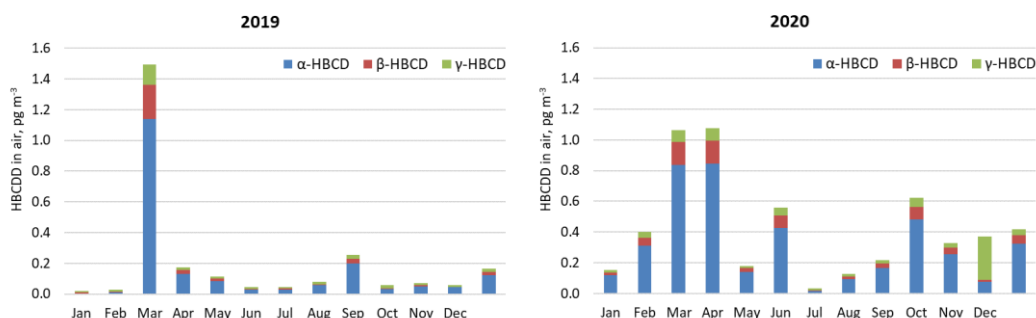


Figure 3.1 Air concentrations of α -, β - and γ -HBCDD measured at Zeppelin monitoring site in 2019 and 2020.

In 2016-2019, at background monitoring sites Pallas and Raö measured atmospheric concentrations of the sum of three HBCDD stereoisomers were at the same level as in Norway below 0.1 pg m^{-3} ($0.020\text{-}0.064 \text{ pg m}^{-3}$ in Raö and $<0.004\text{-}0.092 \text{ pg m}^{-3}$ in Pallas) [Fredricsson *et al.*, 2021]. These levels are in good agreement with the passive sampling of HBCDD performed during 2014 at the Global Atmospheric Passive Sampling (GAPS) Network. Most of the observed concentrations in the background areas in Central Europe (Košetice, Czech Republic), Canada (Alert), USA (Barrow) were also below 0.09 pg m^{-3} [Rauert *et al.*, 2018].

In the Arctic, temporal trend studies on HBCDD reviewed in the AMAP Assessment of Chemicals of Emerging Arctic Concern showed increasing or inconclusive trends for air, ice core, and biota until 2005–2010. At the same time, data after 2010 demonstrated relatively stable or declining concentrations [AMAP, 2016].

HBCDD concentrations are significantly higher in urban air. For instance, in 2014, concentrations of α -HBCDD in Paris ranged from 11 to 40 pg m^{-3} , while concentrations of β -HBCDD and γ -HBCDD were $1.7\text{--}6.8$ and $3.0\text{--}12.0 \text{ pg m}^{-3}$, respectively [Rauert *et al.*,

2018]. Values of observed HBCDD concentrations in urban areas of China were even higher, ranging from 3.21 to 123 pg m⁻³ in Shanghai (2006), from 20 to 1800 pg m⁻³ in Beijing (2008–2009), and from 3.9 to 6700 pg m⁻³ in Harbin (2008–2013) [Li *et al.*, 2012; Hu *et al.*, 2011; Li *et al.*, 2016].

3.5 Modelling

A number of studies were recently performed to evaluate levels of HBCDD concentrations in the environment using available modelling approaches. In particular, modelling study of HBCDD diastereomer profiles in global environment [Li and Wania, 2018] was carried out using BETR-Global model [MacLeod *et al.*, 2011] coupled to dynamic substance flow model, named Chemicals in Products - Comprehensive Anthropospheric Fate Estimation model (CiP-CAFE) [Li and Wania, 2016], which took into account pathways and releases of HBCDD during production, use and waste disposal stages. Modelling results for 2015 indicated that 340–1000 tonnes of HBCDD were emitted globally, with 50–65% of γ -HBCDD and 30–50% of α -HBCDD. It was shown that α -HBCDD dominated in the contamination of the air in populated areas, whereas γ -HBCDD dominated in remote background areas and in the regions with HCBDD production and processing facilities. It was also noted that the relative abundance of α -HBCDD was expected to increase after the production of HBCDD was eliminated.

Mass balance box models and spatially resolved multicompartment models were applied to evaluate long-range transport potential (LRTP) and overall persistence (Pov) of HBCDD [Arnot *et al.*, 2009; Vulykh *et al.*, 2009]. In particular, long-range atmospheric transport and persistence of HBCDD were evaluated using the MSCE-POP multicompartment hemispheric transport model [Vulykh *et al.*, 2009]. The model predicted the residence time of HBCDD mixture in the atmosphere about 3 days and the transport distance about 1800 km.

3.6 Concluding remarks and further activities

Overview of scientific literature on HBCDD demonstrates that information on physical-chemical properties, concentrations in environmental compartments, and levels of emission is not sufficient for detailed assessment of HBCDD fate and pollution levels. To evaluate HBCDD input to the Baltic Sea, inventories of contemporary and historic HBCDD emissions need to be further elaborated to provide spatial distribution of emissions with indication of emissions from particular countries. Model assessment of pollution requires

more detailed monitoring data on their content in the environment and temporal trends. Besides, further improvement of understanding of processes governing HBCDD fate is of importance for the assessment of pollution levels (e.g. of gas-particle partitioning in the atmosphere, air-surface exchange, degradation in media).

4. Information on polychlorinated naphthalenes (PCNs)

4.1 Introduction

Polychlorinated naphthalenes (PCNs) is a group of dioxin-like chemicals that includes 75 theoretical congeners with from one to eight chlorine atoms substituting the hydrogen atoms of the naphthalene ring [Falandysz *et al.*, 2014]. PCNs were among the first commercially produced synthetic industrial chemicals. They are characterized by dielectric, water-repellent, flame retardant, and fungus-resistant properties. PCNs were mainly applied in the electrical industry as separators in storage batteries, capacitor impregnates, as binders for electrical grade ceramics, and in cable covering compositions [Jakobsson and Asplund, 2000]. Also, they were used as additives in cutting and engine oils, in die casting, and as wood and paper preservatives [Yamashita *et al.*, 2000]. Their large-scale production was started in 1920s in the United States and Europe and was discontinued in 1980s. Along with the industrial production, PCNs can also be unintentionally formed during waste incineration, metallurgical and chlor-alkali processes. Besides, they were found as impurities in the commercial PCB mixtures [Yamashita *et al.*, 2000]. Main sources of their releases into environment are the diffusion during production, use, and disposal of PCN mixtures.

PCNs were identified as persistent, toxic substances capable to long-range transport in the environment and bioaccumulation in biota [UNEP, 2012]. Some of PCN congeners cause toxicological effects similar to those of dioxin-like compounds [Hanberg *et al.*, 1990, Blankenship *et al.*, 1999; Villeneuve *et al.*, 2000; Blankenship *et al.*, 2000; Kilanowicz *et al.*, 2011; Zacs *et al.*, 2021; Kilanowicz *et al.*, 2019a, 2019b]. Some of the studies concluded that a number of PCNs may be characterized as carcinogenic contaminants, however they are not currently listed by the IARC [Li *et al.*, 2021; Zacs *et al.*, 2021; IARC, 2022].

Toxicity of PCN mixture can be estimated using Relative Potency Factors (RPFs) which have been suggested for a number of PCN congeners [Blankenship *et al.*, 2000; Falandysz *et al.*, 2014]. Hexa-CNs and hepta-CNs are considered to be the most toxic among PCN congeners, followed by penta-CNs and tetra-CNs. The highest values of RPFs were estimated for PCN-63, PCN-64, PCN-66, PCN-67, PCN-68, PCN-69, PCN-70, PCN-73 [Fang *et al.*, 2019, Falandysz *et al.*, 2014].

This chapter provides a summary of information on PCNs. It briefly describes production, use and emissions of PCNs as well as existed international regulatory activities. In addition

to this, a number of studies are summarized performing assessment of PCN pollution levels based on monitoring of their concentrations in the atmosphere and modelling of their transport and fate in the environment.

4.2 Regulation activities on PCNs

PCNs are listed in the regulatory documents of national and international organizations with the aim to collect information on their environmental levels and trends as well as for the development of measures for the restriction of their usage and reduction of emissions.

In 2009 PCNs were added to the Annex I to the Protocol on Persistent Organic Pollutants to the Convention on Long-Range Transboundary Air Pollution among the new POPs for prohibition of production and use [UNECE, 2009]. However, at present, PCNs are not subject to emission reporting obligations in accordance with the Guidelines for Reporting Emissions and Projections Data under the Convention [UNECE, 2014]. Besides, the Air Pollutant Emission Inventory Guidebook does not provide information on the emission factors for PCNs [EEA, 2019].

Later on in 2015, PCNs were added to the Annexes A (elimination) and C (unintentional production) of the Stockholm Convention on Persistent Organic Pollutants with specific exemptions for the use in the production of polyfluorinated naphthalenes, including octafluoronaphthalene [UNEP, 2015]. It should be noted that mono-CN's are not listed in the Stockholm Convention. PCNs are also listed in the Annex VIII of the Basel Convention on the control of transboundary movements of hazardous wastes and their disposal.

PCNs are considered as POPs under EU Regulation 2019/1021⁶ and are listed in the Annexes I, III and IV of the Regulation⁷. In accordance with the Article 3 of the Regulation, manufacturing, placing on the market and use of PCNs shall be restricted. A specific exemption for PCNs is the possibility of placing on the market and use of the products containing PCNs that were already in use before or on 10 July 2012. The Article 7 of the Regulation establishes specific waste management provisions for PCNs. Release reduction provisions and requirements for PCNs are described in the Article 6. PCNs are also listed in the Annex V (List of Banned or Restricted Chemicals) of EU Regulation 649/2012 concerning the export and import of hazardous chemicals. In accordance with the Article 15,

⁶ Regulation (EU) 2019/1021 of the European Parliament and of the Council of 20 June 2019 on persistent organic pollutants

⁷ In the Regulation (EU) 2019/1021 "polychlorinated naphthalenes means chemical compounds based on the naphthalene ring system, where one or more hydrogen atoms have been replaced by chlorine atoms".

the export of PCNs is not possible.

PCNs are listed in Part C of the OSPAR List of Chemicals for Priority Action as a group of substances which are not currently produced or used in the OSPAR states. However, Contracting Parties should inform OSPAR if they would find any evidence that these substances are being produced, used or discharged. Contracting Parties are also required to report to OSPAR any applications for approvals relating these chemicals, and, if so, what decision has been made.

PCNs were not included in the 2007 HELCOM Baltic Sea Action Plan [HELCOM, 2007]. Updated 2021 HELCOM Baltic Sea Action Plan includes activity with a particular focus on hazardous substances which are not adequately regulated by other policies [HELCOM, 2021].

4.3 PCN production, use, and emissions

PCNs were used mainly in the electrical industry as separators in storage batteries, capacitor impregnates, as binders for electrical grade ceramics and sintered metals, and in cable insulation. Other applications of PCNs included impregnation of wood, paper and textiles to attain waterproofness, flame resistance and protection against insects, molds and fungi. Furthermore, PCNs have been used as an additive in engine oils, electroplating masking compounds, feedstock for dye productions, dye carriers, capacitors and refracting index oils [Jakobsson and Asplund, 2000; ESWI, 2011].

PCNs production was initiated around 1910 in both Europe and the United States. According to *van de Plassche and Schwegler* [2002], most part of PCNs was produced from the 1920s to the 1950s, with the majority occurring in the USA. Total global production of PCNs is estimated at 150,000–400,000 tonnes in the period 1920–1965 [UNEP, 2012]. Until 1970s PCNs remained high volume chemicals.

The annual total world production of PCNs was about 9000 tonnes in the 1920s. In the United States, 3200 tonnes were produced in 1956 which had decreased to 320 tonnes in 1978 due to the replacement of PCNs by a variety of substitutes. Production of PCNs was stopped in 1980 [Jakobsson and Asplund, 2000]. Small amounts of PCNs around 15 tonnes were imported into the USA in 1981, which were mainly used in refractive index testing oils and capacitor dielectrics [US EPA, 1983]. In Japan, about 4000 tonnes of PCNs were produced between 1940 and 1976. In 1979 the production and use were banned [Yamamoto *et al.*, 2016].

In the UK the production was stopped in the mid-1960s, although it was reported that in

1970 small amounts of PCNs were still produced. In Germany about 100-300 tonnes of PCNs per year were produced in 1980-1984 for the use as dye intermediates [UNECE, 2007]. Popp *et al.* [1997] reported that PCNs were used in a German plant producing models and tools for car manufacturing and mining until 1989. Production of PCNs in Germany was stopped in 1989.

PCNs can be formed unintentionally during uncontrolled waste combustion, waste incineration (e.g. municipal, clinical and industrial waste) and other thermal (domestic and industrial) processes. This includes coking processes, different metal processing steps such as secondary copper production, secondary aluminum production, magnesium production as well as iron sintering and electrical arc furnace processes for iron production, industrial solvent production, and cement industry processes which can be considered as emission sources [ESWI, 2011].

Although PCNs are included in the Protocol on POPs to CLRTAP, no official emission data are being collected currently. At the same time, under the Stockholm Convention, the guidance on preparing inventories of PCN production, uses and disposal has been developed to help parties to implement measures on PCN elimination [UNEP, 2021].

Inventory of PCN emissions in Europe was developed for the year 2000 by TNO. The total annual emission of PCNs to the atmosphere was estimated to 1.03 tonnes [Denier van der Gon *et al.*, 2005]. The inventory was based on the data reported by countries and expert estimates where detailed data were missing. Waste incineration contributed 74% to total PCN emissions in 2000. Industrial combustion and processes accounted for 11%, followed by residential, commercial and other combustion with 10% of total PCN emissions. The remaining part was divided between the public power and heat production, as well as solvent production and use [Denier van der Gon *et al.*, 2007].

PCN emission inventory was prepared by the United Kingdom as part of the National Implementation Plan for the Stockholm Convention on Persistent Organic Pollutants. PCN emissions to air and land were estimated for the period 1990-2014. Estimates of PCN releases to the environment in the UK in 2014 were around 104 kg to air and 98 kg to land [UK DEFRA, 2017].

Inventory of PCN emissions was compiled from priority industrial sources in China [Yang *et al.*, 2020]. Estimated emissions from the four typical emission sources in 2014 were about 512 kg. Waste incineration, secondary nonferrous smelting, electric arc furnace steelmaking, and iron ore sintering plants contributed 39, 15, 29, and 17%, respectively, to the total estimated emissions of PCNs.

4.4 Monitoring of PCNs

Monitoring of PCNs in various environmental compartments and biota was performed in Sweden [Haglund *et al.*, 2011]. Atmospheric concentrations of different PCN homologue groups were measured at two monitoring sites Raö and Pallas in 2010 (Fig.4.1). Less halogenated di-CN and tri-CN were found to make the highest proportion to the total PCN concentrations. Concentrations of Σ PCNs at Raö were about 1.5 pg m^{-3} in August and 2.5 pg m^{-3} in November, while at Pallas they were about 0.5 and 1.5 pg m^{-3} , respectively. Monitoring of PCN concentrations in the vicinity of various types of emission sources showed generally higher levels for municipal solid waste incinerators and metal industries. At the same time, importance of long-range atmospheric transport of PCNs was also noted [Haglund *et al.*, 2011].

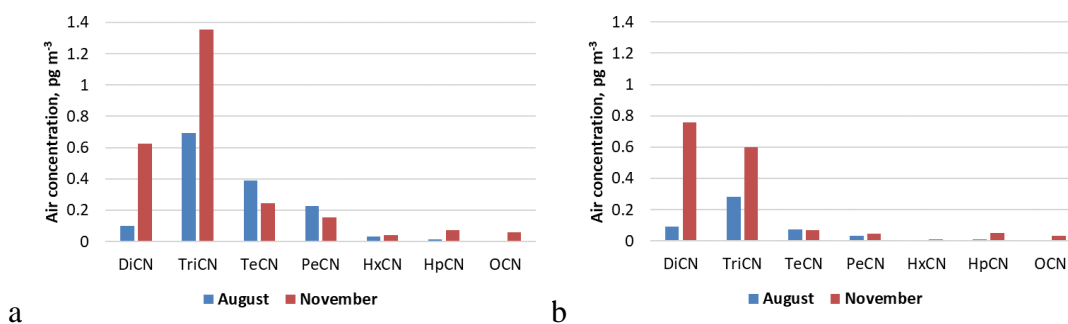


Figure 4.1 Atmospheric concentrations of the PCN congeners observed in August and November 2010 at stations Raö (a) and Pallas (b).

Although PCNs are considered as organic pollutants of emerging concern and are listed in the POP Protocol to LRTAP Convention, they are not currently included in the EMEP monitoring strategy for regular monitoring [ECE/EB.AIR/144/Add.1].

PCNs were measured in the Arctic and sub-Arctic areas in 1993-2005. Total measured atmospheric concentrations ranged from 0.16 to 40 pg m^{-3} [Bidleman *et al.*, 2010]. It was shown that PCNs were widespread in the Arctic, and the European Arctic is characterized by higher levels of Σ PCNs. Besides, it was noted that Σ PCN concentrations were comparable to the concentrations of Σ PCBs. Atmospheric concentrations of Σ PCNs at monitoring sites in Norway in 2001-2003 ranged from 27 to 48 pg m^{-3} (with mean value 35 pg m^{-3}) at Ny-Ålesund and from 9 to 47 pg m^{-3} (with mean value 25 pg m^{-3}) at Tromsø [Herbert *et al.*, 2005]. For both sites, the contribution of tri-CN was the most significant

among PCN homologue groups (65–71%), followed by tetra-CNs (24–31%). The contribution of penta-CNs was lower (<4%) [Herbert *et al.*, 2005].

Atmospheric concentrations of PCNs were measured in 2000-2001 at two rural/semirural sites in the UK and one remote site on the west coast of Ireland [Lee *et al.*, 2005]. In Ireland, Σ PCN concentrations ranged from 1.7 to 55 pg m⁻³ (with mean value 15 pg m⁻³). In northwest part of the UK, Σ PCN concentrations ranged from 31 to 310 pg m⁻³ (with mean 110 pg m⁻³), in southwest part of the UK observed values ranged from 31 to 180 pg m⁻³ (with mean value 85 pg m⁻³). It was noted that the observed concentrations of Σ PCNs were close to or exceeded the concentrations of Σ PCBs for all the sites.

Atmospheric concentrations of Σ PCNs measured in Beijing (China) were comparable to those in Europe. For example, the Σ PCN concentrations in PM_{1.0} ranged from 0.0676 to 2.27 pg m⁻³ (with mean value 1.3 pg m⁻³), whereas concentrations of Σ PCNs in PM₁₀ ranged from 0.157 to 2.65 pg m⁻³ (with mean value 1.65 pg m⁻³) [Zhu *et al.*, 2016].

4.5 Modelling

A number of studies were recently carried out to evaluate physical-chemical properties and levels of PCNs in the environment using available modelling approaches. In particular, partition coefficients, Henry's Law constants, and water solubilities of 75 PCNs were estimated using QSPR models in the studies [Puzyn and Falandysz, 2007; Puzyn *et al.*, 2009]. Partition coefficients and water solubility were also predicted using QSPR model in the study of Chayawan and Vikas [2015] and were recommended for the use in the model assessment of PCN pollution. The half-life values for all PCN congeners due to reaction with the OH radical in the atmosphere were calculated applying QSPR approach [Puzyn *et al.*, 2008]. It was shown that the average half-lives for PCNs of different homologue groups ranged from 2 days for mono-CNs up to 343 days for octa-CNs. The quantum mechanical descriptors and QSPR were also applied to predict supercooled liquid vapor pressure of PCNs [Sosnovska *et al.*, 2014; Vikas and Chayawan, 2015].

The long-range atmospheric transport and overall persistence of PCN-47 congener were estimated using the MSCE-POP multicompartment hemispheric transport model [Vulykh *et al.*, 2005]. The model predicted the residence time of PCN-47 in the environment of about 3.2 months and the atmospheric transport distance of 2271 km that indicated significant long-range transport potential of this compound.

4.6 Concluding remarks and further activities

Overview of scientific literature on PCNs demonstrates that information on concentrations

in environmental compartments, and levels of emission is not sufficient for detailed assessment of PCNs fate and pollution levels. To evaluate PCNs input to the Baltic Sea, inventories of contemporary and historic PCN emissions need to be further elaborated to provide spatial distribution of emissions with indication of emissions from particular countries. Model assessment of pollution requires more detailed monitoring data on their content in the environment and temporal trends. Besides, further improvement of understanding of processes governing PCN fate is of importance for the assessment of pollution levels (e.g. of gas-particle partitioning in the atmosphere, air-surface exchange, degradation in media).

5. Information on pentachlorobenzene (PeCB)

5.1 Introduction

Pentachlorobenzene (PeCB or PeCBz⁸) is a chlorinated aromatic hydrocarbon consisting of a benzene ring with 5 chlorine atoms substituting hydrogen atoms. PeCB occurs as white crystalline solids at room temperatures. Being characterized by relatively high subcooled liquid-vapour pressure [Mackay *et al.*, 2006], PeCB presents in the atmosphere mostly in the gaseous phase. It has a very low solubility in water. At the same time, it has high octanol water partition coefficient. PeCB has been found in air, rain, surface water, sediment and biota samples collected from various locations around the world, including remote regions [UNEP, 2007].

Intentionally produced PeCB was used in PCB products, for the production of quintozene and in dye carriers. Other applications include also its use as a pesticide and as a flame retardant [UNEP, 2007]. As unintentional by-product, PeCB can occur as an impurity in solvents or pesticides. It also can be formed during various combustion, thermal and industrial processes, including waste incineration. It should be noted that combustion of PeCB may result in the formation of other toxic compounds such as polychlorinated dibenzodioxins and polychlorinated dibenzofurans.

PeCB is considered as persistent and bioaccumulative substance, which has hazardous effects to human health and wildlife, especially for aquatic life. Monitoring of environmental levels suggests that PeCB has significant potential for long-range atmospheric transport. It has long residence time in the atmosphere and is characterized by high persistence under anaerobic conditions in sediments and soils [Canada Communication Group, 1993].

This chapter summarizes information on international regulatory activities related to PeCB as well as available data on its production, use and emissions. Along with this, a summary of PeCB pollution assessments based on monitoring and modelling of transport and fate is provided.

5.2 Regulation activities on PeCBz

PeCB is included in a number of programs of various national and international activities, aimed at collection of data on its environmental levels and their trends. Besides, measures have been developed for the restriction of its usage and reduction of emissions to the

⁸ Both PeCB and PeCBz abbreviations are used in the scientific literature for pentachlorobenzene.

environment.

PeCB is one the new POPs that were added in 2009 to the Annex I (prohibition of production and use) to the POP Protocol of the Convention on Long-Range Transboundary Air Pollution [UNECE, 2009]. However, inventories of PeCB emissions are not currently officially reported under the Convention [UNECE, 2015] and emission factors for PeCB are not present in the Air Pollutant Emission Inventory Guidebook [EEA, 2019].

Risk management evaluations, made under the Stockholm Convention [UNEP, 2007, 2008a, 2008b], indicate that PeCB has significant long-range transport potential and can cause significant adverse human health and environment effects. In 2009, PeCB was listed under Annex A (elimination) and Annex C (unintentional production) of the Stockholm Convention on Persistent Organic Pollutants without specific exemptions [UNEP, 2009].

In accordance with the EU REACH⁹ and CLP Regulation¹⁰, PeCB is classified as very toxic for aquatic species with long lasting effects¹¹. PeCB is listed in the Annexes I, III and IV of the EU Regulation 2019/1021 on POPs¹². Article 3 of the Regulation requires a prohibition of manufacturing, placing on the market and use of PeCB. In according with the Article 7 and Annex IV of the Regulation, specific waste management provisions are applied to PeCB. Release reduction provisions and requirements for PeCB are described in Article 6. Besides, PeCB is listed in Part B of Annex III, which however does not require mandatory monitoring of this substance in the environment.

PeCB is considered as a priority substance in the EU Water Framework Directive¹³. The Directive 2013/39/EU¹⁴ sets environmental quality standards (EQS) for PeCB, which are

⁹ Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC

¹⁰ Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006

¹¹ <https://echa.europa.eu/information-on-chemicals/cl-inventory-database/-/discli/details/62913>

¹² Regulation (EU) 2019/1021 of the European Parliament and of the Council of 20 June 2019 on persistent organic pollutants

¹³ Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy

¹⁴ Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy

equal to $0.007 \mu\text{g L}^{-1}$ for inland surface waters and $0.0007 \mu\text{g L}^{-1}$ for other surface waters (annual average concentrations).

PeCB is listed in the OSPAR 1998 List of Candidate Substances [UNEP, 2007]. Under the HELCOM the Baltic Sea Action Plan [HELCOM, 2007] did not have specific activities on PeCB. However, updated HELCOM Baltic Sea Action Plan [HELCOM, 2021] includes activity with a particular focus on hazardous substances which are not adequately regulated by other policies.

5.3 Production, use and emissions

PeCB was intentionally produced in the past as a component of PCB products for the electrical equipment. Besides, it was used as an intermediate chemical for the production of fungicide quintozene. Other applications of PeCB included the use in dyestuff carriers, as a pesticide, and as a flame retardant. The major European and American producers of quintozene have changed their manufacturing processes to eliminate the use of PeCB. It also can present at low levels in herbicides, pesticides and fungicides as an impurity and product of degradation. There is no quantitative information on historic production and use of PeCB [UNEP, 2007a; UNEP, 2008].

At present the most relevant sources of PeCB releases to the environment can be unintentional formation of PeCB during various industrial processes (e.g. combustion of fossil fuels, production of steel and iron, and waste incineration). Further, waste water treatment, which leads to the generation of sewage sludge containing PeCB, has been considered as relevant emission source [ESWI, 2011].

The European Pollutant Release and Transfer Register (E-PRTR) contains specifications for the reporting of PeCB release to the environmental compartments. A small number of EU Member States report emissions of PeCB to air and water (Belgium, Finland, France, Italy, Luxembourg, Portugal, Spain and the United Kingdom).

Within the E-PRTR dataset only a limited number of sites across Europe reported the PeCB emissions to air for the period 2008–2011. According to these data main contribution belonged to manufacturing of pig iron and steel. The other reported minor sources were waste water treatment plants, and plants for the processing of vegetable and animal matter. Reported releases of PeCB to air from iron and steel manufacturing sector ranged from 348 to 1779 kg y^{-1} (based on three metal facilities reporting for 2008 to 2010, and two for 2011).

PeCB releases to water, reported in the E-PRTR (2007-2020), illustrate a small number of sources. Organic chemicals manufacture, waste water treatment works, petroleum

refineries, and hazardous waste treatment reported emissions almost every year. According to E-PRTR, releases of PeCB to water from manufacturing of organic chemicals ranged from 11 to 44 kg y⁻¹, with an average of 30 kg y⁻¹, and from waste water treatment works ranged from 14 and 84 kg y⁻¹, with an average of 40 kg y⁻¹. Petroleum refineries contributed between 2 and 121 kg y⁻¹ with an average of 30 kg y⁻¹.

According to expert estimates [Bailey, 2007], global emissions of PeCB around the year 2000 amounted to 85 t y⁻¹. The largest contributions were made by the combustion of biomass, coal, and solid wastes. However, it was noted that there was a considerable uncertainty in these estimates of PeCB emissions (up to an order of magnitude potentially). Updating of these estimates resulted in higher total annual emissions about 121 t y⁻¹ [Bailey *et al.*, 2009], where more importance was given to pesticide use and degradation of chemicals.

Several national inventories of PeCB emissions were made by particular countries. The total release of PeCB around the year 2003, provided by Environment Canada in the risk management strategy, was 41.9 kg y⁻¹ [Environment Canada, 2005]. The most significant sources in the Canadian risk management report were barrel burning of household waste, municipal solid waste incineration and hazardous waste incineration.

According to US EPA Toxics Release Inventory annual emissions of PeCB in the USA varied from 763 to 1512 kg y⁻¹ in period 2000-2004. The inventory included atmospheric emissions, surface water discharges, underground injection, on site releases to land and transfers off-site for disposal. Atmospheric emissions were about 74 - 100 kg y⁻¹ [UNEP, 2007a; UNEP, 2007b].

Overall discharges of PeCB in Europe in 2010 were estimated to 2632 kg y⁻¹ using mass flow approach [ESWI, 2011]. About 88% of this were released to the atmosphere and soil and only approximately 12% end up as waste. PeCB emissions were dominated by the power production from coal (79%).

An inventory of PeCB emissions in the United Kingdom and Ireland was prepared as part of the National Implementation Plan for the Stockholm Convention on Persistent Organic Pollutants [UK DEFRA, 2017; Ireland EPA, 2018]. PeCB emissions to the atmosphere, water and land were estimated for the period 1990-2014 in the UK and up to 2015 in Ireland. Estimates of PeCB releases to the environment in the UK in 2014 were around 33 kg to the atmosphere, 3 kg to water and 9 kg to land [UK DEFRA, 2017]. In Ireland, emissions of PeCB to the atmosphere, water and land in 2015 were estimated to 14 kg, 0.15 kg and 0.002 kg, respectively [Ireland EPA, 2018].

5.4 Environmental levels

Atmospheric concentrations of PeCB were measured at two EMEP monitoring stations in Norway and the Czech Republic, Zeppelin (NO0042R) and Kosetice (CZ0003R), respectively. In 2004-2006, concentrations of PeCB in air at the Zeppelin station varied from 7.5 to 105 pg m^{-3} with annual mean concentrations 19.5 pg m^{-3} in 2004 and 23.9 pg m^{-3} in 2006. Measurements of PeCB air concentrations at the Kosetice station were performed for longer period starting from 2001 up to the present time. In 2001-2005, annual mean PeCB air concentrations varied from 13 to 55 pg m^{-3} with minimum concentrations 0.5 pg m^{-3} and maximum concentration 441 pg m^{-3} [Dvorska *et al.*, 2008]. In 2011-2020, almost similar levels of annual mean PeCB air concentrations were observed equal to 6.2-11.6 pg m^{-3} , with the exception of 2020, when maximum annual mean concentration 15.5 pg m^{-3} was observed (Fig. 5.1a). Seasonal changes of PeCB concentrations showed minimum values in summer period of the year, while maximum values were measured in winter period (Fig. 5.1b).

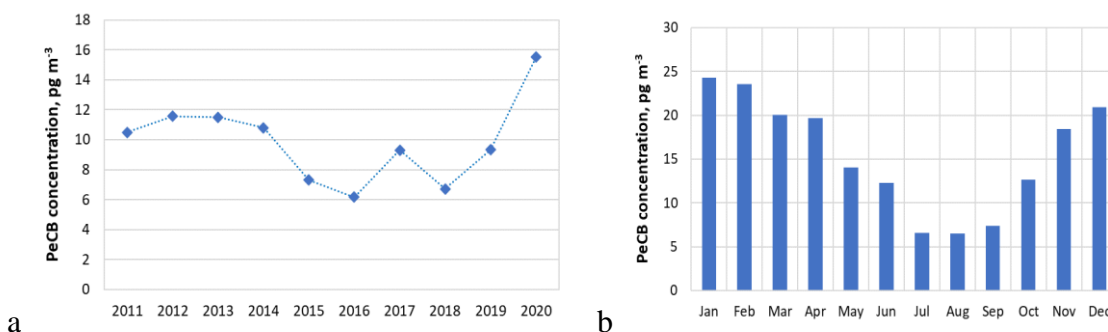


Figure 5.1 Annual mean concentrations of PeCB in air measured at monitoring site Kosetice (CZ0003R) in period 2011-2020 (a) and seasonal variations of observed PeCB air concentrations in 2020 (b).

Spatial distribution of PeCB air concentrations in Norway was analyzed based on the measurements made using passive air sampling [Halvorsen *et al.*, 2021]. PeCB concentrations were measured at 97 locations across Norway in summer 2016. Observed concentrations varied from 16 to 38 pg m^{-3} with mean concentration equal to 22 pg m^{-3} . The ratio of maximum and minimum observed PeCB concentrations was about 2 times indicating low spatial variability of concentrations and potentially significant role of long-range transport of pollution.

5.5. Modelling

Modelling approaches were applied to evaluate physical-chemical properties, expert estimates of emissions and pollution levels of PeCB on global and regional scales. In particular, a complete set of physical-chemical properties (e.g. octanol-water partition coefficient K_{OW} , vapor pressure P , Henry's law constant H , octanol-air partition coefficient K_{OA}) and their temperature dependence, necessary for model assessment, was derived in the study [Shen and Wania, 2005]. The approach is based on the compiling and evaluating measured data from the literature, selecting literature-derived values through averaging or linear regression and making estimates of the uncertainty of these values.

Spatial distribution and long-range transport of PeCB was evaluated in the study [Shen *et al.*, 2005] based on monitoring data of 40 passive air sampling stations across North America. Measurements were performed for the whole year 2000 to obtain annually averaged concentrations. Empirical travel distance for PeCB estimated using monitoring data was about 13000 km. Model predictions of characteristic travel distance, made by the models TaPL3 and ELPOS, showed higher values about 84000 km.

Accuracy of global PeCB emission estimates [Bailey *et al.*, 2007] was evaluated in the study [Bailey *et al.*, 2009] using Globo-POP environmental model [Wania and Mackay, 1995]. The model was run with constant PeCB emission rate of 100000 kg y⁻¹ using physical-chemical properties from [Shen and Wania, 2005]. In spite of considerable uncertainties in model parameterization and properties of PeCB used in these simulations, the model predictions for PeCB were close to the observed atmospheric concentrations of PeCB. It was shown that decline of pollution levels of PeCB would depend on the rate of PeCB degradation in soil, sediments and water. Besides, PeCB concentrations would be observed for a period of years after emissions would be completely stopped. Current PeCB concentrations are likely supported to some extent by re-emission from soil exposed in the past.

The long-range atmospheric transport and overall persistence of PeCB were evaluated in the study [Vulykh *et al.*, 2005] using the MSCE-POP multicompartiment hemispheric transport model. The model predicted the atmospheric transport distance of PeCB about 8300 km using conventional point emission source. The half-life of PeCB in the environment was estimated to approximately 6 months indicating significant long-range transport potential of this contaminant.

5.6 Concluding remarks and further activities

Overview of scientific literature on PeCB demonstrates that information on concentrations

in environmental compartments, and levels of emission is not sufficient for detailed assessment of PeCB fate and pollution levels. To evaluate PeCB input to the Baltic Sea, inventories of contemporary and historic PeCB emissions need to be further elaborated to provide spatial distribution of emissions with indication of emissions from particular countries. Model assessment of pollution requires more detailed monitoring data on their content in the environment and temporal trends. Besides, further improvement of understanding of processes governing PeCB degradation is of importance for the assessment of pollution levels.

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