GLOBAL MONITORING PLAN FOR PERSISTENT ORGANIC POLLUTANTS

UNDER THE STOCKHOLM CONVENTION ARTICLE 16 ON EFFECTIVENESS EVALUATION

SECOND REGIONAL MONITORING REPORT

CENTRAL AND EASTERN EUROPEAN (CEE) AND CENTRAL ASIAN REGION



DECEMBER 2014

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PREFACE

Persistent organic pollutants (POPs) are a group of chemicals that have toxic properties, resist degradation in the environment, bioaccumulate through food chains and are transported long distances through moving air masses, water currents and migratory species, within and across international boundaries. POPs belong to three main groups, however some of the chemicals fit into more than one of these three general categories:

- pesticides used in agricultural applications¹
- industrial chemicals used in various applications²
- chemicals generated unintentionally as a result of incomplete combustion and/or chemical reactions³.

Twelve POPs were initially listed in the Stockholm Convention (shown in bold font in footnotes 1-3). In general, these 'legacy' POPs were first produced and/or used several decades ago, their persistence, bioaccumulative properties and potential for long-range transport are well studied, and they have been globally banned or restricted since 2004. In 2009, nine additional substances were globally regulated by the Convention (chemicals with an asterisk in footnotes 1-3). Finally, two additional chemicals were listed in 2011 and in 2013 (two and three asterisks in footnotes 1-3 respectively).

Article 16 of the Stockholm Convention requires the Conference of the Parties to evaluate periodically whether the Convention is an effective tool in achieving the objective of protecting human health and the environment from persistent organic pollutants. This evaluation is based on comparable and consistent monitoring data on the presence of POPs in the environment and in humans, as well as information from the national reports under Article 15 and non-compliance information under Article 17.

The global monitoring plan for POPs introduced under the Convention is a key component of the effectiveness evaluation and provides a harmonized framework to identify changes in concentrations of POPs over time, as well as information on their regional and global environmental transport.

The present monitoring report is synthesizing information from the first and second phase (i.e. until 2008 and until 2014 respectively) of the global monitoring plan and presents the current findings on POP concentrations of all listed chemicals in the Central and Eastern European Region - including baseline concentrations and trends where available.

¹ aldrin, chlordane, chlordecone*, dichlorodiphenyltrichloroethane (DDT), dieldrin, endosulfan**, endrin, heptachlor, hexachlorobenzene (HCB), gamma-hexachlorocyclohexane (γ -HCH, lindane)* and by-products of lindane [alpha-hexachlorocyclohexane (α -HCH)* and beta-hexachlorocyclohexane (β -HCH)*], mirex, toxaphene.

² tetra- and pentabromodiphenyl ethers (PBDEs)*, hexa- and heptabromodiphenyl ethers (PBDEs)*, hexabromocyclododecane*** (HBCD, HBCDD), hexabromobiphenyl* (HBB), perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOS-F)*, pentachlorobenzene (PeCB)*, **polychlorinated biphenyls (PCBs).**

³ hexachlorobenzene (HCB), pentachlorobenzene (PeCB)*, polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs).

ABBREVIATIONS AND ACRONYMS

AMAP	Arctic Monitoring and Assessment Programme						
CEE	Central and Eastern Europe						
CIS	Commonwealth of Independent States						
COP	Conference of the Parties						
CV	Coefficient of Variation						
DDD /DDE	Metabolites of DDT						
DDT	Dichlorodiphenyltrichloroethane						
dl-PCBs	Dioxin-like PCBs						
EDCs	Endocrine Disrupting Chemicals						
EMAN	Ecological Monitoring and Assessment Network						
EMEP	Co-operative Programme for Monitoring and Evaluation of the Long-Range						
	Transmission of Air Pollutants in Europe						
EPER	European Pollutant Emission Register						
ERL	Effects Range Low						
ERM	Effects Range Median						
EROD	7-ethoxyresorufin-O-deethylase						
EUSES	European Union System for the Evaluation of Substances						
FAO	Food and Agriculture Organisation of the United Nations						
GAPS	Global Atmospheric Passive Sampling Survey						
GEF	Global Environment Facility						
GEMS	Global Environment Monitoring System						
GMP	Global Monitoring Plan						
HCB	Hexachlorobenzene						
HELCOM	Helsinki Commission/The Baltic Marine Environment Protection Commission						
HCHs	Hexachlorocyclohexanes						
HIPS	High Impact Polystyrene						
HPLC	High Performance Liquid Chromatography						
HRGC	High Resolution Gas Chromatography (capillary column)						
HRMS	High Resolution Mass Spectrometer						
HxBB	Hexabromobiphenyl						
IADN	Integrated Atmospheric Deposition Network						
IFCS	Intergovernmental Forum on Chemical Safety						
IMO	International Maritime Organisation						
INSPQ	Centre de Toxicologie du Québec						
INFOCAP	Information Exchange Network on Capacity Building for the Sound						
IDDC	Integrated Pollution Provention and Control						
I TEO	Integrated Fondton Frevention and Control						
I-ILQ KAW	Air/Water Partition Coefficient						
KAW	Octanol/Air Partition Coefficient						
KOA	Octanol/Water Partition Coefficient						
LC50	Median Lethal Concentration						
LC50 LD50	Median Lethal Dose						
LOAFI	I owest Observable Adverse Effect I evel						
LOALL	Limit of Detection						
LOD	Limit of Quantification						
IRT	Long Range Transport						
	Long Kange Hansport						

LRTAP	Long Range Transport Air Pollutants						
LRTP	Long Range Transport Potential						
MDL	Minimum Detectable Level						
MEDPOL	Mediterranean Pollution Monitoring and Research Programme						
MEA	Multi Lateral Environmental Agreements						
MRL	Maximum Residue Limit						
MSCE-East	Meteorological Synthesizing Centre-East						
NAFTA	North American Free Trade Agreement						
NARAPs	North American Regional Action Plans						
ND	Not detected						
NGOs	Non-Governmental Organisations						
NHATS	National Human Adipose Tissue Survey						
NIS	Newly Independent States						
NOAA	National Oceanic and Atmospheric Administration						
NOAEL	No Observable Adverse Effect Level						
NOEL	No Observable Effect Level						
NWT	Northwest Territories						
OCs	Organochlorines						
OCPs	Organochlorine Pesticides						
OECD	Organisation for Economic Co-operation and Development						
OPs	Organophosphates						
OSPAR	Commission for the Protection of the Marine Environment of the North-East						
	Atlantic						
PAHs	Polycyclic aromatic hydrocarbons						
PBDEs	Polybrominated diphenyl ethers						
PCBs	Polychlorinated biphenyls						
PCDDs	Polychlorinated dibenzo- p-dioxins						
PCDFs	Polychlorinated dibenzofurans						
PCP	Pentachlorophenol						
PFOS	Perfluorooctane sulfonate						
PIC	Prior Informed Consent						
POPs	Persistent Organic Pollutants (group of twelve as defined in the Stockholm						
	Convention 2001)						
PRTRs	Pollutant Release and Transfer Registers						
PTS	Persistent Toxic Substances						
PUF	Polyurethane Foam						
PVC	Polyvinylchloride						
QA/QC	Quality Assurance and Quality Control Regimes						
REACH	Registration, Evaluation and Authorisation of Chemicals						
RECETOX	Research Centre for Environmental Chemistry and Ecotoxicology						
ROGs	Regional Organization Groups for the Global Monitoring Plan						
SAICM	Strategic Approach to International Chemicals Management						
SCCPs	Short-chain chlorinated paraffins						
SOP	Standard Operating Procedure						
SPM	Suspended particulate matter						
SPREP	South Pacific Regional Environment Programme						
t	Tonnes						
TBBPA	Tetrabromobisphenol A						
TCDD	Tetrachlorodibenzo-p-dioxin						
TEL	Tetraethyllead						

TEQ	Toxicity Equivalents
TOMPS	Toxic Organic Micropollutants Survey
TPT	Triphenyltin
UNECE	United Nations Economic Commission for Europe
UNEP	United Nations Environment Programme
UNIDO	United Nations Industrial Development Organisation
WFD	Water Framework Directive
WHO	World Heath Organisation
WMO	World Meteorological Organization
XAD	Styrene/divinylbenzene-co-polymer Resin

GLOSSARY OF TERMS

I L-1	Instrumentation level 1 capable to analyze PCDD/PCDF and dioxin-like PCB at ultra-trace concentrations: must be a high-resolution mass spectrometer in combination with a capillary column
I L-2	Instrumentation level capable to analyze all POPs: (capillary column and a mass-selective detector)
I L-3	Instrumentation level capable to analyze all POPs without PCDD/PCDF and dioxin like PCB (capillary column and an electron capture detector)
I L-4	Instrumentation level not capable to do congener-specific PCB analysis (no capillary column, no electron capture detector or mass selective detector)
Intercomparisons	Participation in national and international intercalibration activities such as ring-tests, laboratory performance testing schemes, etc
LOD	Limit of detection. Definition: The lowest concentration at which a compound can be detected; it is defined as that corresponding to a signal three times the noise.
<lod< td=""><td>Result below the of limit detection</td></lod<>	Result below the of limit detection
LOQ	Limit of quantification. Definition: The lowest concentration that can quantitatively be determined is three times higher than LOD.
<loq< td=""><td>Result below limit of quantification. Compounds found at levels between LOD and LOQ can be reported as present, or possibly as being present at an estimated concentration, but in the latter case the result has to be clearly marked as being below LOQ.</td></loq<>	Result below limit of quantification. Compounds found at levels between LOD and LOQ can be reported as present, or possibly as being present at an estimated concentration, but in the latter case the result has to be clearly marked as being below LOQ.
MDL	Method detection limit. The MDL considers the whole method including sampling, sample treatment and instrumental analysis. It is determined by the background amounts on field blanks.
Phase I	Activities to support the Article 16 effectiveness evaluation that will be conducted by the Conference of the Parties at its fourth meeting, information collected between 2000 and 2008.
Phase II	Activities to support the Article 16 effectiveness evaluation that will be conducted by the Conference of the Parties at its seventh meeting, information collected between 2009 and 2013.

EXECUTIVE SUMMARY

This second regional monitoring report synthesizes information from the first and second phase of the global monitoring plan and presents the current findings on POPs concentrations in the Central and Eastern European Region. The UN region of the Central and Eastern Europe covers 23 countries of the Central and Eastern Europe. In addition, five countries of the Central Asia (Kazakhstan, Kyrgyzstan, Tajikistan, Turkmenistan, and Uzbekistan) were also included to the regional report, as agreed in discussion between relevant Regional Organization Groups due to similar pattern of production and use of POPs, geographical proximity and language issues. Thus, this regional report covers 28 countries and more details about the region are provided in chapter 2.

The second phase of the global monitoring plan was undertaken in the period 2009-2014 to determine trends in concentration of persistent organic pollutant in humans and in the environment, and to obtain baseline data on the persistent organic pollutants that have been listed in the Convention after the year 2009. Data available in this report cover 1996-2014 for air and 1987-2014 for breast milk.

It has to be noted that for ambient air monitoring a relatively small amount of international/regional programmes cover the whole CEE GMP region such as EMEP, MONET, and GAPS as described in detail in chapter 4. Some of the monitoring activities are lasting for decades (since 1980s), however they cover a limited scope of Stockholm Convention chemicals (seven or eight chemicals). Other air monitoring activities were only initiated simultaneously with the end of the first phase of GMP data collection round (from 2006 onwards) or by the very end of that period (post-2008). Nevertheless, the long-term sustainability of both the long-term and the most recently established programmes remains crucial for the production of representative and comparable data in the CEE region in the future. This fact is also valid for any future effectiveness evaluation of the implementation of the Stockholm Convention.

For ambient air monitoring, both active sampling and passive sampling techniques organized in the pan-European or global monitoring networks are used to generate data under the global monitoring plan in the CEE region.

For human tissues, the WHO surveys and UNEP/WHO surveys serve are the core data provider, however a number of national monitoring programmes/activities exist, but these cover a limited range of chemicals.

Other matrices, such as water, or other media are not regularly monitored in a regional scale programme. A diverse and limited information exists from various sources that are rather of episodic than of the regular nature. Relevant information is provided through research publications and report, however they do not represent a regular and regional scale activity.

Conclusions on the availability of regional monitoring data are summarized below:

POPs GMP data availability and comparability in the CEE region increased since the first phase. EMEP and RECETOX strategic partnerships for air monitoring were expanded and

significantly contributed to the establishment of monitoring stations in other countries of the region. The good cooperation among EMEP, GAPS and MONET was highlighted and will be continued in the future. Air data are available for the region for 21 chemicals. Human tissues data are available only through the WHO and UNEP/WHO surveys, with certain information gaps identified for South European and Central Asian part of the region. Data on the newly listed POPs are limited. Information related to POP levels in human blood and in water is not at all available in the region in this report, PFOS levels in water only cover western part of the CEE region.

Results indicate decreasing trends in air concentrations on sufficiently long passive sampling time series (minimum 5 years) for HCB, PCB, DDT, alpha, beta and gamma HCH and PeCB. Data from active sampling of air in Košetice also confirmed decreasing trend for HCB, sum 6 PCB, DDT, alpha HCH and PeCB. Series collected for beta and gamma HCH in Košetice, Czech Republic did not provide a statistically significant trend.

For human milk data, due to a limited information (short time series), trends are not quantifiable. Likewise for water and other media, where no regular monitoring is conducted.

Long range transport within the CEE region was assessed in the NILU-MSC-EAST reports for HCB, PCBs and PCDD/PCDFs. Model simulations indicate decrease in total emissions, changes in relative proportion of contributions to transboundary fluxes from anthropogenic emission sources to non-EMEP emissions as well as to a more significant secondary emission sources (re-volatilization from the environmental media). The MSC-E report holds that levels and emissions of all studied POPs have decreased significantly between 1990 and 2012 (i.e. HCB by 90%, PCBs by up to 80%, PCDD/Fs by 40-75%). Decrease in emissions is usually attributed to significant national reductions of emissions (in some countries) as well as to a decrease in anthropogenic EMEP emissions.

Data gaps

Some parts of the CEE region are well monitored through existing air monitoring networks pertaining to international monitoring programmes EMEP, GAPS and MONET, in particular western part of the CEE region. The above air monitoring activities currently cover 21 countries out of 28 that are followed in this GMP region (no information is available for Albania, Azerbaijan, Bosnia and Herzegovina, Georgia, Tajikistan, Turkmenistan, and Uzbekistan). The monitoring combines active and passive sampling and despite the fact that the longest time series are available for chlorinated POPs, more recent information on one site (Košetice, 2011-2013) is available for 97 parameters related to 19 POPs listed in the Stockholm Convention. In addition, in some cases information relevant for 2014 was already made available, however majority of air samples collected in 2013 and 2014 are still processed in laboratories and will only become available at a later stage in many cases.

On the other hand, Central Asian countries have a limited availability of information that only covers several organochlorine POPs (alpha-,beta-,gamma-HCH, HCB, PCB, and DDT in 2008-2010). These activities would require support in the future to ensure continuity of POPs data collection in that sub-region.

Finally, for a large part of the CEE region covering in particular the Russian Federation no information is available with the exception of Valkarkai polar AMAP sampling site (latitude: 70.08, longitude 170.9) operated by Environment Canada in the far east. This gap represents European part of the Russian Federation from latitude 55.1 to further north and whole remaining part of the territory of the Russian Federation located to the east from Ural Mountains. The latest information available covers air monitoring in 2009.

Data availability for human tissues is even more limited. Information generated through WHO and UNEP/WHO surveys covers only 14 countries out of 28 in the CEE region and only half of these countries participated in the surveys more than once. It is impossible to establish trends on the basis of available data and time series are barely available. Support in participation of CEE countries in the milk surveys need to strengthen significantly in particular for South European countries, and for Central Asia and Caucasus countries.

Data on water are scarce and episodic in nature. At present, there is no regional scale program for monitoring PFOS in water except surveys (research projects) undertaken by the European Commission (JRC). Nevertheless, this activity only covers western part of the CEE region and the Southern, Central Asian and Caucasus countries are not involved.

In conclusion, data is available, but the range and regional coverage is limited (50% of countries participate) and no information is available for South European countries and a very limited information is available for Central Asia and Caucasus countries. On the other hand, the UNEP WHO surveys are a perfectly adequate source of information on POP levels.

Recommendations for the future

The experts and members of the CEE ROG propose the following list as priority issues for the next GMP phase in the CEE region:

Include two other countries to the CEE GMP regional report from 3rd data collection campaign Cyprus (UN region Asia) and Turkey (UN region WEOG) as it is pertinent to consider regional levels and long-range transport in the CEE together with those two Parties. Both Cyprus and Turkey are also Parties to the CLRTAP and Turkey is taking steps to ratify also the POPs protocol to the CLRTAP.

Establish closer contacts with relevant institutions in the Russian Federation and consider their involvement in the ROG.

Increase availability of data in relation to human exposure – POP levels in breast milk – and provide support to participation of South European countries + ECCA (Caucasus and Central Asian countries) countries in next rounds of UNEP/WHO surveys.

Ensure availability of human exposure data from general population in the CEE region for reference purposes, as some of undertaken human biomonitoring activities focused only on highly exposed populations and existing information on concentrations of POPs in the region may not be fully accurate.

Monitoring data on occurrence of dioxins and furans and brominated and fluorinated chemicals are scarce, in particular due to lacking analytical equipment in non-EU part of the region and du to high costs of analyses. Nevertheless, capacity to analyze these chemicals exists in the region, in the RECETOX who has state of the art facility and instrumentation as well as trained personnel; however, this capacity needs to be enhanced in the region. Plans for the future include continuing the strategic partnerships for air monitoring with MONET Europe, GAPS and EMEP, support the operation of the 2nd active sampling station in Leova, Moldova, and further support the information collection from Southern Europe, Central Asia and promote greater involvement of the Russian Federation institutions.

The newly developed electronic GMP Data Warehouse, which was used to support regional data storage, analyses, and presentation, was helpful in preparation of the regional monitoring report and should be used also in further campaigns.

The countries in the region recognize the beneficial impact of the capacity building and training activities available for sampling, monitoring and analyses of the samples and hereby acknowledges support provided by the Stockholm Convention Secretariat and its partners to countries in the CEE region. The experts participating in the summer schools, specific training or inter laboratory comparison strengthened their knowledge in undertaking monitoring activities for legacy POPs as well as gradually introduced new sampling techniques to cover newly listed POPs. These activities should also continue in the future as they contribute significantly to the abilities of countries to establish and run sustainable national monitoring or at least fully participate in regional monitoring activities.

1 INTRODUCTION

The present monitoring report synthesizes information from the first and second phase of the global monitoring plan and presents the current findings on POPs concentrations in the Central and Eastern European Region (CEE).

While the first monitoring report, presented at the fourth meeting of the Conference of the Parties in May 2009, provided information on the baseline concentrations of the 12 legacy POPs, this second monitoring report, to be submitted to the seventh meeting of the Conference of the Parties in May 2015, provides first indications as to the changes in concentrations of the chemicals initially listed in the Convention, as well as baseline information on the newly listed POPs and for the CEE region.

At its sixth meeting in May 2013, the Conference of the Parties, by decision SC-6/23 on the global monitoring plan for effectiveness evaluation, adopted the amended global monitoring plan for persistent organic pollutants (UNEP/POPS/COP.6/INF/31/Add.1) and the amended implementation plan for the global monitoring plan (UNEP/POPS/COP.6/INF/31/Add.2). It also adopted the Guidance on the Global Monitoring Plan for Persistent Organic Pollutants (UNEP/POPS/COP.6/INF/31), which has been updated to address the sampling and analysis of the newly listed POPs, providing a useful basis for monitoring of these chemicals in the second phase of the global monitoring plan, as well as for harmonized data collection, storage and handling.

Air, and human tissues (breast milk and/or blood) have been established as core matrices for GMP. They provide information on the sources of POPs, environmental transport and the levels of exposure in human populations. In addition, core matrices of the Global Monitoring Plan were expanded by water as perfluorooctane sulfonic acid (PFOS) and its salts bind preferentially to proteins in the plasma and are hydrophilic.

The global coordination group met four times over the period 2011-2014 in order to oversee and guide implementation of the second phase of the global monitoring plan, with particular emphasis on addressing the sampling and analysis of the newly listed POPs, harmonizing data collection, storage and handling, addressing the needs for ensuring sustainability of ongoing monitoring activities and for further capacity strengthening to fill the existing data gaps, as well as improving data comparability within and across monitoring programmes.

Enhanced comparability within and across monitoring programmes to evaluate changes in levels over time and the regional and global transport of POPs was an equally important milestone in the second phase. QA/QC practices remain essential for ensuring comparability, along with inter-laboratory exercises and intercalibration studies.

Efforts continue to be directed at ensuring comparability within and across programmes, providing for evaluation of changes in concentrations of POPs over time and enabling regional comparisons. Details on monitoring programmes providing information into this report are found in chapter 4.

During the second phase of the global monitoring plan, harmonized data handling was enabled and appropriate support was given to the collection, processing, storing and presentation of monitoring data in regions with limited capacity. A global monitoring plan data warehouse (GMP DWH), online electronic tool supports data storage and analysis and assists the regional organization groups and the global coordination group in producing the regional and global monitoring reports, as well as can support the effectiveness evaluation. The global monitoring plan data warehouse also constitutes a publicly available repository of valuable information that can serve as a useful resource for policy makers and researchers worldwide. This repository is accessible online through data visualization.

2 DESCRIPTION OF THE REGION

The UN region of the Central and Eastern Europe covers 23 countries of the Central and Eastern Europe. In addition, five countries of the Central Asia (Kazakhstan, Kyrgyzstan, Tajikistan, Turkmenistan, and Uzbekistan) were added to the regional report for the first GMP evaluation as well as for this second one, as agreed in discussion between relevant Regional Organization Groups due to similar pattern of production and use of POPs, geographical proximity and language issues. Thus, this regional report covers 28 countries.

2.1. Geography

The region under examination spreads over almost 23 500 000 km2 is populated by 402 800 000 inhabitants. The boundaries of the studied territory are defined by 12 °E (Czech Republic), Chukhotka (170 °W), North land (82 °N) and Tajikistan (35 °N). There are 28 countries.

Wide lowlands as well as highlands and mountains can be found within the studied region. In the western part of the region, the Carpathians and mountains of the Balkan Peninsula are the most important mountain systems. Farther to the east, spacious East-European Plain is situated, which is by the north-to-south range of the Ural Mountains separated from equally wide West Siberian Plain extending up to the Yenisei River. Farther to the east, between Yenisei and Lena Rivers, the Central Siberian Plateau is spreading out. Eastern part of Siberia is mostly mountainous with several mountain ranges (e.g. Verkhoyansk Range) and some active volcanoes in the Kamchatka Peninsula (e.g. Klyuchevskaya volcano). Major part of Central Asia holds the Kazakh Steppe (or Kazakh Plain) and the Kara Kum and Kyzyl Kum Deserts. In the southern part of the region, there are the highest mountain systems - Caucasus (Mt. Elbrus 5 642 m), Pamir Mountains (Ismoil Somoni Peak 7 495 m asl), Tian Shan (Jengish Chokusu 7 439 m), Altai Mountains, Sayan Mountains and other mountain ranges in southern part of Siberia.

2.2. Hydrology

Western part of the studied region belongs to Atlantic Ocean drainage area with these main rivers: Danube and Dnieper Rivers flowing to the Mediterranean or Black Sea and Elbe, Oder and Vistula Rivers drifting towards the German Ocean or Baltic Sea. Great part of the region is drained away to the Arctic Ocean – major part of Siberia, where the south-to-north flow direction is typical (with large streams of Lena, Yenisei and Ob-Irtysh), and northern part of European Russia. Eastern part of the region belongs to the Pacific Ocean drainage area (Amur River).

A significant part of the region has no drainage to any ocean, concerning especially area drained away by Volga River to the Caspian Sea and Central Asia from where water is led away by Amu Darya and Syr Darya Rivers to the Aral Sea (its drying-out is great ecological problem in this region, with significant economical consequences) and by some other rivers to the Lake Balkhash and Lake Yssyk Köl.

Last but not least, Lake Baikal – the world's deepest, purest and most capacious freshwater lake (it contains over one fifth of the world's fresh surface water) is crucially important; other European lakes, especially Lake Lagoda and Lake Onega, are also significant. Large water reservoirs in the region are represented by dam system on Volga, Kama, Dnieper, and on upper streams of Siberian rivers are of major (economic) importance.

2.3. Climate

From climatic point of view, the studied region belongs to following climatic zones: arctic (the northernmost part along the Arctic Ocean), sub arctic (reaching c. 60 °N in European part and c. 55 °N at Lake Baikal), temperate and in the southernmost part rarely also subtropical (Mediterranean coast of the Balkan Peninsula, south of Caucasus and south of Central Asia). Along eastern Asian coast, subarctic zone stretches more to the south due to cooling effect of the cold Oyashio Current. Southern part of East-Asian coast (round about Amur River and Sakhalin Island) is under influence of monsoon of temperate zone, which is expressed especially in winter season as a dry airflow from land to ocean and is linked to the semi-permanent Siberian High. Concerning precipitation, most part of studied region is semi-humid to dry (the driest are Central Asia and Central and Eastern Siberia), only the westernmost part of temperate zone could be classified as prevalent humid. Due to great surface extent of Eurasian continent, for large part of the studied region continental character of climate with the wide annual temperature range (very cold winter and hot summer) and unbalanced annual course of precipitation with remarkable summer maximum is typical.

2.4. Soils

In the northernmost part alongshore the Arctic Ocean and in major part of the Kamchatka Peninsula, a range of arctic and tundra type soils (lithosols) is situated. More southwards, a zone with prevailing occurrence of podzolic character soils is spreading out to large areas – whole Central and Eastern Siberia, only to Amur River territory stretches belt of cambisols. Eastward from upper stream of Yenisei River, podzolic soils verge into a compact zone of chernozems which is stretching to east as far as to lower stream of Dnieper River and to Caucasus region and chernozems also can be found along Danube River (up to Hungary). In Central Asia and in Europe southwards from c. 50°N, cambisols and kastanozems are prevailing. In European part north from the Arctic Circle, in Western Siberia more southwards (c. to 65–60°N) and in whole Central and Eastern Siberia, deep permafrost is extended (in the coldest region of Yana River basin, permafrost reaches 1,493 m deep).

2.5. Vegetation (natural)

From the point of view of natural vegetation (not affected by human activity), the studied region can be classified as follows: the northernmost parts are occupied by tundra which occurs also in the highest parts of Siberian and central-Asian mountain ranges (so-called mountain tundra). Major part of the studied region is occupied by a wide zone of taiga (boreal coniferous forest), whereas so-called mountain taiga could be found also in the highest locations of the Carpathian Mountains. In southern part of Western and Central Siberia, taiga verge into a belt of forest-steppe and steppe spreading westwards (southwestwards) up to the Caucasus and along northern coast of the Black Sea. In Central Asia and along the Caspian Sea, semi-deserts and especially in Aral Sea drainage basin spacious deserts (Kara Kum and Kyzyl Kum) are situated. Only around lower stream of Amur River (under influence of monsoon) alternately-moist leafy forests reach. In Europe, taiga verge directly into a belt of leafy forests of temperate zone. Alongshore the Mediterranean Sea and at the Black Sea in Caucasian area, subtropical forests and shrubbery represent natural vegetation.

3 ORGANIZATION OF REGIONAL IMPLEMENTATION

This chapter summarizes information on the preparation of the second regional report including strategies to collect data, store regional information and making it accessible to ROG members, On the basis of the arrangements leading to the first monitoring report and agreements stemming from the regional strategy, the CEE ROG and its consultants from the Stockholm Convention Regional Centre in the Czech Republic took steps to prepare this second report. The text below describes activities undertaken between end of 2008 and December 2014.

The CEE ROG confirmed from the outset it continues to use the support of the Stockholm Convention Regional Centre in the Czech Republic and its infrastructure for monitoring activities and data storage and handling, in particular through the GENASIS database (www.genasis.cz)

Organization and planning of CEE ROG activities in preparation of the second regional monitoring report took place at the third meeting of the RPGs in September 2013. The following outputs were adopted:

- ROG membership in the CEE region confirmed
- Regional coordinator will send the official letter with all relevant information concerning the GMP II to the responsible ministries and official contact and focal points including the countries of the Central Asia and ask for the persons responsible for the reporting of national POPs data and other relevant information to provide them to the ROG to the GMP Database see timeline below
- CEE ROG agreed with the use of the RECETOX system for data collection, handling and management in the CEECs region and supervision of the RECETOX over the process of collection, storage and analysis of data from GMPII
- CEE ROG confirmed the drafting team from the first regional repůort (Holoubek, Klánová, Kočan) for the second report (with possible help of additional experts such as Branislav Vrana, Kateřina Šebková and others)
- CEE ROG accepted the milestones and timelines for the development of the 2nd GMP phase monitoring reports as proposed by the meeting
- CEE ROG agreed with the collection of all relevant POPs including new ones in abiotic, biotic and anthropogenic matrices for the 2nd Regional Report and use the information database of the Regional Centre
- CEE ROG also suggested the following support would be needed from the Stockholm Convention Regional Centre RECETOX:
 - ✓ Bring all data into MONET database before summer 2014 so that ROG has time to look at it
 - ✓ Assistance to the region with analyses and interpretation of data for the report (IBA-RECETOX
 - ✓ Support the new station in CEE Leova station, existing EMEP site with active sampling of atmospheric POPs provide the station with methodology, align with Košetice + provide the training to produce high-volume data for the second report, start these activities immediately
 - ✓ Water should identify how much is in the EEA database and individual countries. Should do anything to have pilot data in the region based on the gaps encountered.
 - ✓ Send CEE expert Branislav Vrana to the expert group on development methodology on water sampling for the Guidance document (project by UNEP)
 - ✓ Milk find out what is situation in countries + push where needed for as many CEE countries as possible to participate

CEE ROG meetings 2008-2014

2010 – Two meetings of the expert group to update Guidance document for GMP to reflect newly added POPs to the annexes of the Convention as well as to accommodate experience from the first data collection and requirements in the effectiveness evaluation decision of the COP4 were organized.

2011 – Global Coordination Group of the GMP met 8-10 March in Geneva, Switzerland to finalize the revision of the Guidance document on the Global Monitoring Plan (GMP) for Persistent Organic Pollutants (POPs) and submitted the revised guidance document, including consideration of long-range transport, climate effects, specimen banking and the impact of listing nine new chemicals under the Convention to the fifth meeting of the Conference of the Parties to the Stockholm Convention in April 2011. The Global Coordination group also discussed the implementation of the second phase of the GMP, in particular the revised the strategy, process and structure of regional monitoring reports to accommodate the requirements for the second phase of the GMP and timelines for activities to facilitate the preparation of regional monitoring reports were established and agreed by the members of the global coordination group and are embedded in the revised GMP implementation plan. The COP endorsed these changes in the decision SC- 5/18

2012 – Monitoring experts met in June in Brno to discus steps to CEE + ROGs met in Geneva, Switzerland (10-12 October) to discuss harmonized steps to data management and creation of GMP electronic tool and further update of GMP guidance document as required by the decision SC-5/18.

2013 – GCG + ROGs met in Brno, Czech Republic 17-20 September 2013. In the margins of the meeting the CEE ROG agreed on organization and planning activities and timeline + milestones for the second report to be finalized by the end of 2014. The report will contain data 2008-2013 period (or even 2014 where possible) in addition to those reported in the first report in core matrices. CEE region uses monitoring program MONET, GAPS, EMEP database, WHO-UNEP milk database. In addition, the ROG members will identify any other possible source and report drafting team will analyze what information was reported under the EU legislation and European surveys under the EU Water Framework Directive. The ROG also considered and agreed that some countries may need a push – support of ROG and of the Regional Centre to increase the momentum and speed decision on behalf of the particular country to participate in monitoring surveys (in particular for milk).

The second monitoring report will use structure prepared by the secretariat and drafting of the report will be supported by the regional centre and will use information in previous report

Planned Timeline for the 2nd report

- Until mid October 2013 ROG to provide info on focal points and on those who should receive information on new milk survey
- Mid November 2013 Letter by CEE ROG head asking for new information and to collect data for updates
- Mid November 2013 letter by the CEE ROG and CEE Regional Centre to push for participation in the milk survey (note: If a country agreed no need to send the letter)
- Until February 2014 time for response by Parties to ROG with new information and all data for updates
- February-end June 2014 drafting group develops first version of the CEE regional report
- July-25 August 2014 ROG reads over the summer

- September 2014, exact date TBD, meeting in Brno comments from ROG (one week prior the ROG meeting) to drafting group
- Post ROG meeting in September until mid October 2014 Update of the draft Report drafting group+consultants
- End October 2014 Submission of the draft report to the region for comments
- End November 2014 Collect comments from the CEE region
- Mid-end December 2014 submission of the report to the secretariat

2014 - ROG meeting in Brno (October 7-8, 2014)

In line with the report of the 2013 GGCG-ROG meeting the ROG met in Brno (RECETOX premises) to finalize first draft of the regional report and defined steps to its finalization including additional information from research publications in case of the PFOS level in surface waters of the CEE region and information on the long-range transport that would be extracted from the report prepared by the EMEP regional centre EAST MSC-EAST.

In addition, the Global Coordination Group met 10-12 November 2014 in Geneva and discussed steps needed for finalization of the second regional monitoring reports. The minimum requirements for the second GMP reports were defined as follows:

- Air monitoring and human exposure through human breast milk or human blood will be used as core media;
- Comparable and representative core data from core media should be obtained from all five regions;
- Reports will be prepared for the COP summarizing and presenting the data on a regional basis;

4 METHODS FOR SAMPLING, ANALYSIS AND HANDLING OF DATA

This chapter provides overview of monitoring programmes described in greater detail in Chapter 4.1.2. and 4.1.3 that contributed representative regional data from core matrices⁴ to this report as presented further in Chapter 5.

Sampling, analyses and data management procedures are instrumental arrangements to produce quality reports. Global analysis of the first regional reports⁵ revealed that to allow maximum comparability, sampling, data handling and data analyses need to be undertaken in the uniform manner, structure and with globally agreed standards, both retrospectively (where possible), but most importantly towards the future. Any changes in the methodology need to capture also previous data. For the above, the CEE region therefore fully supported development and use of the global electronic data collection system and strict coding of data format, range of additional information covered. Moreover, the CEE region continues using

⁴ Considering the global dimension of the Global Monitoring Plan under the Stockholm Convention, the Conference of the Parties has chosen air, and human milk and/or blood as core matrices in 2007. They provide information on the sources and transport of POPs, and the levels of exposure in human populations. Water was added more recently due to specific properties of perfluorinated chemicals (PFOS) and their low levels in ambient air. More information is available in Global Monitoring Plan Guidance Document, 2013, chapters 2 and 4.

⁵ Klánová J., Dušek L., Borůvková J., Hůlek R., Šebková K., Gregor J., Jarkovský J., Kohút L., Hřebíček J., Holoubek I., The initial analysis of the Global Monitoring Plan (GMP) reports and a detailed proposal to develop an interactive on-line data storage, handling, and presentation module for the GMP in the framework of the GENASIS database and risk assessment tool. Masaryk University, Brno, Czech Republic, 2012.

standard/validated methodologies for sampling, analyses and data handling, so that maximum comparability of collected information is ensured.

More detailed information related to sampling, analytical procedures is provided in greater detail for each POPs air monitoring programme listed below.

Finally, all relevant available representative data for POPs levels in the CEE region are stored in the GMP Data Warehouse in the required format (annually aggregated), covering the maximum time span and diversity (range of chemicals) of available representative data. Though access to this instrument was restricted to experts only in the preparatory phase of this report, the information will be publicly available also in the electronic format (www.pops-gmp.org/visualization) once the report is finalized.

Nevertheless, the CEE region decided to share its monitoring information with its stakeholders continuously. More detailed and gradually updated information on levels of POPs collected in the CEE region is also publicly accessible and permanently available online through the GENASIS database (<u>www.genasis.cz</u>, the Global Environmental Assessment Information System) operated by the Research Centre for Toxic Compounds in the Environment, host of the Stockholm Convention Regional Centre in the Czech Republic.

4.1 Strategy for gathering new information

On the basis of the arrangements leading to the first regional monitoring report and agreements stemming from the regional strategy to collect information, the CEE ROG continues to use the support of the Stockholm Convention Regional Centre in the Czech Republic and its infrastructure for monitoring activities and data handling, in particular through the GENASIS database (www.genasis.cz).

In addition, since early 2009 the ROG members took steps to extend strategic partnerships in support of monitoring in the CEE region. The steps were initiated by the RECETOX and agreed by European experts in April 2009 in Sankt Petersburg (EMEP task force meeting). The outcome of the meeting was to create a pan-European passive sampling network MONET Europe to support a continental collection of information (WEOG+CEE UN regions) in a harmonized monitoring network. This network therefore comprises 31 countries in three UN regions⁶ and started operating from January 2009. It has embedded many sites of the former MONET-CEE network, on the basis of the first pilot monitoring, and added new ones, in particular in the western part of the European continent. It is the only monitoring activity that is undertaken in Europe as a whole and this activity continuously produces harmonized, scientific, evidence based and comparable information in the whole continent.

Moreover, the CEE ROG has also taken steps to broaden cooperation with GAPS to get data from its sampling sites located in the Central and Eastern Europe. into this report. In order to comprise EMEP activities taking place in the CEE region, the steps were taken to extract information and data collected through EMEP activities and placed in the EBAS database.

In terms of human tissues, the CEE ROG acknowledges work of the WHO and joint UNEP/ WHO milk surveys as well as information that is provided through national biomonitoring programmes. Nevertheless, it is necessary to promote participation of countries in the region

⁶ CEE countries (15): Belarus (2 sampling sites), Bulgaria, Croatia, Czech Republic (3 sampling sites), Estonia, Hungary, Latvia, Lithuania (2 sampling sites), Moldova, Poland, Russian Federation (2 sampling sites), Serbia, Slovakia, Slovenia, Ukraine (2 sampling sites); WEOG countries (14): Austria, Finland, France (3 sampling sites), Germany, Iceland, Ireland, Italy, Malta, Netherlands, Norway (3 sampling sites), Spain (discontinued from 2012), Sweden, Switzerland, United Kingdom, Asian countries (2): Cyprus and Turkey

in the future UNEP/WHO surveys as data available for this region are relatively scarce. The ROG believes the Stockholm Convention Regional Centres in the CEE region may be used for supporting such measures/activities.

For water, the CEE ROG agrees that it is necessary to adopt widely recognized methods and techniques as soon as practicable and introduce region-wide activities once a global decisions is taken.

In addition, the CEE ROG emphasizes it is necessary to bridge gaps in knowledge – call upon academia and researchers for support in new and cost effective monitoring and analytical techniques. The Stockholm Convention Regional Centre in the Czech Republic is one of such hubs that helps covering regional gaps as described below in the capacity building part.

Last but not least, in terms of data analyses, it may be necessary to allow for a retrospective analysis of some samples collected and therefore introduction of a specimen banking would be important also in the CEE region. The Stockholm Convention Regional Centre has initiated steps to establish such a specimen bank and have it available prior 2017.

Furthermore, the CEE ROG has also pursued a regional agreement that all relevant national data should be provided to and stored in RECETOX/GENASIS environmental database; national data should be obtained through Stockholm Convention national focal points. Individual national data sources should be indicated to the focal points by national monitoring experts and the CEE ROG members would facilitate that process. The regional organization group members should be in a position to consult primary data where necessary. This activity is fully implemented as data are permanently available online in <u>www.genasis.cz</u>.

Capacity Building and Training

This chapter recognizes the beneficial impact of the capacity building and training activities available for sampling, monitoring and analyses of the samples and hereby acknowledges support provided by the Stockholm Convention Secretariat and its partners to countries in the CEE region. These activities have already borne fruits in the first phase, where experts participating in the summer schools, specific training or inter laboratory comparison strengthened their knowledge in undertaking monitoring activities for legacy POPs as well as gradually introduced new sampling techniques to cover newly listed POPs.

The International Summer School on Environmental Chemistry and Ecotoxicology is a principal global capacity building activity in relation to the Global Monitoring Plan. It is a six day long training course combining both theoretical and practical courses including laboratory exercise and a field visit. The summer school is organized by the RECETOX in its premises in Brno, Czech Republic. A close cooperation of the training programme with UNEP started in 2007, however the summer school was already initiated in 2005. To date, there are 425 participants from 78 countries of all UN regions over ten years of the summer schools with a total of 77 CEE experts trained between 2007-2014. Their participation was either supported by several donors or some participants covered the training fee themselves. We would like to acknowledge and list our donors who made their participation possible – the Ministry of the Environment of the Czech Republic, Stockholm Convention Secretariat, NATO project, UNDP and UNIDO capacity building projects. Furthermore, the ROG would also like to thank the RECETOX research infrastructure for providing excellent facilities and resources for training and knowledgeable staff.

The Czech Republic, in particular its Ministry of Environment of the Czech Republic, supported participation of 22 experts from ten countries in the CEE region between 2010-2014 (Azerbaijan (1 participant), Belarus (1) Bosnia and Herzegovina (3), Czech Republic (2), fYRoM (1), Georgia (3), Moldova (5), Serbia (3), Turkey (1) and Ukraine (1)) and they are greatly acknowledged for this generous support.

UNEP SSC supported participation of nine experts from 7 CEE countries (Albania, Armenia, Belarus, Hungary, Moldova, Russian Federation, and Ukraine) in the period 2007-2014. They received training related to sampling, laboratory analyses, data management and implementation of monitoring activities of the Stockholm Convention focusing on various topic each year.

Additional 60 participants from Armenia, Kazakhstan, and Kyrgyzstan were supported in training in PCB analyses and other related activities through capacity building projects with NATO, UNDP and UNIDO.

In addition, experts from the region also participate in the inter-laboratory training and testing. RECETOX laboratories takes part in the tests for monitoring biota and human tissues regularly since 2009, as well as for other tests and matrices. Other countries receive support through capacity building projects. An example of the recent training took place in Freiburg, Germany 26-27 June 2014 and two experts from the region (Moldova and Russian Federation) were involved in this training provided by UNEP and partner institutions. We would hereby acknowledge their support.

The ROG is also aware of a possibility to get support for capacity building and training from the Global Environment Facility. Since the previous phase GEF projects did not cover CEE region at all, the ROG initiated cooperation with the SCRC in the Czech Republic to prepare a project proposal to fill the gap in this regard to extend support in analytical techniques and using certain analytical equipment to all eligible countries of the CEE region.

4.1.1 Programs/activities related to air monitoring

Ambient air was chosen as core matrix for POPs monitoring under the Stockholm Convention because it has a very short response time to changes in atmospheric emissions. This well-mixed environmental medium is also an entry point into food chains and a global transport medium. In addition, air data are required to validate atmospheric POPs transport models.

In line with the Guidance on the Global Monitoring Plan, there are two ways of sampling ambient air⁷ Within the CEE GMP region there are existing programs using both active sampling and passive sampling techniques described below in greater detail. Overview of existing programmes monitoring POPs in ambient air in the CEE GMP region is provided in Table 1.

It has to be noted that for ambient air monitoring a relatively small amount of international/regional programmes cover the whole CEE GMP region such as EMEP,

⁷ Assessing the POPs levels and trends in each UN/GMP region, the Global monitoring plan (GMP) (UNEP, 2007) should strive for at least: 1) Three to five stations with active high-volume sampling devices; 2) A network of (10 to 15) passive air sampling stations arranged in a grid with spacing of approximately 20° x 20° for an enhancement of the geographical resolution.

MONET, and GAPS. Some of the monitoring activities are lasting for decades (since 1980s), however they cover a limited scope of Stockholm Convention chemicals. Other air monitoring activities were only initiated simultaneously with the first data collection campaign (from 2006 onwards) or by the very end of that period (post-2008). Nevertheless, the long-term sustainability of both long-term and most recently established programmes remains crucial for the production of representative and comparable data in the region in the future. This fact is also valid for any future effectiveness evaluation of the implementation of the Stockholm Convention.

For ambient air monitoring, both active sampling and passive sampling techniques organized in the pan-European or global monitoring networks are used to generate data under the global monitoring plan in the CEE region.

The time range (sampling window) for the first monitoring report aiming at establishment of the initial baseline of POP levels in ambient air was set to 1998-2008, in line with Global Monitoring Plan Guidance Document. This second monitoring report builds on findings from the first regional report and adds more recent monitoring data. In some cases, the most recent information available is for 2014, however majority of air samples collected in 2013 and 2014 are still processed in laboratories and will only become available at a later stage. Table 1 provides information on data availability range for various air monitoring programmes in the region.

Furthermore, chapters 4.1.1.1. to 4.1.1.1.3 describe each monitoring program in more detail.

Table 1: Air monitoring programs providing data to the Global Monitoring Plan in the CEE region (source: GMP Data Warehouse)

Monitoring Programme	Data availabili ty start	Data availability end	Air sampling technique	Amount of Sampling sites	Chemicals analyzed	List of chemicals analyzed
АМАР	2008	2009	Active	1	12	α -HCH, β -HCH, chlordane, DDT, dieldrin, endosulfan, endrin, γ -HCH, heptachlor, mirex, dl-PCB - coplanar, PCB-indicator
ЕМЕР	2009	2010	Active	2	7	α-HCH, chlordane, DDT, γ- HCH, HCB, dl-PCB - coplanar, PCB-indicator
Košetice	1996	2011	Active	1	20	aldrin, α-HCH, β-HCH, chlordane, DDT, dieldrin, endosulfan, endrin, γ-HCH, heptachlor, HCB, mirex, PBDEs, PeCBz, dl-PCB - coplanar, PCB-indicator PCDD/Fs
Košetice - active air sampling	2012	2013	Active	1	21	aldrin, α-HCH, β-HCH, chlordane, DDT, dieldrin, endosulfan, endrin, γ-HCH, heptachlor, HCB, mirex, PBDEs, PeCBz, PFOS, dl- PCB - coplanar, PCB- indicator PCDD/Fs
MONET - CEEC	2006	2008	Passive	54	7	α-HCH, $β$ -HCH, chlordane, DDT, γ -HCH, HCB, dl-PCB - coplanar, PCB-indicator
MONET - CZ	2003	2014	Passive	15	7	α-HCH, β-HCH, chlordane, DDT, γ-HCH, HCB, dl-PCB - coplanar, PCB-indicator
MONET - Europe	2009	2013	Passive	21	7	α -HCH, β-HCH, chlordane, DDT, γ-HCH, HCB, dl-PCB - coplanar, PCB-indicator
APOPSBAL	2004	2004	Passive	1	7	α-HCH, β-HCH, chlordane, DDT, γ-HCH, HCB, dl-PCB - coplanar, PCB-indicator
GAPS	2004	2009	Passive	3	12	aldrin, α-HCH, β-HCH, chlordane, DDT, dieldrin, endosulfan, γ-HCH, heptachlor, PBDEs, dl-PCB - coplanar, PCB-indicator PCDD/Fs

4. 1.1.1 Air Active Sampling Programmes - European Monitoring and Evaluation Programme (EMEP)

Background

The European Monitoring and Evaluation Programme (EMEP) was established under the Convention on Long Range Trans-boundary Air Pollution to provide scientific evidence based information in relation to levels of chemicals in ambient air since 1988. It operates on multiple sampling sites and formerly covered chemicals causing eutrophication and acidification. Over the years, the range of chemicals covered broadened to ozone, volatile organic compounds, and since 1999 also to selected polyaromatic hydrocarbons, persistent organic pollutants, and heavy metals. However, in places there are also data collected from 1988 in the EMEP database.

This programme uses active sampling by high volume devices as described below. Figure 1 provides overview of relevant sampling sites used in EMEP programme in the CEE region.



Figure 1 EMEP Sampling sites providing information on selected POPs under the Stockholm Convention in the CEE region (Košetice, Czech Republic; Leova, Moldova; Borovoe, Kazakhstan. In addition, the figure also shows AMAP sampling site in Valkarkai, Russian Federation, polar station at far north East of Russia (source: GMP DWH)

Sampling and chemicals

Chemicals

The strategic long-term plan on POPs (EB.AIR/GE.1/1997/8) recommended to take a stepwise approach and include the following compounds or groups of compounds in the monitoring: polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), HCB, chlordane, lindane (HCHs), and DDT/DDE. These recommendations are implemented in the EMEP monitoring strategy and measurement program for 2004–2009 (EB.AIR/GE.1/2004/5) as amended. Therefore, 16 US EPA polycyclic aromatic

hydrocarbons (PAHs), 7 indicator polychlorinated biphenyls (PCBs: IUPAC congeners number 28, 52, 101, 118, 153, 138, 180), organochlorine pesticides (OCPs) - p,p'- DDT, p,p'-DDD, and p,p'-DDE, α -, β -, γ -, δ -hexachlorocyclohexane (HCH), hexachlorobenzene (HCB), and pentachlorobenzene are analyzed on regular basis.

Sampling techniques

High volume ambient air samplers PS-1 (Graseby-Andersen, USA, flow: 12-18 m3 h-1, volume: 250-400 m3 per 24 h) and two types of adsorbents were used: a Whatmann quartz filter (QF) (fraction dae $< 50\mu$ m) for collection of particles, and a polyurethane foam (PUF) disk (Gumotex Břeclav, density 0.03 gcm-3) for collection of the gaseous phase. PUF filters were cleaned before the campaign by extraction with acetone and dichloromethane in a Soxtec extractor (8 hours extraction in acetone and 8 hours in dichloromethane). The duration of sampling was 24 hours; quartz filter field blanks and PUF disks field blanks were collected each month (Holoubek et al., 2007a).

Analytical Procedures

Quartz filters and polyurethane foam disks were extracted and analyzed separately in order to determine the gas-particle partitioning of compounds of interest. All filters were extracted with dichloromethane in a Büchi System B-811 automatic extractor. Surrogate recovery standards (PCB 30 and PCB 185 for PCB analysis) were spiked on each sample prior to extraction. PCB 121 was used as internal standard for PCB analyses. The volume was reduced after the extraction under a gentle nitrogen stream at ambient temperature, and fractionation was achieved on a silica gel column; a sulphuric acid modified silica gel column was used for PCB/OCP samples. Samples were analyzed using a GC-ECD (HP 5890) supplied with a Quadrex fused silica column 5% Ph, and a GC-MS (HP 6890 - HP 5975) with a J&W Scientific fused silica column DB-5MS for PCBs and OCPs. 16 US EPA polycyclic aromatic hydrocarbons were determined in all samples using a GC-MS instrument (HP 6890 - HP 5972 and 5973) supplied with a J&W Scientific fused silica column DB-5MS (Holoubek et al.).

Quality assurance, quality control

Recoveries were determined for all samples by spiking with the surrogate standards prior to extraction. Amounts were similar to detected quantities of analytes in the samples. Recoveries were higher than 75 % and 70 % for all air samples for PCBs and PAHs, respectively. Recovery factors were not applied to any of the data. Recovery of native analytes measured for the reference material varied from 88 to 100 % for PCBs, from 75 to 98 % for OCPs, from 72 to 102 % for PAHs. Field blanks were extracted and analyzed in the same way as the samples, and the levels in field blanks never exceeded 1 % of the quantities detected in samples for PCBs, 1% for OCPs, 3% for PAHs, indicating a minimum contamination during the transport, storage and analysis. Laboratory blanks were always lower than 1% of the amount found in the samples (Holoubek et al.).

Data Storage

Data provided to EMEP programme are available from NILU, EBAS database.

4.1.1.2. Arctic Monitoring and Assessment Programme (AMAP)

Background

The only site operating under AMAP programme in the CEE region is the Valkarkai site in the Russian Federation as shown in Figure 1 (top right corner). The sampling site operates

under the same protocol as EMEP (Analytical methods, QA/QC and data storage) and analyzes chemicals as shown below.

Chemicals

 α -HCH, β -HCH, chlordane, DDT, dieldrin, endosulfan, endrin, γ -HCH, heptachlor, mirex, dl-PCB - coplanar, PCB-indicator, data availability 2008-2009.

4.1.1.3. Active sampling of ambient Air - Other existing air active sampling programs and projects in the CEE region

The CEE ROG was unable to identify any other ongoing long-term monitoring programs focused on POP levels in ambient air in the CEE region using active sampling apart from the integrated monitoring in the Czech Republic at the Košetice observatory. This national programme is operated by the Research Centre for Toxic Compounds in the Environment, Czech Republic since 1988. The program is described below.

Košetice Observatory – integrated monitoring

Košetice observatory, hosted and operated by the Czech Hydrometeorological Institute in cooperation with the RECETOX Centre is located in the southern part of the Czech Republic (N49°35'; E15°05'). The climatic classification of the area is moderately warm and moderately humid upland zone with a mean annual temperature of 7.1 °C, mean annual total precipitation of 621 mm, between 60 and 100 days with snow-cover per year, 1800 hours of sunshine per year, and prevailing westerly winds. Observatory was established as a regional station for integrated background monitoring network in the late 1970s (Holoubek et al., 2007a,b).

Ambient air monitoring by active sampling was carried out in Košetice EMEP station since September 1988 which makes a unique data series worldwide in continuous monitoring for toxic chemicals in air. Sampling frequency was a sample every three months between 1988 and 1993 at first. Since 1994, the air samples have been collected once a week (every Wednesday, from 08:00 h to Thursday, 08:00 h) resulting in 52 samples per year (Holoubek et al., 2007a). Sampling technique is the same as described for EMEP program in 4.1.1.1. The only difference is the use of more PUF disks that are cleaned before deployment in various sets of solvents (8 hours extraction in acetone and 8 hours in dichloromethane for OCPs, 8 hours extraction in acetone and 8 hours in toluene for PCDDs/Fs, dl-PCBs and PBDEs and 8 hours in acetone and 8 hours in methanol for PFCs and currently used pesticides).

Košetice EMEP station is the only sampling site collecting samples for POPs analyses also in other environmental matrices (ambient air, wet deposition, surface water, sediment, soil and biota are collected regularly). In addition, ecosystem indicators are used to determine current state, anthropogenic impact, effects, and to predict the future changes of terrestrial and freshwater ecosystems in a long-term perspective (EMEP, 1998). A dataset generated in Košetice integrated monitoring by RECETOX, (Masaryk University, Brno, Czech Republic) between 1988-1998 was used to assess the Central European trends in background levels of persistent organic pollutants.

Scope of chemicals was further expanded since 1996 to cover 20 chemicals as shown in Table 1. Since January 2012 the set also covers all including BDEs and PFOS.

Chemicals analyzed

Polychlorinated dibenzo-p-dioxins and furans (15 congeners) Dioxin-like polychlorinated biphenyls (12 congeners) Indicator polychlorinated biphenyls (7 congeners) Organochlorine pesticides (12 chemicals) $\alpha, \beta, \gamma, -$ hexachlorocyclohexanes (HCHs), o,p' and p,p'-DDT, DDE, DDD, hexachlorobenzene, pentachlorobenzene, aldrin, dieldrin, endrin, heptachlor, mirex, chlordanes, endosulphane, chlordecone Polybrominated diphenyls (10 congeners) Tetra-, Penta-, Hexa-, Hepta-bromdiphenyl ethers (10 congeners) Hexabromocyclododecane (4 isomers) Perfluorinated compounds: Perfluorocarboxylic acids (11 including PFOA) Perfluorosulfonates (5 including PFOS) Perfluoroctane sulfonamides and sulfonamidoethanols (5 PFOS precursors)

Analytical Methods

Analytical methods for the Košetice integrated monitoring analyses of PCBs, OCPs and PAHs are described below in chapter 4.1.1.4.

Parallel Analysis of PCDDs/Fs, dioxin-like PCBs and PBDEs

Samples are extracted with toluene in a Soxhlet extractor (60 minutes warm Soxhlet followed by 30 minutes of solvent rinsing) with toluene in a B-811 extraction unit (Büchi, Switzerland). Prior to extraction, the samples were spiked with 13C PCDDs/Fs (according to EN-1948), 13C dl-PCBs (77, 81, 126, 169, 105, 114, 118, 123, 156, 157, 167 and 189) and 13C BDEs (28, 47, 66, 100, 99, 85, 154, 153, 183, 209).

The concentrated extracts were cleaned-up on a sulphuric acid modified silica gel (30% w/w), eluted with 40 ml DCM/n-hexane mixture (1:1). Fractionation was achieved in a micro column (6 mm i.d) containing from bottom to top: 50 mg silica gel, 70 mg charcoal/silica gel (1:40) and 50 mg of silica gel. The column was prewashed with 5 ml of toluene, followed by 5 ml of DCM/cyclohexane mixture (30%), then the sample was applied and eluted with 9 ml DCM/cyclohexane mixture (30%) in fraction 1 (PBDEs, mono-ortho dl-PCBs) and 40 ml of toluene in fraction 2 (PCDDs/Fs, non-ortho dl-PCBs). Each fraction was concentrated using stream of nitrogen in a TurboVap II (Caliper LifeSciences, USA) concentrator unit and transferred into an insert in a vial. The syringe standards (13C PCDDs, 13C PCBs 70, 111, 138 and 170, 13C BDEs 77 and 138) were added to all samples, the final volume was 50 ul. HRGC/HRMS instrumental analysis (PCDDs/Fs, dl-PCBs) was performed on a 7890A GC (Agilent, USA) equipped with a 60m x 0.25mm x 0.25um DB5-MS column (Agilent J&W, USA) coupled to an AutoSpec Premier MS (Waters, Micromass, UK). The MS was operated in EI+ mode at the resolution of $>10\ 000$. BDEs were analyzed on the same system using 15m x 0.25 mm x 0.10 um DB5 column (Agilent J&W, USA). For BDE 209, the MS resolution was set to >5000.

Hexabromocyclododecane

Samples were extracted with dichloromethane in a Büchi System B-811 automatic extractor. Sample volume was reduced after extraction under a gentle nitrogen stream at ambient temperature. The concentrated extracts were cleaned-up on a sulphuric acid modified silica gel (30% w/w), eluted with 40 ml DCM/n-hexane mixture (1:1). The samples were evaporated and transferred on the acetone: acetonitrile solvent mixture. γ -HBCD (13C12H18Br6) was added into the sample before analysis.

HPLC-MS/MS instrumental analysis was performed on an Agilent 1100 series (Agilent Technologies, Waldbronn, Germany) equipped with a Phenomenex LUNA C-18 endcapped (3 μ m) column (100 x 2 mm), with a pre-column Phenomenex SecureGuard C18 (Phenomenex, Torrance, CA, USA). The mass spectrometer AB Sciex Qtrap 5500 (AB Sciex, Concord, ON, Canada) used electrospray ionization. Ions were detected in the negative mode.

Cyclodien Pesticides

Samples were spiked with the isotopically labeled standards and extracted with dichloromethane in a Soxhlet extractor (Büchi, Switzerland). The concentrated extracts were cleaned-up on a florisil column, eluted with 20 ml 20% DCM/n-hexane and 50 ml DCM. Sample volume was reduced under a gentle nitrogen stream at ambient temperature. Samples were analyzed using a GC-MS/MS (Quattro Micro GC – Watters) supplied with a J&W Scientific fused silica column DB-5MS.

Perfluorinated Compounds

Samples were spiked with the isotopically labelled standards (13C MeFOSA and 13C MeFOSE) and extracted with methanol with the addition of ammonium acetate (5mM) in a Soxhlet extractor (60 minutes warm Soxhlet followed by 30 minutes of solvent rinsing) in a B-811 extraction unit (Büchi, Switzerland). The concentrated extracts were cleaned-up using a syringe filter (nylon membrane, 13 mm diameter and 0,45 μ m pore size). Filtrate was concentrated using stream of nitrogen in a TurboVap II (Caliper LifeSciences, USA) concentrator unit and transferred into a minivial. The syringe standards (13C PFOA, 13C PFOS) were added to all samples, the final volume was 500 ul.

HPLC/MS/MS instrumental analysis was performed on an 1100 HPLC (Agilent, USA) equipped with a SYNERGI 4u Vision RP 80A 50mm x 2 mm column (Phenomenex, USA) coupled to an QTRAP 5500 (ABSciex, CA, USA). The MS was operated in EI- mode using two MRM transition for each compound.

Quality Assurance / Quality Control

As shown in analytical methods above or in 4.1.1.4, recoveries were determined by spiking with appropriate surrogate standards prior to extraction for all samples. Amounts were similar to detected quantities of analytes in the samples. Recoveries were higher than 80% for all PCB samples for PCBs. Recovery factors were not applied to any of the data. Recovery of parent analytes measured for the reference material varied from 88 to 103 % for PCBs, from 75 to 98 % for OCPs. PCB and OCP data were not recovery corrected.

For PCDDs/Fs, recoveries of the isotopically labeled standards were 55-90%. For dl-PCBs, recoveries ranged between 60 and 90 %. For BDEs, recoveries ranged between 60 and 110%. All PCDDs/Fs data are recovery corrected.

Application of the isotopically labeled standards showed recoveries 60-80% for currently used pesticides and 100-105% for PFOS and PFOA, respectively. Data are not recovery corrected.

Limits of quantification (LOQ) varied between the groups of pollutants and analytical instruments. LOQ was 0.01 ng sample-1 for PCBs, 0.02 ng sample-1 for OCPs, 0.15 pg sample-1 for dl-PCBs and PCDDs/Fs, 0.01 pg sample-1 for PBDEs, 0.01 ng sample-1 for HBCD, 0.1 ng sample-1 for PBBs, 0.05 ng sample-1 for cyclodien pesticides, 0.02 ng sample-1 for CUP, and finally 0.002 ng sample-1 for PFCs.

Field blanks consisted of pre-cleaned PUF disks and were taken in each sampling site. These were extracted and analyzed the same way as the samples, and the levels in field blanks never

exceeded 3% of quantities detected in samples for PCDDs/Fs, 5% for dl-PCBs, 3% for indicator PCBs, 1% for OCPs, and 10% for BDEs, indicating minimal contamination during a transport, storage and analysis. No contamination by currently used pesticides and by PFOS and PFOA was observed in the field blanks.

Laboratory blanks were prepared for each set of 20 samples and concentrations found were under the quantification limits for all the compounds.

Data storage

All data collected through integrated monitoring in Košetice Observatory are available in environmental database <u>www.genasis.cz</u>, online, permanently and publicly.

4.1.1.4 Passive sampling - Research Centre for Toxic Compounds in the Environment Monitoring NETwork (RECETOX-MONET Programme)

Passive sampling of ambient air started at the Košetice site in 2004 and piloted in the Czech Republic as MONET-CZ network on four sampling sites and later on expanded to 15 sampling locations. After that successful pilot, the MONET CZ network was expanded to other countries and the MONET CEE was introduced in 2006 and ran in pilot until 2008 in nine CEE countries. In line with the CEE regional strategy (as described in chapter 4.1.), the network was further expanded into MONET Europe covering 31 countries (14 in the CEE region) of the whole continent as described in chapter 3. Figure 2 shows current distribution of MONET Europe sampling sites in the region.



Figure2: Sampling sites of the MONET networks in the CEE region (covering MONET CZ and MONET EU), (source: GMP DWH)

Sampling

Passive air samplers consisting of the polyurethane foam disks (15 cm diameter, 1.5 cm thick, density 0.030 g cm-3, type N 3038; Gumotex Breclav, Czech Republic) housed in the protective chambers are employed in all MONET activities. Average sampling rate was estimated to be between 3.5 and 7 m3/day (based on meteorological conditions at the individual sites) which roughly corresponds to 100-200 m3 of the air sampled during four

weeks of deployment for this kind of sampler. Sampling chambers were washed and solventrinsed with acetone prior to installation. All PUF disks were washed, cleaned (8 hours extraction in acetone and 8 hours in dichloromethane for OCPs, 8 hours extraction in acetone and 8 hours in toluene for PCDDs/Fs, dl-PCBs and PBDEs and 8 hours in acetone and 8 hours in methanol for PFCs and currently used pesticides), wrapped in two layers of aluminum foil, placed into zip-lock polyethylene bags and kept in the freezer prior to deployment. Exposed disks were wrapped in two layers of aluminium foil, labelled, placed into a zip-lock polyethylene bag and transported in a cooler at 5 °C to the laboratory where they were kept in the freezer at -18 °C until the analysis. Field blanks were obtained by installing and removing the PUF disks at all sampling sites for each group of pollutants. PUF disks from one of the samplers were collected every 4 weeks (28 days) until 2009, now they are replaced every 12 weeks (84 days).

Chemicals analyzed

α-HCH, β-HCH, chlordane, DDT, γ-HCH, HCB, dl-PCB - coplanar, PCB-indicator

Analytical methods

This subchapter describes analytical methods used in the MONET program for parallel analysis of PCBs, OCPs, and PAHs. The same analytical method is used for determining concentrations of these chemicals in samples collected by active sampling in the integrated monitoring in Košetice observatory. determination of dl-PCB is described in chapter 4.1.1.3.

All 4-weeks and 12-weeks samples were extracted with dichloromethane in a Büchi System B-811 automatic extractor. One laboratory blank and one reference material were analyzed with each set of ten samples. Surrogate recovery standards (d8-naphthalene, d10-phenanthrene, d12-perylene for PAHs analysis, PCB 30 and PCB 185 for PCBs analysis) were spiked on each filter prior to extraction. Terphenyl and PCB 121 were used as internal standards for polyaromatic hydrocarbon (PAH) and polychlorinated biphenyl (PCB)/organochlorine pesticide (OCP) analyses, respectively.

The sample volume was reduced after extraction under a gentle nitrogen stream at ambient temperature, and fractionation achieved on a silica gel column; a sulphuric acid modified silica gel column was used for PCB/OCP samples.

Samples were analyzed using a GC-MS/MS (Quattro Micro GC – Watters) supplied with a J&W Scientific fused silica column DB-5MS for PCBs: PCB 28, PCB 52, PCB 101, PCB 118, PCB 153, PCB 138, PCB 180, and OCPs : α -hexachlorocyclohexane (HCH), β -HCH, γ -HCH, δ -HCH, 1,1-dichloro-2,2-bis (p-chlorophenyl) ethylene (p,p´-DDE), 1,1-dichloro-2,2-bis (p-chlorophenyl) ethan (p,p´-DDD), 1,1,1-trichloro-2,2-bis (p-chlorophenyl) ethan (p,p´-DDT), o,p´-DDE, o,p´-DDD, o,p´-DDE, hexachlorobenzene (HCB), and pentachlorobenzene (PeCB).

Quality Assurance / Quality Control

As shown in analytical methods of 4.1.1.3 and above, recoveries were determined for all samples by spiking with appropriate surrogate standards prior to extraction. Amounts were similar to detected quantities of analytes in the samples. Recoveries were higher than 80% for all samples for PCBs. Recovery factors were not applied to any of the data. Recovery of parent analytes measured for the reference material varied from 88 to 103 % for PCBs, from 75 to 98 % for OCPs. PCB and OCP data were not recovery corrected.

Limits of quantification (LOQ) varied between the groups of pollutants and analytical instruments. LOQ was 0.01 ng sample-1 for PCBs and 0.02 ng sample-1 for OCPs.

Field blanks consisted of pre-extracted PUF disks and were taken in each sampling site. These were extracted and analyzed the same way as the samples, and the levels in field blanks never exceeded 3% for indicator PCBs, 1% for OCPs indicating a minimum contamination during a transport, storage and analysis.

Laboratory blanks were prepared for each set of 20 samples and concentrations found were under the quantification limits for all the compounds.





Data availability

All data from MONET CZ, MONET CEE and MONET Europe networks are available in environmental database <u>www.genasis.cz</u>, online, permanently and publicly.

Data availability from MONET

Figures 3-5 show data availability over time in the MONET networks. they cover 21 countries of the CEE region and 18 parameters (8 chemicals), the maximum time series is from 2003 to 2014 inclusive.



Figure 4 Data availability overtime and parameters in the MONET networks in fYRoM, Hungary, Kazakhstan, Kyrgyzstan, Latvia, Lithuania, Moldova, Montenegro, Poland, and Romania. The colour represents 18 parametrs. source: GMP DWH



Figure 5 Data availability over time and parameters in the MONET networks for Russian Federation, Serbia, Slovakia, Slovenia, and Ukraine. The lighter color represents 17 parameters, the darker colour covers 18 parametrs. source: GMP DWH

4.1.1.5 – Passive sampling - Global Atmospheric Passive Sampling (GAPS) Network

Background

The Global Atmospheric Passive Sampling Network (GAPS) Network is a key program for producing comparable global-scale data for (POPs) in air. This network using passive sampling was initiated in December 2004 as a two-year pilot study, now it consists of more than 50 sites all continents and contributes to the capacity building and improves global coverage as shown in Figure 6. This program supported by the Environment Canada was the only global-scale program involved in the first phase of the GMP. In addition, the network

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identifies new chemicals in the air, collects information to determine spatial and temporal trends including long-range atmospheric transport. In addition, there are some specific studies that are generating results for specific POPs such as PCDD/F study in GRULAC in 2011/2012 or study on different sorbents (XAD samplers and SIP disks).



Figure 6 - Sampling sites in the GAPS Network (source: Environment Canada Website, <u>http://www.ec.gc.ca</u>)

There are three sampling stations in the CEE region - Danki (Russian Federation), Košetice (Czech Republic) and Pomlewo (Poland), as shown in Figure 8 below. The network focuses on PCBs and organochlorine pesticides as specified below. Data availability in the CEE region is given in Figure 7. In addition, some samples are archived in order to allow for a retrospective analysis at a later stage (this concerns 2010, 2012 and 2013)



Figure 7 Data availability from GAPS in the CEE region, (source: GMP DWH).



Figure 8 GAPS Network stations in CEE region (Danki, Russian Federation, Pomlewo, Poland and Košetice, Czech Republic (source, GMP DWH).

Chemicals

aldrin, α -HCH, β -HCH, chlordane, DDT, dieldrin, endosulfan, γ -HCH, heptachlor, PBDEs, dl-PCB - coplanar, PCB-indicator PCDD/Fs

Sampling Chemicals

Two types of passive air samplers (PAS) are used currently under the GAPS Network for the measurements of persistent organic pollutants (POPs):

One is the polyurethane foam (PUF)-disk sampler that is deployed for three-month periods to capture seasonal differences of the target chemicals. The other is the XAD-type sampler that is deployed for one full year to yield annual average air concentrations.

For the purposes of this report only PUF disk samplers are described (Pozo et al and . PUF disks (14 cm diameter; 1.35 cm thick; surface area, 365 cm2; mass, 4.40 g; volume, 207 cm3; density, 0.0213 g cm-3; PacWill Environmental, Stoney Creek, ON) were housed inside a stainless steel chamber (Figure 1). The chamber consisted of two stainless steel domes with external diameters of 30 and 20 cm. Air is allowed to flow over the sampling surface through a 2.5 cm gap between the two domes and through holes in the bottom surface of the lower dome. The PUF disk chamber protects the sampler from precipitation, UV sunlight, and particle deposition although it is likely that fine particles are sampled. The chamber also reduces the dependence of sampling rate on wind speed resulting in a sample that is equally weighted with time over the integration period.

PUF disks were handled using solvent-rinsed tongs. Sampling chambers were prewashed and solvent-rinsed with acetone prior to installation of the passive sampling media which was done using clean gloves. Sample installation and removal was performed outside to avoid the risk of contamination.

Prior to exposure, PUF disks were precleaned by Soxhlet extraction for 24 h using acetone and then for another 24 h using petroleum ether. PUF disks were changed every 3 months. GAPS sites are mostly in regional/continental background locations, away from local emissions of OCPs and other POPs. The samplers were mounted at least 1.5 m above ground
level and detailed, illustrated protocols, including tools required for changing samplers were sent to each site. One field blank was deployed at each site by inserting and removing a PUF disk from the sampler and then storing and treating it as a sample.

The samplers trap mainly gas-phase contaminants with an air sampling rate of approximately 3-4 m3 day-1, equivalent to $\sim 300 \text{ m3}$ over a 3-month period. Site-specific air sampling rates are determined by adding known amounts of depuration compounds to the PUF disks prior to deployment. These are either isotopically labeled compounds or other chemicals not present in the atmosphere. By analyzing the loss of these chemicals during the deployment period it is possible to estimate the average air-side controlled sampling rate which is similar for all POPs.

Analytical Methods

In preparation for extraction, PUF disk samples were spiked with a recovery standard consisting of 13C PCB-105 (260 ng) (CIL, Andover, MA). PUFs were individually extracted by Soxhlet in petroleum ether for 24 h. Air sample extracts were quantified for 19 OCPs using a mixture of standards: α -, β -, γ -, δ -HCHs, aldrin, heptachlor, heptachlor epoxide, cischlordane, trans-chlordane, trans-nonachlor, endosulfan I, endosulfan II, endosulfan sulfate (SO4), o,p'-DDE p,p'-DDE, o,p'-DDD, p,p'-DDD, o,p'-DDT, p,p'-DDT, obtained from Ultra Scientific (North Kingstown, RI, U.S.A. and U.S. Environmental Protection Agency, Research Triangle Park, NC) and toxaphene (Supelco Inc, USA). PCBs were quantified separately using a 48 component mixture (PCB-8, -18, -17, -15, -16+32, -28, -33, -52, -49, -44, -42, -37, -74, -70, -66, -95, -56+60, -101, -99, -87, -110, -123, -149, -118, -114, -153, -105, -137+138, -126, -187, -183, -128, -185, -174, -177, -171, -156, -157, -180, -200, -170, -203, -195, -205, and -206) (Ultra Scientific, North Kingstown, RI). Samples were also analyzed for 13 polybrominated diphenyl ethers (PBDE congeners 17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, and 190) obtained from Cambridge Isotope Laboratories (Andover, MA).

PCBs, OCPs, and PBDEs were analyzed by GC-MS on a Hewlett-Packard 6890 GC-5973 MSD. PCBs were determined in EI–SIM (electron impact–selected ion monitoring), and OCPs and PBDEs were determined in negative chemical ionization (NCI) in SIM mode with methane as reagent gas with a flow of 2.2 mL min-1.

Limit of detection (LOD) was defined as the average field blank (n = 30) plus three standard deviations (SD). When target compounds were not detected in blanks, the 1/2 instrumental detection limit (IDL) value was substituted for LOD. For data values that fell below the LOD, 1/2 LOD was used for calculating means. All qualified data (i.e., those exceeding the LOD) were blank corrected.

Quality Assurance / Quality Control

Surrogate recoveries for 13C PCB-105 ranged from 68.7 to 94.3% (mean 83.6% \pm 7.7%). Recoveries of PCBs were further assessed for PCBs by spiking PUF disks (n=2) with the calibration solution and treating as samples. Average recoveries for all PCBs were satisfactory (75% \pm 4.0%), and no recovery correction was applied to the samples. Method recoveries were assessed previously in the same laboratory for OCPs (Meier et al.) and PBDEs (Shoeib et al.) and found to be good.

Blank levels were assessed from the two field blanks and two laboratory blanks. All blanks levels were below the detection limit for OCPs except for γ -HCH, TC, and endosulfan I which were also low and ranged from 0.4% to 3% of the sample amounts. Results for p,p⁻DDE and endosulfan SO4 were either excluded or flagged because of high blanks that were ~40% of the sample amounts. For PCBs, field blanks had quantifiable levels of di- (PCB-8), penta- (PCB-101, PCB-123), and hepta- (PCB-170) congeners. Solvent (method) blank

values for individual PCB congeners were low and not detectable for most higher molecular weight PCBs.

Method detection limits (MDL) in air samples were defined as the average blank (n=4) plus three standard deviations (SD). When target compounds were not detected in blanks, 2/3 of the instrumental detection limit was used as the MDL. All qualified data (i.e. exceeding the MDL) has been blank corrected.

Data storage

Data from GAPS Network are stored in an electronic database GAPS data browser that is for authorized users only. It is a sister database to GENASIS (www.genasis.cz).

4.1.2 Programs/activities related to human tissues (milk and blood)

For human tissues, the WHO surveys and UNEP/WHO surveys serve are core data provider, however a number of national monitoring programmes/activities exist, but cover a limited range of chemicals.

4.1.2.1 Programs/activities related to human milk

WHO survey of Human Milk for Persistent Organic Pollutants

Background

In 2005, at the second meeting of the Conference of the Parties to the Stockholm Convention, it was recognized that human biomonitoring is essential to evaluate whether human exposure to POPs is indeed decreasing over time. Monitoring of human milk allows thus countries and regions to identify contamination problems and formulate measures to reduce and prevent human and environmental exposure to these chemicals.

Building on the previous WHO human milk monitoring studies, the United Nations Environment Programme (UNEP) and the World Health Organisation (WHO) jointly implement a global study to monitor changes in human exposure over time. The survey measures POPs concentrations in human milk and is implemented in a wide range of countries with large differences in food consumption patterns and environmental levels of POPs.

Concentrations of POPs in human milk are considered good indicators of the actual body burden. In addition, human milk is considered as one of the best sampling matrices for biomonitoring due to its availability and non-invasive approach when collecting individual samples. Its high lipid content makes the extraction method for POPs easier and the precision of the measurements higher. Over the last decades, human milk has generally been used as a medium to measure contamination in humans, and analytical techniques have been well established for most POPs included in the Stockholm Convention.

Furthermore, the uptake of these chemicals by the infant via human milk is of high toxicological relevance. The risk-benefit assessment of breastfed infants represents one of the most challenging aspects of human toxicology, as possible adverse health effects associated with exposure to POPs concur with significant health benefits of breastfeeding. In this

perspective, the results of the human milk survey are not meant to derive a "ranking" of countries with respect to risks for the breastfed infant. The surveys are primarily aimed at identifying worldwide quantitative differences of human milk contamination with these POPs, and provide a baseline for those countries for which such information was previously not available. This will allow in the future evaluating the effectiveness of measures taken to reduce POPs exposure. The quantitative differences observed in these surveys may provide a suitable basis for possible source-directed measures to further reduce levels of specific POPs on a country-by-country basis. Therefore it is useful to interpret the results in a national/regional context, and introduce targeted measures to further decrease human exposure.

Early WHO surveys performed mainly in Europe and North America in 1987-1989 and 1992-1993 exclusively focused on PCB, PCDD and PCDF. In 2001-2003, a larger global survey was implemented, covering the twelve POP compounds initially listed in the Stockholm Convention. Following the ratification of the Stockholm Convention, WHO and UNEP started their collaboration, and two additional global surveys were completed in 2005-2007 and 2008-2012. These significantly enlarged the geographical scope of the study to provide representative results for all regions of the globe. The results of these surveys have been compiled in document UNEP/POPS/COP.6/INF/33.

The second phase of the human milk survey (2013-2014) aimed at detecting changes in the levels of legacy POPs measured in human populations and building a consistent baseline for human exposure to the newly listed POPs.

Sampling

In order to promote reliability and comparability, participating countries are encouraged to adhere as closely to WHO protocol as much as possible. However, it is also recognized that the situations in countries vary considerably so that some flexibility is required. Guidance is provided to assist countries in developing their national protocols, including:

Number of donors: A minimum of 50 individual donors should each provide 50 ml of human milk for preparing the pooled sample. Note that one additional participant per million population over 50 million is recommended for large countries and in some cases, more than one pooled sample may need to be prepared. On the other hand, a lower number samples may be necessary for small countries.

Strategies for selecting donors: The following criteria for selection of donating mothers shall be applied: a) they should be primiparae, b) healthy, c) exclusively breastfeeding one child (i.e. no twins), and d) residing in the area for about five years. Interviewing of potential donors can take place pre- or post-natal or in well-baby clinics. The stratification of donors should represent the presumed national exposure profile of each country. This would include consideration of diet, occupational exposure, rural and urban residence and proximity to potential POPs releasing sources such as industries and waste sites.

Biosafety: In general, the handling of any milk sample should comply with biosafety rules to protect workers who will handle samples. The National Coordinators should decide whether HIV-positive donors can participate in the survey.

Consequently, the sampling protocol will vary among countries and therefore, comparison of results between countries should be approached with caution. However, once the national

protocol is established, it should be applied in subsequent rounds so that changes/trends can be followed. In these cases, observation of temporal trends should be scientifically valid provided information on the distribution of levels in individual samples is available.

Analytical procedures

Procedure for PCDDs, PCDFs and PCBs

After freeze-drying of the whole sample, fat and contaminants of interest are extracted in a hot extraction device ("Twisselmann extractor") with cyclohexane/toluene (50/50) for 8 hrs. After evaporation of the solvent, an aliquot of fat is spiked with 13C-labeled internal standards (17 PCDD/Fs, 5 non-ortho PCBs [37, 77, 81, 126, 169], 6 mono-ortho PCBs [28, 60, 105, 118, 156,189] and 7 di-ortho PCBs [52, 101, 153, 138, 180, 194 and 209]). Gel permeation chromatography on Bio Beads S-X3 removes fat. A silica column impregnated with sulfuric acid removes remaining oxidizable substances. A florisil column separates PCDD/F from PCBs. The PCDD/F-fraction is purified on a Carbopack C-column. After addition of 1,2,3,4-13C12-TCDD, determination is performed by HRGC/HRMS (Fisons Autospec; resolution 10,000; DB5-MS). The PCBs are separated on a Carbopack B-column into three fractions of first di-ortho PCBs (elution with hexane), then mono-ortho PCBs (elution with hexane/toluene; 92.5/7.5) and finally non-ortho PCBs (reversed elution with toluene). After addition of 13C12-PCB 80, the different PCB groups are determined by HRGC/HRMS (Fisons Autospec; resolution 10,000; DB5-MS) in three separate runs. Marker PCBs are PCB 28, 52, 101, 138, 153 and 180.

Procedure for analytically simple POPs

The milk samples were analysed for POP pesticides. Fats and POPs of interest were extracted from freeze-dried human milk as described above for PCDDs, PCDFs and PCBs. Up to 0.5 g of the fat extract was re-dissolved in cyclohexane/ethyl acetate and the internal standards (2,4,5-Trichlorobiphenly and Mirex), dissolved in cyclohexane, were added. The applied clean up-parts of the analytical method followed the principles of the European standardized methods for pesticide residue analysis for fatty food - Determination of pesticides and PCBs", EN 1528 part 1-4, 1996-10 (confirmed 2001). To remove fat, gel permeation chromatography was performed on a chromatography column using Bio-Beads S-X3 with cyclohexane/ethyl acetate as eluting solvent. After concentration and transfer into iso-octane, chromatography on a small column of partially deactivated silica gel was used as final clean up steps with toluene as eluent. Determination was performed with GC/ECD using a GC (Fisons Mega 2) with two parallel columns of different polarity (fused silica no. 1:30 m PS-088 [97.5% Dimethyl -2.5% diphenyl siloxane copolymer] 0.32 mm id., 0.32 μm film thickness, fused silica no. 2:30 m OV-1701-OH, 0.32 mm id., 0.25 µm film thickness, both columns customs column made). Results were confirmed by GC-LRMS (GC: HP 6890 / MS: HP 5973; 30 m HP5-MS, 0.25 mm id., 0.25 µm film thickness + 2.5 m pre-column; detection mode: MSD –EI). The limit of quantification (LOQ) was 0.5 ngg⁻¹ fat.

Procedure for PFOS

Milk samples were extracted using weak anion exchange, solid-phase extraction (Waters Oasis[®] WAX, Waters Corporation, Milford, USA) using a previously reported method (Kärrman et al. 2007). Internal standard (${}^{13}C_4$ -PFOS) and 2 mL formic acid/water (1:1) were added to 1 mL milk. The solution was sonicated for 15 min and centrifuged at 9000 x g for 30 minutes. The supernatant was extracted on Oasis WAX and PFOS was eluted with 1 mL 2% ammonium hydroxide in methanol, after washing the column with 2 mL sodium acetate buffer solution (pH 4) and 2 mL 40% methanol in water. After evaporation the final extract volume was 20 µL, then 30 µL 2mM ammonium acetate in water and performance standard

 $(^{13}C_8$ -PFOS) were added. Milk extracts were injected (10 µL) on an Acquity UPLC Xevo TQ-S tandem mass spectrometer (Waters Corporation, Milford, USA) with an atmospheric electrospray interface operating in negative ion mode. The analytes were separated on an Acquity BEH C18 column (2.1 x 100 mm, 1.7 µm) and analyzed on a MS/MS system run in electrospray ionization mode (ESI). Multiple reaction monitoring (MRM) was used and three product ions were monitored for PFOS. Milk samples were quantified using external standards in solvent and the internal standard method. The performance standard was used to assess the recovery of the internal standard.

Data comparability

To ensure reliability of exposure data and to improve comparability of analytical results from different laboratories, WHO has coordinated a number of inter-laboratory quality assessment studies. The State Institute for Chemical and Veterinary Analysis of Food Freiburg met all the pre-set criteria for analyses of PCDDs, PCDFs, dioxin-like PCBs, marker PCBs and fat in human milk and was thus selected as the WHO Reference Laboratory for the WHO human milk studies. Perfluorinated chemicals are likewise analyzed in a single laboratory at the MTM Research Centre, Örebro University, Sweden.

It should also be noted that the sampling concept for the mothers' milk exposure studies changed between 2000 and 2012. Whereas in 2000-2003 countries were encouraged to prepare two or more pooled samples to address differences within a country, the guidance document for the Global Monitoring Plan under the Stockholm Convention asks for one representative sample for up to 50 million citizens. In order to obtain comparable results, the median concentration from all national pools that were submitted is commonly used.

Correlation study on PFOS between milk and blood

Among the newly listed POPs, PFOS and its salts do not follow the "classical" pattern of partitioning into fatty tissues, but instead bind preferentially to proteins in the plasma, such as albumin and gamma-lipoproteins, and in the liver, such as liver fatty acid binding protein. Due to higher albumin content, blood is considered the preferable and recommended medium to determine fluorinated compounds, but analyzing PFOS in milk samples is also a viable option with today's technology. The levels in human milk are generally much lower than those in blood, but a strong association between serum and milk concentrations of PFOS has been reported.

Kärrman and Davies (2013) collected milk and serum samples from primipara women in Uppsala, Sweden in the period from 2004 to 2011. 48 serum samples and 48 milk samples were collected and analyzed on a MS/MS system run in electrospray ionization mode. PFOS (linear isomer) was quantified in all samples and concentrations ranged from 1.3 to 20 ng/mL in serum and 0.028 to 0.354 ng/mL in milk. The limit of detection was 0.05 ng/mL for serum and 0.012 ng/mL for milk. Serum levels of PFOS were compared with levels of PFOS in human milk from the same mother. The regression analysis showed that levels of PFOS measured in milk and serum were highly correlated, with a Pearson's correlation coefficient of 0.9171. Milk levels in this study are on average 1.55% of the corresponding serum levels. This value is in agreement with previous studies on similar serum to milk relationships, that have reported 1.09% (Kim et al. 2011), 1% (Kärrman et al. 2007), and 1.4% (Thomsen et al. 2010).

Data storage

All available data from WHO and UNEP/WHO surveys are stored in the password protected part of the GMP data warehouse, available at <u>www.pops-gmp.org</u>.

Data availability

Figures 9 and 10 show participating countries in WHO and UNEP/WHO milk surveys in the CEE region and data availability over time respectively.



Figure 9 - Data availability from WHO and UNEP/WHO surveys in the CEE region in the following 14 countries: Albania, Bulgaria, Croatia, Czech Republic, Georgia, Hungary, Lithuania, Republic of Moldova, Poland, Romania, Russian Federation, Slovakia, Tajikistan, Ukraine (source: GMP DWH)



Figure 10 – Data availability for breast milk data of the CEE region in the GMP Data Warehouse. Describes participation by 28 countries of the CEE GMP region. The darker the colour, more chemicals were analyzed in the individual survey (min = 17 - dioxins, furans, max = 97)

4.1.3 Programs/activities related to water

PFOS in water is not currently monitored in a regional scale programme. A diverse and limited information exists from various sources i.e. surface water, ground water and through various activities (NORMAN - NORMAN Association former NORMAN project of EU FP6 - Network of reference laboratories, research centres and related organizations for monitoring of emerging environmental substances), or Joint Danube Survey (2009), undertaken by the JRC in Ispra, Italy (Joint Research Centre of the European Commission). PFOS in water bodies of the CEE region is not regularly monitored except the EU countries in the region (it is required by the EU legislation since 2013, where Water Framework Directive amendment included PFOS to the priority substance list as priority hazardous substance)⁸.

⁸ Directive 2013/39/EU amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy, entry 35 in the Annex I

Furthermore, a pilot data collection was also initiated in 2013 through MONET Europe monitoring network, but the results of chemical analyses were not yet available at the time of finalizing this report.

Information on PFOS levels in water in the CEE region collected in this chapter and in chapter 5 therefore only comprises a selection of publicly available information from research publications and international reports and it represents a limited information on the baseline levels in the western part of the CEE region. Information on the non-EU part of the CEE region that is not part of the Danube survey is completely lacking at present.

Analytical Methods⁹

Solid-phase extraction (SPE)

The water samples were extracted at the JRC by solid-phase extraction (SPE) with Oasis HLB (200 mg) cartridges. Most water samples contained particles (suspended particle material; SPM) which settled to the bottom of the plastic bottles. The water was not filtered, but decanted into a 500 mL glass bottle (Schott-Duran). Thus, only the dissolved (liquid) water phase was investigated. Before extraction, the samples (500 mL) were spiked with the internal standard (50 µL), which contained the labeled substances PFOA 13C4, PFOS 13C4, carbamazepine d10, simazine 13C3, atrazine 13C3, ibuprofen 13C3, and 4n- nonylphenol d8. The spiking level in the water samples was 10 ng/L for PFOA 13C4 and PFOS 13C4, and 100 ng/L for the other labeled compounds. The glass bottles were closed, and then the samples were mixed by shaking. The SPE procedure for the clean-up and concentration of water samples was performed automatically using an AutoTrace© SPE workstation (Caliper Life Sciences). 200 mg (6 mL) Oasis® HLB columns (Waters, Milford, MA, USA) were used. The cartridges were activated and conditioned with 5 mL methanol and 5 mL water at a flow- rate of 5 mL min-1. The water samples (400 mL) were passed through the wet cartridges at a flow-rate of 5 mL min-1, the columns rinsed with 2 mL water (flow 3 mL min-1), and the cartridges dried for 30 min using nitrogen at 0.6 bars. Elution was performed with 6 mL methanol. Evaporation of the extracts with nitrogen to 500 µL was performed at a temperature of 35°C in a water bath using a TurboVap© II Concentration Workstation (Caliper Life Sciences).

Liquid chromatography tandem mass spectrometry (LC-MS2)

Analyses were performed by reversed-phase liquid chromatography (RP-LC) followed by electrospray ionization (ESI) mass spectrometry (MS) detection using atmospheric- pressure ionization (API) with a triple-quadrupole MS-MS system. Quantitative LC-MS2 analysis was performed in three separate LC-MS2 runs (methods 1-3) in the multiple reaction monitoring (MRM) mode. Method 1 comprised the compounds in the negative ionization mode, method 2 those in the positive ionization mode, and method 3 alkylphenolic compounds and estrogens which were analysed with a different HPLC mobile phase.

LC was performed with an Agilent 1100 Series LC systems consisting of a binary pump, vacuum degasser, autosampler and a thermostated column compartment. LC separations were performed with a Hypersil Gold column (Thermo Electron Corp., 100 x 2.1 mm, 3μ m particles). Tandem mass spectrometry was performed on a bench-top triple- quadrupole quattro micro MS from Waters-Micromass (Manchester, UK) equipped with an electrospray probe and a Z-spray interface.

⁹ information reproduced from Loos et al.

The eluants used for the separations of the target analytes were water and acetonitrile. The water phase used was acidified with 0.1 % acetic acid (pH 3.5) when analyzing PFCs, pharmaceuticals, and pesticides in the negative and positive ionization modes. The flow-rate was 0.25 mL min-1. The gradient started with 90 % water and proceeded to 90 % acetonitrile over 25 min, conditions hold for 5 min, returned back to the starting conditions over 5 min, and followed by 5 min equilibration.

Instrument control, data acquisition and evaluation (integration and quantification) were done with MassLynx software. Nitrogen is used as the nebulizer gas and argon as the collision gas. Capillary voltage was operated at 3.2 kV, extractor lens at 1.0 V, and RF lens at 0.0 V. The source and desolvation temperatures were set to 120 and 350 °C under chromatographic HPLC conditions. Cone and desolvation gas flows were 50 and 600 L h-1, respectively. The applied analyser parameters for MRM analysis were: LM 1 and HM 1 resolution 11.0, ion energy 1 1.0, entrance -1 (negative mode), 2 (positive mode), exit 1, LM 2 and HM 2 resolution 11.0, ion energy 2 2.0, multiplier 600 V. The MRM inter-channel delay was 0.05 and the inter-scan delay 0.15.

Collision-induced dissociation (CID) was carried out using argon at approx. 3.5 x 10- 3 mbar as collision gas at collision energies of 7 - 40 eV. The optimized characteristic MRM precursor \rightarrow product ion pairs monitored for the quantification of the compounds together with the cone voltage and collision energy are given in Table 2.

Identification, quantification, QA/QC and LODs

The internal standards PFOS and PFOA 13C4 from Wellington Laboratories (Guelph, Canada) were used. The recoveries were determined with spike experiments in the concentration range of 10 and 100 ng L-1 using Milli-Q water (replication n = 6); they were in the range of 50 – 90 % Good performance of the developed analytical methods was demonstrated by successful participation in several interlaboratory exercises. All perfluorinated carboxylates were quantified with PFOA 13C4, and PFOS with PFOS 13C4. The compound-dependent method detection limits (MDLs or LODs) for the SPE- LC-MS2 procedure were calculated from the mean concentrations of the blanks of the real water samples plus 3 times the standard deviation; 400 mL water was extracted and concentrated to 0.5 mL, which results in an enrichment factor of 800. LOD for per fluorinated chemicals was 1 ng L-1

Uncertainty

Measurement uncertainties of analytical methods can be calculated by the analysis of certified reference materials (CRM), or from the Z-scores derived from interlaboratory studies. CRMs for polar organics in water samples do not exist. The JRC-IES laboratory participated in two interlaboratory studies on non-steroidal anti-inflammatory drugs NSAIDs (Farré et al.), the 3rd international interlaboratory study on PFCs (van Leeuwen et al.,2008), and a dedicated study on nonyl- and octylphenol (Loos et al., 2008b). Another possibility to calculate the uncertainty is from the single uncertainty sources in the

Another possibility to calculate the uncertainty is from the single uncertainty sources in the laboratory, if known (standards, glass ware, balance, etc.). Examples how to calculate the uncertainty of a SPE-GC-MS method by this procedure can be found in (Quintana et al., 2001; Planas et al., 2006). These examples show that typical uncertainties for the analysis of water samples by SPE-GC-MS are around 25-50 %.

Statistical analyses

Frequency of positive detection (freq) in [%], average, median (med), and percentile 90% (Per90), were quantified with excel software (Microsoft).

Data storage

Data are only available through research publications and specialized survey reports so far. Information provided in this report is reproduced from the EU survey performed by the JRC (Loos et al).

4.1.4 Programs/activities related to other media

Monitoring activities related to other media exist in some countries in the CEE region. These include human blood, soil, sediments and biota (fish). However, the information from other media does not describe regional situation but provide information relevant locally/at a country level.

This is valid in particular for soils and sediments. For example, a long term soil monitoring of POPs exists in the Czech Republic, where it is preformed each year since 1980s. Data are available, but they do not always represent background levels but rather a hot-spots or burdened area(s).

Sediment monitoring is available in some countries and covers catchment area and usually reflects local contamination.

For human blood - there is no regular blood monitoring in the CEE region apart from the Czech Republic and Slovakia that provided information for the first monitoring report, but no specific information have been made available to the ROG for the period of this report. Some activities also exist in establishing POP levels in biota (fish) or in food and feed (monitoring in the Czech Republic).

For example, in Bulgaria a pilot study was undertaken to sample fish in Black Sea to screen for pesticides and PCB¹⁰, activities of HELCOM SCREEN project (2009) or MORE looked at fish - flounder and herring in seas in Estonia, Latvia, Lithuania and Poland as well as other countries of the Baltic Sea¹¹.

ROG decided not to use information generated from these activities further as the sources are too variable, episodic and the information generated reflects rather national or local situation then a regional perspective.

4.2 Strategy concerning analytical procedures

The following brief text shows a summary of analytical methods/procedures used in programs that contributed to this report. Description of sample preparation procedures as well as individual analytical techniques for a particular group of chemicals are described above, together with the relevant monitoring programme in chapter 4.1. A summary overview of analytical procedures is provided in Table 2.

Moreover, international monitoring programmes operating in the CEE region (in particular air monitoring) have embedded into their standard operating procedures for sampling as well as for sample processing a series of field and laboratory blanks that ensure levels of the background noise and potential cross-contamination are kept as low as possible. Detailed QA/QC measures as described above for each programme.

Data generated in the UNEP/WHO human milk survey come from two laboratories. The first one analyzing all listed POPs but PFOS was selected as the WHO Reference Laboratory for the WHO human milk studies on the basis of meeting the pre-set criteria in inter-laboratory

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¹⁰ National implementation Plan of Bulgaria

http://helcom.fi/Documents/HELCOM%20at%20work/Projects/Completed%20projects/MORE/OverviewMarin eMonitoring2013_V3.1.pdf

quality assessment studies. the other laboratory provides information on PFOS concentrations in breastmilk. For details see table 2 below.

4.3 Strategy concerning participating laboratories

Laboratory capacities and state of the art facilities able to analyze all groups of POPs are somewhat limited in the region except the Czech Republic and Slovakia, and to a limited extent some laboratories in the Russian Federation. However, a detailed information on the equipment available across the region is limited as participation of an institution/country in international monitoring programs operating in the CEE region (such as MONET or GAPS) does not necessarily require the use of laboratory capacities in individual countries. On the contrary, MONET, GAPS, as well as samples collected in the UNEP/WHO milk surveys) samples are usually analyzed in one main laboratory to keep the results comparable across the programme. In addition, some programmes such as EMEP do rely on data generated through national monitoring programmes, but they only cover a limited scope of chemicals - see table 1 in 4.1.1. or table 2 below.

Decreasing quantities of POPs in the environment as well as listing of brominated and fluorinated POPs require the use of more sensitive analytical equipment such as liquid chromatography coupled with mass spectroscopy (ideally high resolution). Such kind of instrumentation is not readily available throughout the region and external support would be required if more establishments are needed in the region. However, this is a matter of priority setting for needs to take place at individual country level.

On the other hand, the Stockholm Convention Regional Centre in the Czech Republic receives a number of requests for cooperation and support in providing chemical analyses of various kinds of environmental samples each year for various countries and stakeholders and its laboratory capacity have been so far sufficient.

Despite the fact that a long term capacity building and training activities have been initiated and undertaken by the Stockholm Convention Regional Centre in the Czech Republic in 2005 to train many experts and laboratory specialists in using new methodology and equipment for analytical procedures, as described in greater detail in chapter 4.1., comparability of data among laboratories may be an issue should more laboratories be involved in analyzing the collected samples.

Monitoring Programme and matrix	sampling technique	Amount of Sampling sites	Chemicals analyzed	List of chemicals analyzed	Analytical Methods	Data provider
AMAP/air	Active	1	12	α -HCH, β -HCH, chlordane, DDT, dieldrin, endosulfan, endrin, γ -HCH, heptachlor, mirex, dl-PCB - coplanar, PCB-indicator	GC-MS	Environment Canada
EMEP/air	Active	2	7	α-HCH, chlordane, DDT, γ- HCH, HCB, dl-PCB - coplanar, PCB-indicator	GC-MS	EMEP/NILU
Košetice - active air sampling	Active	1	21	aldrin, α-HCH, β-HCH, chlordane, DDT, dieldrin, endosulfan, endrin, γ-HCH, heptachlor, HCB, mirex, PBDEs, PeCBz, PFOS, dl- PCB - coplanar, PCB- indicator, PCDD/Fs	GC-ECD, GC-MS, GC-MS/MS, GC-HRMS	RECETOX

Table 2 Overview of analytical methods used in monitoring programms in the CEE region

GAPS/air	Passive	3	12	aldrin, α-HCH, β-HCH, chlordane, DDT, dieldrin, endosulfan, γ-HCH, heptachlor, PBDEs, dl-PCB - coplanar, PCB-indicator, PCDD/Fs	GC-MS/MS	Environment Canada
APOPSBAL	Passive	1	7	α-HCH, β-HCH, chlordane, DDT, γ-HCH, HCB, dl-PCB - coplanar, PCB-indicator	GC-ECD, GC-MS	RECETOX
MONET - CEEC/air	Passive	54	7	α-HCH, β-HCH, chlordane, DDT, γ-HCH, HCB, dl-PCB - coplanar, PCB-indicator	GC-MS, GC-MS/MS	RECETOX
MONET - CZ/air, (+ water, soil)	Passive	15	7	α-HCH, β-HCH, chlordane, DDT, γ-HCH, HCB, dl-PCB - coplanar, PCB-indicator	GC-ECD, GC-MS, GC-MS/MS	RECETOX
MONET - Europe (MONET- EU)/air, (+water, soil)	Passive	21	7	α-HCH, β-HCH, chlordane, DDT, γ-HCH, HCB, dl-PCB - coplanar, PCB-indicator	GC-MS, GC-MS/MS	RECETOX
UNEP/WHO milk survey	pooled sample/W HO protocol	participation varies each survey round; ranges 3-8	varies in the survey round	all PCDDs, PCDFs, dl-PCB PBDEs PFOS other remaining listed POPs	HRGC/HR MS GC-MS/MS, GC-HRMS UPLC/MS/ MS GC-ECD, GC-LRMS	The State Institute for Chemical and Veterinary Analysis of Food Freiburg (all POPs but PFOS) and MTM Research Centre, Örebro University, Sweden (PFOS only)

However, in order to boost sustainability of the Global Monitoring Plan activities in the CEE region and support national activities and ownership it is necessary to have more laboratories capable of analyzing various POPs and samples coming from various core media.

4.4 Data handling and preparation for the regional monitoring report

The CEE ROG and experts have agreed to use the electronic tool under the Global Monitoring Plan once plans for its establishment were presented in 2012.

In addition, as many data providers operating in the CEE region have already stored data in the GENASIS environmental database (in 2009 onwards), it was considered beneficial to continue using this electronic data repository for primary data and only ensure transfer of relevant representative data to the Global Monitoring Plan Data Warehouse. Any new monitoring data that would fulfill the compatibility check regarding QA/QC for sampling, analytical methods, and data interpretation could be added to the GENASIS environmental database should data provider decide to provide this information to the ROG. As the requirements for data comparability, structure, accompanying information, and other information are in place ensuring maximum use of available information, this information would be then automatically used in any subsequent reporting round.

Collected information elements in the GENASIS database are the same as those required by the GMP data warehouse and their reporting forms so the two systems are fully compatible. The outcome in the GMP DWH is presented as annually aggregated concentration and the data evaluation procedure in place (in the GMP Data Warehouse) guarantees comparability of the different samples, especially from the point of view of the type of site, matrix, sampling method, time span and sampling frequency. The embedded processing procedures in place also limit the impact of uncontrolled covariates and thus reduce the risk of false trend detection or neglecting truly significant changes.

Details on statistical considerations and their implementation in the second phase GMP are available in the guidance document (UNEP/POPS/COP.6/INF/31).

GMP information warehouse

Harmonized data handling and appropriate support given to the collection, processing, storing and presentation of monitoring data in regions with limited capacity was a major focus of the work in the second phase GMP. A global monitoring plan data warehouse supports data collection and assists the regional organization groups and the global coordination group in producing the regional and global monitoring reports, and the effectiveness evaluation. It includes an interactive on-line data capture system, handling, and presentation module.

The global monitoring plan data warehouse also constitutes a publicly available repository of valuable information that can serve as a useful resource for policy makers and researchers worldwide. The tool is available at <u>www.pops-gmp.org</u>.

4.5 Preparation of the monitoring reports

CEE Regional Organization Group decided in its meeting in Brno in September 2013 that its second report will build on the content of the extensive first regional report from 2008 and new information will be added, in particular covering levels of POPs for the period 2008-2014 (where applicable). The second regional report would mirror the reporting template prepared by the Stockholm Convention Secretariat.

First draft of the regional report was supported by the same team of consultants and data managers from the Stockholm Convention Regional Centre hosted in RECETOX, Czech Republic since majority of CEE data is collected and made available through electronic tools and environmental databases operated by the RECETOX. Regional Organization Group members were to inform RECETOX by end of March 2014 whether any new POPs data has been made available in their respective sub-region so that they could be transferred to the GMP data warehouse for consideration. No such information was made available. It was decided that available data from existing monitoring programmes as described in 4.1.1-4.1.4 are to be incorporated into the GMP data warehouse and made available to the CEE regional organization group for a subsequent consideration and validation analysis. Access to information from ongoing existing monitoring programmes and activities is thus provided to the regional organization groups online, as soon as data was available. This is efficient and user friendly manner for the development of monitoring reports, and ensures harmonized data analysis and presentation across whole region as well as comparable globally (with other regions).

Once this first draft made available by the supporting team, CEE ROG members considered the information therein in a meeting 7-8 October 2014 and prepared further work on chapters 4, 5, 6 and 7. When drafting the report, the GMP electronic tool was extensively used and found very useful.

Chapter of the report	Drafting team
Executive summary	ROG members
1 Introduction	ROG members based on secretariat's draft
2 Description of the Region	Ivan Holoubek
3 Organization of Regional Implementation	Ivan Holoubek
4 Methods for Sampling, Analysis and Data Handling	Stockholm Convention Regional Centre in Czech Republic
5 Results	ROG + consultants from SCRC and MSC-East
5.1 Ambient air (active and passive sampling)	Stockholm Convention Regional Centre in Czech Republic (Klanova)
5.2 Human tissues (milk and / or blood)	ROG members
5.3. Water	Stockholm Convention Regional Centre in Czech Republic (Vrana)
5.4 Other media (non-core media)	Stockholm Convention Regional Centre in Czech Republic
5.5 Long Range Transport (Regional and Global Environmental Transport)	Stockholm Convention Regional Centre in Czech Republic with materials from the MSC-East + ROG members
6 Conclusions and Recommendations	ROG

The division of tasks were as follows:

The CEE ROG with support of the SCRC Czech Republic finalized the report after two rounds of comments and sent it to the Stockholm Convention Secretariat in line with the set deadline in early 2015 to allow production of materials for the 7th meeting of the Conference of the Parties to the Stockholm Convention.

5 **RESULTS**

This chapter describes data provided by the monitoring programmes and activities described in Chapter 4. It also provides information on sources of POPs, comments on changes in concentrations of studied POPs over time from regional perspective and provides other relevant information.

The attention of the first evaluation focused on the twelve POP substances listed in the Annexes of the Stockholm Convention and on collection of available information on some new POPs (hexachlorocyclohexanes, pentachlorobenzene). In addition, the first report comprised data other toxic substances - polycyclic aromatic hydrocarbons (PAHs) - that are not subject to the Stockholm Convention, but are regulated by the UN ECE Convention on Long-Range Transboundary Air Pollution (CRLTAP) and its Protocols. PAHs are not included in this report this time.

In its first report, the CEE region has successfully established baseline and trends for: DDTs, PCBs, HCB and some new POPs such as all three isomers of HCHs and pentachlorobenzene. In addition, information on other compounds listed in the Convention (dieldrin, chlordane) was also collected, but short time series generated during monitoring consisting of two to three years (by passive sampling) did not allow for determination of trend at that time. However the period was sufficient for establishing the baseline, longer time series would be necessary for the trend identification.

Moreover, other newly included chemicals will have their baseline established by this report (i.e. fluorinated chemicals, PBDEs and some other chemicals that were not monitored previously, including some legacy POPs, however their levels are very low and in some case were even below limit of quantification of analytical methods used.

The results in chapters 5.2. and 5.3. are complemented by charts and tables generated from the GMP DWH, however full reprint of available data is not provided. Detailed information for each site, compound or concentration levels are available in yearly aggregated form online from the GMP Data warehouse in its data visualization (www.pops-gmp.org/visualization-2014).

5.1 The results in context

This chapter further comments on the production and use of POPs in the CEE region. The text builds on the information made available in the first regional report and is organized in the same manner as monitoring data in the core matrices in chapters 5.2.1. and 5.2.2. below; at first it covers seven organochlorine pesticides from Annex A followed by HCB, PCBs, DDTs, and dioxins and furans. New POPs are described in the following order HCHs, chlordecone, endosulfan, PBDEs, hexabromobiphenyl, pentachlorobenzene, PFOS and hexabromocyclododecane.

5.1.1. Cyclodiene Insecticides/ Organochlorine Pesticides

Several POP pesticides were produced in various countries of the CEE region. Information on the former pesticide production, use, import and export and stocks is not fully available in some countries of the region. Despite the existing legislation and use bans, obsolete stocks and hotspots still remain in the region. Much work was performed since early 1990s to identify these obsolete pesticides, and ensure their imminent environmentally sound storage or disposal have been carried out in all countries of the region, but the job is far from completed. This chapter covers production and use of aldrin, chlordane, dieldrin, endrin, heptachlor, chlordecone, mirex, and toxaphene in the CEE region. Based on available information, aldrin, dieldrin, endrin, chlordane, heptachlor, mirex, and toxaphene have never been registered and applied in the Russian Federation. Some of these pesticides were, however, used in the former Soviet Union.

Aldrin

The use was banned in 1980 in the Czechoslovakia, in the former Soviet Union before 1987 and in Ukraine since 1997.

Chlordane use banned in Ukraine since 1997

Dieldrin

used for pesticide production in Poland, use banned in Ukraine since 1997. Never used in the Czech Republic (former Czechoslovakia).

Endrin

The use was banned in the Czechoslovakia in 1984, in the former Soviet Union before 1987, and in Ukraine since 1997.

Heptachlor

The agricultural use was banned in the Czechoslovakia in 1989, in the former Soviet Union before 1987 and in Ukraine since 1997.

Chlordecone never produced in the region and nor registered

Mirex

It was used in Kazakhstan for protection of cotton crops and in Poland, but it was never registered/used in the former Soviet Union.

Toxaphene

use banned in the former Soviet Union before 1987, in the Czechoslovakia in 1986. Plant protection products containing toxaphene were imported to the Czechoslovakia between 1963-1986.

5.1.2. Hexachlorobenzene (HCB)

Intentional production in the Czech Republic ceased in 1968. Use as pesticide banned in the Czechoslovakia in 1977, in Ukraine since 1997.

Used for pesticide production in Poland; HCB is still unintentionally produced in the production of perchlorinated ethylene in the Czech Republic, but it is in the closed system and it is disposed of as waste /by incineration under controlled conditions/.

5.1.3. Polychlorinated biphenyls (PCBs)

As described in detail in the first monitoring report, several countries of the CEE region produced PCB technical mixtures. – See Table II-1, annex II of the first monitoring report.

PCBs were manufactured between 1959 and 1984 in Eastern Slovakia (Chemko Strážske, about 22500 tons) and used extensively in production of capacitors, paints and varnishes in the former Czechoslovakia and former east Germany.

Other significant PCB production, in Dzerzhinsk in the region of Nizhni Novgorod and in Novomoskovsk in Tula Region (300 km east from Moscow and 200 km south of Moscow

respectively), was in operation between 1939 and 1993, producing about 180 000 tons of PCBs for paints, varnishes, lubricants, transformers and capacitors. The equipment produced was extensively used in the countries of the former Soviet Union. Small quantities of PCBs were also produced in Poland. PCBs were never produced in the former Yugoslavia, but the country manufactured transformers and capacitors in Slovenia, Serbia and in Croatia. Both the previous and present industrial use of PCBs is responsible for current PCB emissions. The major source of atmospheric contamination are due to evaporation from the old open systems (paint and wood protecting layers, softeners etc.), from landfills, dumping sites and waste incinerators, and from transformers, condensers, hydraulic systems and other PCB containing devices that are either in use or waiting to be disposed of.

5.1.4. DDT

DDT was produced in the Czech Republic and in Poland. It was used quite extensively until 1970s/1984 in the region (i.e. phase out in Poland in 1975, CZ:1975, import and use banned in 1982 in former Yugoslavia, end of use in the Soviet Union in 1986 (used since 1946), and the use was banned in Ukraine since 1997.

5.1.5. PCDDs and PCDFs

These compounds are unintentionally produced by combustion in the whole region.

5.1.6. New POPs

This chapter cover all remaining POPs listed in the Stockholm Convention and their situation in the region

Hexachlorocyclohexanes (HCHs)

Hexachlorocyclohexanes (technical mixture) were extensively produced in the region since 1950s, in particular in the Czech Republic, Poland, Romania, Azerbaijan, and former Soviet Union. Obsolete stocks still remain in many countries on landfills and dumping sites throughout the region or in the former production facilities that ceased their operation.

Endosulfan

used in agriculture (past use) or as wood preservative in some countries of the region.

PBDEs

not produced in the region, but used (in articles)

Hexabrombiphenyl never produced or used in the region

Pentachlorobenzene

unintentionally produced, releases/transfer as waste reported in the Czech Republic - similarly to hexachlorobenzene.

PFOS

Not produced in the region, but some use reported, also available from use of products/articles.

HBCD (hexabromocyclododekan)

Not produced in the region but imported and currently used in the Czech Republic in the manufacture of the construction material for insulation of houses.

5.2 Review of concentrations and their changes over time in the CEE region

5.2.1 Ambient air

Both active and passive sampling networks and programmes contributed data to this chapter. It covers maximum span of data available – i.e. 1996 onwards for DDT, HCB, PCBs, pentachlorobenzene, and all HCHs. Other POPs were added gradually, depending on monitoring programme, sites and analytical equipment (and expertise) available. Information on large majority of listed POPs as of 2011 (but toxaphene and hexabrombiphenyl) is continuously collected by active sampling at the Košetice EMEP station since January 2011. The most recent data also show levels for 2014, but only for selected chemicals.

5.2.1.1. Cyclodiene Insecticides/ Organochlorine Pesticides

This chapter addresses seven chlorinated pesticides included in Annex A to the Stockholm Convention in the following order: aldrin, chlordane, dieldrin, endrin, heptachlor, mirex, and toxaphene.

Aldrin was sampled at two sites, Danki (2009-2010) and Košetice (2011-2013) as shown in the Table 3 below. The values detected are predominantly below level of quantification and therefore no trend could be observed. Baseline level is below LOQ.

Sampling Site	Time series start Year	Time series end Year	Length (Years)	Minimum concentration (mean) (pg m ⁻ ³)	Maximum concentration (mean) (pg m ⁻ ³)	Total amount of measurements	Concentration values below LOQ observed N times	Values below LOQ
Danki	2009	2009	1	0,487452	0,487452	4	4	100%
Kosetice, EMEP station	2009	2013	4	0,0257447	0,487452	104	103	99%

Table 3 - Overview of levels observed for aldrin in the CEE region, 2009-2013

Chlordane

Isomers of chlordane and its transformation products were monitored at six sites in the CEE region: Košetice EMEP station, Leova II, Valkarkai, and Borovoe by active sampling and at Danki, Košetice EMEP station, and Pomlewo as shown in the Table 4.

It can be noted that values for polar site at Valkarkai were very low, the 83 and 88% of values observed for alpha and gamma isomers of chlordane respectively were below LOQ. Values for degradation products were also predominantly below LOQ. Baseline level is thereby established, lower levels were observed in Leova II, Borovoe and Valrkaikai than in

Danki, Pomlewo and Košetice. Trend observed at all these sites is statistically not significant, in particular due to a short duration of time series.

Samplin g Site	Time series start Year	Time series end Year	Length (Years)	Compound	Minimum concentratio n (mean) (pg m ⁻³)	Maximum concentratio n (mean) (pg m ⁻³)	Total amount of measuremen ts	Concentratio n values below LOQ observed N times	Value s below LOQ
Danki	2005	2009	3	Cis-chlordane	0,249368	3,35	12	4	33%
				Trans-chlordane	0,125	0,5525	12	7	58%
				Trans- nonachlor	0,057967	1	12	4	33%
Kosetice,	2005	2013	3+3	Cis-chlordane	0,249368	2,25	112	42	38%
station				Trans-chlordane	0,126538	0,775	112	73	65%
				Oxychlordane	0,0185106	0,888077	100	100	100%
				Trans- nonachlor	0,057967	1,3	12	4	33%
Leova II	2009	2010	2	Cis-chlordane	0,4969	0,5405	14	0	0%
				Trans-chlordane	0,6333	0,7105	14	0	0%
				Cis-Nonachlor	0,057	0,2346	14	0	0%
				Trans- nonachlor	0,54575	0,56	14	0	0%
Pomlew o	2004	2006	3	Cis-chlordane	0,5	2,9	8	0	0%
				Trans-chlordane	0,01	1,13333	8	1	13%
				Trans- nonachlor	0,3	1,93333	8	0	0%
Valkarka	2008	2009	2	Cis-chlordane	0,25	0,26	41	34	83%
1				Trans-chlordane	0,25	0,27	41	36	88%
				Cis-Nonachlor	0,12	0,13	31	28	90%
				Oxychlordane	0,35	0,4	41	33	80%
				Trans- nonachlor	0,17	0,22	41	28	68%
Borovoe	2010	2010	1	Cis-chlordane	0,35075	0,35075	4	0	0%
				Trans-chlordane	0,08175	0,08175	4	0	0%
				Cis-Nonachlor	0,04725	0,04725	4	0	0%
				Trans- Nonachlor	0,31625	0,31625	4	0	0%

Table 4 - Overview of levels observed for chlordane in the CEE region, 2005-2013

Dieldrin

Monitoring of dieldrin occurred at four sampling sites - in Danki (2005-2009) and Pomlewo (2004-2006) by passive sampling and in Valkarkai (2009-2010) and Košetice EMEP station (2005-2013) by active sampling.

Occurrence in very low quantities was observed for Valkarkai station (88% of measured values were below LOQ), and Danki site (75% values below LOQ). Observed ranges are provided in the Table 5 below, trend is not statistically significant, in particular due to relatively short time series.

Sampling Site	Time series start Year	Time series end Year	Length (Years)	Minimum concentration (mean) (pg m ⁻ ³)	Maximum concentration (mean) (pg m ⁻ ³)	Total amount of measurements	Concentration values below LOQ observed N times	Values below LOQ
Danki	2005	2009	3	0,6	7,34	12	9	75%
Kosetice, EMEP station	2005	2013	3+3	0,891064	23,78	112	53	47%
Pomlewo	2004	2006	3	5	26,3333	8	1	13%
Valkarkai	2008	2009	2	0,27	0,29	41	36	88%

 Table 5 - Overview of levels observed for dieldrin in the CEE region, 2005-2013

Endrin

Sampling sites in Valkarkai and Košetice monitored endrin by active sampling as shown in the Table 6 below. Time series are short (two and three years respectively) and values detected are predominantly below level of quantification. In conclusion, no trend could be observed at this time, but baseline level is established.

Sampling Site	Time series start Year	Time series end Year	Length (Years)	Minimum concentration (mean) (pg m ⁻ ³)	Maximum concentration (mean) (pg m ⁻ ³)	Total amount of measurements	Concentration values below LOQ observed N times	Values below LOQ
Kosetice, EMEP station	2011	2013	3	0,0185106	1,68673	100	100	100%
Valkarkai	2008	2009	2	0,42	0,45	41	36	88%

 Table 6 - Overview of levels observed for endrin in the CEE region, 2008-2013

Heptachlor

Monitoring of heptachlor took place at four sampling sites - Danki (2005-2009) and Pomlewo (2004-2006) by passive sampling and in Valkarkai (2008-2009) and Košetice EMEP station (2005-2013) by active sampling.

As shown in the Table 7, concentration observed were very low, majority of measurements are below LOQ. Trend is not statistically significant, in particular due to relatively short continuous time series, but the baseline level is established.

Sampling Site	Time series start Year	Time series end Year	Length (Years)	Minimum concentration (mean) (pg m ⁻³)	Maximum concentration (mean) (pg m ⁻ ³)	Total amount of measurements	Concentration values below LOQ observed N times	Values below LOQ
Danki	2005	2009	3	0,075	0,3	12	12	100%
Kosetice, EMEP station	2005	2013	3+3	0,0423404	0,3	112	106	95%
Pomlewo	2004	2006	3	0,075	0,3	8	8	100%
Valkarkai	2008	2009	2	0,63	0,68	41	36	88%

Table 7 - Overview of levels observed for heptachlor in the CEE region, 2005-2013

Mirex

Air samples for mirex were collected at two sites, Danki (2009-2010) by passive sampling and at the Košetice EMEP station (2011-2013) by active samplers as shown in the Table 8. The values detected are predominantly below level of quantification. No trend could be observed, but the baseline is thereby established.

Table 8 - Overview of levels observed for mirex in the CEE region, 2009-2013

Sampling Site	Time series start Year	Time series end Year	Length (Years)	Minimum concentration (mean) (pg m ⁻ ³)	Maximum concentration (mean) (pg m ⁻ ³)	Total amount of measurements	Concentration values below LOQ observed N times	Values below LOQ
Kosetice, EMEP station	2011	2013	3	0,067963	0,0969231	100	49	49%
Valkarkai	2008	2009	2	1,1	1,2	41	36	88%

Toxaphene

This chemical was not measured regularly, episodic measurements took place in Košetice, but it was not detected. No relevant data were identified for this compound as there is no source.

5.2.1.2. Hexachlorobenzene (HCB)

Hexachlorobenzene is monitored quite extensively on 77 sampling sites of 17 countries in the CEE region however, the total duration of time series ranges from one year up to thirty years. Baseline for this chemical was established in the first phase of the GMP data collection. As shown in the map in Figure 11, passive sampling sites cover well the western part of the CEE region and statistically significant trends were observed on two sites in the Czech Republic. A border mountain sampling site Děčínský Sněžník (marked red in Figure 11) experienced increase in HCB concentrations over nine years (2006-2014) and site in Plaňavy

(green circle in the Figure 11) shows a statistically significant decreasing trend over 11 years long time series (monitoring started in 2004).

The increasing trend for Děčínský Sněžnik site may be caused by emissions transported from other neighboring countries, due to prevailing westerly winds.

Sampling sites shown in blue do not exhibit statistically significant trend, the time series are insufficiently long. Grey circles represent sites where monitoring occurred in a short term period (i.e. about one year during pilot study in 2006 or 2007) and was further discontinued. Note that the diameter of the sampling site circle marker is also related to a POPs concentration level (mean) observed on that site. Detailed concentration levels are provided in Annex in Table HCB and online in the GMP DWH.

In addition to passive sampling, active sampling of HCB also takes place at the Košetice EMEP station. Figure 12 shows changes in HCB concentrations and a statistically significant decreasing trend for 18 year long time series (1996 onwards).



Figure 11 - Trends observed in the CEE region for HCB concentrations gathered by passive sampling between 1996-2014. Decreasing trend is shown in green, increasing trend in red, statistically non-significant trend in blue, and no trend in grey. (source: GMP DWH)



Figure 12 - Changes in the HCB concentration levels and resulting long-term trend as analyzed from the samples collected at the Košetice EMEP station by active sampling over 18 years. (source: GMP DWH)

5.2.1.3. PCBs

PCBs in air were monitored by passive sampling on 80 sampling sites of 17 countries in the CEE region quite broadly. However, the total duration of time series differs significantly; it ranges from one year up to thirty three years. Table containing data summary is provided in Annex, Table PCBs. Baseline for this chemical was established in the first phase of the GMP data collection.

As shown in the regional map in Figure 13, several passive sampling sites detected statistically significant decreasing trends. They were observed in the remote site Lahemaa in Estonia (2006-2012), sub-urban site in Zagreb Siget, Croatia (2007-2012) and on twelve sites in the Czech Republic, where eight out of twelve are located in the border mountains (remote), one is urban site in Prague, and three remaining sampling sites are rural sites (Svratouch, Plaňavy, Mikulov-Sedlec) in Moravia. The trends are observed on longer time series (5 and 6 years for Croatia and Estonia respectively), and 8-11 years for the Czech Republic.



Figure 13 – Trends observed in the CEE region for changes in PCB concentrations 1996-2014. Decreasing trend is marked in green, statistically non-significant trend in blue, and no trend in grey. (source: GMP DWH)

Sampling sites expressed by blue circles in Figure 13 do not exhibit statistically significant trend, largely due to short time series available so far. Grey circles represent sites where monitoring occurred in a short term period (i.e. about one year during pilot study in 2006 or 2007) and was/is further discontinued. The diameter of the sampling site circle marker is also related to a POPs concentration level (mean) observed on that site. Detailed concentration levels are provided in Table PCBs in the Annex.

Moreover, a trend for PCBs was also observed for samples collected by active sampling at the Košetice EMEP station as shown in Figure 14. This sampling site (Košetice) is also represented in the map in Figure 13 above by jade (darker greenblue) colour.



Figure 14 - Changes in the concentration levels of sum PCBs collected by active sampling and resulting decreasing trend at the Košetice EMEP station over 18 years. (source: GMP DWH)

dlPCBs

In the MONET networks, the only dl-PCB congener analyzed is the PCB118, other congeners are not available. In the GAPS network, only nine out of 12 of the dl-PCBs congeners are analyzed (77, 81, 105, 114, 118, 123, 126, 156 and 157) in the collected samples, however the values reached are predominantly below LOQ (fg/m3) for all studied congeners except PCB118. In that case, the median values reached in samples from both MONET and GAPS were in the range of up to 79-77000 fg/m3. The relevant LOQ ranged from 150-3200 fg/m3 and about 45% of values were below LOQ.

In addition, dl-PCBs are also analyzed in samples from the integrated monitoring in Košetice. Therein, the full set of dl-PCBs is sampled from 2011 onwards. Currently, analyses are ready for 2011-2013 as shown in the Table 9 below for the sum of twelve dl-PCBs.

Sampling site	Time series start Year	Time series end Year	Length (Years)	Minimum concentration (mean) (pg m-3)	Maximum concentration (mean) (pg m-3)	Total amount of measurements	Concentration values below LOQ observed N times	Values below LOQ
Kosetice, EMEP station	2011	2013	3	628,097	9522,25	100	0	0%

Table 9 - Overview of levels observed for sum dl-PCBs in the CEE region, 2011-2013

The trends observed for dl-PCBs are statistically not significant, the time series is too short. Nevertheless, it was possible to calculate the WHO TEQ. The levels as shown in Figure 14a and Figure 14b (for TEQ1998 and 2005 respectively).

PCBs WHO1998-TEQ UB0.6-2.15 fg/m3 as provided in detail in Figure 14aPCBs WHO2005-TEQ UB0.56-1.89 fg/m3 as given in Figure 14b



Figure 14a - Observed PCBs TEQ1998 UB levels in air (active sampling) at the Košetice sampling site 2011-2013. (source: GMP DWH)



Figure 14b - Observed PCBs TEQ2005 UB levels in air (active sampling) at the Košetice sampling site 2011-2013.(source: GMP DWH)

5.2.1.4. DDT

DDT is another POPs extensively studied in the region. It was monitored on 79 sampling sites of 17 countries in the CEE region by both passive and active sampling. However, the total duration of time series varies from one year up to thirty one years. Baseline for this chemical was established in the previous phase of the GMP.

As shown by green circles in Figure 15 for the situation observed by passive sampling, several sampling sites in the region experience statistically significant decreasing trends. All these sites are located in the Czech Republic, time series length ranges 8-11 years for passive sampling. Seven of sites with decreasing trend are located in border mountains of the Czech Republic (remote), two sites are at rural background sites (Svratouch and Plaňavy) and one site is urban background site in Prague. Sampling sites expressed by blue circles do not exhibit statistically significant trend. Grey circles represent sites where monitoring occurred in a short term period (i.e. about one year during pilot study in 2006 or 2007) and was/is further discontinued. The diameter of the sampling site circle marker is also related to a POPs concentration level (mean) observed on that site. Detailed concentration levels are provided in Table DDT Annex and online in GMP DWH.



Figure 15 - Trends observed in the CEE region for changes in DDT concentrations between 1996-2014. Decreasing trend is marked in green, statistically non-significant trend in blue, and no trend in grey. (source: GMP DWH)

Moreover, a mild decreasing trend was also observed for DDTs resulting from air samples collected by active sampling at the Košetice EMEP station since 1996 as shown in Figure 16.



Figure 16 - Changes in the levels of sum DDT collected by active sampling and resulting decreasing trend at the Košetice EMEP station over 18 years. (source: GMP DWH)

5.2.1.5. PCDD and PCDF (fg/m3)

Dioxins and furans (all 17 parameters) were monitored by active sampling only in Košetice EMEP station, Czech Republic 2011-2013. Changes observed do not represent statistically

significant trend as the time series is too short. Table 10 below shows minimum and maximum values observed and thereby establishes a baseline.

Table 10 - Overview of levels observed for sum of 17 congeners PCDD/PCDF in the CEE region, 2011-2013, source GMP DWH

Sampling Site	Time series start Year	Time series end Year	Length (Years)	Minimum concentration (mean) (fg m ⁻³)	Maximum concentration (mean) (fg m ⁻³)	Total amount of measurements	Concentration values below LOQ observed N times	Values below LOQ
Kosetice, EMEP station	2011	2013	3	218,515	297,894	100	0	0%

In addition, both the individual as well as summary concentrations can also be expressed in TEQ values as follows:

PCDDs:

- PCDDs WHO1998-TEQ UB 4.19-6.6 fg/m3 • PCDDs WHO2005-TEQ UB 4.21-6.63 fg/m3 • **PCDFs** 4.82-8.87 fg/m3
- PCDFs WHO1998-TEQ UB
- 3.88-6.74 fg/m3 • PCDFs WHO2005-TEQ UB PCDDs/Fs
 - PCDFs WHO1998-TEQ UB
- PCDFs WHO2005-TEQ UB
- 12.34-14.07 fg/m3 in Figure 16a 10.87-11.79 fg/m3 in Figure 16b



Figure 16a - Observed PCDD/Fs TEQ1998 UB levels in air (active sampling) at the Košetice sampling site 2011-2013.(source: GMP DWH)



Figure 16b - Observed PCDD/Fs TEQ2005 UB levels in air (active sampling) at the Košetice sampling site 2011-2013.(source: GMP DWH)

5.2.1.6. New POPs – HCHs

Hexachlorcyclohexanes (three isomers: alpha-, beta- and gamma- lindane, HCHs) are another well studied chemical in the CEE region. Individual isomers were analyzed/detected in air collected by passive sampling at 80 sampling sites of 17 countries in the CEE region. However, the duration of time series differs significantly; it ranges from one year up to 33 years. Nevertheless, regional baseline for all isomers was established earlier. As shown in the regional maps in Figures 18, 19, and 21 several passive sampling sites detected statistically significant decreasing trends. The trends are observed on longer time series and are discussed for each isomer individually below.

Alpha HCH

As shown in the regional map in Figure 18, eleven passive sampling sites in the region detected statistically significant decreasing trends for alpha HCH levels in ambient air. They were observed in two the rural sites in Lithuania between 2006-2012 (Plateliai and Rugsteliskes, EMEP station) and on nine sites in the Czech Republic between 2004-2014. Six out of nine sites with the trend in the Czech Republic are located in the border mountains (remote), one is urban site in Prague, and two remaining sampling sites are rural sites in Moravia (Plaňavy, Mikulov-Sedlec). The trends are observed on longer time series - five years for Lithuania and 8-11 years for the Czech Republic.

Sampling sites expressed by blue circles do not exhibit statistically significant trend, largerly due to short continuous time series available so far. Grey circles represent sites where monitoring occurred in a short term period (i.e. about one year during pilot study in 2006 or 2007) and was/is further discontinued. The diameter of the sampling site circle marker is also related to a POPs concentration level (mean) observed on that site. Detailed overview of concentration levels observed is provided in Table alpha-HCH in the Annex.

Alpha HCH was also analyzed in samples collected by active sampling at the Košetice EMEP station since 1996 as shown in Figure 17 and a mild statistically significant decreasing trend was observed.



Figure 17 - Changes in the levels of alpha HCH collected by active sampling and resulting decreasing trend at the Košetice EMEP station over 18 years. (source: GMP DWH)



Figure 18 - Trends observed in the CEE region for changes in alpha-HCH concentrations between 1996-2014. Decreasing trend is marked in green, statistically non-significant trend in blue, and no trend in grey. (source: GMP DWH)

Beta-HCH

As shown in the regional map in Figure 19, six passive sampling sites in the Czech Republic detected statistically significant decreasing trends. They were observed in five sampling sites (remote) in border mountain chains and in one rural site in Mikulov, Sedlec over 8-10 years long time series. Analyses have shown increased proportion of values below LOQ for this isomer in analyses – this is valid for Celje and Iskrba, Slovenia (80-100%), Diabla Gora, Szarow and Zabierzow, Poland (80-100%), Plateliai, Lithuania (92%), Podgorica, Montenegro (80%), Danki, Obninsk and Valkarkai, Russian Federation (54-100%) Zagreb, Croatia (80-100%), Ručava EMEP and Starina dam in Slovakia (59-69%) and Plovdiv and Sofia, Bulgaria (50-80%). Values observed in Valkarkai polar site were also one order of magnitude lower than the rest of the region. Sampling sites expressed by blue circles do not exhibit statistically significant trend, largerly due to short time series available so far. Grey circles represent sites where monitoring occurred in a short term period (i.e. about one year during pilot study in 2006 or 2007) and was/is further discontinued. The diameter of the sampling site circle marker is also related to a POPs concentration level (mean) observed on that site. Detailed concentration levels are provided in Table beta-HCH in the Annex. Beta HCH was also analyzed in samples collected by active sampling at the Košetice EMEP station since 1996 as shown in Figure 20, nevertheless a statistically significant trend was not observed.



Figure 19 - Trends observed in the CEE region for changes in beta HCH concentrations between 1996-2014. Decreasing trend is marked in green, statistically non-significant trend in blue, and no trend in grey. (source: GMP DWH).



Figure 20 - Changes in the levels of gamaHCH collected by active sampling at the Košetice EMEP station over 18 years. Statistically significant trend line cannot be determined (source: GMP DWH)

Gamma HCH

As shown in the regional map in Figure 21, twenty passive sampling sites detected statistically significant decreasing trends. Similarly to alpha HCH, trends were also observed in two rural sites in Lithuania between 2006-2012 (Plateliai and Rugsteliskes, EMEP station)

and in the Czech Republic on six remote sites in border mountains (Děčínský Sněžník, Churáňov, Jeseník, Liberec, Rudoltice, Rýchory), urban site in Prague, and two rural sites Mikulov-Sedlec and Plaňavy between 2004-2014. In addition, decreasing trends were also observed in Estonia (Lahemaa), Poland (Diabla Gora), Russian Federation (EPRC), Slovenia (Iskrba) and on five additional sites in the Czech Republic including a rural site in Svratouch and four remote sites (Bílý kříž, Kleť, Přimda and Šerlich) in the border mountain chains. Trends were observed on longer time series - five years for Lithuania, Poland, Russian Federation, six years for sites in Estonia and Slovenia, and 7-11 years for sites the Czech Republic.

Sampling sites expressed by blue circles in the map do not exhibit statistically significant trend, largerly due to short time series available so far. Grey circles represent sites where monitoring occurred in a short term period (i.e. about one year during pilot study in 2006 or 2007) and was/is further discontinued. The diameter of the sampling site circle marker is also related to a POPs concentration level (mean) observed on that site. Detailed concentration levels are provided in Table gamma-HCH in the Annex.



Figure 21 - Trends observed in the CEE region for changes in gHCH concentrations between 1996-2014. Decreasing trend is marked in green, statistically non-signifcant trend in blue, and no trend in grey. (source: GMP DWH)

Gamma HCH was also analyzed in samples collected by active sampling at the Košetice EMEP station since 1996 as shown in Figure 22. Even such a long time series did not yield a statistically significant trend.



Figure 22 - Changes in the levels of gammaHCH collected by active sampling at the Košetice EMEP station. Statistically significant trend was not determined. (source: GMP DWH)

5.2.1.7. New POPs – Chlordecone, Endosulfan

Chlordecone

Chlordecone is monitored by active sampling in Košetice EMEP station, Czech Republic. the monitoring covers period 2011-2013. Trend cannot be determined as all levels observed are below LOQ. Table 11 below shows minimum and maximum values observed and establishes a baseline for this chemical.

						,_,_,		
Sampling Site	Time series start Year	Time series end Year	Length (Years)	Minimum concentration (mean) (pg m-3)	Maximum concentration (mean) (pg m-3)	Total amount of measurements	Concentration values below LOQ observed N times	Values below LOQ
Kosetice, EMEP station	2011	2013	3	0,0185106	11,4302	100	100	100%

Table 11 - Overview of levels observed for chlordecone in the CEE region, 2011-2013

Endosulfan

Monitoring of endosulfan isomers and transformation products took place at four sampling sites in the CEE region - Danki (2005-2009) and Pomlewo (2004-2006) by passive sampling and in Valkarkai (2008-2009) and Košetice EMEP station (2005-2013) by active sampling. As shown in the Table 12 below, majority of concentration levels observed for Valkarkai station were below LOQ. On other sampling sites, alpha endosfulfan was a predominant parameter observed, beta endosulfan and endosulfan sulphate levels were at least an order of magnitude lower and sulphate levels were two up to four orders of magnitude lowr. Changes in concentrations observed at any site do not represent a statistically significant trend as the time series available are too short. Nevertheless, baseline for this chemical is established.

Table 12 - Overview of levels observed for endosulfan parameters in the CEE region in the period 2005-2013.

Sampling Site	Time series start Year	Time series end Year	Length (Years)	Compoun d / Parameter	Minimum concentratio n (mean) (pg m-3)	Maximum concentratio n (mean) (pg m-3)	Total amount of measurement s	Concentratio n values below LOQ observed N times	Values below LOQ
Danki	2005	2009	3	Endosulfa n I (alpha)	7,85513	26	12	0	0%
				Endosulfa n II (beta)	0,210454	1,35	12	8	67%
				Endosulfa n SO ₄	0,10537	0,2875	12	8	67%
Košetice EMEP station	2005	2013	3+3	Endosulfa n I (alpha)	1,50077	272,75	112	10	9%
				Endosulfa n II (beta)	0,0185106	39,025	112	104	93%
				Endosulfa n SO ₄	0,0777778	3,4275	112	96	86%
Pomlewo	2004	2006	3	Endosulfa n I (alpha)	22	188,667	8	0	0%
				Endosulfa n II (beta)	1,2	21,6667	8	0	0%
				Endosulfa n SO ₄	0,055	1,7	8	2	25%
Valkarka i	2008	2009	2	Endosulfa n I (alpha)	0,17	0,18	41	36	88%

5.2.1.8. New POPs – PBDE and Hexabromobiphenyl (HBB)

Polybrominated diphenyl ethers (PBDEs)

PBDE were analyzed in samples collected by passive sampling in three sites in the Region (Pomlewo, Poland, Danki, Russian Federation and Košetice Czech Republic in 2004-2005. As shown in the Table 13 below, levels determined in Poland and Russian Federation are below LOQ. These activities determined baseline levels of PBDEs in the region. In addition, whole set of PBDEs is determined in samples stemming from active sampling in Košetice EMEP station, Czech Republic since 2012, however changes observed at Košetice site do not represent a statistically significant trend as the time series is yet too short. Table 13 below shows minimum and maximum values observed.

Table 13 - Overview of levels observed for PBDE parameters in the CEE region in the period 2005-2013.

Samplin g Site	Time series start Year	Time series end Year	Length (Years)	Compoun d / Parameter	Minimum concentratio n (mean) (pg m-3)	Maximum concentratio n (mean) (pg m-3)	Total amount of measurement s	Concentratio n values below LOQ observed N times	Values below LOQ
Danki	2005	2005	1	BDE 47	0,005	0,005	4	4	100%
				BDE 99	0,0212872	0,0212872	4	4	100%
				BDE 100	0,0187204	0,0187204	4	4	100%
Košetice EMEP station	2005 2012	2006 2013	2+2	BDE 47	0,159937	0,385729	104	3	3%
				BDE 99	0,129756	0,277375	104	3	3%
				BDE 100	0,0334111	0,0890403	104	3	3%
Pomlew o	2004	2005	2	BDE 47	0,005	0,005	4	4	100%
				BDE 99	0,0212872	0,0212872	4	4	100%
				BDE 100	0,0187204	0,0187204	4	4	100%

Hexabromobiphenyl (HBB)

Hexabromobiphenyl was banned in 1970s in Europe. Since there is no source, no air data were identified for this compound. (monitoring/analyses not performed in this period).

5.2.1.9. New POPs – Pentachlorobenzene (PeCB)

This chemical is included in the monitoring by active samplers at the Košetice EMEP station since 2001. It is the only site in the CEE region and PeCB levels observed are shown in Table 14. A statistically significant decreasing trend is observed, as depicted in Figure 23. Baseline was established in the first regional report. A statistically significant decreasing trend is observed, as depicted in Figure 23.

Table 14 - Overview of levels observed for PeCB in the CEE region, Košetice EMEP station, Czech Republic since 2001.

Sampling site	Time series start Year	Time series end Year	Length (Years)	Minimum concentration (mean) (pg m-3)	Maximum concentration (mean) (pg m-3)
Kosetice, EMEP station	2001	2013	13	1,83269	55,5245



Figure 23 – Changes in the levels of pentachlorobenzene as analyzed from the samples collected at the Košetice EMEP station, Czech Republic by active sampling and resulting trend observed over 13 year long time series. (source: GMP DWH)

5.2.2.10. New POPs – PFOS

A set of parent chemical, isomers and transformation products is collected and analyzed from samples gathered by active sampling at the Košetice EMEP station since 2012 as shown in Table 15. Baseline levels are thereby established. Since the time series are still very short a trend observed is not statistically significant. Values observed for transformation products are very low and majority of them is below LOQ.

Table 15 - Overview of concentrations established for PFOS and its transformation products in the CEE region 2012-2013. Samples are collected by active sampling at the Košetice EMEP station since 2012.

Parameter/Compoun d	Time series start Year	Time series end Year	Length (Years)	Minimum concentratio n (mean) (pg m-3)	Maximum concentratio n (mean) (pg m-3)	Total amount of measurement s	Concentratio n values below LOQ observed N times	Values below LOQ
PFOS				0,145471	0,337174	52	0	0%
PFOSA				0,0065801	0,0286688	52	26	50%
NEtFOSA	2012	2013	2	0,00461729	0,0278416	52	46	88%
NEtFOSE				0,0263281	0,0370864	52	31	60%
NMeFOSA				0,00695871	0,0260219	52	40	77%
NMeFOSE				0,0222207	0,0804179	52	22	42%
5.2.1.11. New POPs – HBCDD

No air data were identified for this compound yet. The samples are collected but results of analyses were not available at the time of submitting this report. Nevertheless, it is expected that a HBCDD baseline relevant to 2013 will be made available in the next GMP report for the CEE region.

5.2.2 Human tissues (milk and/or blood)

This chapter contains data collected in the WHO human milk monitoring studies on PCBs and dioxins and furans in 1987-1989 and 1992-1993. A global WHO survey between 2001-2003 comprised twelve POPs initially listed in the Stockholm Convention. Two additional UNEP/WHO global surveys (round 4 and 5) were conducted in 2005-2007 and 2008-2012. The scope for round 5 study (2008-2012) was extended to all POP parameters including new POPs, however information available for CEE region does not include chlordecone and fluorinated compounds. On the other hand, information is provided for POPs whose levels in air are so far unknown for the CEE region, such as toxaphene, hexabromobiphenyl (HBB) and hexabromocyclododekane (HBCDD).



Figure 24 - Overview of data availability over time in the CEE region. The darker the colour, the more parameters are analyzed. For samples in 2009, whole set of POPs was analyzed.

The scope for round 5 study (2008-2012) was extended to all POP parameters including new POPs, however information available for CEE region does not include chlordecone and fluorinated compounds. On the other hand, information is provided for POPs whose levels in

air are so far unknown for the CEE region, such as toxaphene, hexabromobiphenyl (HBB) and hexabromocyclododekane (HBCDD).

Second phase of global UNEP/WHO study was initiated in 2013 and data collection finished in mid 2014.

Data from the second phase are available for Bulgaria and Romania so far and there are additional data expected. They will be made available in the next regional report.

General availability of data in the CEE region regarding POPs levels in human tissues (breast milk) generated through WHO and WHO/UNEP surveys is shown in Figure 24. As seen from that figure, participation of CEE countries in survey is limited – only 14 countries out of 28 in the CEE GMP region participated in various surveys and only nine countries participated in more than one survey (Bulgaria, Croatia, Czech Republic, Hungary, Lithuania, Romania, Russian Federation, Slovakia, and Ukraine).

5.2.1.1. Cyclodiene Insecticides/ Organochlorine Pesticides

This chapter addresses seven chlorinated pesticides included in annex A to the Stockholm Convention: aldrin, chlordane, dieldrin, endrin, heptachlor, mirex, and toxaphene.

Aldrin levels are available for seven CEE countries participating in 4th round (Czech Republic, Hungary, and Slovakia) and 5th round (Georgia, Lithuania, Moldova, and Tajikistan) surveys (2006-2009) for as shown in Figure 25.

Aldrin levels in all participating countries were lower than 0,5 ng/g lipid weight (fat).



Figure 25 - Observed aldrin levels in breast milk in the CEE region between 2006-2009 (ng/g fat). Data generated through WHO and UNEP/WHO surveys rounds 4-5, first phase. Pooled samples. (source: GMP DWH)

Chlordane

Concentration values for chlordane are available for ten CEE countries participating in 3rd round (Bulgaria, Czech Republic, Russian Federation, and Ukraine), 4th round (Czech Republic, Hungary, and Slovakia) and 5th round (Georgia, Lithuania, Moldova, and Tajikistan) surveys covering period 2001-2009 for as shown in Figures 26 and 27. Observed levels of cis-chlordane and trans-chlordane in all participating countries showed the same pattern and were lower than 0,5 ng/g lipid weight (fat) respectively as shown in Figure 26. Levels of oxychlordane differ more significantly, as shown in Figure 27 below.



Figure 26 - Observed cis-chlordane and trans-chlordane levels in breast milk in the CEE region between 2001-2009 (ng/g fat). Data generated through WHO and UNEP/WHO surveys, first phase. Charts are identical for both parameters. (source: GMP DWH)



Figure 27 - Observed oxychlordane levels in breast milk in the CEE region between 2001-2009 (ng/g fat). Data generated through WHO and UNEP/WHO surveys, first phase, pooled samples. (source: GMP DWH)

Dieldrin

Dieldrin levels are available for ten CEE countries participating in 3rd survey (Bulgaria, Czech Republic, Russian Federation, and Ukraine), 4th round (Czech Republic, Hungary, and Slovakia) and 5th round (Georgia, Lithuania, Moldova, and Tajikistan) surveys covering period 2001-2009 for as shown in Figure 28.



Figure 28 – Observed dieldrin levels in breast milk in the CEE region between 2001-2009 (ng/g fat). Data generated through WHO and UNEP/WHO surveys, first phase, pooled samples. (source: GMP DWH)

Endrin

Concentration values for endrin are available for ten CEE countries participating in 3rd round (Bulgaria, Czech Republic, Russian Federation, and Ukraine), 4th round (Czech Republic, Hungary, and Slovakia) and 5th round (Georgia, Lithuania, Moldova, and Tajikistan) surveys covering period 2001-2009 for as shown in Figure 29. Observed levels in all participating countries were lower than 0,5 ng/g lipid weight (fat) respectively.



Figure 29 - Observed endrin levels in breast milk in the CEE region between 2006-2009. Data generated through WHO and UNEP/WHO surveys rounds 3-5, first phase. (source: GMP DWH)

Heptachlor

Heptachlor concentrations are available for ten CEE countries participating in 3rd round (Bulgaria, Czech Republic, Russian Federation, and Ukraine), 4th round (Czech Republic, Hungary, and Slovakia) and 5th round (Georgia, Lithuania, Moldova, and Tajikistan) surveys covering period 2001-2009. Unfortunately, heptachlor analyses were not the same for all years. The cis-heptachlorepoxide was the only parameter analyzed in the 3rd survey; more recent surveys comprised all parameters of the heptachlor group. Figures 30-32 show levels observed for heptachlor, cis-heptachlorepoxide and trans-heptachlorepoxide. Observed levels

both heptachlor and trans-heptachlorepoxide were lower than 0,5 ng/g lipid weight (fat) in all participating countries (Figures 30 and 32 respectively). Comparison of Czech Republic's levels of cis-heptachlorepoxide for 2001 and 2006 in Figure 31 suggests a decrease in concentration of the chemical.



Figure 30 - Observed heptachlor levels in breast milk in the CEE region between 2006-2009 (ng/g fat). Data generated through WHO and UNEP/WHO surveys rounds 3-5, first phase. Pooled samples. (source: GMP DWH)



Figure 31 - Observed cis-heptachlor levels in breast milk in the CEE region between 2001-2009 (ng/g fat). Data generated through WHO and UNEP/WHO surveys rounds 3-5, first phase. Pooled samples. (source: GMP DWH)



Figure 32 - Observed trans-heptachlorepoxide levels in breast milk in the CEE region between 2006-2009 (ng/g fat). Data generated through WHO and UNEP/WHO surveys rounds 3-5, first phase. Pooled samples. (source: GMP DWH)

Mirex

Mirex levels are available for seven CEE countries participating in 4th round (Czech Republic, Hungary, and Slovakia) and 5th round (Georgia, Lithuania, Moldova, and Tajikistan) surveys (2006-2009) for as shown in Figure 33. The levels observed in all participating countries were lower than 0,5 ng/g lipid weight (fat).



Figure 33 - Observed mirex levels in breast milk in the CEE region between 2006-2009. Data generated through WHO and UNEP/WHO surveys rounds 4-5, first phase. (source: GMP DWH)

Toxaphene

Toxaphene levels are available for ten CEE countries participating in 3rd round (Bulgaria, Czech Republic, Russian Federation, and Ukraine), 4th round (Czech Republic, Hungary, and Slovakia) and 5th round (Georgia, Lithuania, Moldova, and Tajikistan) surveys covering period 2001-2009. Figures 34-36 show levels observed for Parlar 25, Parlar 50 and Parlar 60. Comparison of Czech Republic's levels 2001 and 2006 do not show any significant change neither for Parlar 26 or Parlar 50. Levels for Parlar 62 are identical for majority of participating countries (lower than 0,5 ng/g lipid weight (fat)).



Figure 34 - Observed toxaphene (Parlar 26) levels in breast milk in the CEE region between 2001-2009 (ng/g fat). Data generated through WHO and UNEP/WHO surveys rounds 3-5, first phase. Pooled samples. (source: GMP DWH)



Figure 35 - Observed toxaphene (Parlar50) levels in breast milk in the CEE region between 2001-2009 (ng/g fat). (source: GMP DWH)



Figure 36 - Observed toxaphene (Parlar 62) levels in breast milk in the CEE region between 2001-2009 (ng/g fat). Data generated through WHO and UNEP/WHO surveys rounds 3-5, first phase. Pooled samples. (source: GMP DWH)

5.2.2.2. Hexachlorobenzene (HCB)

Concentration values for hexachlorobenzene are available for ten CEE countries participating in 3rd round (Bulgaria, Czech Republic, Russian Federation, and Ukraine), 4th round (Czech Republic, Hungary, and Slovakia) and 5th round (Georgia, Lithuania, Moldova, and Tajikistan) surveys covering period 2001-2009 for as shown in Figure 37. Observed values vary significantly, but comparison for Czech Republic between 2001 and 2006 suggests a significant decrease in levels for these two periods.



Figure 37 - Levels observed for HCB in _{concentration ng/gfat} breast milk in the CEE region between 2001-2009 (ng/g fat). Data generated through WHO and UNEP/WHO surveys rounds 3-5, first phase. Pooled samples. (source: GMP DWH). (source: GMP DWH)

5.2.2.3. PCBs

Polychlorinated biphenyls were analyzed in samples since 1992 till 2009. Analyses are available for 13 CEE countries (Albania, Bulgaria, Croatia, Czech Republic, Georgia, Hungary, Lithuania, Moldova, Romania, Russian Federation, Slovakia, Tajikistan, and Ukraine). Four countries participated in three consecutive surveys (Czech Republic, Hungary, Russian Federation and Slovakia).

Figure 38 shows that for all countries with repeated participation in WHO surveys levels decrease over time (Bulgaria, Croatia, Czech Republic, Hungary, Lithuania, Romania, Russian Federation, Slovakia and Ukraine).

Decrease in Croatia, Czech Republic, Slovakia, and Lithuania exhibit a steeper slope than that of Hungary, Russia and Ukraine. The more significant decrease is seen in countries that

used PCB in paints for improvement of adhesive properties of the paint. This use was stopped and therefore the levels decreased.

In terms of the congeners partition, lighter congeners (28, 52 and 101) were observed in lower concentrations than higher ones (138, 153 and 180). PCB28 was observed in concentrations 0,5-10 ng/g fat, PCB52 (0,2-3,2 ng/g fat), and PCB101 (0,2-2,6 ng/g fat); higher congeners were found in levels as follows: PCB138 (4,8-260 ng/g fat), PCB153 (5-360 ng/g fat), and PCB180 (3-200 ng/g fat). Figure 38 shows sum of 6 indicator PCBs.



Figure 38 - Observed sum of six PCBs (indicator) levels in breast milk in the CEE region between 1992-2009. Data generated through WHO and UNEP/WHO surveys rounds 2-5, first phase. (source: GMP DWH)

For the dioxin-like PCBs and their congeners, the sum of 12 dl-PCBs is shown in Figure 39 and concentration ranges for medians observed for individual congeners were as follows:

PCB 77 0,5-20 pg/g fat

PCB 81 1,3-16 pg/g fat

PCB 126 8.2-119.4 pg/g fat

PCB 169 4.3-47.7 pg/g fat

for non-ortho PCBs and

- PCB 105 472.4-12066.7 pg/g fat
- PCB 114 70-1927.2 pg/g fat
- PCB 118 2025-64443 pg/g fat
- PCB 123 2.5-256.5 pg/g fat
- PCB 156 710-36000 pg/g fat
- PCB 157 138-5250 pg/g fat
- PCB 167 210-11350 pg/g fat
- PCB 189 50-4900 pg/g fat

for mono-ortho PCBs.



Figure 39 Observed dl-PCBs levels for sums of 12 dl-PCBs congeners in breast milk in the CEE region between 2001-2009. Data generated through WHO and UNEP/WHO surveys (source: GMP DWH)

It was possible to calculate the WHO TEQ levels only for 18 out of 25 samples as the levels of PCB81, PCB114, and PCB123 were not determined in those collected in 1992. Ranges of the TEQ values (medians) observed in the region were as follows:

PCBs WHO1998-TEQ2.06-19.94 pg/g fat as provided in detail in Figure 39aPCBs WHO2005-TEQ1.5-10.7 pg/g fat as given in Figure 39b



Figure 39a Observed PCBs TEQ1998 LB levels in breast milk in the CEE region between 2001-2009. Data generated through WHO and UNEP/WHO surveys. (source: GMP DWH)



Figure 39b Observed PCBs TEQ2005 levels in breast milk in the CEE region between 2001-2009. Data generated through WHO and UNEP/WHO surveys (source: GMP DWH)

5.2.1.4. DDT

DDT analyses were performed for ten CEE countries participating in 3rd round (Bulgaria, Czech Republic, Russian Federation, and Ukraine), 4th round (Czech Republic, Hungary, and Slovakia) and 5th round (Georgia, Lithuania, Moldova, and Tajikistan) surveys covering period 2001-2009. Figures 40 a-d show levels observed for DDT and its isomers.



Figure 40a - Observed o,p-DDT levels in the breast milk in the CEE region between 2001-2009. Data generated through WHO and UNEP/WHO surveys. (source: GMP DWH)



Figure 40b - Observed p,p-DDT levels in the breast milk in the CEE region between 2001-2009. Data from UNEP/WHO surveys (source: GMP DWH)

While levels of o,p DDE and o,p-DDD were below level of quantification (i.e. below 0,5 ng/L), levels of the parent DDT shown in Figures 40a and 40b mean that in many cases there must be some stocks of DDT still present in the countries. Former large/frequent application of the pesticide is shown in Figure 40c for p,p DDE by high levels (over 1000 ng/L) in some countries. Overall summary picture for sum of 3 DDTs is given in Figure 40d.



Figure 40c - Observed p,p DDE levels in breast milk in the CEE region between 2001-2009. Data generated through WHO and UNEP/WHO surveys rounds 3-5, first phase. (source: GMP DWH)



Figure 40d - Observed sum of three DDTs (p,p-DDTs) levels in breast milk in the CEE region between 2001-2009. Data generated through WHO and UNEP/WHO surveys rounds 3-5, first phase. (source: GMP DWH)

5.2.2.5. PCDDs and PCDFs

Polychlorinated dibenzo dioxins (PCDDs) and furans (PCDFs) were the most studied compounds in the milk surveys. Levels are available for 13 CEE countries (Albania, Bulgaria, Croatia, Czech Republic, Georgia, Hungary, Lithuania, Moldova, Russian Federation, Tajikistan, and Ukraine). Four countries participated in three consecutive surveys (Czech Republic, Hungary, Russian Federation and Slovakia), other countries (Croatia, Lithuania and Ukraine).

Figure 41 shows sum PCDD/Fs concentrations and reveal that for the majority of countries with repeated participation in WHO surveys levels decrease over time. A decrease observed for Croatia, Czech Republic, Hungary, Slovakia, and Lithuania exhibit a steeper slope than that for Russia and Ukraine. When testing for trends, the statistical tests do not prove a statistically significant trends as of yet. Longer time series would be necessary.

Figures 42 and 43 show a similar pattern for sum of PCDDs and sum of PCDFs, respectively. Baseline levels were established in the first report, but statistically significant trends are not yet quantifiable.



Figure 41 - Observed levels for sumPCDDs/Fs (17) in breast milk in the CEE region between 19926-2009. Data generated through WHO and UNEP/WHO surveys rounds 2-5, first phase. (source: GMP DWH)



Figure 42 - Observed levels for sum of 7 PCDDs in breast milk in the CEE region between 1987-2009. Data generated through WHO and UNEP/WHO surveys rounds 1-5, first phase. (source: GMP DWH)



Figure 43 - Observed levels for sumPCDFs (10) in breast milk in the CEE region between 1992-2009. Data generated through WHO and UNEP/WHO surveys rounds 2-5, first phase. (source: GMP DWH)

5.2.2.6. New POPs – Hexachlorocyclohexanes (HCHs)

Alpha-HCH

Levels for alphaHCH are available for ten CEE countries: Bulgaria, Czech Republic, Ukraine (3rd round) participating in 4th round (Hungary and Slovakia) and 5th round (Georgia, Lithuania, Moldova, Tajikistan and Ukraine) surveys (2001-2009) for as shown in Figure 44. Values are similar to those observed for gamma-HCH and about at least an order of magnitude lower than those observed for beta-HCH. Values below LOQ were observed in the Czech Republic, Hungary, Lithuania, and Slovakia.



Figure 44 - Observed alpha HCH levels in the human tissues (breast milk) in the CEE region between 2006-2009. Data generated through WHO and UNEP/WHO surveys rounds 4-5, first phase. (source: GMP DWH)

Beta-HCH

Concentration values for beta-HCH are available for ten CEE countries participating in 3rd round (Bulgaria, Czech Republic, Russian Federation, and Ukraine), 4th round (Czech Republic, Hungary, and Slovakia) and 5th round (Georgia, Lithuania, Moldova, and Tajikistan) surveys covering period 2001-2009 for as shown in Figure 45.

Observed values vary significantly, median concentation ranges observed are between 8.5-476 ng/g fat.



Figure 45 - Observed beta-HCH levels in the human tissues (breast milk) in the CEE region between 2001-2009. Data generated through WHO and UNEP/WHO surveys rounds 3-5, first phase. (source: GMP DWH)

Gamma-HCH

Concentration values for gamma HCH are available for ten CEE countries participating in 3rd round (Bulgaria, Czech Republic, Russian Federation, and Ukraine), 4th round (Czech Republic, Hungary, and Slovakia) and 5th round (Georgia, Lithuania, Moldova, and Tajikistan) surveys covering period 2001-2009 for as shown in Figure 46. Observed values vary, but comparison of concentrations determined in the Czech Republic between 2001 and 2006 suggests a decrease in levels between these two periods. In addition, levels are of the same order of magnitude as those observed for alpha-HCH.



Figure 46 - Observed gamma HCH levels in the human tissues (breast milk) in the CEE region between 2001-2009. Data generated through WHO and UNEP/WHO surveys rounds 4-5, first phase. (source: GMP DWH)

5.2.2.7. New POPs – Chlordecone, Endosulfan

Chlordecone

No data for levels of chlordecone were identified in the CEE region.

Endosulfan

Concentration values for endosulfan isomers and endosulfan sulphate are available for ten CEE countries participating in 3rd round (Bulgaria, Czech Republic, Russian Federation, and Ukraine), 4th round (Czech Republic, Hungary, and Slovakia) and 5th round (Georgia, Lithuania, Moldova, and Tajikistan) surveys covering period 2001-2009 for as shown in Figure 47.

Levels for all three chemicals (cis-endosulfan, trans- and endosulfan sulphate) are identical for all participating countries (lower than 0,5 ng/g lipid weight (fat)).



Figure 47 - Observed levels for all individual parameters related to endosulfan (same for cis-, trans- and sulphate) in breast milk in the CEE region between 2001-2009. Data generated through WHO and UNEP/WHO surveys rounds 3-5, first phase. (source: GMP DWH)

5.2.2.8. New POPs – PBDE and Hexabromobiphenyl (HBB) PBDEs

Levels for polybrominatediphenylethers were analysed in samples collected between 2001 and 2014 for Bulgaria, Croatia, Czech Republic, Georgia, Hungary, Moldova, Romania, Russian Federation, Slovakia, Tajikistan, and Ukraine. Five countries Bulgaria, Czech Republic, Hungary, Romania, and Slovakia have results from two rounds. Levels vary between countries. However a difference is observed for countries with two measurements, no clear indication of increase or decrease can be determined. Baseline levels were already established by the first GMP report.

Results are as shown in Figures 48-50 for BDE 47, 99, and 100 respectively. All other BDE isomers (BDE 17, BDE 28, BDE 153, BDE154) were detected in all countries, though for BDE 17 the median values seen were predominantly below LOQ (0.002 ng/g fat), for BDE28 a range of 0.017-0.059 ng/g fat, BDE 153 0.09-0.33 ng/g fat, and BDE154 0.013-0.05 ng/g fat were obtained.



Figure 48 - Observed BDE47 levels in breast milk in the CEE region between 2006-2009. Data generated through WHO and UNEP/WHO surveys rounds 4-5, first phase. (source: GMP DWH)



Figure 49 - Observed BDE99 levels in breast milk in the CEE region between 2006-2009. Data generated through WHO and UNEP/WHO surveys rounds 4-5, first phase. (source: GMP DWH)



Figure 50 - Observed BDE100 levels in breast milk in the CEE region between 2006-2009. Data generated through WHO and UNEP/WHO surveys rounds 4-5, first phase. (source: GMP DWH)

Hexabromobiphenyl

Analyses for hexabromobiphenyl were performed in the 5th round of the UNEP/WHO survey in 2009. Data are available for Georgia, Lithuania and Tajikistan as shown in Figure 51. Observed levels were identical for all participating countries (lower than 0,5 ng/g lipid weight (fat)).



Figure 51 - Observed hexabromobiphenyl levels in breast milk in the CEE region between 2006-2009. Data generated through WHO and UNEP/WHO surveys rounds 4-5, first phase. (source: GMP DWH)

5.2.2.9. New POPs – Pentachlorobenzene (PeCB)

Analyses for pentachlorobenzene were performed in the 5th round of the UNEP/WHO survey in 2009. Data are available for Georgia, Lithuania and Tajikistan as shown in Figure 52.



Figure 52 - Observed pentachlorobenzene levels in breast milk in the CEE region between 2006-2009. Data generated through WHO and UNEP/WHO surveys rounds 4-5, first phase. (source: GMP DWH)

5.2.2.10. New POPs - PFOS

PFOS data in the CEE region are only available for survey in 2009 in three countries. Levels observed vary as shown in Figure 53.



Concentration ng/l

Figure 53 - Observed PFOS levels in breast milk in the CEE region. Data generated through WHO and UNEP/WHO surveys round 5, first phase. (source: GMP DWH)

5.2.2.11. New POPs – HBCDD

Hexabromocyclododecane was analyzed in samples collected in five countries – Hungary and Slovakia in 2006 and Georgia, Moldova and Tajikistan in 2009. Levels observed are shown in Figures 54 and 55 for alphaHBCDD and beta-HBCDD, respectively. Levels observed for gammaHBCDD were identical to those observed for beta-HBCDD and they were all below LOQ (see Figure 55).



Figure 54 - Observed alphaHBCD levels in breast milk in the CEE region between 2006-2009. Data generated through WHO and UNEP/WHO surveys rounds 4-5, first phase. (source: GMP DWH)



Figure 55 - Observed betaHBCDD and gammaHBCDD levels in breast milk in the CEE region between 2006-2009. Data generated through WHO and UNEP/WHO surveys rounds 4-5, first phase. (source: GMP DWH)

5.2.3. Water

A limited information is available in relation to the CEE region. There are no systematic regional nor national monitoring programmes related to PFOS in water, however the PFOS was included among priority substances under the EU Water Framework Directive in 2013 and thus should be monitored by all EU countries since 2013.

Data presented in this chapter in Table 16 are stemming from research project undertaken by European Union in 23 countries along Danube river including its tributaries (summer 2007). The survey looked into occurrence of 34 polar organic contaminants including PFOS and PFOA in major European rivers and their tributaries. The results show that occurrence of both chemicals were observed in 94 and 97% cases/samples respectively. For the CEE region, a relatively high perfluorooctanoate (PFOA) levels were detected in the Rivers Danube and "elevated" perfluorooctansulfonate (PFOS) concentrations in Krka. A higher median concentration for all river samples was found for PFOS (6 ng/L), compared to PFOA (3 ng/L). Data are not included into the GMP Data Warehouse.

In addition, the same research group looked into occurrence of polar organic contaminants in Danube river (Loos et al 2010) and found that the PFOS concentration was quite constant in the upstream part of the Danube (about10 ng/L). Then, at the river mouth in Romania 6 ng/L were reached. In the following tributaries higher PFOS concentration levels were detected: Morava (CZ) (20 ng/L), Jantra (57 ng/L), and Arges (RO) (101 ng/L). In Tisza River, low concentrations of PFOA (3 ng/L) and PFOS (3 ng/L) were detected, however high concentration level of PFNA (108 ng/L).

Table 16 - Overview of PFOS concentrations in CEE rivers and their tributaries from Danube survey (Loos et al 2008). Samples collected in 2007 in 23 countries. Results analyzed in 40 laboratories. Zero level means LOD.

Country	River	PFOS concentration (ng/L)	PFOA concentration (ng/L)
BG	Iskar	3	2
BG	Lesnovka	1	1

CZ	Elbe/Labe	19	7
CZ	Vltava	5	3
CZ	Svrtka	4	6
CZ	Luž. Nisa	81	4
CZ	Odra	6	0
EE	Emajogi	1	1
EE	Purtse	0	1
EE	Narva	1	0
HU	Sio	41	5
HU	Sajo	5	2
HU	Raba	9	3
HU	Pecsi víz	6	4
HU	Tisza	3	1
HU	Hossureti Patak	33	32
Lithuania	Nemunas	0	1
Lithuania	Nemunas	1	1
Lithuania	Neris	1	1
Lithuania	Neris	1	1
PL	Vistula	4	2
PL	Vistula	3	1
PL	Vistula	6	1
RO	Somez Mic	1	1
RO	Somez Mic	4	1
RO	Somez Mic	1	1
RO	Somez Mare	0	1
SI	Krka	4	1
SI	Krka	1371	40
SI	Krka	3	1
SI	Sava	5	1
SI	Ljubljanica	3	1
SI	Ljublanica	2	1

SI	Drava	2	1
SI	Drava	2	1

5.2.4 Other media

Information on POP levels in other media is scarce. No regular monitoring of POPs occurs in blood with the exception of the Czech Republic and Slovakia that provided information for the first monitoring report, but not to the second report.

Other information is available for biota (fish), soil, and sediments. The CEE ROG decided not to use information generated from these activities further as the sources are too variable, episodic and the information generated reflects rather national or local situation then a regional perspective.

5.3 Long-range transport

Information in this chapter stems from the report provided by the MSC-East and CCC (NILU)¹² and covers only a limited range of Stockholm Convention POPs – HCB, PCBs and PCDD/PCDF.

Model assessment of transboundary transport within the EMEP region was carried out for 1990 and 2012 to evaluate changes in transboundary fluxes between the EMEP countries and contributions of different sources. Model simulations indicate decrease in total emissions, changes in relative proportion of contributions to transboundary fluxes from anthropogenic emission sources to non-EMEP emissions as well as to a more significant secondary emission sources (re-volatilization from the environmental media).

The report holds that levels and emissions of all studied POPs have decreased significantly between 1990 and 2012 (i.e. HCB by 90%, PCBs by up to 80%, PCDD/Fs by 40-75%). Decrease in emissions is usually attributed to significant national reductions of emissions (in some countries) as well as to a decrease in anthropogenic EMEP emissions.

¹² EMEP Status Report 3/2014. POPs in the Environment.

6 CONCLUSIONS AND RECOMMENDATIONS

The second phase of the global monitoring plan was undertaken in the period 2009-2014 to determine trends in concentration of persistent organic pollutant in humans and in the environment, and to obtain baseline data on the persistent organic pollutants that have been listed in the Convention after the year 2009.

This regional monitoring report regional scale in two core matrices out of four; regional data for POP levels in ambient air span over 1996-2014 and 1987-2014 for breast milk.

Data for water sampling are available only from research publications as no regional scale monitoring takes place as of yet and they represent a baseline relative to 2007. Data from pilot study in water collected through the MONET network were not yet available at the time of finalizing this report.

Data from other matrices such as blood or other matrices (biota, sediments and soil) are produced only occasionally, they represent rather a local situation. In addition, these additional matrices do not cover many of the POPs listed under the Stockholm Convention.

It can be concluded that POPs GMP data availability and comparability in the CEE region increased since the first GMP phase. Strategic partnerships for air monitoring were expanded and significantly contributed to the establishment of monitoring stations in many countries of the CEE region. Air data are available for 21 chemicals and in some cases statistically significant decreasing trends were detected in parts of the region.

Human tissues data are available only through the WHO and UNEP/WHO surveys, with certain information gaps identified for South European and Central Asian part of the region. So far data on the newly listed POPs are limited. Information related to POP levels in human blood and in water is available neither through regional nor through national programmes

Monitoring activities related to other media exist in some countries in the CEE region. These include soil, sediments and biota (fish). However, the information from other media does not describe regional situation but provide information relevant locally/at a country level.

The CEE ROG decided not to use information generated from these activities further in this report as the sources are too variable, measurement is episodic and the information generated reflects rather a national or local situation then a regional perspective.

6.1. Summary of the baseline concentrations

POPs GMP data availability and comparability in the CEE region increased since the first phase.

Air

Baseline concentrations for legacy POPs were available from passive sampling of the air for two pesticides (chlordane, DDT), and two industrial chemicals (HCB and PCBs) in the first GMP phase. In addition, all three isomers of hexachlorocyclohexanes and pentachlorobenzene had their baseline established prior 2008, too.

It can also be underlined that the unique set of ambient air POPs concentrations data, generated through integrated monitoring based on active air sampling at the Košetice sampling site over a period of more than 20 years represents the Central European background, and the MONET networks, based on passive air sampling, provide a comprehensive set of data since 2006 to date and significantly contributed to identification of trends.

Furthermore, the current report established baseline for 14 additional chemicals listed below:

dieldrin, dioxins and furans (PCDDs/PCDFs), endosulfan, PBDEs, and PFOS;

In addition, the levels observed for aldrin, endrin, heptachlor, mirex, and chlordecone in the CEE region are predominantly below level of quantification.

No data were identified for toxaphene and hexabromobiphenyl in the region. And finally, hexabromocyclododekane levels are yet to be determined in samples collected since 2013 that are still in the pipeline to be analyzed. It is expected that the next report will contain this information.

Breast Milk

Baseline concentrations are available for the following 15 Stockholm Convention listed chemicals (both legacy POPs and new POPs) since the first GMP report : chlordane, DDT, dieldrin, dioxins and furans, endosulfan, endrin, heptachlor, hexachlorobenzene, PBDEs, PCBs, toxaphene.

The current report established baseline for eight additional chemicals listed below:

Aldrin levels in all participating countries were lower than 0,5 ng/g lipid weight (fat). Mirex levels in all participating countries were lower than 0,5 ng/g lipid weight (fat). Hexachlorocyclohexanes (alpha, beta and gamma) - their levels vary in the region 0,5-3 ng/g lipid weight (fat) for alpha-HCH; 5-470 ng/g lipid weight (fat) for beta HCH, and 0,3-12,4 ng/g lipid weight (fat) for gamma-HCH.

Hexabromobiphenyl levels in all participating countries were lower than 0,5 ng/g lipid weight (fat).

Pentachlorobenzene levels in all participating countries were lower than 0,55 ng/g lipid weight (fat).

PFOS levels were determined in three countries so far, the levels range between HBCDD levels vary in the region, they range from 0,25 to 2.9 ng/g lipid weight (fat) for alpha HBCDD, and 0.05-0.2 ng/g lipid weight (fat) for beta and gamma isomers. Chordecone - no data were identified in the CEE region

Water

In case of monitoring activities in water, PFOS baseline was established in the western part of the CEE region around the Danube River and its tributaries. Levels vary between 1-80 ng/L median on average and this constitutes baseline levels in many cases.

6.2. Summary of evidence of temporal trends

Air

Trends in changes of levels over time were identified for a number of chemicals in air by both passive and active sampling. Results indicate decreasing trends in POP concentrations on sufficiently long passive sampling time series (minimum 5 years) for HCB, PCB, DDT, alpha, beta and gamma HCH and PeCB in several sampling sites in some countries the region. Details on the trends are provided in chapter 5.

Data from active sampling of air in Košetice also confirmed decreasing trend for HCB, sum 6 PCB, DDT, alpha HCH and PeCB. On the other hand, time series collected for beta and gamma HCH by passive sampling in Košetice, Czech Republic did not provide a statistically significant trend.

Trends for other new POPs except HCHs are not confirmed as existing time series are not sufficiently long to observe statistically significant trends.

Breast Milk

No statistically significant trends are identified for milk data due to limited availability of data (insufficient participation of CEE Parties in surveys) in the region and limited length

(time points) in these time series. In addition, the modus operandi of the UNEP/WHO surveys - two rounds in six years - also do not significantly increase the amount of points in the time series from the GMP phase one. Moreover, participation of countries change so despite increased efforts, statistically significant trends are not yet quantifiable in the region as the time series are too short. Maximum availability of data is for PCDD and PCDF (4 rounds)

Other media

No trends are available for the CEE region for water and other media, where no regular monitoring is conducted.

6.3. Summary of evidence of long-range transport

Model assessment of transboundary transport within the EMEP region was carried out for 1990 and 2012 to evaluate changes in transboundary fluxes between the EMEP countries and contributions of different sources. Model simulations indicate decrease in total emissions, changes in relative proportion of contributions to transboundary fluxes from anthropogenic emission sources to non-EMEP emissions as well as to a more significant secondary emission sources (re-volatilization from the environmental media).

The report holds that levels and emissions of all studied POPs have decreased significantly between 1990 and 2012 (i.e. HCB by 90%, PCBs by up to 80%, PCDD/Fs by 40-75%). Decrease in emissions is usually attributed to significant national reductions of emissions (in some countries) as well as to a decrease in anthropogenic EMEP emissions.

6.4. Summary of gaps in data coverage and the resources needed to overcome the gaps or establish/strengthen the capacity within the region

The sampling window for the first monitoring report aiming at establishment of the initial baseline was set to 1998-2008, in line with Global Monitoring Plan Guidance Document. The second monitoring report therefore builds on this information from the first regional report and adds more recent data.

In some cases information relevant for 2014 was also made available, however majority of air samples collected in 2013 and 2014 are still processed in laboratories and will only become available at a later stage in many cases.

Some parts of the CEE region are relatively well monitored through existing air monitoring networks pertaining to international monitoring programmes EMEP, GAPS and MONET, in particular western part of the CEE region. The above monitoring activities currently cover 21 countries out of 28 that are followed in this GMP region (no information is available for Albania, Azerbaijan, Bosnia and Herzegovina, Georgia, Tajikistan, Turkmenistan, and Uzbekistan). The monitoring combines active and passive sampling and despite the fact that the longest time series are available for chlorinated POPs, more recent information on one site (Košetice, 2011-2013) is available for 97 parameters related to 19 POPs listed in the Stockholm Convention.

Central Asian countries have a limited availability of information that only covers several organochlorine POPs (alpha-,beta-,gamma-HCH, HCB, PCB, and DDT). These activities would require support in the future to ensure continuity of POPs data collection in that sub-region. The information available covers at present years 2008-2010.

Finally, for a large part of the CEE region covering in particular the Russian Federation no information is available with the exception of Valkarkai polar AMAP sampling site (latitude: 70.08, longitude 170.9) operated by Environment Canada in the far east. This gap represents European part of the Russian Federation from latitude 55.1 to further north and whole remaining part of the territory of the Russian Federation located to the east from Ural Mountains. The latest information available covers air monitoring in 2009.

Data availability for human tissues is even more limited. Information generated through WHO and UNEP/WHO surveys covers only 14 countries out of 28 in the CEE region and only half of these countries participated in the surveys more than once. It is impossible to establish trends on the basis of available data and time series are barely available. Support in participation of CEE countries in the milk surveys need to strengthen significantly.

Data on water are scarce and episodic in nature. At present, there is no regional scale program for monitoring PFOS in water except surveys (research projects) undertaken by the European Commission (JRC). Nevertheless, this activity only covers western part of the CEE region and the Southern, Central Asian and Caucasus countries are not involved.

6.5. Summary of ongoing programs/activities

Data availability – sampling frequency for air data in the CEE region is provided in detail in chapter 4. In general, air data are generated through international programmes by both passive and active sampling of ambient air – MONET, GAPS and EMEP - that allow harmonized approach, enhance data comparison and provide a online data storage with public access to data visualization.

Information used in this report data generated by passive sampling ranges from 2004 onwards on several sites (Czech Republic, Poland and Serbia) and the most recent information is available also for 2014.

Some data generated by active sampling exist in time series over 30 years long, though this is only available for a limited range of compounds alpha-,beta-,gamma-HCH, HCB, PCB, and DDT. The three decades monitoring period is valid for Košetice EMEP observatory, Czech Republic only, however data used in this report for Košetice observatory span over 1996-2013. Other data generated by active sampling are available are from three sites: Leova II, Republic of Moldova (EMEP 2009-2010), Valkarkai station, Russian Federation operated by AMAP, supported by Environment Canada (2008-2009), and Borovoe, Kazakhstan (EMEP, 2009-2010).

Generation of information for human matrices (breast milk) occurs through the global WHO or UNEP/WHO human milk surveys. First data available for CEE region relate to studies on PCBs and dioxins and furans in 1987-1989 and 1992-1993. A global survey between 2001-2003 comprised twelve POPs initially listed in the Stockholm Convention. Two additional UNEP/WHO global surveys (round 4 and 5) were conducted in 2005-2007 and 2008-2012. The coverage for round 5 study (2008-2012) was extended to all POP parameters including new POPs, however information available for CEE region does not include chlordecone and fluorinated compounds. On the other hand, some information is provided for POPs whose levels in air are so far unknown for the CEE region, such as toxaphene, hexabromobiphenyl (HBB) and hexabromocyclododekane (HBCDD). In addition, second phase of the UNEP/WHO global study was initiated in 2013 and data collection will finish in 2014, but analyses will be made available later than due date of this second monitoring report. In conclusion, data is available, but the range and regional coverage is limited (50% of countries

participate) and no information is available for South European countries and a very limited information is available for Central Asia and Caucasus countries.

6.6. Comment on the adequacy of monitoring arrangements for the purpose of effectiveness evaluation

POPs GMP data availability and comparability in the CEE region increased since the first phase. EMEP and RECETOX strategic partnerships for air monitoring were expanded and significantly contributed to the establishment of monitoring stations in other countries of the region. The unique set of ambient air POPs concentrations data, generated through integrated monitoring based on active air sampling over a period of more than 20 years represents the Central European background, and the MONET networks, based on passive air sampling, provide a comprehensive set of data since 2006.

The newly developed electronic GMP Data Warehouse, which was used to support regional data storage, analyses, and presentation, was helpful in preparation of the regional monitoring report and should be used also in further campaigns.

Current monitoring arrangements – using international programmes and combining active and passive sampling of ambient air - are adequate with the limited availability of air data for large part of the Russian Federation, though this information may be available from other sources/national monitoring and could be made accessible at a later stage.

6.7. Recommendations for the future

The newly developed electronic GMP Data Warehouse, which was used to support regional data storage, analyses, and presentation, was helpful in preparation of the regional monitoring report and should be used also in further campaigns.

The experts and members of the CEE ROG propose the following list as priority issues for the next GMP phase in the CEE region:

- Include two other countries to the CEE GMP regional report from 3rd data collection campaign Cyprus (UN region Asia) and Turkey (UN region WEOG) as it is pertinent to consider regional levels and long-range transport in the CEE together with those two Parties. Both Cyprus and Turkey are also Parties to the CLRTAP and Turkey is taking steps to ratify also the POPs protocol to the CLRTAP.
- Establish closer contacts with relevant institutions in the Russian Federation and consider their involvement in the ROG.
- Increase availability of data in relation to human exposure POP levels in breast milk and provide support to participation of South European countries + ECCA (Caucasus and Central Asian countries) countries in next rounds of UNEP/WHO surveys.
- Ensure availability of human exposure data from general population in the CEE region for reference purposes, as some of undertaken human biomonitoring activities focused only on highly exposed populations and existing information on concentrations of POPs in the region may not be fully accurate.
- Monitoring data on occurrence of dioxins and furans and brominated and fluorinated chemicals are scarce, in particular due to lacking analytical equipment in non-EU part of the region and du to high costs of analyses. Nevertheless, capacity to analyze these chemicals exists in the region, in the RECETOX who has state of the art facility and instrumentation as well as trained personnel; however, this capacity needs to be enhanced in the region.

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8 ANNEX

This annex contains overview of levels observed for HCB, PBs (sum six indicator PCBs), PCB118, sum 3 p,p DDTs, and of individual isomers of HCHs in ambient air observed in individual countries of the CEE region.

More details are available in the electronic data warehouse (www.pops-gmp.org)