

GLOBAL MONITORING PLAN FOR PERSISTENT ORGANIC POLLUTANTS

UNDER THE STOCKHOLM CONVENTION ARTICLE 16
ON EFFECTIVENESS EVALUATION

2ND REGIONAL MONITORING REPORT WESTERN EUROPE AND OTHERS GROUP (WEOG) REGION 2015

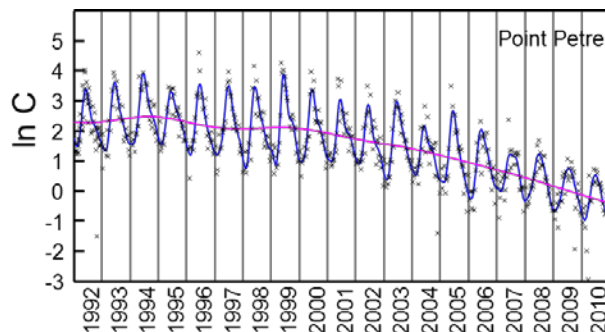
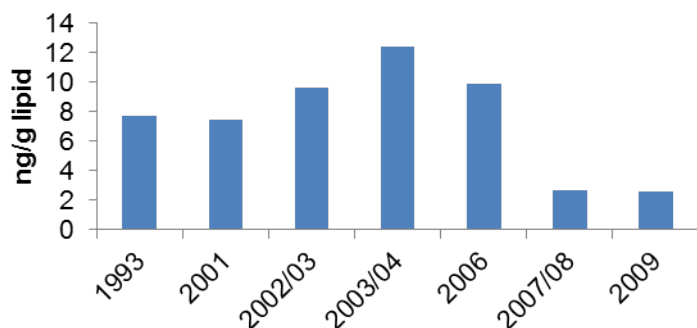
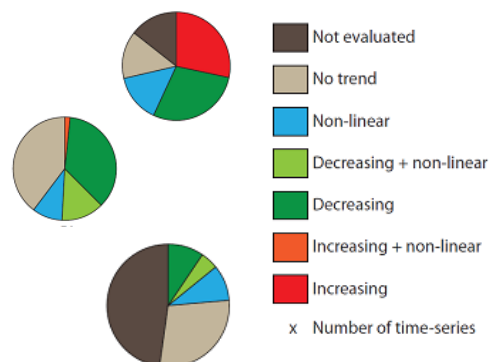


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PREFACE

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 more substances were added to the Convention (chemicals with an asterisk in footnotes 1-3). 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, which has been put in place under the Convention, is a key component of the effectiveness evaluation and provides a harmonized framework to

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), hexabromobiphenyl*, 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)**.

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 of the global monitoring plan and presents the current findings on POPs concentrations in the Western Europe and Others Group (WEOG) Region. While the first monitoring report, presented at the fourth meeting of the Conference of the Parties, 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 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.

ABBREVIATIONS AND ACRONYMS

ACP	Arctic Contamination Potential
ADI	Acceptable Daily Intake
AFN	Assembly of First Nations
AGAM	Australian Pilot Monitoring Programme
ALRT	Atmospheric Long Range Transport
AMAP	Arctic Monitoring and Assessment Programme
ANCOVA	Analysis of Covariance
ANOVA	Analysis of Variance
APEs	Alkylphenol Ethoxylates
BCF	Bioconcentration Factor
BFR	Brominated Flame Retardants
BHC	Benzenhexachloride
BPH	Benzo(a)pyrene oxidation
CBz	Chlorobenzenes
CCC	Chemical Coordinating Centre
CCEHIP	Coordinating Center for Environmental Health and Injury Prevention
CDC	Centers for Disease Control and prevention
CEE	Central and Eastern Europe
CEMP	Coordinated Environmental Monitoring Programme
CEP	Caspian Environment Programme
CHL	Chlordane-related Compounds
CHMS	Canadian Health Measures Survey
CLRTAP	Convention on Long Range Transboundary Air Pollution
CRM	Certified Reference Material
CIS	Commonwealth of Independent States
COP	Conference of the Parties
CTD	Characteristic Travel Distance
CUPs	Current Use Pesticides
CV	Coefficient of Variation
DDD /DDE	Metabolites of DDT
DDT	Dichlorodiphenyltrichloroethane
DLPCBs	Dioxin-like PCBs
EAC	Ecological Assessment Criteria
ECA	Environmental Contamination in Antarctica
ECF	Electrochemical Fluorination
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
EPA	(US) Environmental Protection Agency
EPER	European Pollutant Emission Register
ERL	Effects Range Low
ERM	Effects Range Median

EROD	7-ethoxyresorufin-O-deethylase
ESB	Environmental Specimen Bank
EtFOSA	Ethyl Perfluorooctane Sulfonamide (sulfluramid)
EtFOSE	Ethyl Perfluorooctane Sulfonamidoethanol
EUSES	European Union System for the Evaluation of Substances
FAO	Food and Agriculture Organisation of the United Nations
FERTIMEX	Fertilizantes Mexicanos, S.A.
FNBI	First Nations Biomonitoring Initiative
FOSA	Perfluoro-octanesulfonamide
FOSE	Perfluorooctane Sulfonamidoethanol
FTOH	Fluorotelmer Alcohol
GAPS	Global Atmospheric Passive Sampling Survey
GAW	Global Atmospheric Watch
GEF	Global Environment Facility
GEMS	Global Environment Monitoring System
GerES	German Environmental Survey
GEOS	Global Earth Observation Systems
GLBTS	Great Lakes Bi-national Toxics Strategy
GLWQA	Great Lakes Water Quality Agreement
GMP	Global Monitoring Plan
HBB	Hexabromobiphenyl
HBCD	Hexabromocyclododecane
HCB	Hexachlorobenzene
HELCOM	Helsinki Commission/The Baltic Marine Environment Protection Commission
HCHs	Hexachlorocyclohexanes
HHAG	Human Health Assessment Group
HIPS	High Impact Polystyrene
HPLC	High Performance Liquid Chromatography
HRGC	High Resolution Gas Chromatography (capillary column)
HRMS	High Resolution Mass Spectrometer
HTAP	Hemispheric Transport of Air Pollutants
HxBB	Hexabromobiphenyl
IADN	Integrated Atmospheric Deposition Network
IARC	International Agency for Research on Cancer
ICES	International Council for the Exploration of the Sea
IFCS	Intergovernmental Forum on Chemical Safety
ILS	Interlaboratory Studies
IMO	International Maritime Organisation
INSPQ	Centre de Toxicologie du Québec
INFOCAP	Information Exchange Network on Capacity Building for the Sound Management of Chemicals
IPCC	Intergovernmental Panel on Climate Change
IPPC	Integrated Pollution Prevention and Control
I-TEQ	International Toxicity Equivalence
JGOFS	Joint Global Ocean Flux Study

KAW	Air/Water Partition Coefficient
KOA	Octanol/Air Partition Coefficient
Kow	Octanol/Water Partition Coefficient
LC50	Median Lethal Concentration
LC-MS/MS	Liquid Chromatography-tandem Mass Spectrometry
LD50	Median Lethal Dose
LOAEL	Lowest Observable Adverse Effect Level
LOD	Limit of Detection
LOQ	Limit of Quantification
LRT	Long Range Transport
LRTAP	Long Range Transboundary Air Pollution
LRTP	Long Range Transport Potential
MAP	Mediterranean Action Plan
MDL	Minimum Detectable Level
MEDPOL	Mediterranean Pollution Monitoring and Research Programme
MEA	Multi Lateral Environmental Agreements
MeFOSA	Methyl perfluorooctane sulfonamide
MeFOSE	Methyl perfluorooctane sulfonamidoethanol
MONARPOP	Monitoring Network in the Alpine Region for Persistent and other Organic Pollutants
MORS	Monitoring Of Radioactive Substances
MRL	Maximum Residue Limit
MSCE-East	Meteorological Synthesizing Centre-East
MSFD	Marine Strategy Framework Directive
NAFTA	North American Free Trade Agreement
NARAPs	North American Regional Action Plans
NAWQA	National Water-Quality Assessment Program
NCEH	National Center for Environmental Health
NCP	Northern Contaminants Program
ND	Not detected
NDAMN	National Dioxin Air Monitoring Network
NGOs	Non-Governmental Organisations
NHANES	National Health and Nutrition Examination Survey
NHATS	National Human Adipose Tissue Survey
NILU	Norwegian Institute of Air Research
NIS	Newly Independent States
NOAA	National Oceanic and Atmospheric Administration
NOAEL	No Observable Adverse Effect Level
NOEL	No Observable Effect Level
NS&T	National Status and Trends Program
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
PAS	Passive Air Sampler
PBDEs	Polybrominated diphenyl ethers
PBT	Polybutylene Terephthalate
PCBs	Polychlorinated biphenyls
PCDDs	Polychlorinated dibenzo- p-dioxins
PCDFs	Polychlorinated dibenzofurans
PCP	Pentachlorophenol
PeCB	Pentachlorobenzene
PFAA	Perfluoroalkyl acids
PFAS	Perfluoroalkyl sulfonates
PFCA	Perfluoroalkyl Carboxylic Acids
PFSA	Perfluoroalkyl Sulfonic Acids
PFOA	Perfluorooctanoic Acid
PFOS	Perfluorooctane sulfonate
PIC	Prior Informed Consent
PLC	Pollution Load Compilation
PNRA	Polar Chemistry Project of the Italian Research Program in Antarctica
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
QSAR	Quantitative Structure-Activity Relationship
QSPR	Quantitative Structure-Property Relationship
REACH	Registration, Evaluation and Authorisation of Chemicals
RECETOX	Research Centre for Environmental Chemistry and Ecotoxicology
RENAPAP	Regional Network on Pesticide Production in Asia and Pacific
ROGs	Regional Organization Groups for the Global Monitoring Plan
ROPME	Regional Organisation for the Protection of the Marine Environment
ROWA	Regional Organisation of West Asia
SAICM	Strategic Approach to International Chemicals Management
SC	Stockholm Convention
SCAR	Scientific Committee of Antarctic Research
SCCPs	Short-chain chlorinated paraffins
SIP	Sorbent impregnated
SCOR	Scientific Committee of Oceanic Research
SOLAC	State of the Lakes Ecosystem Conferences
SOP	Standard Operating Procedure
SPM	Suspended particulate matter
SPMD	Semi-Permeable Membrane Device
SPREP	South Pacific Regional Environment Programme

SRES	Special Report: Emissions Scenarios
t	Tonnes
TBBPA	Tetrabromobisphenol A
TCDD	Tetrachlorodibenzo- <i>p</i> -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
USGS	U.S. Geological Survey
VOC	Volatile Organic Compound
WEOG	Western Europe and Others Group
WFD	Water Framework Directive
WHB	Western Hudson Bay
WHO	World Health Organisation
WMO	World Meteorological Organization
WWTP	Waste Water Treatment Plants
XAD	Styrene/divinylbenzene-co-polymer Resin

GLOSSARY OF TERMS

Activity	Any programme or other activity or project that generates data or information on the levels of POPs in the environment or in humans that can contribute to the effectiveness evaluation under Article 16 of the Stockholm Convention Core matrices These are the matrices identified by the Conference of the Parties to the Stockholm Convention at its second meeting as core for the first evaluation: A = ambient air; M = (human) mother's milk and / or B = human blood
CTD	The characteristic travel distance– defined as the “half-distance” for a substance present in a mobile phase
Hot spots	An area of high contamination
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	Result below the limit of detection
LOQ	Limit of quantification. Definition: The lowest concentration that can quantitatively be determined is three times higher than LOD.
<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 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 Western Europe and Others Group (WEOG) Region. The second phase of the global monitoring plan focused on the inclusion of the newly listed POPs in ongoing monitoring activities, addressed the need for harmonized data handling and ensured support to the collection, processing, storing and presentation of monitoring data in regions with limited capacity through a global monitoring plan data warehouse. Enhancing the comparability within and across monitoring programmes to evaluate changes in concentrations of POPs over time and their regional and global transport was also an important milestone in the second phase.

0.1 Contributing programs

The data in this report and from the first GMP report comes from a relatively small number of long-term national and international programs. A number of new programs have been implemented in the past several years, which adds to the information on POPs available in the WEOG region.

0.2 Key messages from the data on baseline concentrations and temporal trends

Adequacy of information: Existing and new programs in the WEOG region provide adequate monitoring data for POPs in core and other media, which includes baseline information on many of the new POPs. For many of the new POPs however, temporal trends are not yet established.

Measurements in air: Most older and previously banned POPs are now showing slower rates of decline or slight increases in some isolated cases, as secondary sources and effects of climate change and warming become increasingly important. Time trends for many of the new POPs are not yet established although baseline data has become available.

Measurements in human media: Levels of older POPs continue to decline and in some cases are no longer detected in human tissues. Time trends for PFOS are also declining in response to regulation and PBDEs are declining in some countries but not in others (e.g. Australia). Due to many factors that contribute to human burdens of POPs,

comparability of data and development of temporal trends relies on individual programs. It is important that these programs maintain internal consistency.

Measurements of PFOS in water: Measurements of PFOS levels in water (rivers, lakes, estuaries and oceans) in the WEOG region are abundant, especially in western Europe, the North Sea and in the North Atlantic and Canadian Archipelago. Information is much more limited for North America and Australia and no information was found for New Zealand. However, information on temporal trends is limited. It is suggested that the measurement of PFOS precursor compounds (e.g. FOSA, MeFOSA, EtFOSA, MeFOSE and EtFOSE) is very helpful in understanding PFOS concentrations and these are not currently well represented in the literature or in monitoring programmes.

Measurements in Other Media: There is a wealth of information on POPs levels and temporal trends in other media across the WEOG region, reported under a variety of international programs, *inter alia*, AMAP, HELCOM, OSPAR, MEDPOL. A few regions and species are well studied for most POPs. For other regions and newly listed POPs the information is sparse.

Challenges with new POPs: The growing number of listed POPs and candidate substances presents a resource pressure for existing monitoring programs. The emission and environmental fate and partitioning of new POPs differs from their legacy counterparts. This presents challenges for assessing the transport and fate of these chemicals.

In response to the growing future demand for information on POPs and new POPs it is important that data and samples be maintained in a coordinated and sustainable way and that programs operate efficiently and collaboratively to address these challenges.

0.3 Long range transport

Integrated assessment of POPs emissions, transport in the environment, and levels and trends observed at monitoring stations is the most effective way to quantify the extent of long range transport of POPs and forecast the effectiveness of emission reductions. A variety of modeling tools and approaches are available for this purpose, and experience with modeling existing POPs has beneficial synergies with identification and risk profiling of candidate POPs. Climate variability and climate change impact the emissions and cycling of POPs in the environment, however the influence of climate

change on levels and trends of POPs in the global environment on the time-scale of decades is likely to be much smaller than the influence of policies that would reduce emissions.

0.4 Description of data gaps and capacity building needs

Although baseline information for most POPs is adequate, temporal trends are not yet established for some of the newer POPs in the core media. It is important that monitoring programs are maintained and continue to establish analytical methods and time series for the newer POPs and to develop strategic partnerships with other expert labs/programs to deal with the increased demands and complexities of sample analysis for the newer POPs.

0.5 Future evaluations

As times series for newer POPs are developed within existing programmes, future evaluations will provide temporal trend information to inform on the effectiveness of the Convention. More broadly, monitoring programs should continue to identify and target priority POP-like chemicals as this information is useful to the evaluation and assessment of candidate POPs e.g. the work of the POP Review Committee. Efforts should continue to be made to integrate monitoring programs and activities across regions for future reporting of comparable data under the GMP. Areas for cooperation include *inter alia*, continued monitoring across the Arctic region (e.g. AMAP), WHO human milk surveys, measurement of PFOS in global oceans, and regional and global-scale passive air monitoring (e.g. GAPS, MONET).

0.6 Conclusions and recommendations

0.6.1 Media specific conclusions and recommendations

Air: Passive air samplers should continue to be implemented as a cost-effective approach for improving spatial information for POPs in air and their performance for measuring particle-associated POPs should be further assessed. To increase the usefulness of the data collected on concentrations in air for POPs beyond the GMP, it is suggested that strategies for linking concentration information for air with toxicity should be explored and developed. This could include consideration of mixture effects. In vitro methods are now available with the required sensitivity to be applied to air sample extracts. Such toxicity studies address the broader goals of the Convention and contribute to the Effectiveness Evaluation in assessing the efficacy of actions towards the protection of human health and the environment from POPs.

As many new POPs are associated with commercial chemicals and are used in consumer and household items and construction material, important release and exposure pathways involve the indoor and urban environments, and emissions from waste disposal and treatment facilities. Accordingly, monitoring and research programs that are aiming to understand current exposure levels and emissions to the broader environment should include indoor and urban studies as well as studies targeting the emissions from the waste sector. Indoor air surveys with linkages to human exposure should be investigated to assess risks. This information will also be useful for interpreting levels in human tissue reported under the GMP.

Human media: Human monitoring programs should be implemented in countries and sub-regions where they are lacking as human exposure to POPs is not homogeneous across the region. Existing programs including pilot programmes should be maintained and should continue to target new POPs in representative samples of the population so that temporal trends can be developed.

Water: For studying the global distribution of PFOS in oceans, collaborative monitoring programs along key cruise transects sites should be encouraged.

For developing temporal trends of PFOS in water, systematic studies are needed at a few key sites based on past measurements. Studies in rivers are considered to be best suited for trend studies as rivers are expected to respond relatively quickly to reductions in emissions whereas ocean water is subject to a substantial time-lag.

Information on the sources, emissions and environmental levels of PFOS precursor compounds is key to understanding PFOS concentrations and temporal trends in water and hence complementary work on this would be beneficial to understanding the levels reported under the GMP.

Other Media: Efforts should be made to make use of the vast body of information that is available for POPs in other media, in collaboration with modelers, to develop a better understanding of the fate of POPs in the multi-media environment.

0.6.2 Generic conclusions and recommendations

Challenges with new POPs: In order to improve the performance of fate models, studies of partitioning to particles and particle-associated transport and fate are needed for high molecular weight POPs and polar / ionizable chemicals (e.g. PFOS) that exist in air primarily on the particle-phase. This will improve understanding of regional and global transport of particle-associated POPs and help to interpret temporal trend information from monitoring programmes that contribute to the GMP.

Emissions of newer POPs include a wide range of indoor sources associated with commercial products, where human exposure can be a significant concern. Emissions from the waste sector are also relevant for the newer POPs. Monitoring and research studies should include assessment of these sources and attempt to link emissions of these chemicals to human and environmental burdens. This knowledge will be beneficial for understanding human monitoring data for POPs reported in the GMP.

Efficiencies for Monitoring Programs: In order to deal with analysis pressures for new POPs, monitoring programs may need to adjust their protocols and resources to better align with new priorities. Possible strategies include reduced analysis frequency for legacy POPs (e.g. PCBs, organochlorine pesticides), optimized analytical methods, and partnerships among laboratories to address specialized analytical needs. It is not necessary for every laboratory to be an expert for every class of POPs.

Sample Archiving / Sample Banks: Long term monitoring programs should invest resources to ensure the integrity and sustainability of sample banks as they are useful for conducting retrospective analysis on current and future POPs, and for screening studies on candidate POPs.

Data archiving and accessibility: Databases play an important role in identifying, documenting and making accessible reliable and comparable data sets on POPs. These data are needed for assessing environmental levels and trends for POPs and for combining with emission estimates and model in integrated assessments of sources, fate and transport of POPs. Effort should be invested to make databases easily accessible (e.g. data downloadable) and in to integrate / link databases. Further development of simple visualization tools such as those implemented under the GMP database is useful.

The ROG wishes to emphasize that the information reviewed to provide a baseline and to inform the COP of current trends in the WEOG region is mainly available from only a relatively small number of existing international programs. An important element of their long-term viability is the continued efficacy of the contributing national programs on which they often depend. The ability to compare POPs levels over time within these national and international programs therefore makes their long-term viability of utmost importance for future trends analysis.

Finally, on the 10 year anniversary of the Stockholm Convention (SC) coming into force, the following general statements can be made regarding its effectiveness and the GMP. First, the GMP has shown that primary sources of old POPs have been substantially reduced and current low levels can be attributed to effectiveness of regulations (mostly implemented prior to the SC and integrated into it). Secondly, the SC and the GMP have raised awareness of POPs and POP-like chemicals and provide a framework for collaboration and integration at the national, regional and global scales.

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 Western Europe and Others Group (WEOG) Region. 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.

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.

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.

Long term viability of existing monitoring programmes (air and human bio-monitoring) is essential to ensure that changes in concentrations over time can be investigated. National air monitoring activities having contributed data to the first monitoring reports continued during the second phase, and new programmes have been identified to support the development of the second reports. Likewise, the continued operation of global and regional air monitoring programmes was a major pillar in the second phase. For the new monitoring activities, collaboration with strategic partners has ensured cost-effective

generation of data and use of harmonized protocols for POPs monitoring. The implementation of the second phase of the UNEP/WHO human milk survey is another important pillar of the global monitoring plan, providing useful long-term results showing how human exposure to POPs changed over time as measures are implemented to enforce the Convention.

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 have been and continue to be 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.

Considering the global dimension of the monitoring plan under the Stockholm Convention, air, and human milk and/or blood have been established as core matrices as they provide information on the sources of POPs, environmental transport and the levels of exposure in human populations. The listing of new POPs in the Convention brought additional challenges in the implementation of the global monitoring plan. Perfluorooctane sulfonic acid (PFOS) and its salts do not follow the “classical” pattern of partitioning into fatty tissues, but instead bind preferentially to proteins in the plasma and are hydrophilic. Water has thus been added to the list of core matrices for these particular substances. This report also provides first results as to the concentrations of such chemicals in water.

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 supports data collection and assists the regional organization groups and the global coordination group in producing the regional and global monitoring reports that contribute to 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.

2 DESCRIPTION OF THE REGION

2.1 Background

The Western European and Others Group (WEOG) is composed of twenty eight nations in Western Europe, North America, and Australasia.

A comprehensive summary of the characteristics of the region can be found in the reports of the 2002. UNEP/GEF: Regionally Based Assessment of Persistent Toxic Substances (PTS). This study used a different division of regions as was adopted by the conference of the Parties to the Stockholm Convention (COP) for the purposes of effectiveness evaluation. Therefore, the WEOG countries can be found in six different volumes of the PTS study. These are volumes on: the Arctic; North America; Europe; the Mediterranean; South East Asia and South Pacific; and, the Antarctic. These reports are recommended for providing a synthesis of geographical, physical, and biological characterization of these areas, as it relates to the sources and fates of POPs released to the environment. They provided the basis for the following brief political, geographical, and social and economic overview.

2.2 Political

Specific membership is as follows: Australasia- Australia; and, New Zealand.

North America - Canada; and, United States. Western Europe - Andorra; Austria; Belgium; Denmark; Finland; France; Germany; Greece; Iceland; Italy; Liechtenstein; Luxembourg; Malta; Monaco; Netherlands; Norway; Portugal; Republic of Ireland; San Marino; Spain; Sweden; Switzerland; Turkey; and, United Kingdom.

2.3 Geographical

The region is not a coherent geographical unit. Its membership is divided into three continents, and two hemispheres. However, Canada and the United States collectively occupy similar latitudinal zones as those occupied by Western Europe while Australia and New Zealand occupy generally the similar corresponding latitudes in the southern hemisphere.

The climate in Australia is mainly arid or semi arid. It is temperate in the south and tropical in the north. New Zealand is temperate with some regional contrasts.

In North America, climatic variation is large extending from the Arctic in the north to a sub-tropical climate in the south. Within this pattern there is much variation. For example, within the Arctic, there is considerable moderating maritime influence on the coastal strip of Alaska but intense cold in the central and high eastern Canadian sectors.

Western Europe includes four climatic zones – A sector of the circumpolar Arctic in the north, alpine climate in the main mountain ranges such as the Alps and Pyrenees, a temperate zone in the central area and the Mediterranean zone to the south. The latter is generally characterised by mild wet winters and hot dry summers with more than 90% of annual precipitation falling in winter. Superimposed on this pattern is the moderating and wet influence of the Atlantic to the west, with drier and more extreme temperature ranges to the east.

2.4 Social and economic considerations

Australasia: Australia and New Zealand are developed countries with mixed economies and substantial agricultural sectors. Available information suggests that environmental levels and human exposure to POPs in both countries has always been low in relation to most regions elsewhere. Regulations are well established concerning the environmental release of the original twelve POPs.

North America: The USA and Canada are developed, industrialised countries. Of particular interest in terms of historical and potential source characterization is the Great Lakes Basin. It covers an area of approximately 774,000 square kilometers including much of Ontario, and the eight Great Lakes States: Illinois, Indiana, Michigan, Minnesota, New York, Ohio, Pennsylvania and Wisconsin. The Great Lakes basin is home to a total of about 33 million people, more than one-tenth of the population of the United States and one-quarter of the population of Canada. It is also a focus of both the U.S. and Canadian industrial capacity, while agriculture in Ontario and Quebec accounts for the largest single use of Canadian land in the basin, contributing about 40 percent of the value of agricultural output in the Canadian economy. Nearly 7 percent of the American agricultural production is located in the basin. The emissions and environmental fate of POPs in the Great Lakes and St Lawrence basins have been extensively studied and have provided much of the information for North America in the present report. Comprehensive regulations are well established concerning the environmental release of POPs.

Western Europe: In Western Europe the chemical industry, metal production and processing and agriculture are all significant parts of the economy. There is a range from highly industrialised economies to other countries with greater reliance on agriculture and / or a more developing economic structure.

Generally in Western Europe there is considerable information relating to industrial point source emissions to the atmosphere. Sources to air of well studied compounds such as PCBs and PCDDs/Fs are generally well characterised and inventories have been calculated and updated regularly via EMEP. A number of European countries such as the UK, and Germany also have a long industrial history, involving combustion activity in the form of wood and coal burning. The smelting of metals, cement kilns, and the production of iron and steel also have a long history in Europe, activities known to produce significant PCDDs/Fs emissions.

Most of the Western Europe region is today part of the European Union and, comprehensive regulations concerning the environmental release of POPs are well established with progressive development of harmonized regulation.

The Arctic: North America and Western Europe collectively include a large segment of the Arctic. This area is of particular interest in terms of the fate of POPs in the environment because it is lightly populated and with a generally low intensity of industrialization. However historical uses of POPs have occurred in the Arctic and waste disposal is continuing. The eight Arctic countries that are members of the Arctic Council contribute monitoring information on POPs to the Arctic Monitoring and Assessment Programme (AMAP) which produces extensive periodic assessment reports.

The Antarctic: The Antarctic is not defined by national boundaries. Because a number of WEOG region countries are parties to the Antarctic Treaty and are maintaining research activities in the area, the Antarctic has been given brief attention in this report (see section 4). The Antarctic is completely surrounded by ocean and is largely snow and ice covered. It is therefore remote from any significant primary source of the POPs listed in the Convention.

2.5 Considerations in relation to sampling strategies

The WEOG ROG report is based mainly upon existing programmes. Although it is difficult to provide a good categorization, the following illustrates the range of objectives observed from the programmes contributing to the WEOG report:

- ❖ Studies aimed to investigate levels and / or processes in areas close to historical local sources of POPs (e.g. HELCOM and studies in the Great Lakes region of North America such as IADN).
- ❖ Studies aimed to investigate levels and / or processes in areas distant from local sources of POPs where long-range transport and other processes are believed to be important in determining environmental levels and / or human exposure (e.g. AMAP; ARCRISK, MONARPOP; and NCP)
- ❖ Studies aimed at understanding regional and / or global transport (e.g., ARCRISK, EMEP and GAPS)
- ❖ Studies aimed at providing a wide survey of levels (e.g., WHO coordinated human milk surveys; NHANES)

It is important to be aware of the historical objectives of the different programmes that have been the source of information used by the ROG. This information is contained in the programme summaries that are provided in Annex 1 and 2 of this report.

3 ORGANIZATION OF REGIONAL IMPLEMENTATION

The WEOG regional Organizational Group (ROG) for the second evaluation was composed of six experts from each of the following countries: Australia; Spain; Canada; Sweden; Norway; and, Portugal.

3.1 Organization of activities

The ROG met exclusively by tele-conference calls supplemented by internet communication. A record of each meeting was kept which documented key decisions and work responsibilities until the next meeting when progress would be reviewed. Fourteen such teleconferences were held before the draft report was sent to the WEOG focal points for their review. The chair rotated with each meeting. Early decisions were taken upon general responsibilities for coordination and drafting of the regional report (see acknowledgements section). A critical path was developed of work to be performed in sequence leading up to the finalization of the report and which included the elements detailed below. In general, this plan was followed throughout the data gathering and drafting process.

3.2 Strategy to locate and collect information from existing programmes

At its initial meetings, the ROG reviewed information from programmes that contributed to the first WEOG region report. These programs were initially identified based upon survey responses obtained by the Secretariat. The basis of the selection was the application of the criteria contained in the “Implementation Plan for the First Evaluation Reports”. For this 2nd WEOG region report, new programs were included if they also met these criteria.

Programmes were contacted and invited to provide “programme summaries” according to a template developed by the ROG. In a few cases, the programme summaries were provided by ROG members, or by arrangements established by ROG members. This usually occurred when a single organization is host to the data bases for several programmes as is the case of the Norwegian Institute of Air Research (NILU) with the air information of both EMEP and AMAP. In cases where updated programmes information was available in reports or on-line, chapter leads summarized the most relevant information in their chapters.

Water was included for the first time in the WEOG report as a second tier core medium for PFOS. Information was compiled by a WEOG expert based on a literature review of published papers and reports.

The drafting of the WEOG region report benefitted from recent efforts under AMAP to assess temporal trends for POPs in Arctic datasets. The AMAP assessment contributed directly to the air, human and other media chapters and is also included in the Annex 5 to this report.

3.3 Identified data gaps and strategies to fill them, including strategies and activities to generate monitoring data

Following the compilation of the first WEOG region report, the ROG concluded that information from existing programmes in the WEOG region provides an adequate overview of the status of POPs in the core media for the first evaluation and therefore decided not to attempt to initiate any new monitoring activities. However, some new activities were implemented by some countries to further enhance data coverage across the WEOG region and data from these programmes are included in this report (e.g. The Canadian Health Measures Survey, CHMS).

Although most of the data included in the regional report originates from existing long-term programmes, data from smaller scale programmes and even “snapshot” data were included in some cases to improve geographic resolution and completeness of reporting for POPs. The ROG decided on the strategy to include such data if it otherwise was consistent with the criteria specified in the implementation plan for the first evaluation. Information on PFOS in water originates primarily from these types of data sets.

3.4 Capacity strengthening needs

The first WEOG region report identified the Mediterranean rim as an area where improvements in POPs monitoring were required. This has since improved in the open sea monitoring and northern shores of the Mediterranean Sea (e.g. Castro-Jiménez et al., 2013; and Annex 2 and 4). Capacity building is still needed in the southern rim.

4 METHODS FOR SAMPLING, ANALYSIS AND HANDLING OF DATA

4.1 Background

This 2nd report for the WEOG region builds upon activities and arrangements that contributed baseline information from the WEOG region for the 1st GMP report. At that time and when initiating its activities to obtain monitoring information, the ROG took careful note of two concepts outlined in Article 16 of the Convention. First, it is stated that Parties shall make arrangements to obtain comparable monitoring data. The operational procedure to achieve comparability is the application of the criteria for programme selection outlined in the Implementation Plan for the first evaluation and the measures listed in the “Guidance Document”. Second, Article 16 further states that the arrangements to gather data should be implemented using existing programmes and mechanisms to the extent possible.

As noted in section 3 of this report, the ROG decided that for the first effectiveness evaluation, it would base its review of POPs levels in the region using information derived entirely from existing programmes and activities. These same programs have again contributed to this 2nd report and have been supplemented by newly initiated programmes and information on water for the purpose of reporting for PFOS (see Ch. 5.3). The ROG has not initiated any sampling, analytical, or data handling activities and therefore has nothing to report on such matters. However, the practices to conduct these elements were carefully considered when the ROG reviewed information on existing programmes based upon survey responses obtained by the Secretariat, and selected candidate programmes to provide the basis for the first evaluation report. The selection was performed by application of the above noted criteria which resulted in the identification of more than 16 established international and national programmes to be the main “comparable” information sources for the first evaluation. At least one member of the ROG (according to the expertise of that individual) then carefully examined the sampling, analytical, data quality, and data storage arrangements of each of the programmes. This enabled the ROG to satisfy itself that such arrangements are being maintained and will enable comparable data from the identified programmes to be used by the COP now and in the future to look for changes in POPs levels over time within those programmes.

4.1.1 Key Message regarding “comparable data” from existing programmes and activities

Although the ROG believed that it is practical and realistic to expect intra-programme (internal) comparability, it noted that each of the established programmes has its own procedures for conducting its work, usually including constraints on the use of different analytical laboratories within each programme. It is important to note that very few programmes share the same analytical laboratory with other programmes. Since the use of different analytical laboratories is a major source of variance, the ROG concluded that it would be very difficult to achieve levels of comparability between programmes necessary for effectiveness evaluation. Therefore in preparing this report, the ROG focused on using information from programmes where measures and procedures are expected to provide intra-programme comparability over time for present and future effectiveness evaluations. While this conclusion generally means that there will be very limited direct comparability between programmes and regions, significant exceptions are evident, such as when a programme operating in several regions has maintained a centralized analytical facility servicing all regions, such as with the WHO coordinated human milk programme. The extensive use of such measures as utilization of common analytical laboratories and data centres has demonstrated the possibility of achieving adequate comparability between well established programmes in the WEOG region. An example is the collaborative practices of AMAP, EMEP, OSPAR, and HELCOM.

4.1.2 Availability of information to allow data to be independently evaluated

This report provides the COP with the information requested in a concise fashion but in an easily accessible form. The information is provided in four tiers: They are:

- 1 The short “Executive Summary” and “Chapter 6 Summary” elements of this report which inform the COP of the essential features of the levels and temporal trends of POPs in the region;
- 2 The concise synthesis of information derived from the contributing existing monitoring programmes (Chapter 5 of this report);
- 3 More detailed information on the nature of operation and data used from each of the contributing programmes. These are termed “programme summaries” and are provided in Annex 1 and 2 of the WEOG report. They were chiefly prepared by experts working in the existing contributing programmes; and,
- 4 Ensuring that full details on any aspect of an existing programme can be accessed, usually through direct contact with the management or secretariats of each contributing programme.

Therefore if an individual would like to obtain more information for example on the analytical methodologies, quality assurance and control, data handling, and data availability practices of a contributing programme, that individual has a choice of the degree of detail that can be accessed.

4.2 Description of national and international programmes and activities that have contributed information for the regional report

The following tables (Table 4.2a and Table 4.2b) briefly summarize the nature of each of the main sources of information on environmental levels of the core media (air and human milk / blood) used by the ROG for this report. More details can be found in the programme summaries provided in Annex 1 and 2 including in many cases maps to indicate geographical coverage, while a collective synthesis of the programme results is provided in chapter 5. The ROG found it difficult to develop a summary map of the geographic coverage due in part to the evolving nature of programmes.

4.2.1 Programmes/activities related to air monitoring

Table 4.2a Monitoring programmes which contributed to the assessment of POP temporal trends and levels (23 priority substances) in the WEOG region.

Monitoring program	Abbrev.	Region of interest	Current # of monitoring sites in WEOG	Monitoring period	Monitored compounds (Stockholm conv. POPs)
Arctic Monitoring and Assessment Programme ^a	AMAP	Arctic	5 long-term 2 satellite	1993 - present	HCHs, PCB, chlordanes, DDTs In addition: Alert reports: Dieldrin, Heptachlor, Endrin, Aldrin, HBCD, α - and β -Endosulfan, HCB, PFAS, PBDEs Storhofdi reports: Dieldrin, HCB, PBDEs Zeppelin reports: HBCD, HCB, PFAS Pallas reports: α -Endosulfan, PBDEs Station Nord reports: HCB, Heptachlor, Aldrin, Dieldrin, Endrin, α - and β -Endosulfan, DDTs
Australian Pilot Monitoring Programme - air (Antarctic Air)	AGAM	Antarctica	1	2009-present	PeCB, HCB, Dieldrin, Aldrin, Endrin, Heptachlor, chlordanes, Toxaphene, Endosulfan, Mirex, HCH, DDTs, PCBs, PBDEs
Australian Pilot Monitoring Programme - air (Hazardous Substances in Air)	AGAM	Australia	11	2010-present	PBDEs, PCDDs, PCDFs, PCBs, PFAS, Toxaphene, HBB, Aldrin, chlordanes, HCHs, Dieldrin, Endrin, HCB, Heptachlor, α - and β -Endosulfan, Endosulfan sulfate, Mirex, DDTs, PeCB
Australian Pilot Monitoring Programme - air (Long Term Air Monitoring Network)	AGAM	Australia	44	2011-present	Samples archived, not analysed
European Monitoring and Evaluation Programme	UNECE-EMEP	Europe	7	1993 - present	PCB, DDT, chlordanes, HCB Note that AMAP sites Storhofdi, Zeppelin and Pallas are also EMEP sites. Please see additional analytical compounds above under AMAP.
Global Atmospheric Passive Sampling network	GAPS	Global	23	2004 - present	PCB, chlordanes, HCB

Table 4.2a continued...

Monitoring program	Abbrev.	Region of interest	Current # of monitoring sites in WEOG	Monitoring period	Monitored compounds (Stockholm conv. POPs)
Integrated Atmospheric Deposition Network	IADN	Great Lakes (North America)	5 (master stations); 2 urban and 1 rural satellite stations	1990 - present	Aldrin, Chlordanes, DDTs, Dieldrin, Heptachlor, α - and β - Endosulfan, Endosulfan sulfate, HCHs, PCBs, chlordanes, HCB (US only), PBDEs, HBCD (US sites only), Mirex (Canada only)
Northern Contaminants Program (Canada) ^a	NCP	Arctic	2	1992 - present	HCHs, PCB, chlordanes, DDTs, Dieldrin, Heptachlor, Endrin, Aldrin, HBCD, α - and β - Endosulfan, HCB, PFAS, PBDEs
Norwegian Troll Station	Troll	Antarctica	1	2007-present	PeCB, PCBs, HCHs, DDTs, chlordanes, HCB
Monitoring Network in the Alpine Region for Persistent and other Organic Pollutants	MONARPOP	European Alpine regions	33	2005 - present	PCB, chlordanes, HCB
MONET (EU)	MONET (EU)	Europe	23	2009-present	PCBs, HCHs, DDTs, HCB, PeCB. Analysed but not yet reported: PCDDs/Fs and PBDEs
U.S. EPA's National Dioxin Air Monitoring Network	NDAMN	USA	34	1998 - 2004	PCDD/F, co-planar PCB
UK-Norwegian Transect		UK and Norway	11	1994 - present	PCBs, OCPs, PBDEs
The UK Toxic Organic Micro Pollutants (TOMPs) program	TOMPs	UK	7	1991 - present 1999 - present	PCDD/F, co-planar PCB, PCBs, PBDEs

^a The Northern Contaminants Program (NCP) is the Canadian National Implementation Plan of Arctic Monitoring and Assessment Programme (AMAP). Data from 5 long-term and 2 satellite AMAP stations are presented in the current assessment, within which 1 long-term (Alert, NU Canada) and 1 satellite (Little Fox Lake, YK Canada) stations are operated under NCP. The other satellite AMAP station, Valkarkai, is in Russia. In total 14 atmospheric monitoring programmes contributed results to this assessment.

4.2.2 Programmes/activities related to human tissues (milk and blood)

Table 4.2b Programmes and activities related to human media (human milk and/or blood) that have contributed to the regional report.

Programme	Media	Geographic coverage	Time period	POPs measured
AMAP	Blood	Arctic region	1993 – present	DDT, PCB, toxaphene, mirex, chlordanes, dieldrin, heptachlor, HCB,
CDC/CCEHIP/-NCEH	Blood	United States	1999 - present	All 12 Stockholm Convention POPs
CHMS and FNBI	Blood	Canada	2007 -	Oxychlordanes, transnonachlor, HCH, DDT, PFOS, PBDE
Uppsala	Human Milk	Sweden	1996 - present	DDT, PCB, PCDD/PCDF, HCB, chlordanes,
Stockholm	Human milk	Sweden	1967 - present	DDT, PCB, HCB, chlordanes
WHO	Human Milk	All UNEP regions	1988 - present	PCDD/PCDF, PCB
GerES	Blood and urine	Germany	1985- present	HCB,DDE, and PCB
ESB	Blood	Germany	1984 - present	HCB, PCB 153
Australia “snap shot” surveys (under the Australian pilot monitoring programme)	Blood and mother's milk	Australia	repetitive to date: 2002/03; 2004/05; 2006/07; 2008/09; 2010/11; 2012/13	PCDD/PCDF, PCB,PBDEs, OCPs (HCB, B-HCCH, G-HCCH, oxychlordanes, trans-nonachlor, PP-DDE, OP-DDT, PP-DDT, Mirex), PFAS, HBCD (2012/13 only)
New Zealand “snap shot” surveys	Human milk	New Zealand	Not repetitive	PCDD/PCDF, PCB, HCB, dieldrin, heptachlor epoxide, pp-DDT / pp-DDE

It is important to note that the results from national programmes could either be reported individually (such as the German human media GerES and ESB activities), or “invisibly” through their pre-existing participation in an international programme (such as the Canadian Northern Contaminants Programme, which provides data from the Canadian Arctic to AMAP). When opportunities for the latter approach exist, they were used by the ROG, because it enabled full advantage to be taken of the “comparability” measures maintained by the international programme.

4.2.3 Programmes/activities related to water

Regional monitoring and assessment programmes within the WEOG such as HELCOM, OSPAR, MEDPOL, AMAP, as well as national programmes in Norway, Sweden, Canada, Denmark, the USA, have generally not focused on measurements of PFOS or other PFAS in water. However, early measurements in lake and seawaters were made in Scandinavia under the Nordic Council of Ministers (Kallenborn et al., 2004) and the Joint Research Centre initiated a European wide surveillance of PFAS in the mid-2000s (Loos et al., 2008a). The International Council for Exploration of the Sea (ICES) database includes results for PFOS from the North Sea from 2005 only (ICES 2005). Results were also available for coastal waters of Antarctica from the Australian Pilot Monitoring Programme. The majority of the available data for this assessment is from the peer reviewed scientific literature. These are from both independent university-led studies and from government laboratories that are involved in monitoring and surveillance of contaminants in water.

All results are from near surface waters collected by manual grab sampling using standard protocols of the various regional or national agencies involved (e.g. see Loos et al 2008). In the case of ocean sampling, collections have been either by sampling water from an intake under the ship or by use of oceanographic rosette bottles triggered at specific depths. Most reports were for whole (unfiltered) water samples, however, as some studies did use filtration; this has been noted (see Annex 3, Table 1) and is discussed further in Chapter 6.

Only data for studies published from about 2004 and utilizing high performance liquid chromatography-tandem mass spectrometry (LC-MS/MS) with mass labelled standards were included because this approach has been used by all studies of PFOS in water since the mid-2000s.

All of the available peer reviewed literature and government technical reports on PFOS and related per-fluoro and polyfluoroalkyl substances (PFAS) in water were reviewed, however, reports on municipal waste waters and drinking waters were not considered for this assessment on the grounds that they would be too site-specific. With the focus mainly on background sites, results from samples immediately downstream of wastewater outfalls, or from harbours and urban watersheds were not also included. However, sufficient information on samples from background or “far field” sites was

available to permit assessment of the levels of PFAS in most WEOG countries and in nearby coastal areas, seas and ocean environments.

4.2.4 Programmes/activities related to other media

Following the same logic that was used in the 2009 GMP report the information relating to data concerning POPs monitored in other media is based on a brief overview of the published outcomes from a number of well established long term monitoring programmes (AMAP, NCP, Great Lakes, HELCOM, OSPAR and MEDPOL) and data from Antarctica provided by Australia. The data reported cover legacy POPs: PBDEs, PFOS, endosulfan and HBCD.

These programmes have well established QA/QC procedures and publish regular updates on the results in the regions of interest. The uninterrupted work of these monitoring programmes since the early 1990s has yielded an extraordinary corpus of knowledge concerning the presence and pathways of POPs in the abiotic and biotic environments. To a large extent the collections of consistent monitoring data reported by the programmes and briefly summarized here, have been deposited in recent years in publicly accessible repositories (www.amap.no, www.helcom.fi, and others) opening up and enabling a vast new field of research for environmental scientists in years to come.

The continued existence of these long term programmes and data collections is indispensable to improve accuracy of assessments and the effectiveness of policies. AMAP has contributed to this GMP report an extensive study on trends in POPs monitored in biota (Annex 5).

4.3 Antarctica

New air monitoring information for Antarctica (chapter 5.1) is now available from the Norwegian Antarctic station “Troll” that was established in 2006/07. The station operations are based upon the sampling and analytical protocols established for the ongoing monitoring programme at the “Zeppelin” atmospheric research station (Ny-Ålesund, Svalbard). The first years of data have become available for the WEOG report and continuous POP atmospheric monitoring data for Antarctica will be available for future evaluations for assessing temporal trends and baselines for new POPs. Information was also compiled for PFOS in other media from Antarctica and summarized in Ch. 5.4.

Because human exposure of POPs is primarily derived from diet and all provisions at Antarctic field stations will be imported, human exposure studies would not have value in the context of effectiveness evaluation.

The ROG believes that in future evaluations the engagement of the Antarctic Treaty and the Scientific Committee of Antarctic Research (SCAR) would be very beneficial.

4.4 Data handling and preparation for the regional monitoring report

Most of the measurements on POPs that are available across the WEOG region originate from a small number of existing programs. In many cases these programs have been operating for more than a decade and exercise well established QA/QC protocols for sample collection and analyses. These methods are consistent with the standards outlined in the GMP guidance document. Scientists and researchers involved with these programs are at the forefront of the field and employ what are deemed to be the most appropriate data analysis methods based on the latest scientific expert opinion.

The WEOG ROG has therefore relied on these programme experts for summarizing information on temporal trends on POPs in their respective monitoring programs. Additional details on data analysis and interpretation is provided in the Annexes to this report and/or is referenced to program reports and publications.

Many of the WEOG region programs continue to deliver data to long term databases (e.g. EBAS). These databases are integral for making the monitoring data available to modelers for assessing regional and global transport of POPs, making connections between emissions and environmental burdens, and for exploring climate change and climate variability effects on POPs.

The GMP data warehouse is recognized as a useful tool for archiving GMP data and for comparing data and data availability across different regions. WEOG monitoring programs that are not already contributing data to existing databases have been encouraged to submit data to the GMP warehouse.

4.5 Preparation of the monitoring reports

The ROG drafted its own report, with the assistance of several chapter leads, Hayley Hung, Athanasios Katsoyiannis, Britta Hedlund, Derek Muir, Ramon Guardans, Matthew

Macleod and Tom Harner. The drafting responsibilities were as follows: Executive Summary, and Chapters 1-4 (Tom Harner); Chapter 5 – 5.2.1 Air (Hayley Hung and Athanasios Katsoyiannis); 5.2.2 Human tissue (Kristin Larsson and Britta Hedlund); 5.2.3 Water (Derek Muir); 5.2.4 Other Media (Ramon Guardans); 5.3 Long range transport (Matthew Macleod); and Chapter 6 (Tom Harner). ROG members Sara Broomhall, Rui Mendes and Tor Johannessen provided programme summaries and annexed material and assisted with the review of the report. The WEOG report also benefitted from the contributions from the AMAP trends report for POPs (contained in its entirety in Annex 5). We acknowledge the following lead authors of this report: Air – Hayley Hung, Athanasios A. Katsogiannis, Deguo Kong; Human Tissues – Jay Van Oostdam; Other Media - Frank Rigét, Simon Wilson, Anders Bignert.

5 RESULTS

5.1 The results in context

This 2nd GMP report for the WEOG region builds on measurements reported in the 1st GMP report in 2009. The 2009 report established baseline information for the original POPs in the core media of air and human milk and/or blood. It was concluded that geographic coverage for the WEOG region as presented in the 2009 report was adequate for reporting baselines for most POPs. It was also recognized that some sub-regions would benefit from supplemental monitoring efforts.

For this 2nd GMP report (and for subsequent monitoring reports), the WEOG region continues to rely on the long-term programs for deriving temporal trends for the older POPs and for baseline measurements for some of the newly listed POPs. A few new programs that were implemented in the WEOG region since 2009 are helping to improve spatial resolution for POPs reporting across the region.

In addition to POPs measurements in the original core media, this 2nd GMP report includes information on PFOS in water. This 2nd report also takes advantage of the wealth of data from existing programs that report POPs in non-core media (“Other Media”) for generating additional information on baseline and temporal trends for older and newly listed POPs.

5.2 Review of concentrations and their changes over time in the regions

5.2.1 Ambient air

5.2.1.1 Background

This chapter summarizes temporal trends and levels of POPs measured in air in the WEOG region. For the past two decades, multiple air monitoring networks provided air measurement data for various POPs. The results from the networks listed in **Table 5.2.1a** are presented in this chapter.

Table 5.2.1a Monitoring programmes which contributed to the assessment of POP temporal trends and levels (23 priority substances) in the WEOG region.

Monitoring program	Abbrev.	Region of interest	Current # of monitoring sites in WEOG	Monitoring period	Monitored compounds (Stockholm conv. POPs)
Arctic Monitoring and Assessment Programme ^a	AMAP	Arctic	5 long-term 2 satellite	1993 - present	HCHs, PCB, chlordanes, DDTs In addition: Alert reports: Dieldrin, Heptachlor, Endrin, Aldrin, HBCD, α - and β -Endosulfan, HCB, PFAS, PBDEs Storhofdi reports: Dieldrin, HCB, PBDEs Zeppelin reports: HBCD, HCB, PFAS Pallas reports: α -Endosulfan, PBDEs Station Nord reports: HCB, Heptachlor, Aldrin, Dieldrin, Endrin, α - and β -Endosulfan, DDTs
Australian Pilot Monitoring Programme - air (Antarctic Air)	AGAM	Antarctica	1	2009-present	PeCB, HCB, Dieldrin, Aldrin, Endrin, Heptachlor, chlordanes, Toxaphene, Endosulfan, Mirex, HCH, DDTs, PCBs, PBDEs
Australian Pilot Monitoring Programme - air (Hazardous Substances in Air)	AGAM	Australia	11	2010-present	PBDEs, PCDDs, PCDFs, PCBs, PFAS, Toxaphene, HBB, Aldrin, chlordanes, HCHs, Dieldrin, Endrin, HCB, Heptachlor, α - and β -Endosulfan, Endosulfan sulfate, Mirex, DDTs, PeCB
Australian Pilot Monitoring Programme - air (Long Term Air Monitoring Network)	AGAM	Australia	44	2011-present	Samples archived, not analysed
European Monitoring and Evaluation Programme	UNECE-EMEP	Europe	7	1993 - present	PCB, DDT, chlordanes, HCB Note that AMAP sites Storhofdi, Zeppelin and Pallas are also EMEP sites. Please see additional analytical compounds above under AMAP.
Global Atmospheric Passive Sampling network	GAPS	Global	23	2004 - present	PCB, chlordanes, HCB

Table 5.2.1a continued...

Monitoring program	Abbrev.	Region of interest	Current # of monitoring sites in WEOG	Monitoring period	Monitored compounds (Stockholm conv. POPs)
Integrated Atmospheric Deposition Network	IADN	Great Lakes (North America)	5 (master stations); 2 urban and 1 rural satellite stations	1990 - present	Aldrin, Chlordanes, DDTs, Dieldrin, Heptachlor, α - and β - Endosulfan, Endosulfan sulfate, HCHs, PCBs, chlordanes, HCB (US only), PBDEs, HBCD (US sites only), Mirex (Canada only)
Northern Contaminants Program (Canada) ^a	NCP	Arctic	2	1992 - present	HCHs, PCB, chlordanes, DDTs, Dieldrin, Heptachlor, Endrin, Aldrin, HBCD, α - and β - Endosulfan, HCB, PFAS, PBDEs
Norwegian Troll Station	Troll	Antarctica	1	2007-present	PeCB, PCBs, HCHs, DDTs, chlordanes, HCB
Monitoring Network in the Alpine Region for Persistent and other Organic Pollutants	MONARPOP	European Alpine regions	33	2005 - present	PCB, chlordanes, HCB
MONET (EU)	MONET (EU)	Europe	23	2009-present	PCBs, HCHs, DDTs, HCB, PeCB. Analysed but not yet reported: PCDDs/Fs and PBDEs
U.S. EPA's National Dioxin Air Monitoring Network	NDAMN	USA	34	1998 - 2004	PCDD/F, co-planar PCB
UK-Norwegian Transect		UK and Norway	11	1994 - present	PCBs, OCPs, PBDEs
The UK Toxic Organic Micro Pollutants (TOMPs) program	TOMPs	UK	7	1991 - present 1999 - present	PCDD/F, co-planar PCB, PCBs, PBDEs

^a The Northern Contaminants Program (NCP) is the Canadian National Implementation Plan of Arctic Monitoring and Assessment Programme (AMAP). Data from 5 long-term and 2 satellite AMAP stations are presented in the current assessment, within which 1 long-term (Alert, NU Canada) and 1 satellite (Little Fox Lake, YK Canada) stations are operated under NCP. The other satellite AMAP station, Valkarkai, is in Russia. In total 14 atmospheric monitoring programmes contributed results to this assessment.

5.2.1.2 Contributing Air Monitoring Programmes

This section provides a brief overview of the key programmes that have contributed data and information to the air chapter of the present report. **Figure 5.2.1a** shows the locations of currently-operating sites where measurements were made under these programmes. **Figure 5.2.1b** shows new sites that have been established and will be able to provide time trends on POPs in the near future. Figure A1 in Annex 1 summarizes past air monitoring sites that were previously in operation and may be restarted to assess concentration changes in the future. Details on the objectives, sampling methods, operation and analytical information and spatial coverage of the various monitoring programmes are included in the programme executive summaries given in Annex 1.

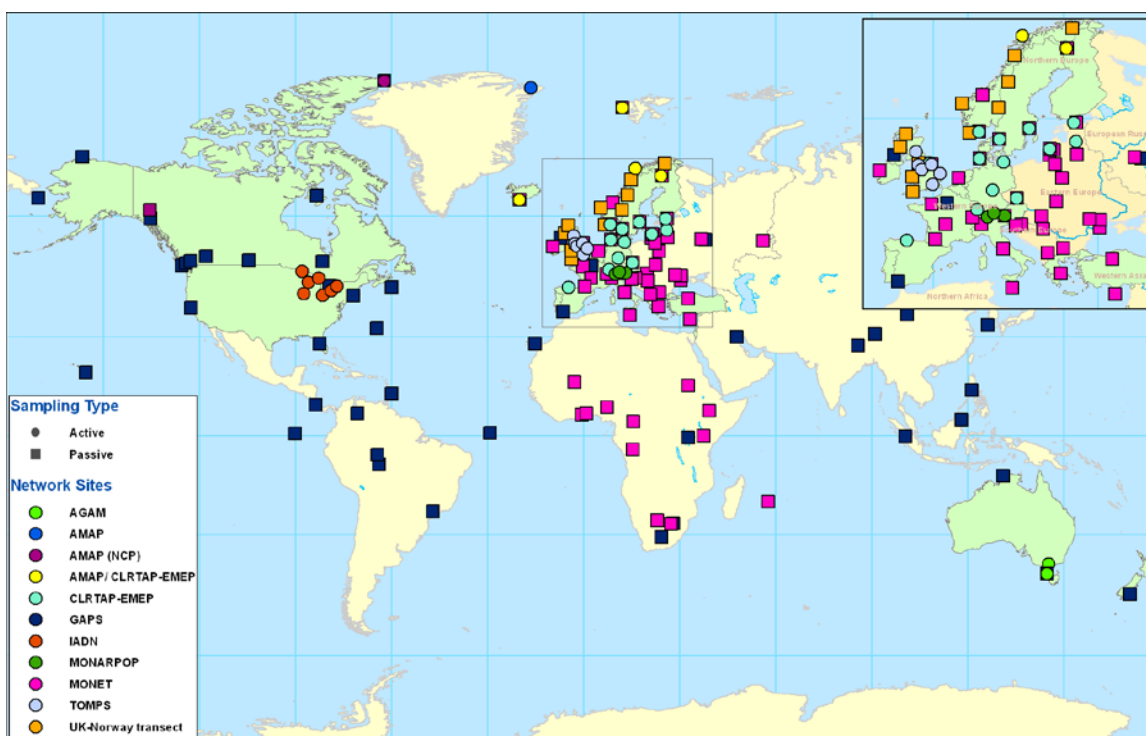


Figure 5.2.1a Site map for currently operating air monitoring sites for POPs. WEOG region is shaded in pale green. See **Table 5.2.1a** for definition of program acronyms. Symbol shapes represent sampling types (passive ■, active ●) and symbol colors represent program/network.

AMAP/EMEP monitoring programme and Northern Contaminants Program (NCP)

AMAP and CLRTAP-EMEP are the largest long-term international monitoring networks with overlapping geographical coverage which represents atmospheric monitoring activities for POPs in a large part of Europe, including the European Arctic. AMAP is based largely on ongoing national monitoring and research activities of the eight Arctic countries on pollutants issues.

AMAP coordinates these activities and works to ensure harmonization, and to promote quality assurance activities, and compiles results for use in circum-Arctic assessment activities. EMEP is a scientifically based and policy driven programme under the Convention on Long-range Transboundary Air Pollution (CLRTAP) for international co-operation to solve transboundary air pollution problems. The Chemical Coordinating Centre EMEP (EMEP-CCC) was established at NILU (Norwegian Institute for Air Research) in 1977 to harmonize previous international monitoring efforts. EMEP monitors POPs but also heavy metals, ozone, particulate matter, VOCs etc. In total 52 sampling sites have been involved in POPs monitoring in air or precipitation samples, for short, or longer periods, as it is summarized in <http://www.nilu.no/projects/ccc/emepdata.html>.

As part of AMAP, Canadian-operated NCP features the longest time series for atmospheric POPs at the North American Arctic station of Alert (Canada). These three programmes were established in the early 1990s with the goal of assessing contaminant impact on the European and circumpolar environment. With their long records of atmospheric POP concentrations, temporal trends were derived and reported here.

Australian Pilot Monitoring Programmes - Air

The Australian Pilot Monitoring programme for air operates three complementary programmes aiming at monitoring POPs in Australia and the Australian Antarctic station of Casey, which contributed to the current assessment. The Hazardous Substances in Air component contributed high-volume air sampling results from 2011, 2012 and 2013 from 3 sites (two urban sites and one background site). The Antarctic Air component contributed measurement results from the Casey station collected from November 2009 to November 2010 using a flowthrough air sampler developed for sampling of POPs in cold, remote environments (Xiao et al., 2007). The Long Term Air Monitoring component started passive air sampling at 44 sites with samples being archived but not analyzed. This could potentially contribute results to future assessments.

Global atmospheric passive sampling network for POPs

The GAPS programme was initiated in December 2004 as a two-year pilot study before evolving into a network consisting of more than 50 sites worldwide. Its objectives are to i) demonstrate the feasibility of passive air samplers (PAS) for POPs; ii) determine spatial and temporal trends for POPs in air; and iii) contribute useful data for assessing regional and global long-range atmospheric transport of POPs. Results from 37 stations under this network in the WEOG region are reported here.

Integrated Atmospheric Deposition Network (IADN)

The Integrated Atmospheric Deposition Network (IADN) is a collaboration between Canada and the US which conducts air and precipitation monitoring in the Great Lakes Basin. The network consists of 5 Master Stations, located on each of the 5 Great Lakes, along with a number of satellite stations in urban, rural and remote locations. Measurement results from the 5 Master Stations and 2 urban stations obtained between 1990 and 2011 are included in the current assessment.

MONET Europe

MONET EU was established in 2009 and is a passive air sampling network with 23 stations in 17 countries within the WEOG region; of which, 4 stations collocate at EMEP sites. Measurement results from 2009 and 2010 are reported here.

Norwegian Troll Station

Air monitoring of POPs started at the Norwegian Antarctic station of Troll in 2007. Data reported from 2007 to 2010 are included in this assessment (Kallenborn et al., 2013).

U.S. EPA's National Dioxin Air Monitoring Network (NDAMN)

NDAMN was a US national network with 34 geographically dispersed monitoring stations in the United States. It operated from June 1998 through November 2004 and collected ambient air measurements of PCDD/Fs and coplanar PCBs in 23 rural, 7 remote and 4 urban sites.

UK Toxic Organic Micro Pollutants (TOMPs) programme

TOMPs (Toxic Organic Micro Pollutants) is a monitoring network which measures the atmospheric concentrations of PCBs, co-PCBs, PAHs, PBDEs and PCDD/Fs within the U.K. Currently, the monitoring sites include 2 urban (London and Manchester) and 4 rural stations (Hazelrigg, Auchencorth, Weybourne and High Muffles). Two stations (Middlesbrough and Stoke Ferry) have ceased operation. Data are reported quarterly and temporal trends were reported for all stations since the early 1990s.

The UK – Norwegian transect programme

This programme started in 1994 and includes passive air sampling collected from 5 sites in the UK and 6 in Norway. All sampling sites are "remote" with the closest residences being few

kilometres away. Passive samplers are deployed for a two-year period and the analysed compounds include PCBs, PBDEs and PAHs.

Monitoring Network in the Alpine Region for Persistent and other Organic Pollutants (MONARPOP)

MONARPOP aims to provide spatial and altitudinal monitoring information of POPs and other organic pollutants to decision makers in the European Alpine regions. The network consists of 40 remote alpine sites in Austria, Germany, Italy, Slovenia and Switzerland. In addition, seven altitude profiles with several subplots were selected to investigate the vertical variation of POPs. Three summit stations above the timberline are equipped with remotely controlled active direction-specific samplers which collect air approaching the stations from different directions separately. Air concentrations at these stations are assessed with a combination of active and semi-permeable membrane device (SPMD) passive sampling techniques. This network intends to help to assess the success of the Stockholm Convention on POPs. Mean air concentrations measured at the three summit stations in 2006-2010 of priority POPs under the Stockholm Convention, except chlordecone, toxaphene, HBB and PFAS, are reported here.

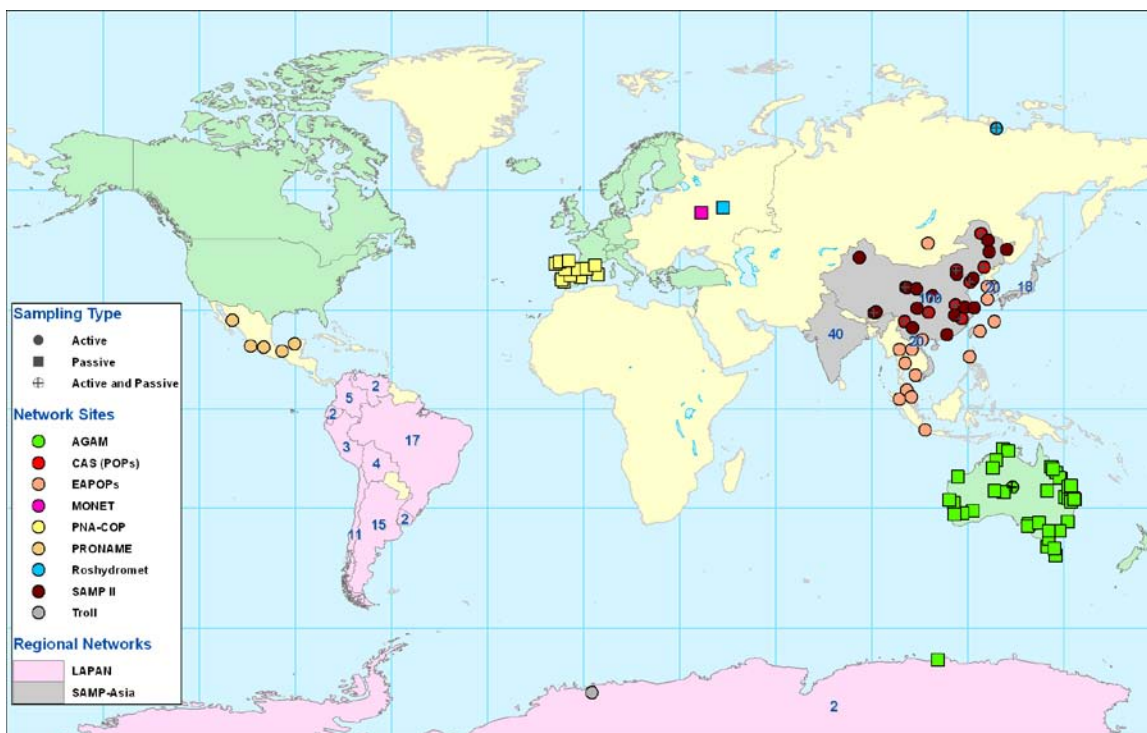


Figure 5.2.1b Newly established air monitoring sites for POPs. WEOG region shaded in green. See Table 5.2.1a and Table A1 in Annex 1 for definition of program acronyms. Symbol shapes represent sampling types (passive ■, active ● or both ⊕) and symbol colors represent program/network.

5.2.1.3 Levels and Trends of POPs in the WEOG Region

For evaluation of long-term temporal trends, a decline in air concentrations over time is often quantified by an apparent first order half-life or halving-time, $t_{1/2}$, which refers to the time required for the air concentration of a chemical to decline to half its original value. $t_{1/2}$ is estimated by dividing $\ln 2$ with the negative value of the linear regression slope of the time trend between the natural log of air concentrations, C (pg/m^3), and time (year). Similarly, for increasing time trends, doubling times, t_2 (or negative $t_{1/2}$), can be estimated. Note that half-life in this context assumes that air concentrations decline exponentially as a result of atmospheric clearance processes (e.g. photodegradation and deposition) which differs from radioactive decay that refers to the unstable decay of radioactive atoms themselves. Many compounds do not necessarily decline/increase linearly or consistently in the first order manner throughout the monitoring periods. Half-lives or doubling times are only presented here when the trends are declining or increasing more or less linearly and consistently. These values are only used to compare the relative rates of decline between stations or regions. Readers are advised to use the absolute values of these half-lives or doubling times with caution. **Table 5.2.1a –Table 5.2.1f** summarize $t_{1/2}$ and t_2 (represented as negative $t_{1/2}$) observed for different chemicals and regions. The focus of the current assessment is on the temporal trends of POPs. Only rarely would actual concentration values be presented here. Actual measured values reported by various programs can be found in the program executive summaries given in Annex 1.

Aldrin, Endrin and Dieldrin

Few monitoring programmes report levels of aldrin, endrin and dieldrin in air. The Great Lakes stations of Point Petre on Lake Ontario and Burnt Island on Lake Huron showed continuous decline of dieldrin from 1992 to 2010 with $t_{1/2}$ of 11.8 y and 10.3 y, respectively. Similar decline was observed at the satellite station of Egbert on Lake Ontario (1997-2003) ($t_{1/2}$ = 9.5 y). Declines were also observed for aldrin at all 3 sites with slightly shorter $t_{1/2}$ of 6-8.5 y. The Arctic stations of Alert (Canada) and Storhofdi (Iceland) reported time trends of dieldrin since 1993 and 1995, respectively, and have shown no discernible increase or decrease in trends. Air concentrations of aldrin and endrin measured at Alert also did not show any consistent trends, with aldrin being mostly non-detectable after 2008. Air concentrations tend to be lower in the colder months and higher in the warmer months for both Great Lakes and Arctic sites. Slight decreases in the warmest months were observed for dieldrin in all years at Alert which may be related to greater photodegradation during Arctic summer under 24 hour sunlight. Station Nord in Iceland also reported relatively low concentrations of dieldrin in air with statistically significant correlation with temperature (Bossi, Skj  thb and Skovac, 2013). Dieldrin in air probably results from re-emission from historical sources and the use of aldrin, which can be converted to dieldrin in the environment. This indicates that dieldrin in air has probably reached

some sort of steady state with other environmental media as it has been banned under various national and international initiatives worldwide for more than 30 years.

In Australia (2011-2013), dieldrin was found to be highest at the urban sites of Darwin (mean of 32-46 pg/m³) and Aspendale (mean of 33-38 pg/m³) while the background site, Cape Grim, sampling only under baseline conditions (i.e. wind coming from the Southern Ocean) had mean values ranging from 5.6 to 7.8 pg/m³. A new active sampling site established in 2013 at Alice Springs, a small inland city in the north of the continent, had a mean of 43.7 pg/m³.

5.2.1.2 Chlordanes, Nonachlor, Methoxychlor and Oxychlordane

Declining trends of *trans*- and *cis*-chlordane were observed at most Arctic stations and at the 5 Great Lake sites representing each of the lake, with $t_{1/2}$ ranging from about 12-16 y for *c*-chlordane and 6-11 y for *t*-chlordane in the Arctic; and 11-15 y for individual isomer on Lakes Ontario and Huron and 8-10 y for Σ chlordane (*t*- and *c*-chlordane and *t*-nonachlor) on Lakes Erie, Michigan and Superior. In the Arctic, *trans*- and *cis*-nonachlor declines at $t_{1/2}$ of 17 and 10 y, respectively, at Zeppelin and 19 and 17 y, respectively, at Alert. In the Great Lakes, *t*-nonachlor shows $t_{1/2}$ of 12-14 y on Lakes Ontario and Huron. Slow declines for *c*- and *t*-chlordane have been recorded also in the Swedish station in Rao (8.9 and 6.1 y, respectively) and a decline of 12 y for *t*-nonachlor. Methoxychlor seems to show declining tendency in air in the Great Lakes but few detectable data were available after 1995 to develop a reasonable trend. Oxychlordane, as the major metabolite of the chlordanes and nonachlors, showed consistent declining trends on Lakes Ontario and Huron with $t_{1/2}$ of 12 and 14 y, respectively. Globally, the GAPS network reported no consistent increasing or decreasing tendency for chlordane or heptachlor from 2005 to 2011; but results from 2005 to 2008 in Europe showed declining tendencies for *c*-chlordane. Similar to the drins, slow declines in the air with $t_{1/2}$ mostly longer than 10 years for all chlordane and nonachlor-related isomers reflects the fact that chlordane has been banned in the WEOG region since the 1980s and time trends seems to indicate a tendency towards equilibrium with other media.

In terms of seasonality, *t*- and *c*-chlordane and oxychlordane peaked during the warmer summer season in the Great Lakes region implying re-emission from historical sources. However, *t*-chlordane measured in the Arctic generally showed higher winter time concentrations. This seasonality is especially apparent at Zeppelin. Since *t*-chlordane is less stable than *c*-chlordane, this seasonality may have resulted from enhanced photodegradation during the Arctic summer when there is 24-hour daylight. No consistent seasonality was observed for *c*-chlordane in Arctic air, except at Alert where concentrations are slightly higher in the spring and fall.

DDTs

Among the 4 Arctic sites with long-term time series, Zeppelin is the only station where all DDT isomers show consistent declining trends (**Table 5.2.1c**). For *p,p'*- and *o,p'*-DDT, $t_{1/2}$ were found to be 5 y and 8.5 y, respectively, at this site. Declines were also observable at Storhofdi from the late 1990s to early 2000s for *p,p'*-DDT, DDE and DDD and at Pallas from 1999 to 2011 for *p,p'*-DDT. Air concentrations at other Arctic sites seem to have reached steady state and no discernible decreasing trends can be found.

For the Great Lakes sites, consistent declining trends can be found for almost all isomers and for Σ DDT from 1992 to 2010 with $t_{1/2}$ ranging from 7.4 to 11 y. At all sites, *p,p'*-DDT tends to decline faster than other isomers probably because it reflects fresh DDT application which continues to decline despite its allowance for use for malaria control in some tropical countries.

Air concentration maxima for all DDT isomers at the Arctic site of Zeppelin and *p,p'*-DDE at Alert and Pallas generally occurred in the winter, as opposed to summer maxima observed in the Great Lakes region corresponding to greater volatilization. It has been reported that DDT-related compounds tend to associate with particles which show greater input in the winter to the Arctic due to the Arctic Haze season. Also, higher precipitation rates in summer may result in their lower summertime concentrations due to enhanced scavenging. On the other hand, Bossi et al. (2013) reported that higher *p,p'*-DDT concentrations were observed in the summer at Station Nord in Greenland, showing significant correlation with temperature and negative correlation with ice cover. However, temperature can only account for about 27% of DDT variability in air, meaning that long-range transport (LRT) sources may not be excluded. *p,p'*-DDE concentrations were not correlated with temperature, indicating a predominance of LRT rather than re-emission.

The highest levels of DDTs were detected in the warmer parts of Western Europe, Greece and Spain under the MONET programme. *p,p'*-DDE prevailed at all monitoring sites indicating weathered sources. In Greece and Spain, the concentrations of *p,p'*-DDE were one order of magnitude higher comparing to other DDT isomers.

A similar finding was observed in Kosetice, in the Czech Republic (EMEP), where *p,p'*-DDE was constantly 3-5 times higher from *p,p'*-DDT and *p,p'*-DDD, respectively. The DDTs showed an increase in the period 2001-2003, and then a continuous decrease of the annual average. Overall, during the period 1999-2010 the half-lives were rather high, being 9.7 y, 9.8 y and 24.8 y, for *p,p'*-DDT, *p,p'*-DDE and *p,p'*-DDD, respectively. At the Swedish station of Rao, *p,p'*-

DDE and *p,p'*-DDD did not exhibit any clear decline, while *p,p'*-DDT's concentrations decreased over the period 2002-2012 with a half-life of 6.8 y. A slower decline (16 y) was observed at Aspvreten (Sweden) for *p,p'*-DDE.

Heptachlor and Heptachlor Epoxide

Heptachlor and heptachlor epoxide in air were reported for the Canadian Arctic station of Alert and 3 Great Lakes sites on Lakes Huron and Ontario. While heptachlor showed no discernible trend and heptachlor epoxide showed a very slow declining trend ($t_{1/2}=22$ y) at Alert, consistent declining trends for both compounds were observed at the Great Lake sites with $t_{1/2}$ ranging from 5.4 to 9 y. It is known that heptachlor degrades readily to heptachlor epoxide once it is released to the environment. Thus, the air concentrations of heptachlor measured at most sites are generally lower than those of heptachlor epoxide and appear to be more sporadic. Heptachlor epoxide tends to show higher concentrations in the summer in the Great Lakes region which is consistent with enhanced revolatilization of a degradation product during a warmer season. Higher air concentrations were also observed at Alert during the warm period with a slight dip in concentration in the midst of summer which may be related to greater photodegradation and enhanced scavenging during this time.

Hexachlorobenzene (HCB)

HCB in air was reported at 3 Arctic stations showing increasing trends at Zeppelin and Storhofdi in the last decade and very slow decline ($t_{1/2}>20$ y) at Alert. The air concentrations of HCB measured at Zeppelin were highest during the 1990s, but Alert and Zeppelin showed similar concentrations after 2000. Note that HCB has a tendency to breakthrough in air samples collected using polyurethane foam plugs (PUFs), for instance at the Alert site HCB broke through in about 30 % of all samples; thus air concentrations may be underestimated. Among the Arctic sites, the lowest HCB air concentrations were found at Storhofdi in Iceland. Time trends of HCB were reported for the Great Lakes sites of Eagle Harbour on Lake Superior and Chicago on Lake Michigan, with steady and slow decline showing half-lives of 34 and 44 years, respectively. Such slow decline reflects the fact that HCB has been banned in the US since 1966 and its air concentration is tending towards equilibrium with surface media. HCB was not reported for the Canadian Great Lakes stations because of potential breakthrough during sampling with a single PUF.

At Station Nord in Greenland, where samples should not be affected by breakthrough as measurements were conducted with PUF-XAD sandwich to capture the gas phase, Bossi et al. (2013) found that there was a lack in seasonal variations in HCB air concentrations between

2008 and 2010 with a weak correlation with temperature, and no correlation with ice cover. These observations suggest that HCB concentrations were not substantially influenced by re-emission, and may still be controlled by primary sources (e.g. byproducts of chlorinated chemicals and incomplete combustion processes).

Globally, XAD passive air sampler measurements have shown reducing tendency for HCB in air under GAPS from 2005 to 2008 (Shunthirasignhan et al., 2010). A pilot study conducted under the GAPS network using sorbent impregnated PUF or SIP as sampling medium showed that HCB is fairly uniformly distributed globally with concentrations ranging from 37 to 240 pg/m³.

MONET reported HCB air concentrations at 23 sites in Europe between 2009 and 2011 with median concentrations ranging from 2.6 to 19.6 ng/sample.

In Australia (2011-2013), HCB was found to be highest at the background site of Cape Grim in the south of the continent, sampling under baseline conditions (mean of 23-32 pg/m³) as compared the 2 urban sites of Aspendale (mean of 28-31 pg/m³) and Darwin (mean of 28-32 pg/m³) and the new site of Alice Springs in the north which had a mean of 32 pg/m³ in 2013. Considering that HCB has not been used in Australia since 1987, the concentrations observed at all three sites may represent a long-range transport source for HCB.

As part of the EMEP programme, HCB has been monitored in various stations in 20 countries. The highest concentration was 137 pg/m³ and was detected in Lista (Norway) in 1991. The lowest concentration ever recorded was in Leova (Moldavia) in 2005 and was 1.99 pg/m³. Time trends have been estimated for the two Norwegian Sites Lista (1991-2004 with some "gap years") and Birkennes (2003-2012) and the HCB half-lives were 10.6 y and 16.9 y, respectively. In neither site is there a clear trend regarding seasonality.

Mirex and Photomirex

Air concentrations of mirex and degradation product photomirex were only reported at the Great Lakes stations of Burnt Island and Egbert on Lake Huron and Point Petre on Lake Ontario. Both are declining with $t_{1/2}$ ranging from 10-16 y for mirex and 3-7.5 y for photomirex. It can be seen that the decline has started to level off for both compounds, especially at the more remote site of Burnt Island. Since all uses of mirex were cancelled in 1978 in the US and it was never registered for use as a pesticide in Canada, air concentrations seem to tend towards equilibrium with the environment.

Polychlorinated Biphenyls (PCBs)

PCBs in air in the WEOG region tend to be generally declining in trends at all monitoring stations since the 1990's. The decline seems to have become less rapid in recent years as the concentrations become much lower resulting in longer half-lives **Table 5.2.1b**). Estimated apparent first-order half-lives are given in **Table 5.2.1b**. Negative $t_{1/2}$ for PCB 52 and 101 at Storhofdi indicates steadily increasing trends, especially after 2000 (**Figure 5.2.1c**). Since Storhofdi is a coastal site and is in close proximity to Icelandic ice caps, e.g. the Mýrdalsjökull and Eyjafjallajökull ice caps, sea ice retreat around Iceland and deglaciation of ice caps in a warming Arctic may result in re-emission of previously deposited PCBs from oceans and ice, rendering increasing concentrations of relatively lighter PCBs such as PCB 52 and 101.

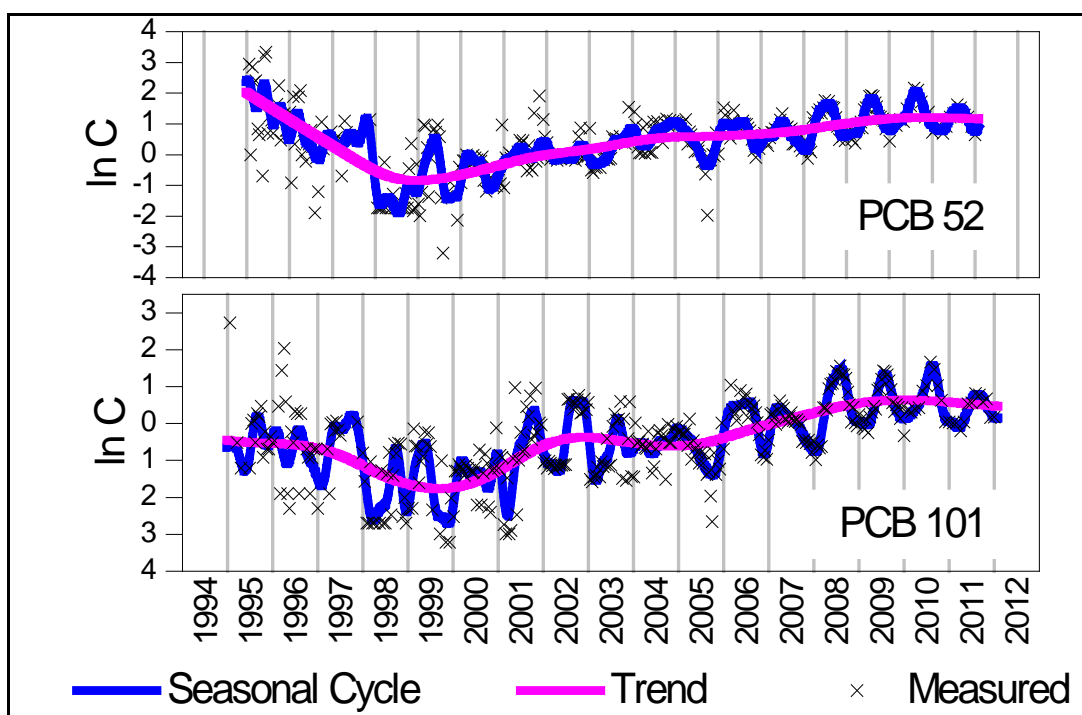


Figure 5.2.1c PCB 52 and 101 measured in air at Storhofdi, Iceland.

At the 3 summit sites in the European Alps, significant decline in air concentrations of PCBs was detected between 2006-2010. The PCB concentrations (sum of the six standard PCBs) decreased on average by 1.3 pg/Nm³ per year (Sonnblick), by 3.1 pg/Nm³ per year (Weißfluhjoch) and by 2.1 pg/Nm³ per year (Zugspitze). Dioxin-like PCBs with consistent time series also showed significant trends of decline in air. PCB air concentrations measured at the western site (Weißfluhjoch, CH) was higher than those measured at the eastern-most site (Sonnblick, A).

For temperate locations closer to urban centers, the rates of decline for PCBs at different TOMPs sites in the UK were not found to be statistically different from each other suggesting similar sources have been, and still are, contributing to the measurements. The calculated atmospheric clearance rate averaged across all sites was 4.7 ± 1.6 y (equivalent to $t_{1/2}$ of 3.3 ± 1.1 y). Air concentrations are found to be correlated with local population density for both the UK sites (TOMPs executive summary in Annex 1) and the Great Lakes sites in the US (Venier and Hites, 2010); indicating that primary sources from PCBs stocked in urban environments (e.g. in PCB transformers, electrical equipment and in landfills) still contribute to measured atmospheric levels.

PCBs have been monitored since 2003 in Birkennes, Norway, under EMEP. For the seven indicative PCB congeners, halflives ranged between 4.5 y and 8.0 y for PCB 118 and PCB 52, respectively. It should be mentioned, however, that all seven congeners followed a similar pattern over the studied period which probably reflects common sources, similarly to what was reported by TOMPs. In all cases, the decline became faster after 2008. Other EMEP stations that have monitored PCBs include the two Swedish stations, namely Aspvreten and Rao. Both stations reported the seven common congeners, namely PCB 28, 52, 101, 118, 138, 153 and 180; for Aspvreten the treated data included the years 1995-2012, while for Rao, the available data cover the period between 2002-2012. For Aspvreten, all PCB congeners exhibited slow declines with halflives ranging between 11 y (PCB 180) and 20 y (PCB 52), while for Rao, no clear trend can be estimated for the whole studied period. However, for all seven congeners, it can be seen that an initial slow decline (2002-2006/2007) is followed by a similarly slow increase (2007-2012) (**Figure 5.2.1d**).

In the Great Lakes, declining trends are observed at all US and Canadian sites with halflives ranging from 6.5 to 34 y and is congener specific. The halflives tend to be rather long (>10 y) for most congeners, implying the tendency towards equilibration with surrounding environmental surfaces.

For coplanar PCBs, the highest concentrations were found for PCBs 118 and 105, with concentrations in the hundreds to thousands of fg/m^3 at US NDAMN sites. The lowest mean concentrations ($<10 \text{ fg}/\text{m}^3$) were seen for PCBs 126, 169 and 189, among which PCB 126 is the most toxicologically significant coplanar PCB which was detected 100 % of time with an average concentration of $6.9 \text{ fg}/\text{m}^3$. Coplanar PCBs accounts for an average of 7 % of total TEQ (PCDD/Fs + coplanar PCBs) measured in air at US sites.

Under the MONET programme the median concentrations of 7 PCBs (EMEP congeners) (2009-2011) at 23 sites varied from 0.7 ng/sample at High Muffles (UK) and Camkoru (Turkey) to 8 ng/sample at De Zilk (Netherlands).

In Australia, the TEQ-PCB species display lower concentrations than the ortho-PCB species at all sites under the Australian Pilot Monitoring Programme - air (Hazardous Substances in Air) and median concentrations of TEQ-PCB and ortho-PCB species at the urban site of Aspendale are greater than concentrations at the smaller city of Darwin, which are in turn greater than concentrations at the background site of Cape Grim. PCB 118, followed by PCB 105, contributes to the highest concentration of PCB-TEQ at each site. Among the dioxin-like PCBs, the highest concentration congener measured at Aspendale, Darwin and Cape Grim were PCB 52, PCB 101 and PCB 28, respectively. Homologue distribution remained the same between 2011 and 2012 at all sites. Higher contribution of penta- and hexa-PCB to the total PCB mass at Darwin and Aspendale than at Cape Grim suggests a more localized source at urban sites since commercial PCB mixtures are often dominated by penta- and hexa-chlorinated congeners.

Globally, no clear temporal tendency was observed under the GAPS network from 2005 to 2011. As PCBs are now “legacy POPs”, air concentrations would mostly be dominated by secondary emission sources and the rate of decline is more closely associated with environmental persistence of PCBs.

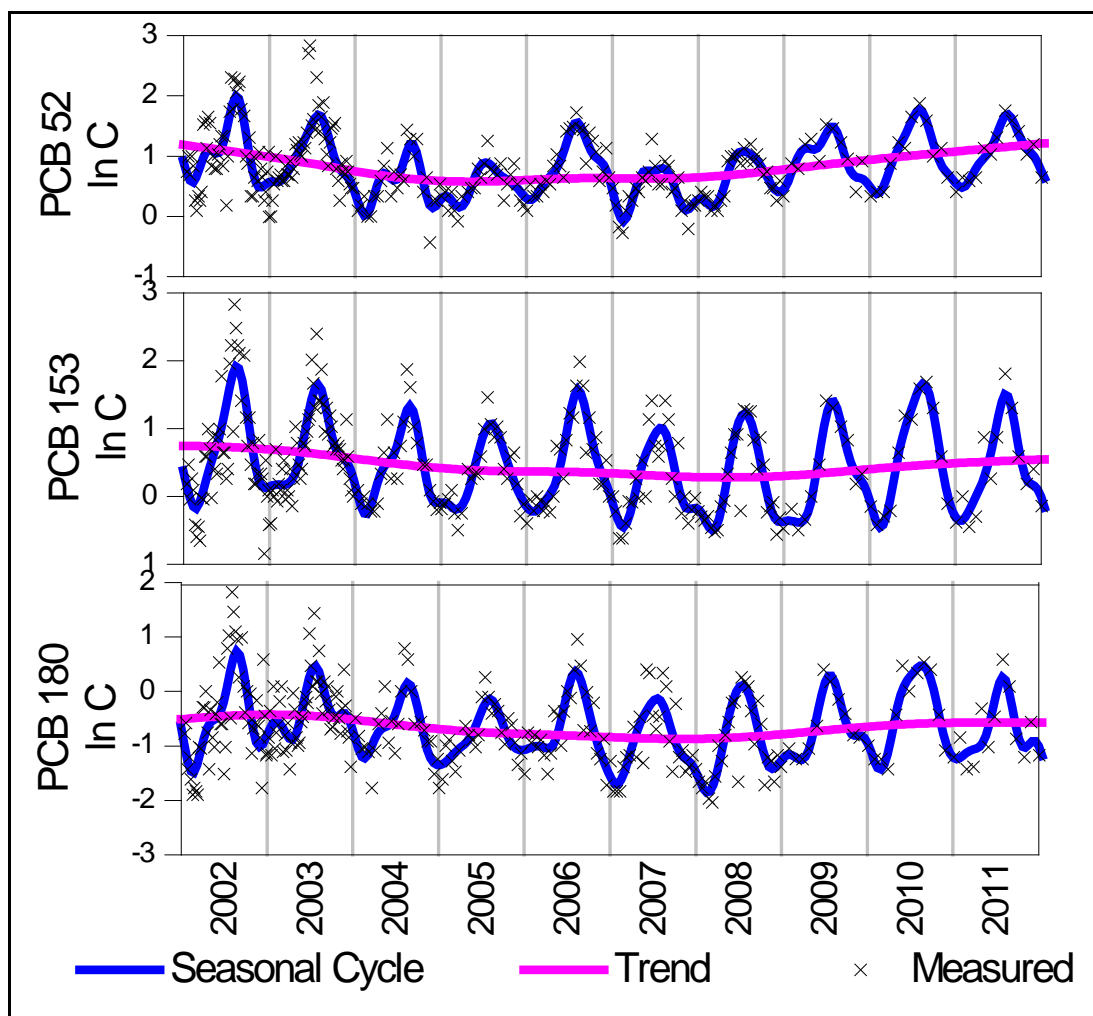


Figure 5.2.1d PCBs 52 and 180 in air at Rao.

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs)

While dioxin concentrations in air at three UK urban sites, namely London, Middlesbrough and Manchester, were found to be declining (1992-2010) and correlated with annual atmospheric emission trends reported, both UK rural and US (urban, rural and remote) air concentrations show no discernible change (TOMPs and NDAMN executive summaries in Annex 1). Urban concentrations are now similar to those in rural areas; thus, implying that most major, readily controllable sources were reduced and current levels in both rural and urban areas may remain similar unless there are major changes in energy requirements and generation options. Winter concentrations were found to be generally higher than summer concentrations at UK and US rural sites, implying contribution of combustion sources due to space heating in winter.

PCDD/Fs in air at 3 summit sites in the European Alps were found to be significantly decreasing between 2006 and 2010. The mean annual PCDD/F TEQ air concentrations decreased on average by 0.15 fg TEQ/Nm³ per year (Weißfluhjoch) and by 0.19 fg TEQ/Nm³ per year (Zugspitze). Air concentrations measured on the Alps were similar to those measured at US remote sites, but 1-2 orders of magnitude lower than at US urban sites.

PCDD/Fs (210 congeners) were measured between 2011 and 2012 at 3 sites under the Australian Pilot Monitoring Programme for Air. The average concentrations measured during 2012 are similar to those measured during 2011 with the exception of the homologue groups total TCDD ($p=0.04$) and total HpCDF ($p=0.028$) at Cape Grim, which were significantly lower in 2012. No significant difference between 2011 and 2012 average concentrations at the 95% confidence level for any of the congeners at any site was observed. During both 2011 and 2012, highest concentrations were measured at the urban site of Aspendale (Melbourne) and lowest concentrations at the background site of Cape Grim (Tasmania). At the small urban site of Darwin (Northern Territory), concentrations were greater than blank concentrations during the dry season.

α -, β - and γ -hexachlorocyclohexane (HCH)

The HCHs were used globally as a pesticide which were available in two formulae: (1) Technical HCH which is made up of a mixture of isomers, mainly γ -HCH (10–15%), α -HCH (60–70%) and β -HCH (5–12%); and (2) lindane which contains almost pure γ -HCH, the active ingredient. α - and γ -HCH were most widely measured in air, while the air concentrations of β -HCH were usually found to be very low and were mostly below the detection limits, with no discernible time trends or consistent seasonality.

In the Arctic, α - and γ -HCH were found to be declining in air at all long-term monitoring stations. The halflives of α -HCH range from 4.8 to 5.7 y; and those of γ -HCH were found to be about 4 y for all sites, except at Storhofdi where it was 7.7 y. At the master stations in the Great Lakes region, α -HCH was declining in air with $t_{1/2}$ ranging from 2.9 to 4.8 y and γ -HCH showed $t_{1/2}$ of 2.5 to 5 y. Usage of technical HCH has declined significantly since the 1980s, and lindane use was phased out in Canada by 2004 and in the US by 2009, with the exception of a government registered pharmaceutical use as a second-line treatment for lice and scabies in the United States. It is notable that the atmospheric decline rates of lindane have accelerated in both the Arctic (**Figure 5.2.1e**) and the Great Lakes region after its use has been restricted in North America (Venier et al., 2012; Hung et al., 2010).

At Station Nord in Greenland, γ -HCH measured in air (2008-2010) did not show significant correlation with temperature, implying direct atmospheric transport from sources (Bossi et al., 2013).

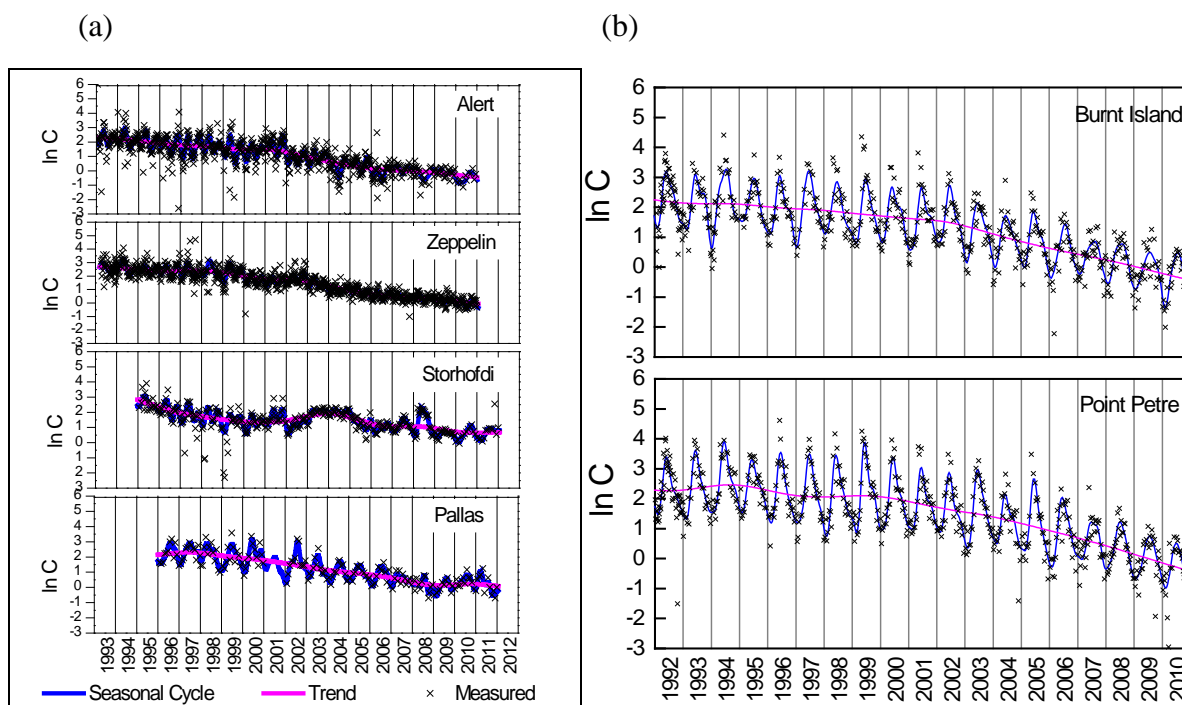


Figure 5.2.1e Time trends of γ -HCH (lindane) measured at (a) 4 Arctic sites and 2 Great Lakes sites.

The air concentrations in the Great Lakes region for α - and γ -HCH tend to maximize over the summer which is consistent with enhanced volatilization during warmer periods. Those in the Arctic generally showed a ‘bimodal’ seasonal cycle which may be the result of a combination of factors, including increased tillage in the spring and fall in the south releasing HCHs from the soil, enhanced photodegradation and depletion by OH-radicals during the summer, and scavenging by forests along the transport pathway during the growing season (Hung et al., 2002).

Under the MONET programme, 4 HCH isomers were measured between 2009 and 2011 at 23 sites. α -, β -, and γ -HCH isomers were identified at all sampling sites, with γ -HCH and α -HCH being the most abundant, while δ -HCH was close to the detection limit. The highest median concentrations were detected at Sonnblick (Austria), Storhofdi (Iceland), De Zilk (Netherlands) and High Muffles (UK).

Under the EMEP programme, long time series for α - and γ -HCH isomers exist for Birkennes (Norway) and Kosetice (Czech Republic), while at Lista (Norway), concentrations were recorded only for α -HCH. For Lista and Birkennes, the observed decline apparent halflives are similar to the above mentioned values for Zeppelin and other Arctic sites, being 5.2 y and 3.5 y for α -HCH in Birkennes and Lista, respectively, and 3.9 y for γ -HCH in Birkennes. For Kosetice, the halflife for α -HCH was 18.5 y, while for γ -HCH was 1.15 y.

The afore-mentioned seasonality of HCH isomers is observed in both Birkennes and Lista, where consistently the concentrations are noticeably higher in summer. This is not observed though in Kosetice. Fast declines for both α -HCH and γ -HCH have been observed in Rao and Aspvreten. α -HCH declined with a halflife of 3.3 y in Aspvreten and 5.5 y in Rao, while γ -HCH decreased with half-lives of 2.9 y in Aspvreten and 4.4 y in Rao.

Globally, the GAPS network reported declining tendency for α - and γ -HCH from 2005 to 2011 and no consistent trends for β -HCH.

Hexabromobiphenyl (HBB or BB-153)

Hexabromobiphenyl (HBB or BB-153) was only reported at 3 sites in Australia. The concentrations of BB-153 were reported to be 0.057 and 0.050 pg/m³ in 2011 and 2012, respectively, at the city of Aspendale in Melbourne. Measurements at the background site of Cape Grim and small city of Darwin were below the blank level.

Perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl

Per- and polyfluorinated compounds include a large number of substances, in which perfluoroalkyl acids (PFAAs), such as the perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs), were found to have widespread presence in the environment, humans and wildlife and tend to bioaccumulate through the food webs. PFAAs can be emitted directly into the environment but can also result from biotic and abiotic degradation of neutral precursors (Schenker et al., 2008). The focus of this review is on PFOS; however, since many PFOS precursors can transform or degrade to PFOS in the environment, they are included here. Also included are PFCAs and perfluorooctanoic acid (PFOA), and their precursors which are often measured in air.

PFOS and PFOA in air-borne particles were measured at the Arctic site of Zeppelin from mid-2006 to 2012. The air concentrations for both compounds seem to remain constant throughout the monitoring period and no consistent seasonality was observed (**Figure 5.2.1f**). At Alert, neutral per- and polyfluoroalkyl substances (PFASs) were monitored in air (gas+particle) from August 2006 to 2012. The 8:2 fluorotelomer alcohol (FTOH) was the most dominant compound detected in all air samples collected at Alert. This is consistent with previous cruise-based measurements performed across the North Atlantic and Canadian Archipelago in 2005 (Shoeib et al., 2006), in the Atlantic Ocean/ Southern Ocean/ Baltic Sea in 2007 and 2008 (Dryer et al., 2009); as well as globally under the GAPS study at land-based stations (Gawor et al., 2014). Piekarz et al. (2007) calculated the estimated atmospheric residence times for 6:2, 8:2 and 10:2 FTOH which were 50, 80 and 70 d. The relative order of these residence times coincides with their observed atmospheric concentrations which may explain the relative enhancement of 8:2FTOH in ambient air. Spring maxima were observed at Alert, particularly for methyl perfluorooctane sulfonamido ethanol (MeFOSE), which may be associated with the increase in particulate input during the Arctic Haze. Summer maxima were also apparent for FTOH and MeFOSE which may be related to volatilization due to higher temperatures. PFOS precursors MeFOSE and EtFOSE showed non-changing and declining trends ($t_{1/2}=1.3$ y), respectively (**Figure 5.2.1g**); reflecting the voluntary phaseout of the production of PFOS, PFOA, and PFOS-related products by their largest producer 3M in 2000. In contrast, PFCA precursors 6:2, 8:2 and 10:2 FTOHs, which were not regulated at the time of measurement, showed increasing tendencies in air at Alert with doubling times of 2.3 to 3.3 y.

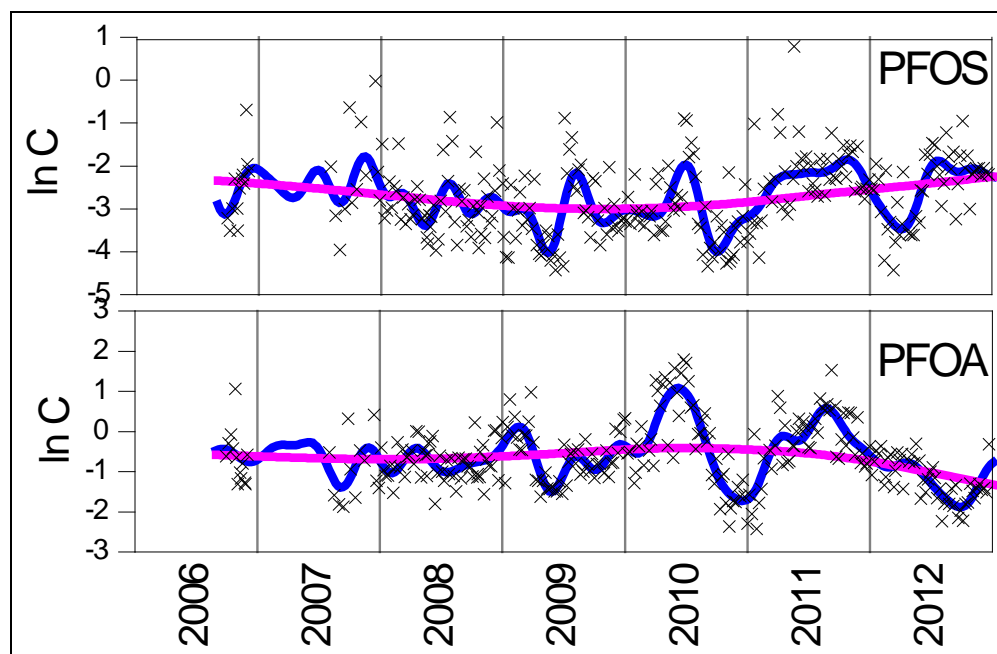


Figure 5.2.1f Time trends of PFOS and PFOA (particle phase only) measured in air in Zeppelin

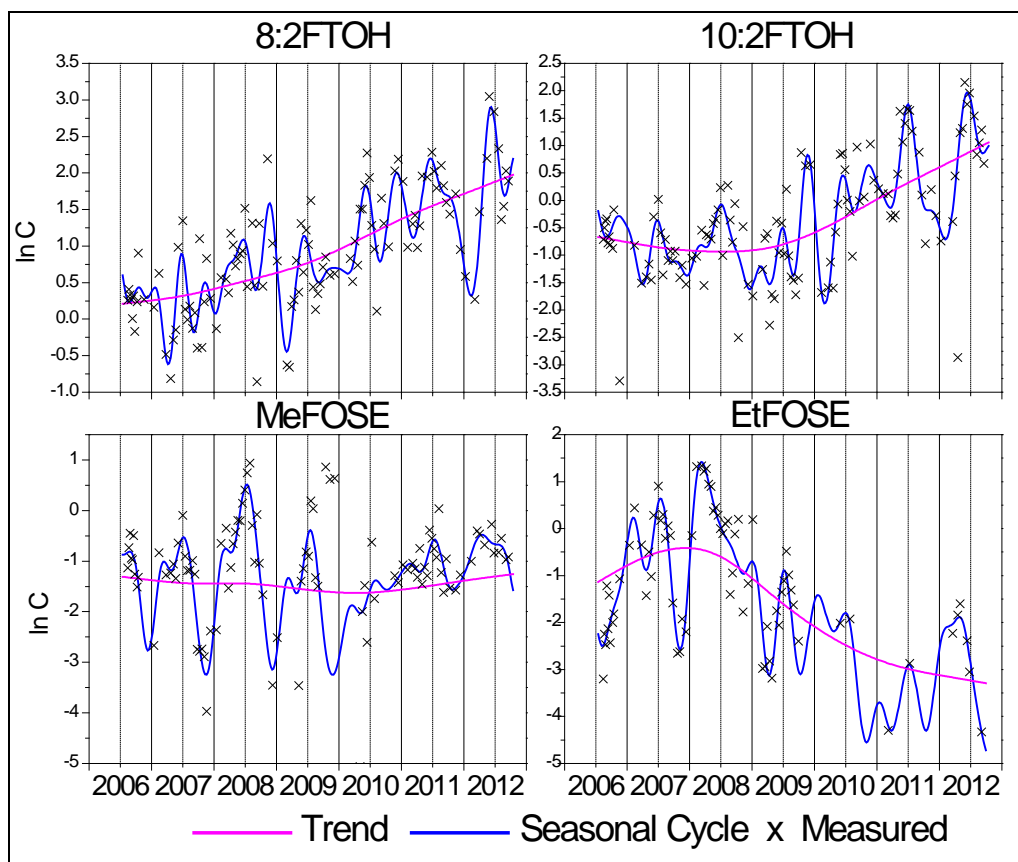


Figure 5.2.1g 8:2 and 10:2 FTOH and MeFOSE and EtFOSE measured in air at Alert.

The declining trend of EtFOSE at Alert is consistent with reported global decline of FOSAs and FOSEs between 2006 and 2011 measured under the GAPS programme with XAD-based passive air samplers deployed for one year at between 17 and 46 sites globally (Gawor et al., 2014) (**Figure 5.2.1h**). However, the observed increase in FTOH concentrations in Arctic air is different from reported global trends where a decrease of 60-70% in mass was reported for 8:2 and 10:2FTOH with no observable trend for 6:2FTOH. It is notable that the declining trend of FTOHs from 2006 to 2008 did not continue in 2009 to 2011. In the GAPS study, higher levels of FTOHs were found at all sites compared to FOSAs and FOSEs. Urban sites had the highest levels of neutral PFAS compared to rural and remote sites with a positive correlation with proximity to high population density.

In Australia (2011-2012), the highest concentrations of perfluorinated compounds are seen at the city of Aspendale and PFOS is the dominant compound showing the highest concentrations at Aspendale (mean of 16-17 pg/m^3) and Darwin (mean of 0.77-1.5 pg/m^3). At Cape Grim, PFOS and most other species are below the LOD, except PFOSA (mean of 0.14-0.27 pg/m^3). The PFOS precursor compounds NEtFOSAA and NMeFOSAA are only detectable at Aspendale.

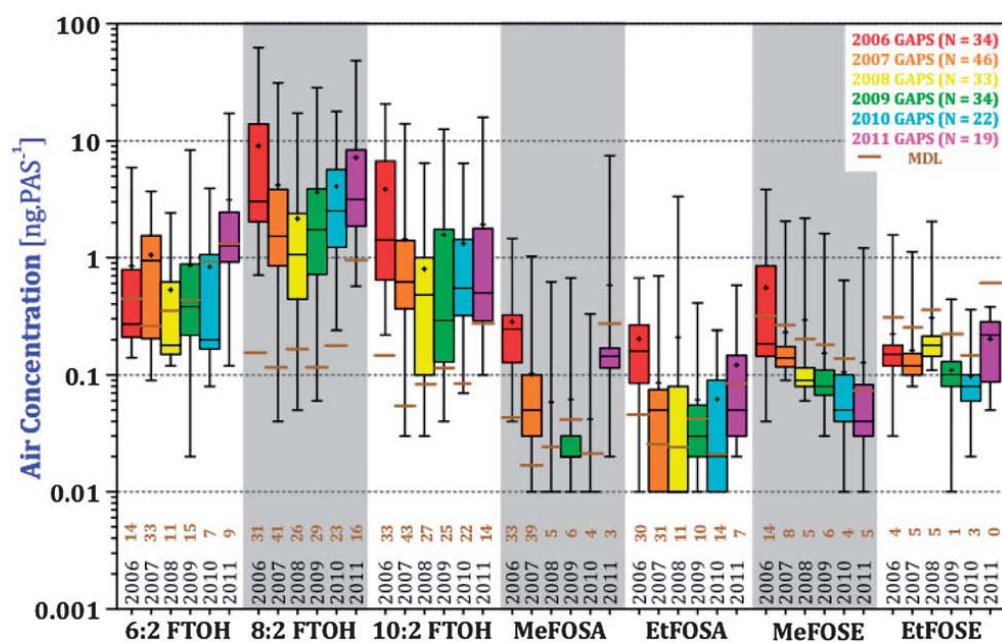


Figure 5.2.1h Box and whiskers plot of individual nPFAS concentrations analyzed in the GAPS Network study. Five boxes per compound illustrate different sampling years. Boxes contain 50% of the data, whereby the lower and upper ends correspond to 25th and 75th percentiles respectively. Whiskers show the minimum and maximum concentrations of the compounds. Medians and arithmetic averages are illustrated with a bar crossing the box and ‘+’ sign, respectively. nPFAS detection limits are displayed as horizontal brown lines, and the number of sites where a nPFAS was detected is shown below the boxes (from Gawor et al., 2014).

A summary of PFAS measured in air in surveillance-type studies (not part of a long-term monitoring programme) is given in the Annex 1 (Table A1).

Technical Endosulfan and Its Related Isomers

The air concentrations of α -endosulfan measured at the Arctic sites of Alert (1993-2011) and Pallas (2009-2011) showed non-changing or slightly declining ($t_{1/2}=37$ y) time trend. β -endosulfan was found to be mostly below detection limit and no time trend or consistent seasonality was observed at the Arctic sites of Pallas and Alert. At Station Nord in Greenland, α -endosulfan measured between 2008 and 2010 did not correlate with temperature indicating transport from direct sources (Bossi et al., 2013).

In the Great Lakes region, slight decline in α -endosulfan ($t_{1/2}$: 17-21 y), β -endosulfan ($t_{1/2}$ ~10 y) and endosulfan sulfate ($t_{1/2}$: 10-16 y) were observed at the Canadian master stations on Lake Ontario and Huron; and Σ endosulfans (sum of α - and β -endosulfan and endosulfan sulfate) was reported to decline at a $t_{1/2}$ of 13 y in the vapour phase and 11 y in the particle phase as an average among 5 US sites. As endosulfan is still being used in North America (to be phased out in Canada by December 31, 2016 and in the US by July 31, 2016), the rate of decline is relatively slow compared to other POPs.

The GAPS network reported declining tendencies for endosulfans globally. Between 2005 and 2008, α -endosulfan showed apparent decline at European sites and unchanging levels in North America.

Polybrominated Diphenyl Ethers (PBDEs)

PBDEs measured in air in the UK from 1999 to 2010 indicated that the atmospheric time trend of Σ PBDE (sum of congeners BDE47, BDE49, BDE99, BDE100, BDE119, BDE154, BDE153, BDE138, BDE183) for an average of the four studied sites show a decrease that is highly correlated ($r^2=0.79$, $p=0.0084$) with modelled historical estimates of PBDE emission, taking into account PBDE manufacture, incorporation into products and subsequent emission from each product type using specific emission factors over their respective life cycles (TOMPS executive summary Figure 1.4 in Annex 1). Dominating congeners were BDE47 followed by BDE99 indicating extensive use of the penta-technical mixture, indicating continued releases from articles containing PeBDE products is likely to be controlling the long-term trends in the UK atmosphere.

Similar to the UK sites, dominating congeners in Arctic and Great Lakes air were also BDE 47 and 99, reflecting influence from the penta-technical mixture. In the Arctic, most BDE congeners remain more or less unchanged in air concentrations at Alert with apparent summer maxima corresponding to increased volatilization during warmer times. Contrarily, the air concentrations at Pallas and Zeppelin showed significant declining trends with halflives of 2.6-4.5 y for BDE 47, 99 and 100. Also, the air concentrations at Pallas and Zeppelin were generally much lower than those observed at Alert. Air concentrations at Alert were probably more strongly influenced by the nearby military base, which contains articles that were treated with PBDEs, and the generally much higher usage of these compounds in North America as compared to the rest of the world. At the US Great Lakes sites, PBDE concentrations were found to be related to population density within 25 km radius of the sampling sites. BDE 47 and 99 vapour phase concentrations were increasing with doubling times of 5-10 years (negative values on Table 2c

Annex 1) at 3 US background sites; but BDE 47 was slowly decreasing at Chicago and Cleveland in both vapour and particle phases ($t_{1/2}$ of 5-9 y). On the other hand, declining trends for BDE 47 and 99 were observed at the 2 Canadian Great Lakes sites with faster decline at Point Petre ($t_{1/2}$ of 3-6 y) which is closer to urban development, probably reflecting the replacement of these substances in cities.

In Australia (2011-2013), the urban site of Aspendale showed the highest total BDE concentrations with BDE 209 at the highest concentrations (mean of 14-16 pg/m³ contributing ~80% of mean mass) followed by BDE 47 and 99; indicating influence from both deca and penta-BDE mixtures. BDE 47 and 99 were the dominant congeners at the small city of Darwin. At Cape Grim, BDE209 was dominant followed by BDE 47 and 99. Although BDE209 (decaBDE) is not a Stockholm Convention listed POP, it is included here to provide context for the PBDE suite measured.

Hexabromocyclododecane (HBCD)

Air concentrations of α -, β -, γ -HBCD were measured at the Arctic station of Zeppelin showing declining trends for α - and γ -HBCD with $t_{1/2}$ of 2.9 and 1.5 y, respectively. Total HBCD air concentrations were reported at Alert (2002-2011) but the concentrations were found to be mostly non-detectable and no trend can be derived.

In the Great Lakes region, highest concentrations of HBCDs were observed in Chicago on Lake Michigan followed by Eagle Harbour on Lake Superior. While Chicago is an urban site and HBCD being used mainly as a flame retardant on polystyrene foam, it is not surprising that its air concentration is high at an urban site. On the other hand, air concentrations observed at another urban site, Cleveland, was relatively low, showing similar concentrations as two other rural sites on Lakes Erie and Michigan. However, it is surprising to find that HBCD air concentrations were high at the remote site of Eagle Harbour. The reason for this observation is not apparent. No observable time trends can be derived from measurements obtained from Chicago and Eagle Harbour from 2005 to 2011. At the two Canadian master stations on Lakes Ontario and Huron, HBCD was found to be mostly non-detectable in air samples from 2009 and 2010.

Covaci et al. (2006) has summarized HBCD measurement results in air in Scandinavian countries and the United States. HBCDs were detected in urban and rural areas of Sweden ranging from 2 to 610 pg/m³. Atmospheric levels of HBCDs in remote locations, e.g. Greenland and Svalbard, can be correlated with their levels in animals suggesting long-range atmospheric

transport from western Europe and eastern North America to the Arctic. Much higher values (up to 28,500 ng/m³) were measured in air from plants producing HBCDs or extruded polystyrene foam flame retarded with HBCDs.

Pentachlorobenzene (PeCB)

No time trend data are available for pentachlorobenzene because it has a tendency to breakthrough PUFs used in active air sampling programmes. MONET reported air concentrations of PeCB measured with passive air samplers at 23 sampling sites measured from 2009 to 2011, showing relatively uniform levels with median concentrations ranging from 0.8 to 2.8 ng/sample.

The GAPS network reported seasonal results for PeCB in a pilot study using SIP as sampling medium showing that PeCB has fairly uniform global distribution with air concentrations ranging from 2.5 to 75 pg/m³.

In Australia, over three years from 2011-2013, PeCB concentrations ranged from a mean of 9 to 14 pg/m³ at Aspendale, 4 to 7 pg/m³ at Darwin and 6 to 7 pg/m³ at the background baseline site of Cape Grim.

Toxaphene

No trend data were available for toxaphene.

Only Parlar-26 was found to be above the limit of detection (LOD) among 3 sites in Australia (mean of 0.048 pg/m³ in Aspendale, 0.050 pg/m³ at Darwin, 0.097 pg/m³ at Cape Grim in 2011), but concentrations were close to the LOD values and would not pass a limit of quantification (LOQ) criteria.

Chlordecone

No air measurement data were reported for chlordecone.

5.2.1.4 Summarised Compound Specific Trends

Figure 5.2.1i-k below is compiled in an attempt to understand the general trends for all individual compounds in air in the WEOG region. In this figure, the half-lives estimated for each compound in all the studied stations were pooled together. Note that the half-lives were calculated

over the entire period of monitoring and for different programs, the data time series span over different time frame (Table 5.2.2a-e), with some of them starting as early as 1990. Arbitrarily, it was decided that:

- ❖ A decline of 0.01 to 5.99 y ($>11\%$ per year) is considered a "sharp decline";
- ❖ A decline of 6.00 to 19.99 y ($3.4\text{--}11\%$ per year) is considered a "slow decline";
- ❖ Declines with halflives >20 y ($<3.4\%$ per year), and/or trends that were characterised by insignificant correlation coefficients are considered as "no clear trend"
- ❖ An increase with doubling times of 0.01 to 19.99 y ($>3.4\%$ per year) is considered an "increasing trend";

From **Figure 5.2.1i-k**, it can be seen that α -HCH and γ -HCH are the chemicals that are mostly characterised by fast declines. The chemicals for which increases are also observed include PCB congeners 52, 101 and 138. These increases may be due to revolatilisation of PCBs from soil or water, or simply due to recent local emissions. PBDEs are also declining fast, however the number of monitoring sites is rather limited. Generally speaking, the majority of POPs in the most stations are declining slowly. Note that POPs that do not have many reported time series, e.g. PCDD/Fs, PFOS and related compounds, and HBCD, are not included in **Figure 5.2.1i-k**.

Table 5.2.1b Apparent first order half-lives ($t_{1/2}$, year) of PCBs.

Station	Period	28		52		101		118		138		153		180	
		$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2
Arctic															
Alert (93-01)	1993-2001	7.1	0.76	4.6	0.81	6.9	0.77	8.3	0.28	20	0.17	8.3	0.32	3.6	0.84
Alert (03-11)	2003-2011	-31	0.17	17	0.39	42	0.43	42	0.07	-13	0.26	-51	0.023	-23	0.046
Pallas	1996-2011	18	0.51	38	0.37	17	0.65	11	0.73	8.9	0.68	9.8	0.71	5.1	0.76
Storhofdi	1995-2011	20	0.28	-11	0.22	-6.1	0.62	-	-	12	0.25	19	0.15	8.4	0.35
Zeppelin	1998-2012	8.2	0.68	4.4	0.71	11	0.90	6.1	0.91	5.1	0.60	6.2	0.84	4.4	0.81
		28		52		101		118		138		153		180	
Europe		$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2
Birkennes	2003-2012	6.6	0.79	8.0	0.76	7.0	0.83	4.5	0.83	5.3	0.77	4.7	0.77	4.7	0.84
Kosetice	1999-2011	-	-	-	-	-	-	24	0.76	28	0.36	8.6	0.66	-	-
Apvretten	1995-2012	14	0.59	20	0.25	19	0.69	15	0.69	18	0.49	15	0.73	11	0.63
Rao	2002-2012	47	0.11	-41	0.06	25	0.32	25	0.55	30	0.22	28	0.26	41	0.12
U.K.		ΣPCBs													
		$t_{1/2}$	\pm SE												
Average TOMPs sites ^a	1992-2008	3.26	1.11												

^a Converted from clearance rate (y) ($t_{1/2}$ =clearance rate \times ln 2).

Table 5.2.1b *continued...*

Station	Period										
Great Lakes		ΣPCBs									
		t_{1/2}	±SE								
5 US Great Lakes sites (vapor phase only)	1991-2008	15	±1.1								
Sturgeon Point (Lake Erie)	1992-2010	23	±9.1								
Sleeping Bear Dune (Lake Michigan)	1992-2010	12	±3.0								
Eagle Harbour (Lake Superior)	1992-2010	13	±2.8								
		ΣPCBs		18		28		31		52	
		t_{1/2}	r²	t_{1/2}	r²	t_{1/2}	r²	t_{1/2}	r²	t_{1/2}	r²
Point Petre (Lake Ontario)	1992-2010	11	0.93	9.0	0.94	30	0.39	12	0.89	13	0.87
Burnt Island (Lake Huron)	1992-2010	12	0.91	8.9	0.93	-	-	13	0.86	31	0.55
Egbert (Lake Huron)	1997-2003	11	0.63	6.5	0.72	13	0.24	6.7	0.70	9.7	0.61
		101		118		138		153		180	
		t_{1/2}	r²	t_{1/2}	r²	t_{1/2}	r²	t_{1/2}	r²	t_{1/2}	r²
Point Petre (Lake Ontario)	1992-2010	17	0.84	14	0.84	15	0.48	13	0.75	8.3	0.84
Burnt Island (Lake Huron)	1992-2010	34	0.45	27	0.28	13	0.42	25	0.62	8.0	0.68
Egbert (Lake Huron)	1997-2003	24	0.27	20	0.33	-	-	9.0	0.90	7.3	0.45

Table 5.2.1c Apparent first order half-lives ($t_{1/2}$, year) of organochlorine pesticides

Station	Period	α -HCH		γ -HCH		c-chlordane		t-chlordane		c-nonachlor		t-nonachlor	
		$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2
Arctic													
Alert	1993-2011	4.8	0.97	4.2	0.98	17	0.59	11	0.60	17	0.31	19	0.38
Pallas	1996-2011	5.7	0.96	4.2	0.98	12	0.70	9.7	0.78	-	-	13	0.65
Storhofdi	1995-2011	5.6	0.93	7.7	0.75	12	0.64	5.9	0.60	-	-	-	-
Zeppelin	1993-2012	4.9	0.99	4.1	0.96	14	0.95	9.3	0.98	9.9	0.85	17	0.84
		p,p'-DDT		p,p'-DDE		p,p'-DDD		o,p'-DDT		o,p'-DDE		o,p'-DDD	
		$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2
Alert	1993-2011	-	-	-	-	-	-	-	-	-	-	-	-
Pallas	1996-2011	10	0.67	43	0.22	-	-	-	-	-	-	-	-
Storhofdi	1995-2011	4.8	0.45	8.9	0.47	5.1	0.67	-	-	-	-	-	-
Zeppelin	1993-2012	5.0	0.92	8.0	0.74	8.8	0.63	8.5	0.83	6.0	0.69	8.3	0.85
		dieldrin		HCB		α -endosulfan		heptachlor epoxide					
		$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2				
Alert	1993-2011	12	0.72	25	0.69	37	0.21	22	0.47				
Pallas	1996-2011	-	-	-	-	-	-	-	-				
Storhofdi	1995-2011	28	0.23	20	0.27	-	-	-	-				
Zeppelin	1993-2012	-	-	-	-	-	-	-	-				

Table 5.2.1c continued...

	Period	HCB		α -HCH		γ -HCH		p,p'-DDT		p,p'-DDE		p,p'-DDD	
Europe (EMEP)		$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2
Birkennes	2003-2012	17	0.46	5.2	0.95	3.9	0.98	-	-	-	-	-	-
Lista	1991-2004	11	0.85	3.5	0.96	-	-	-	-	-	-	-	-
Kosetice	1999-2011	-	-	18	0.73	1.2	0.27	9.7	0.78	9.8	0.24	25	0.6
Aspvreten	1995-2012	-	-	3.27	0.92	2.91	0.89	-	-	16	0.49	-	-
Rao	2002-2012	-	-	5.5	0.94	4.4	0.94	6.8	0.91	63	0.08	114	0.00023

	Period	c-chlordane		t-chlordane		t-nonachlor	
		$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2
Rao	2002-2012	8.9	0.85	6.1	0.94	12	0.83

Table 5.2.1c *continued...*

Great Lakes	Period	α -HCH		γ -HCH		dieldrin		Σ DDT ^a		Σ chlordanes ^b		Σ endosulfans ^c	
		t _{1/2}	±SE	t _{1/2}	±SE	t _{1/2}	±SE	t _{1/2}	±SE	t _{1/2}	±SE	t _{1/2}	±SE
5 US Great Lakes sites (vapor phase only)	1991-2008	3.4	0.1	4	0.1	-	-	8.2	0.4	11	0.8	13.1	1.9
5 US Great Lakes sites (particle phase only)	1991-2008	4	0.7	5.1	0.4	-	-	5.8	0.6	5.7	0.4	11.1	1.2
Sturgeon Point (Lake Erie)	1992-2010	2.9	0.3	2.5	0.1	7.4	1	8.9	0.8	8.1	0.7	-	-
Sleeping Bear Dune (Lake Michigan)	1992-2010	3.4 ^d	0.4	2.6 ^d	0.2	8	1.3	8.4	1.1	8.6	1.2	-	-
Eagle Harbour (Lake Superior)	1992-2010	3.9 ^d	0.3	3.1 ^d	0.2	8.3	1.2	10.4	2	10	1.6	-	-

^a Sum of p,p'-DDT, p,p'-DDD and p,p'-DDE.

^b Sum of c- and t-chlordane and trans-nonachlor.

^c Sum of α - and β -endosulfan and endosulfan sulfate.

^d Regression applied to 1999-2010 air concentration data

Table 5.2.1c continued...

	Period	aldrin		α -HCH		γ -HCH		c-chlordane		t-chlordane		t-nonachlor	
		t _{1/2}	r ²	t _{1/2}	r ²	t _{1/2}	r ²	t _{1/2}	r ²	t _{1/2}	r ²	t _{1/2}	r ²
Point Petre (Lake Ontario)	1992-2010	8.5	0.41	4.5	0.98	4.8	0.90	14	0.76	11	0.85	12	0.82
Burnt Island (Lake Huron)	1992-2010	6.0	0.76	4.8	0.98	4.9	0.93	14	0.79	14	0.92	13	0.90
Egbert (Lake Huron)	1997-2003	7.0	0.65	3.7	0.94	7.1	0.84	13	0.55	15	0.41	14	0.61

	Period	p,p'-DDT		p,p'-DDE		p,p'-DDD		o,p'-DDT		o,p'-DDE		dieldrin	
		t _{1/2}	r ²	t _{1/2}	r ²	t _{1/2}	r ²	t _{1/2}	r ²	t _{1/2}	r ²	t _{1/2}	r ²
Point Petre (Lake Ontario)	1992-2010	7.5	0.87	11	0.88	8.6	0.92	10	0.71	7.4	0.93	12	0.84
Burnt Island (Lake Huron)	1992-2010	7.2	0.90	9.2	0.93	11	0.72	9.1	0.80	7.9	1.00	10	0.92
Egbert (Lake Huron)	1997-2003	7.3	0.53	16	0.24	11	0.63	12	0.32	17	0.51	9.5	0.50

Table 5.2.1c continued...

	Period	α -endosulfan		β -endosulfan		endosulfan sulfate		heptachlor		heptachlor epoxide		oxychlordane	
		$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2
Point Petre (Lake Ontario)	1992-2010	17	0.68	10	0.71	16	0.37	6.2	0.69	7.8	0.88	12	0.85
Burnt Island (Lake Huron)	1992-2010	21	0.59	11	0.77	10	0.51	9.0	0.41	7.8	0.93	14	0.84
Egbert (Lake Huron)	1997-2003	17	0.25	-	-	5.0	0.87	-	-	5.4	0.88	31	0.20
		mirex		photomirex									
		$t_{1/2}$	r^2	$t_{1/2}$	r^2								
Point Petre (Lake Ontario)	1992-2010	11	0.88	7.5	0.80								
Burnt Island (Lake Huron)	1992-2010	16	0.45	6.0	0.72								
Egbert (Lake Huron)	1997-2003	13	0.21	3.0	0.79								

Table 5.2.1d Apparent first order half-lives ($t_{1/2}$, year) of PBDEs and HBCD.

Station	Period	BDE47		BDE99		BDE100		BDE138		BDE209 ^a	
		$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2
Arctic											
Alert	2002-2011	-	-	38	0.13	-36	0.12	-	-	-	-
Pallas	2003-2011	4.5	0.70	2.7	0.95	78	0.88	-	-	-	-
Zeppelin	mid-2006-2012	2.6	0.98	2.6	0.92	4.1	0.97	-	-	2.63	0.65

Station	Period	α -HBCD		β -HBCD		γ -HBCD		Σ HBCD	
		$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2
Zeppelin	mid-2006-2012	2.89	0.69	-	-	1.55	0.87	2.44	0.76

Station	Period	BDE47		BDE99		BDE209 ^a		α -HBCD		β -HBCD		γ -HBCD	
		$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2
<i>Europe (EMEP)</i>													
Birkennes I	2006-2010	1.5	0.99	1.3	0.97	0.46	0.77	3.4	0.11	4.5	0.1	1.7	0.36
Birkennes II	2009-2013	3.8	0.96	2.0	0.95	3.7	0.62	-	-	-	-	-	-
Andoya	2009-2013	1.1	0.87	1.2	0.89	9.2	0.37	-	-	-	-	-	-

^a Although BDE209 (decaBDE) is not a Stockholm Convention listed POP, it is included here to provide context for the PBDE suite measured. For the Great Lakes region, BDE 209 is part of the sum of the PBDE suite measured.

Table 5.2.1d continued...

Station	Period	Σ PBDEs (including BDE209) ^a		BDE 47		BDE 99	
		$t_{1/2}^b$	\pm SE	$t_{1/2}^b$	\pm SE	$t_{1/2}^b$	\pm SE
<i>Great Lakes</i>							
Sturgeon Point (Lake Erie)	2005-2011	-6.4 (vap)	2.5	-9.4 (vap)	2.8	-4.6 (vap)	0.9
		7.3 (part)	2.6	-	-	-	-
Sleeping Bear Dune (Lake Michigan)	2005-2011	-3.7 (vap)	0.8	-7.0 (vap)	2.0	-4.3 (vap)	1.0
		1.9 (part)	0.3	-	-	-	-
Eagle Harbour (Lake Superior)	2005-2011	-3.0 (vap)	0.5	-7.4 (vap)	2.1	-4.7 (vap)	1.2
		-6.0 (part)	1.7	-	-	-	-
Chicago	2005-2011	-	-	5.2 (vap)	1.1	-9.5 (vap)	3.5
		-	-	5.3 (part)	0.9	10.1(part)	3.5
Cleveland	2005-2011	-	-	8.9 (vap)	2.9	-	-
		4.8 (part)	1.4	9.2 (part)	2.5	9.1 (part)	3.0
Point Petre (Lake Ontario)	2002-2010			3.3	0.96	5.6	0.64
Burnt Island (Lake Huron)	2002-2010			12	0.72	10	0.42

^a Although BDE209 (decaBDE) is not a Stockholm Convention listed POP, it is included here to provide context for the PBDE suite measured. For the Great Lakes region, BDE 209 is part of the sum of the PBDE suite measured.

^b vap=vapour phase, part=particle phase

Table 5.2.1d *continued...*

Station	Period	Σ PBDEs ^c
		$t_{1/2}^c$
UK	1999-2010	2.43
London	1999-2010	1.39
Manchester	1999-2010	2.36

^c Σ PBDEs = Sum of BDE47, 49, 99, 100, 119, 154, 153, 138, 183. Halfives converted from clearance rates ($t_{1/2} = \text{clearance rate} \times \ln 2$)

Table 5.2.1e *Apparent first order halfives ($t_{1/2}$, year) of PCDD/Fs*

Station	Period	$t_{1/2}^a$
UK		
London	1992-2008	2.2-4.1
Manchester	1992-2008	2.8-4.1
Middlesbrough	1992-2008	2.7-7.7

^a Halfives converted from clearance rates ($t_{1/2} = \text{clearance rate} \times \ln 2$)

Error! Not a valid link. ^a Only 1 detectable sample in 2007. Regression performed between 2008 and 2012 Jan.

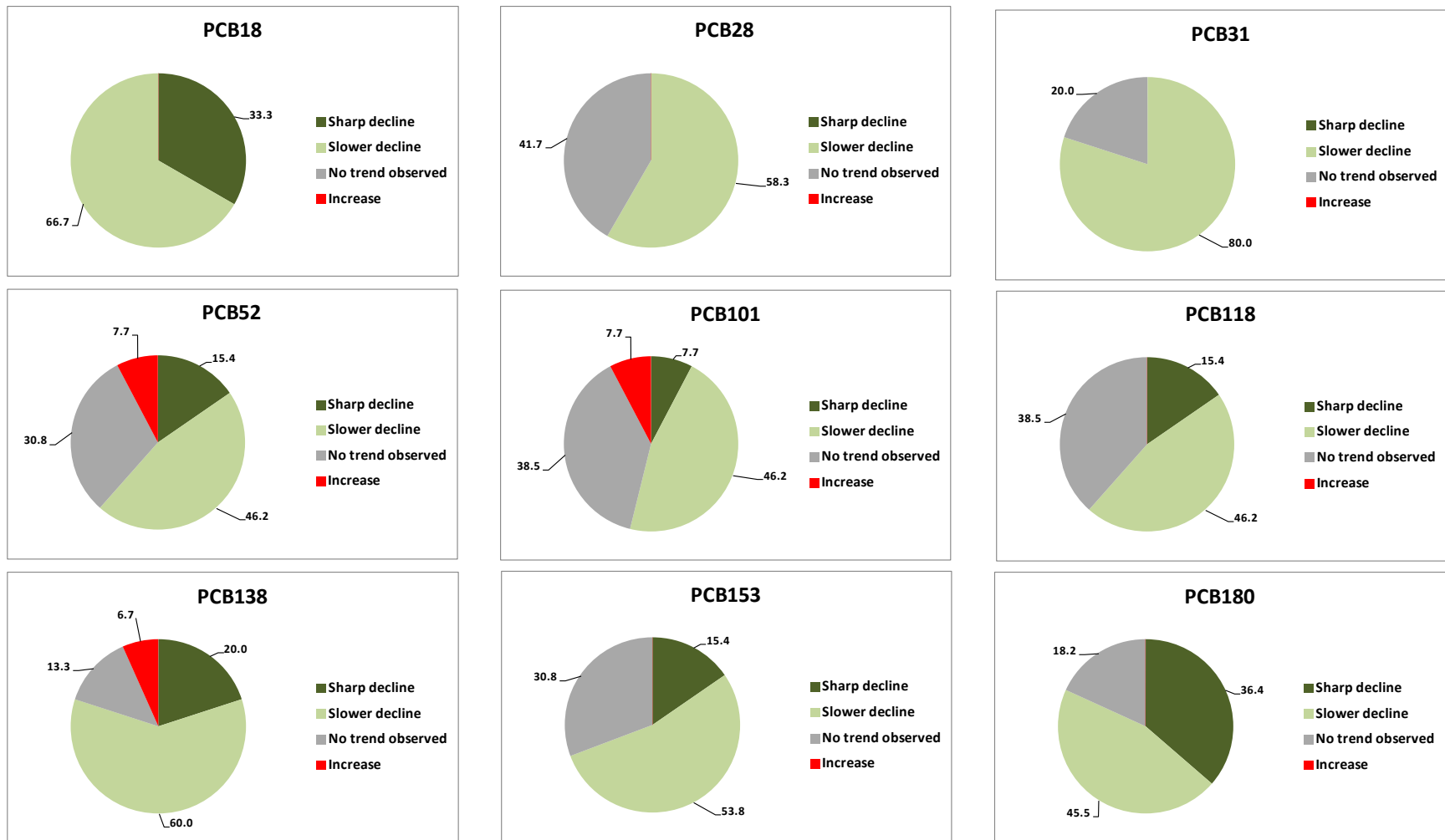


Figure 5.2.1i PCB trends in the WEOG Region.

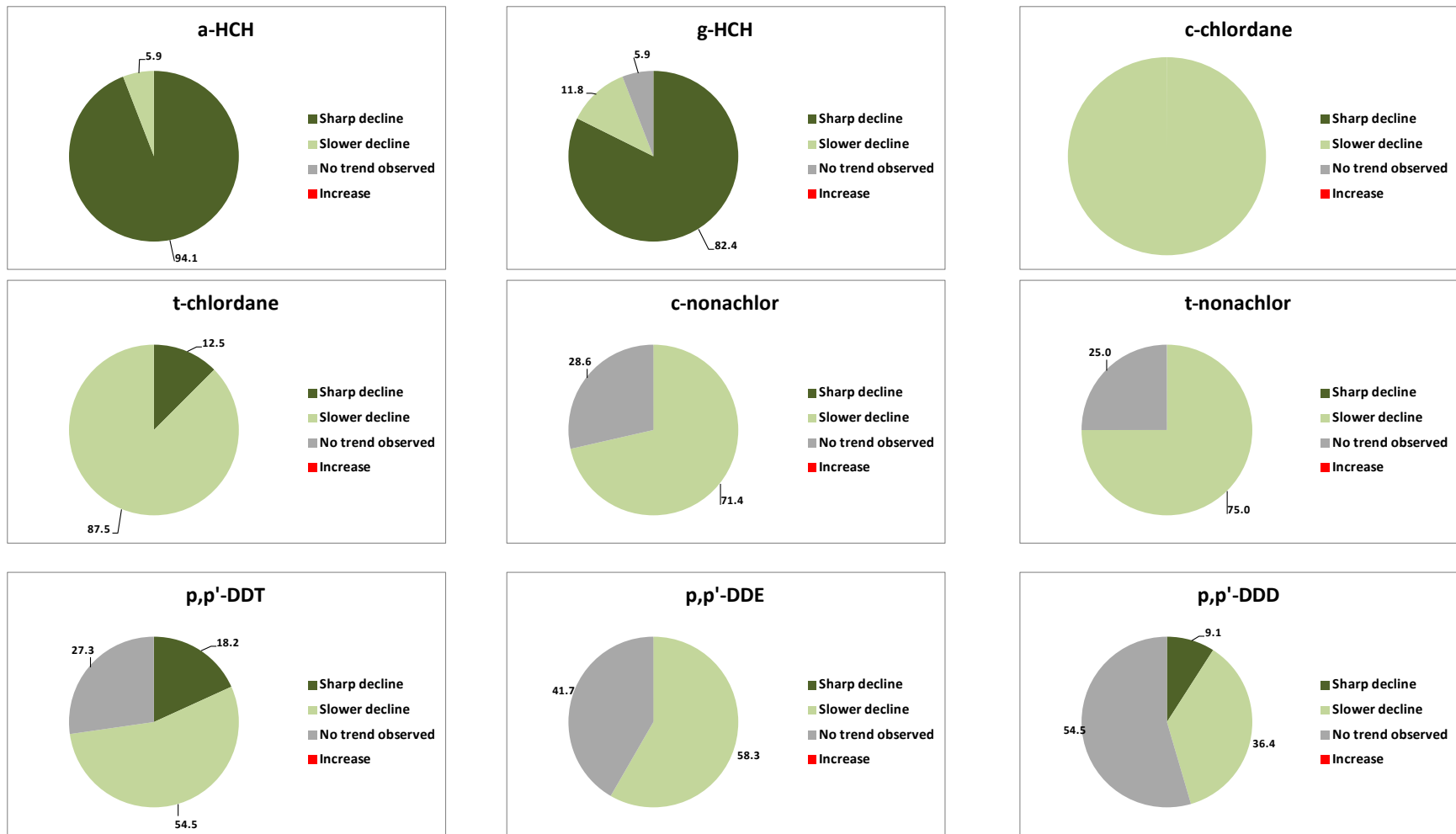


Figure 5.2.1j OC trends in the WEOG Region (con't).

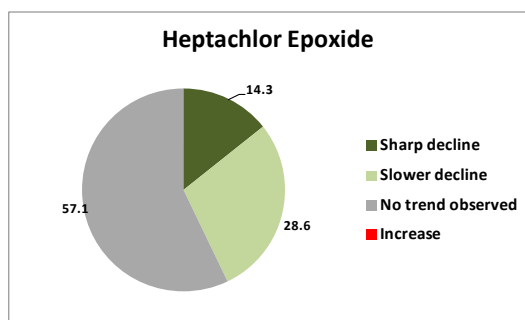
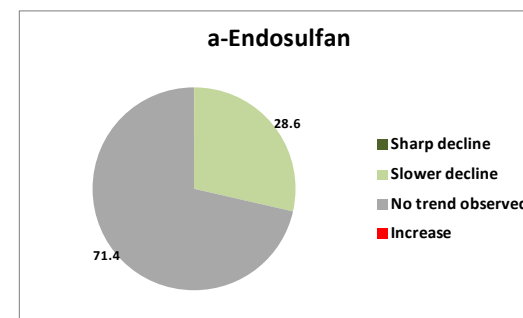
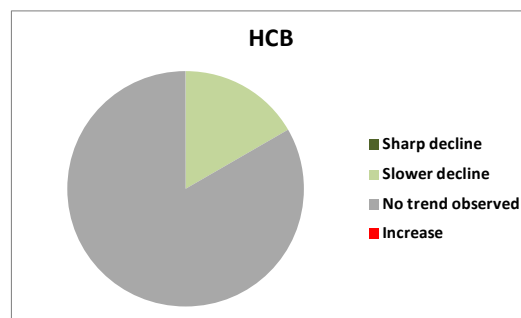
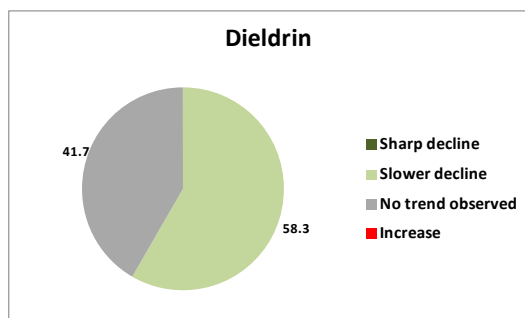
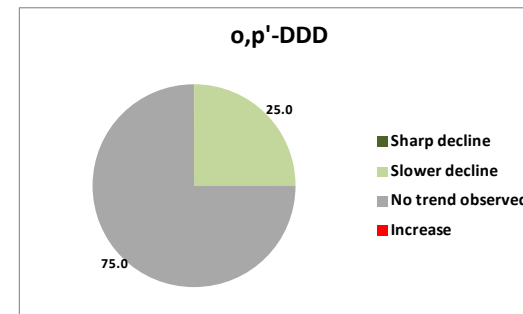
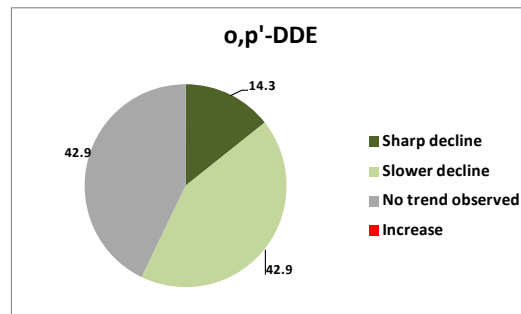
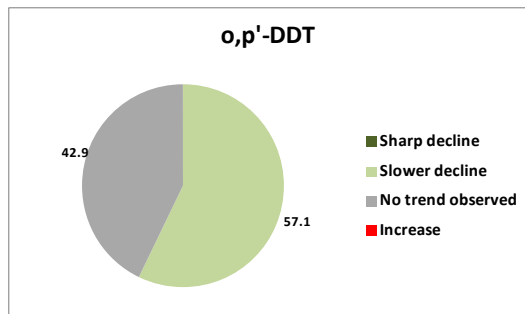


Figure 5.2.1j continued...

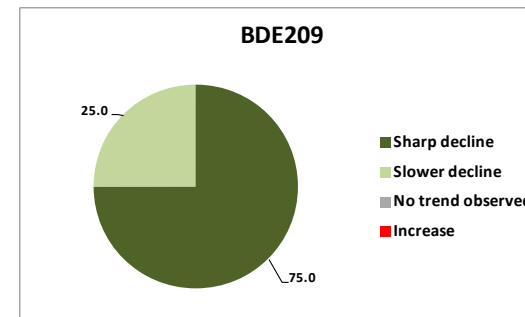
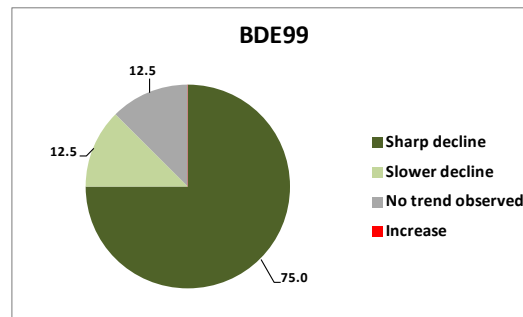
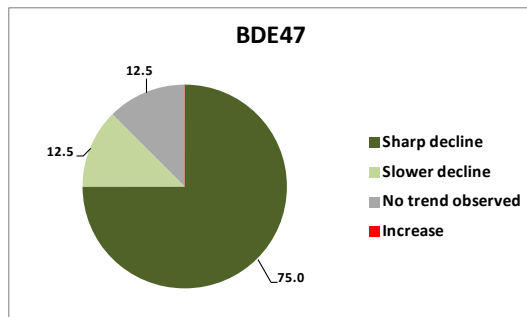


Figure 5.2.1k PBDE trends in the WEOG Region.

5.2.1.5 Summary and Conclusions

- ❖ Most POPs that have been banned for extended period of time (>20-30 years) in the WEOG region, e.g. DDTs, the drins, PCBs and chlordanes, are now showing slower rates of decline, indicating that they are approaching steady state with other environmental media and secondary sources now dominate.
- ❖ HCB and PCBs are showing varying trends, however in Arctic air at specific locations increases are also observed; this may be related to revolatilization from open ocean due to significant ice retreat or melting glaciers in recent years as a result of warming.
- ❖ PCDD/F concentrations are declining, reflecting the fact that most controllable sources are reduced. Unless there are major changes in energy requirements and generation options, levels would probably remain similar.
- ❖ While PBDEs generally showed declining trends in European sites, their trends are more variable at North American locations. It seems that concentrations are declining at urban sites, probably reflecting the replacement of these substances in cities; but declining trends were not observed in North American background sites in the Great Lakes and the Arctic.
- ❖ Accelerated decline of lindane (γ -HCH) was observed in air as its usage was phased out in North America. α -HCH has also been generally declining at a faster rate, compared to other legacy POPs.
- ❖ Time trends of newer POPs, e.g. PFAS, HBB and HBCD, are lacking. Only 3 Australian sites reported data for HBB.
- ❖ PFOS precursors MeFOSE and EtFOSE showed non-changing and declining trends in Arctic air reflecting the voluntary phaseout of the production of PFOS, PFOA, and PFOS-related products by their largest producer 3M in 2000. In contrast, PFCA precursors showed increasing tendencies in Arctic air.
- ❖ No trends were available for toxaphene or chlordecone.

5.2.2 Human tissues (milk and/or blood)

5.2.2.1 Background

The chapter on persistent organic pollutants in human tissues focuses on international and national programmes evaluating trends of pollutants in mother's milk and blood. Two international programmes were available for the WEOG region; the WHO milk survey and the Arctic Monitoring and Assessment Programmes (AMAP). National trend studies were available from the US, Canada, Germany, Sweden, Australia and New Zealand. In addition, a literature search of biomonitoring studies that are not part of any programme was performed.

5.2.2.2 Levels and trends of POPs reported by international programmes

5.2.2.2.1 WHO Milk survey

Since the mid-1980s, the WHO Regional Office for Europe has coordinated a comprehensive programme on possible health risks of polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) (Environmental Health in Europe No 3 1996; Environmental Health Series No 43 1989; Van Leeuwen and Malisch 2002). In some countries milk samples to the WHO survey are delivered as a part of ongoing national monitoring programmes. One such programme (with samples collected in the Uppsala area in Sweden) is discussed later in this chapter as an example.

The WHO programme has concentrated particularly on the possible health risk to infants, due to exposure to POPs via mother's milk, and is aimed to assist measures to prevent and control environmental exposure to PCDDs, PCDFs and PCBs. It can be assumed that the levels of PCDDs, PCDFs and PCBs in breast milk are representative for those in plasma, serum lipid and adipose tissue. Therefore levels of these contaminants in human milk will reflect body burden and can thus be used as an indicator for the overall exposure of the sampled population (Environmental Health in Europe No 3 1996; Environmental Health Series No 43 1989; Van Leeuwen and Malisch 2002, UNEP 2013). Participation by WEOG countries in the WHO surveys has varied with some countries participating in several of the surveys while some have not participated in any. Nonetheless, the geographical and temporal coverage for WEOG region is the best of any of the UNEP regions used for the Stockholm Convention evaluation.

Dioxins and PCBs

Five WHO-coordinated human milk surveys have taken place since 1987. A summary of the results are presented in **Table 5.2.2a, b, and c**. In the most recent survey (2009-2012) Australia, New Zealand, Ireland, Israel and Switzerland participated with one pooled sample per country.

In the 2009-2012 survey, the levels of dioxin-like PCBs ranged from 1.5 to 4.8 pg WHO-TEQ₂₀₀₅/g lipid and the levels of indicator PCBs ranged from 12.0 to 78.9 ng/g lipid. The levels of PCDD/Fs ranged from 3.2 to 5.0 pg WHO-TEQ/g lipid.

The number of participating countries has varied over the years. For PCDDs and PCDFs, some countries have participated in up to four survey rounds and data for countries participating multiple times suggest a continuing decline in levels of these pollutants. For dioxin-like PCBs and indicator PCBs, declining levels in milk are indicated in the countries with repeated measurements. Note that the toxic equivalence factors used to calculate the levels of PCDDs/PCDFs and dioxin-like PCBs differ between the first and later measuring points, and direct comparison should therefore be performed with caution.

Table 5.2.2a Levels of PCDD/PCDFs in WHO milk surveys 1987-2009.

PCDD/PCDFs (pg/g lipid)					
	1987-1988 Nordic-TEQ Range ¹⁾	1992 WHO-TEQ₂₀₀₅ Median (range) ²⁾	2000-2003 WHO-TEQ₂₀₀₅ Median (range) ²⁾	2006-2007 WHO-TEQ₂₀₀₅ Median (range) ²⁾	2009-2012 WHO-TEQ₂₀₀₅ One pooled sample ²⁾
Australia			5.2 (4.9-5.4)		4.4
Austria	17.1 – 18.6	10.9 (10.4-13.5)			
Belgium	33.7 – 40.2	26.0 (20.2-26.2)	14.4 (12.5-16.2)		
Canada	15.6 – 23.0				
Denmark	17.8	15.7			
Finland	15.5 – 18.0	16.5 (12.0-21.0)	8.0 (7.9-8.2)	4.8 (3.7-6.4)	
Germany	27.6 – 36.8	17.6	10.6 (9.5-10.7)		
Ireland			6.1 (5.5-7.5) 7.7		4.6
Israel					3.8
Italy			10.6 (7.8-12.4)		
Luxemburg			12.6 (11.5-13.7)	8.9	
Netherlands	37.4 – 39.6	22.6	15.9 (15.2-18.6)		4.5
New Zealand	5.8		6.4 (5.7-6.5)		3.2
Norway	15.0 – 19.4	10.2 (9.1-12.2)	6.3 (6.2-6.3)	4.6	
Spain		21.9 (18.9-25.0)	10.2 (9.0-16.1) 9.9 (9.0-10.7)		
Sweden	20.2 – 22.8		8.3	5.0	
Switzerland					5.0
United Kingdom	16.6 – 37.0	17.6 (16.1-19.2)			
United States	16.7		6.6 (5.7-7.4)		

1) Environmental Health Series No 34, 1989

2) Hulek et al 2014

Table 5.2.2b Levels of dioxin-like PCBs in WHO milk surveys 1987-2009.

Dioxin-like PCBs (pg/g lipid)				
	1992 I-TEQ Range ¹⁾	2000-2003 WHO-TEQ₂₀₀₅ Median (range) ²⁾	2006-2007 WHO-TEQ₂₀₀₅ Median (range) ²⁾	2009-2012 WHO-TEQ₂₀₀₅ One pooled sample ²⁾
Australia		1.8 (1.5-2.2)		1.7
Austria	11.7 – 19			
Belgium	4.7 – 7.8	7.7 (7.0-8.5)		
Canada	3.0 – 6.8			
Denmark	4.5			
Finland		3.7 (3.6-3.7)	2.1 (1.6-3.3)	
Germany	11.7	8.5 (7.8-8.9)		
Ireland		3.3 (1.7-3.4) 2.9		2.0
Italy		9.5 (5.7-11.3)		
Israel				2.5
Luxemburg		9.1 (8.8-9.4)	6.7	
Netherlands	11.0	7.7 (7.6-7.9)		2.7
New Zealand		2.9 (2.3-3.2)		1.5
Norway	9.5 – 19.5	4.7 (3.6-5.8)	3.2	
Spain	8.2 – 10.6	6.0 (5.5-10.8) 5.1 (4.0-5.8)		
Sweden		6.0	4.2	
Switzerland				4.8
United Kingdom	4.0 – 4.3			
United States		2.6 (1.9-3.3)		

¹⁾ Environmental Health in Europe No 3, 1996

²⁾ Hulek et al 2014

Table 5.2.2c Levels of indicator PCBs (sum of PCB 28, 52, 101, 138, 153 and 180) in WHO milk surveys 1987-2009 (Hulek et al., 2014).

Indicator PCB (ng/g lipid)					
	1987-1988 Median (Range)	1992 Median (Range)	2000-2003 Median (Range)	2006-2007 One pooled sample	2009-2012 One pooled sample
Australia			30.2 (24.9-35.5)		16.4
Austria		381 (303-449)			
Belgium	609 (525-734)	276 (260-306)	191 (169-213)		
Canada		137 (57.9-1361)			
Denmark		209			
Finland	177 (150-203)	161 (134-189)	90.0 (84.0-97.9)	36.2	
Germany	765	375	220 (188-238)		
Ireland			61.4 (40.8-64.5) 58.5		31.8
Italy			253 (195-323)		
Israel					23.9
Luxemburg			217 (196-237)	115	
Netherlands		253	191 (178-210)		40.1
New Zealand			37.1 (29.9-41.2)		12.0
Norway		273 (265-302)	119 (106-132)	65.7	
Spain		457 (452-461)	399 (279-467) 201 (162-203)		
Sweden			146	84.3	
Switzerland					78.9
United Kingdom		130 (129-131)			
United States	206 (197-215)		53.6 (43.4-63.8)		

Other POPs in the Stockholm Convention

In the later survey rounds the analysis of pooled human milk samples was expanded to include the other POPs presently included in the Stockholm Convention. Consequently, data on such POPs from pooled samples are available from the 2006-2007 survey from Belgium, Finland, Norway, Luxembourg and Sweden and from the 2009-2012 survey from New Zealand, Israel, Ireland, Belgium, Switzerland and Australia.

- ❖ *Aldrin and dieldrin*: Aldrin was not detected in any sample. Aldrin has been banned for many years and any present aldrin would have degraded into dieldrin. Dieldrin was found in levels ranging from 1.6 to 16.8 ng/g lipid. Due to the long time ban, the levels of dieldrin in the WEOG-region are expected to be low.
- ❖ *Chlordane*: cis-Chlordane and trans-chlordane were not detected in any milk sample. However, the degradation product oxychlordane was detected in milk samples from all participating countries in levels ranging from 0.6 to 8.1 ng/g lipid.
- ❖ *DDT Complex*: The levels of the DDT Complex (including DDE, DDT and DDD) in the reporting countries ranged from 26.5 to 552 ng/g lipid. The levels in Australia and New Zealand were remarkably higher than in the European countries. The compound that contributed most to the DDT Complex was p,p'-DDE, indicating that these residues are the result of DDT use in the distant past. Having been banned in the WEOG region for many years, the levels of DDT in breast milk have declined significantly (Smith 1999). In countries where the current levels are low, further decline in human milk are expected to be slight.
- ❖ *Endosulfan*: The levels of endosulfan I and endosulfan II were below the limit of detection in all reporting countries.
- ❖ *Endrin*: The levels of endrin were below the limit of detection in all reporting countries.
- ❖ *Hexachlorobenzene (HCB)*: HCB was detected in milk samples from all reporting countries. The levels ranged from 2.8 to 17.8 ng/g lipid.
- ❖ *Mirex*: The levels of mirex were below the limit of detection in all reporting countries.
- ❖ *Pentachlorobenzene (PeCB)*: PeCB was measured only in the 2009-2012 survey and the levels were below the limit of detection in all reporting countries.
- ❖ *Toxaphene*: The levels of Parlar 26 ranged from <LOQ to 1.3 ng/g lipid and the levels of Parlar 50 ranged from <LOQ to 2.6 ng/g lipid in the reporting countries.
- ❖ *Hexachlorocyclohexanes (HCH)*: the levels of α -HCH were below the limit of detection in all reporting countries. The levels of β -HCH ranged from 3.9 to 17.7 ng/g lipid and the levels of γ -HCH ranged from <LOQ-1.0 ng/g lipid.

- ❖ *Heptachlor*: The levels of heptachlor were below the limit of detection in all reporting countries. However, a persistent metabolite of heptachlor, cis-heptachlorepoxyde, was detected in all but two samples. The highest level was 5.6 ng/g lipid. Another metabolites of heptachlor, trans-heptachlorepoxyde, was not detected in any sample.
- ❖ *Polybrominated diphenyl ethers (PBDE)*: PBDEs were only measured in milk samples from Luxembourg, Finland and Sweden (2006-2007) and New Zealand and Israel (2009-2012). The levels of BDE-47 ranged from 1.3 to 4.1 ng/g lipid. It is noteworthy that an American sample from an earlier survey round in 2003 contained much higher levels (144 ng/g lipid) than the later samples from Europe, Australia and New Zealand.
- ❖ *Hexabromocyclododecane (HBCD)*: HBCD was only measure in samples from Israel (2012), New Zealand (2011), Finland (2007) and Luxembourg (2006). The levels of α -HBCD ranged from <LOQ to 1.4 ng/g lipid and levels of γ -HBCD were ranging from <LOQ to 0.19 ng/g lipid. β -HBCD was not detected in any sample.
- ❖ *Hexabromobiphenyl (HBB or BB-153)*: The level of HBB was only measured in the 2009-2012 survey. The levels were below the limit of detection in four European countries and New Zealand, but were detected at 1.5 ng/g lipid in milk from Australia.

5.2.2.2.1 Arctic Monitoring and Assessment Programme (AMAP). Inter-country Comparisons and Temporal Trends in the Arctic

The sampling of human tissue (blood and breast milk) for contaminants has taken place in a number of circumpolar countries since the early 1990s. These data sets provide an opportunity to assess temporal trends and additional inter-country comparisons of organochlorines and heavy metals in pregnant women and, in some cases, in adults (both men and women).

This analysis is based on the various population samples available for each country. The studied population and the time periods covered for each country differ, but overall comparisons can be made. Some countries have two sampling time points, while others have several. The pattern of declining concentrations in countries that have two data points are similar to trends seen among mothers from parts of Arctic Canada and Greenland where more frequent population sampling took place over a similar period. The similar patterns strengthen the overall findings.

5.2.2.2.1.1 Maternal blood and breast milk comparisons

AMAP has generally used blood as the medium of choice for evaluating human exposure, although in some cases breast milk has been used where maternal blood data were not available.

Although breast milk is useful in specific instances, notably when evaluating perinatal health risks, it suffers from several limitations that make it less than ideal for population exposure monitoring. Because concentrations in breast milk can only be determined after the birth, in *utero* exposure is not addressed. Also, because not all environmental contaminants are found in breast milk, child exposure from other sources may go unnoticed. Additionally, in some cultures, women are unwilling to provide breast milk, but will provide blood samples.

Blood concentrations accurately reflect the body burden of most contaminants, whether lipophilic, protein-bound, or ionic. For weakly lipophilic compounds, concentrations are much higher in blood than in milk. As an example, perfluorooctane sulfonate (PFOS) serum concentrations were found to be 100-fold greater than breast milk concentrations in paired maternal-newborn samples (Karrman et al., 2007). For lipophilic compounds, which include most POPs, blood concentrations expressed on a lipid basis are well-correlated with concentrations in other compartments such as stored fat and breast milk. Blood concentrations obtained from pregnant women enable public health action, if required, during the pregnancy when the fetus is very susceptible to damage. Occupational and environmental exposure guidelines based on blood concentrations exist for many compounds.

In conclusion, blood and breast milk are both useful and complementary media for monitoring environmental contaminants. With regard to blood, the focus on QA/QC related to the AMAP human health monitoring has been highly successful and has made inter-regional and time-trend evaluations meaningful for Arctic residents, scientists, and policy makers and as a component of the Stockholm Convention efforts to evaluate its effectiveness.

Persistent organic pollutants

The results of recent biomonitoring studies suggest that the concentrations of certain POPs (e.g., oxychlordan, DDE) are two- to ten- fold higher among Inuit living in eastern parts of the Canadian Arctic (Baffin and Nunavik) and Greenland compared to other populations in the Arctic (Norway, Sweden, Iceland, Dene-Métis from Inuvik Canada), as was seen in previous assessments (AMAP 1998; AMAP 2003). There are several cases where various organochlorines are similarly elevated in specific regions of Russia. For oxychlordan and CB153, the highest concentrations were found in maternal blood of Inuit and Chukchi living in the Chukotka Peninsula coastal region.

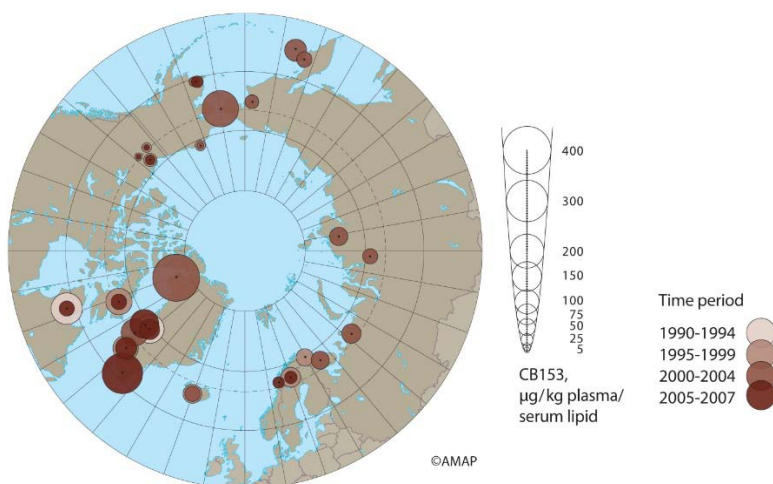


Figure 5.2.2a PCB (CB153) concentrations in blood of mothers, pregnant women and women of childbearing age in the circumpolar countries.

These concentrations were slightly higher than the more recent concentrations among Inuit mothers from Arctic Canada and Greenland but not as high as some of those seen in the 1990s from these regions. Data for organochlorines in Inuit men are also available for Canada, Greenland, and Russia. The highest concentrations of oxychlordan and CB153 were seen in Qaanaaq, Greenland (**Figure 5.2.2a**). These varying inter-country comparisons indicate the need for further time trend and regional monitoring. In Russia, the DDE concentrations in maternal blood were elevated in non-indigenous (ethnic Russian) and indigenous populations. The highest DDE concentration (452 µg/ kg plasma lipids) was found among pregnant ethnic Russian women in the Norilsk area (**Figure 5.2.2b**). This elevation of DDE in the Russian population is likely to be due to the use of DDT in the commercial Russian food supply or its use for residential or environmental pest control.

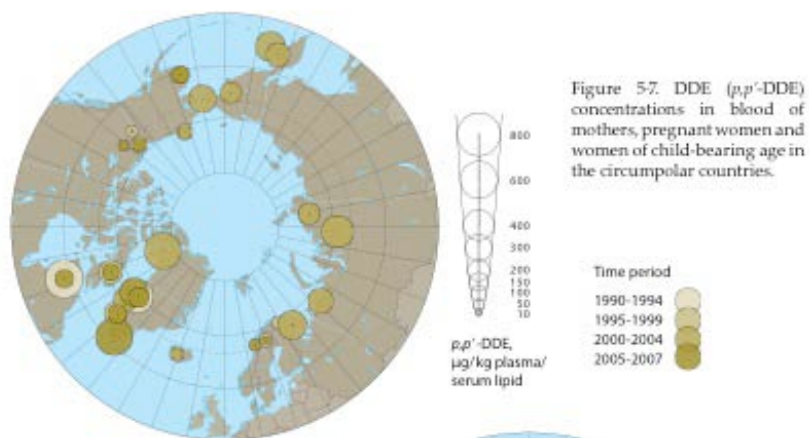


Figure 5.2.2b DDE (*p,p'*-DDE) concentrations in blood of mothers, pregnant women and women of childbearing age in the circumpolar countries.

The data sets suggest that concentrations of legacy POPs have decreased in many populations compared to the data presented in the two previous AMAP assessments (AMAP 1998; AMAP 2003). Notable decreases occurred in concentrations of oxychlordan, DDE and CB153 in maternal blood of Inuit living in parts of the eastern Canadian Arctic (Baffin and Nunavik) and Disko Bay in Greenland.

There are exceptions to the overall decreases in POPs concentrations in maternal blood samples in the circumpolar region. In Nuuk, Greenland, where only intermediate concentrations of contaminants were found in mothers during the 1990s, due to lower marine mammal consumption, annual changes are variable and there has been no significant decline in the concentrations of oxychlordan, DDE and CB153. People living in Nuuk have always had greater access to store-bought food and may not have changed their marine food consumption as much as other communities where people relied more heavily on traditional marine foods.

Dietary studies help to interpret trends in POPs concentrations in human populations. Unfortunately, dietary studies were not carried out in parallel with many of the contaminant trend assessments. Initial dietary trend analyses have been assessed in the Inuvik region of Canada and Disko Bay in Greenland and provide support for the changes in maternal contaminant concentrations. In the Inuvik region, Inuit mothers were eating more fish that have lower concentrations of contaminants, (see AMAP 2009 for further details) and less marine mammal fats (which have higher concentrations of contaminants). In Greenland, mothers are also eating smaller amounts of the more highly contaminated marine mammals, which support the declining trends observed in maternal contaminant concentrations.

The more moderate decrease in organochlorine concentrations in Norway, Sweden, Iceland, and Finland is likely to be due to the banning and/or restriction of many of these compounds in these regions during the 1970s, and the resulting decline in the concentrations of these contaminants in the commercial/store-bought food chain. In Russia, the results of this assessment suggest that exposure to several organochlorines could be associated with household or environmental use of insecticides, possible use in the commercial food supply, or contamination during food processing.

The breast milk studies carried out in Finland and Russia complement the data in the maternal blood studies. Breast milk studies are available for southern, central and northern Finland and the Murmansk, Arkhangelsk, and Chukotka regions in Russia. For the cases where two time points were available in Finland and Russia, there was a decrease in concentrations of oxychlordan, DDE, and CB153 as was seen elsewhere in the Arctic in maternal blood (**Figure 5.2.2c**). Also, the highest concentrations of DDE occur in ethnic Russian mothers as was seen in the maternal blood comparisons.

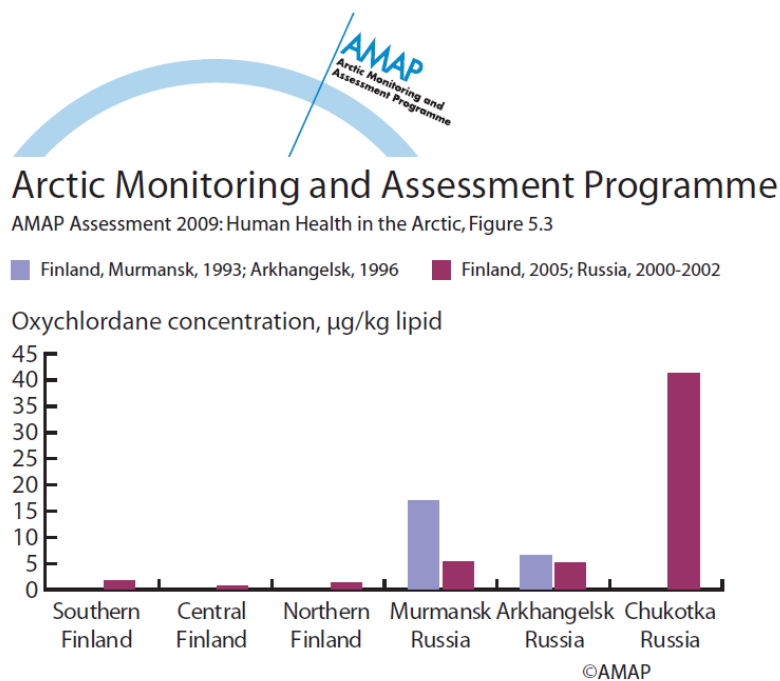


Figure 5.2.2c Oxychlordan concentrations in breast milk from various regions of Finland and northern Russia (AMAP 2009).

5.2.2.2.1.2 Emerging contaminants of concern for humans in Arctic regions

In addition to the legacy POPs discussed in the previous section, a growing number of other compounds are being detected in humans from the Arctic regions of the world. Some of these are

fairly ‘new’ compounds whereas others have been around for decades but have only recently been detected due to advances in analytical techniques. This new biomonitoring and additional toxicological / epidemiological work has indicated that a number of these compounds raise significant human and environmental concerns. The boundary between legacy POPs and emerging compounds is very much an overlapping spectrum and it will be possible for a much more integrated discussion in future assessments. The main compounds addressed in this section are the brominated flame retardants and the perfluorinated compounds (PFAS), in particular the polybrominated diphenylethers (PBDEs), perflourooctane sulfonate (PFOS), and perflourooctanoic acid (PFOA). Until recently, there were few data available on human concentrations of these compounds.

5.2.2.2.1.3 Circumpolar Comparisons

Polybrominated diphenylethers

Elevated human concentrations of PBDEs are now reported in the Arctic, but these findings seem to be limited to Alaska (U.S. Arctic). Levels in mothers for all other countries reporting PBDE concentrations in this assessment are considerably lower with concentrations from the European Arctic being the lowest (**Figure 5.2.2d**). The concentrations reported from Alaska are comparable to, or even somewhat higher than, those recently reported for the general U.S. population (Sjodin et al., 2008).

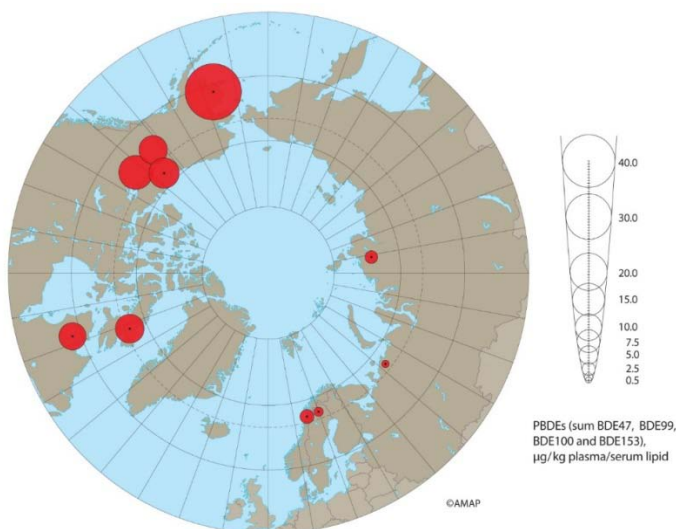


Figure 5.2.2d PBDE (sum of BDE-47, BDE-99, BDE-100 and BDE-153) concentrations in blood of mothers, pregnant women and women of childbearing age in the circumpolar countries.

The mean BDE47 concentration in Alaska (Yupiks) was reported to be 26 µg/kg lipids, which is

considerably higher than that reported for the Canadian arctic communities, with mean concentrations of 6 to 11 µg/kg lipids. Concentrations in the European Arctic are considerably lower, with mean concentrations for BDE-47 in the range from < 0.6 to 2.2 µg/kg lipids. Within Canada, concentrations seem slightly higher in the non-indigenous population from Inuvik compared to Dene-Métis and Inuit from the Inuvik, Baffin and Nunavik regions, although the sample size among non-indigenous northern Canadians is quite small. Concentrations in Norway, Russia, and Finland are comparable, even though the Naryan Mar (Russia) data seem slightly lower than for the other populations. Again, these concentrations are all low and close to detection limits, and are thus associated with greater uncertainty. The predominant PBDE is still BDE-47, but data from Norway indicate that BDE-209 is found in comparable concentrations to BDE-47. The finding of elevated concentrations of BDE-209 together with BDE-207 is supported by a Swedish study where high concentrations of BDE-207, together with BDE-209 and BDE-47, were observed (Karlsson et al., 2007). Despite the higher uncertainty associated with BDE-207 and BDE-209, this clearly indicates the need to determine this compound in future assessments.

The ratio of BDE-153 to BDE-47 is highly variable between the countries, with BDE-153 concentrations constituting only 25% of BDE-47 concentrations in the Alaskan data. In other countries like Norway and Canada, concentrations are comparable. The reason for this could be that the diet constitutes a larger proportion of the exposure for people that are exposed to lower concentrations. The men also consumed more traditional food and thus a larger proportion of BDE-153. The differences in exposure to the different mixtures in different countries may also contribute to higher concentrations of BDE-47 relative to BDE-153. Therefore, a shift towards BDE-153 and a decrease in BDE-47 is expected in the most remote Arctic communities where exposures are more related to the food chain. Others have also reported that there seems to be a general trend with increasing proportions of BDE-153 in populations with non-occupational exposure (Thuresson et al., 2006).

There are few available data on trends in these compounds in humans from the Arctic. An increasing trend in PBDE concentrations has recently been demonstrated in Nunavik (Canada). In contrast, concentrations are reported to be leveling off or decreasing in the southern parts of Sweden and Norway. For the more persistent congeners like BDE-153 it might take longer before a similar decline occurs because this will dominate in the marine food chain.

The limited human data on TBBPA and HBCD show that concentrations are still low and mostly undetected (Knutsen et al., 2008;

Perfluorinated compounds

The main perfluorinated compound reported here is PFOS with only limited data on PFOA. Discussions are therefore focused on PFOS. It should be noted that this is a compound with greater analytical uncertainty than the legacy POPs. There is reason to believe that the estimated concentrations are associated with an uncertainty of 10 % to 40 % depending on the laboratory. PFOS and PFOA were only recently introduced in the AMAP external quality assessment scheme (Ring Test). In addition, PFOS is not associated with lipids and thus only wet weight concentrations of this compound are considered here.

Of all the contaminants reported in this assessment, PFOS is currently the predominant compound in human plasma. The maximum concentration reported in this assessment is 470 µg/L plasma found in an Inuit male from Nunavik.

Even though it is by far the predominant compound in plasma, the fact that PFOS is not associated with lipids implies that the total burden of PFOS might not be higher than the more lipid-soluble compounds (legacy POPs). However, this has not been completely evaluated and PFOS is also associated with organs such as the liver.

The geographical distribution of human PFOS exposure across the Arctic provides no clear spatial distribution or distinct differences between countries (**Figure 5.2.2e**). In addition, sample size for most countries is limited, reducing the availability of firm conclusions. However, concentrations reported from Sweden, Alaska, and Naryan Mar (Russia) (mean concentrations 8.1 µg/L plasma, 7.4 µg/L plasma, and 9.3 µg/L plasma, respectively) seem slightly lower than the majority of the other concentrations. The highest mean concentration (20.6 µg/L plasma) was reported among men from Nunavik. Initial time trend data for women of childbearing age in Nunavik suggest PFOS concentrations are decreasing; this is in contrast to recent data from Nuuk, Greenland that indicate an increasing concentration between 1997 and 2006. A recent study using samples collected in 2001/02 compared Greenlandic Inuit men to men from Poland and Ukraine and found markedly higher concentrations of PFOS in the Inuit men (52 µg/L serum) than those seen in men from Poland and Ukraine (19 and 8.1 µg/L serum, respectively) (Lindh et al., 2012). This study found that for Greenlandic men's marine food consumption and tea intake were important determinants of PFOS concentration, though all the determinants only explained 22% of the variation. The PFOS concentrations cited by Lindh et al 2012 for Greenlandic men are higher than any other population presented here.

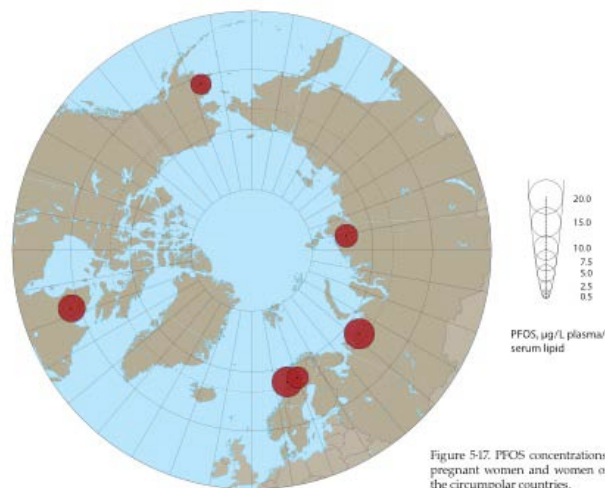


Figure 5-17. PFOS concentrations in blood of mothers, pregnant women and women of child-bearing age in the circumpolar countries.

Figure 5.2.2e *PFOS concentrations in blood of mothers, pregnant women and women of childbearing age in the circumpolar countries.*

For Nunavik, gender-specific data indicated that men had significantly higher concentrations of PFOS than women from the same communities. Significantly higher concentrations among men are in accord with the findings by Calafat et al. (2007).

The range of PFOS exposure in the different populations is narrow compared to other contaminants, with considerable uncertainty linked to the possible routes of exposure. Dietary data were only available from Nunavik, where increasing concentrations of PFOS were associated with the consumption of fish and marine mammal meat. Marine mammal meat was also identified as a source of PFOS exposure in a recent study on the Faroe Islands (Weihe et al., 2008). Fromme et al. (2007) summarized the overall exposure assessment for adults, and concluded that dietary exposure is the dominant intake pathway for both PFOS and PFOA for the western European population.

PFOA data from Norway, Russia, and Alaska are comparable and the concentrations are considerably lower than for PFOS. Nevertheless, compared to legacy POPs, concentrations are high, which is of concern considering that higher concentrations of this compound are reported in cord plasma than maternal plasma. More data on PFOA are required to understand both trends and spatial distribution.

The AMAP HHAG is undertaking a new assessment of the human exposure to environmental contaminants and the possible human health impacts in the circumpolar arctic. This report will be available in 2015.

5.2.2.3 Levels and trends of POPs reported by national programmes

5.2.2.3.1 National Health and Nutrition Examination Survey (NHANES)

The levels of persistent organic pollutants in blood serum from the general U.S. population (aged 12 years and older) have since 1999 continuously been measured in the National Health and Nutrition Examination Survey (NHANES), initiated by the Centers for Disease Control and Prevention (CDC 2009; CDC 2013; Sjodin et al., 2014). In the early survey periods (1999-2000, 2001-2002 and 2003-2004) POPs were analysed in individual serum samples, whereas in the later survey periods (2005-2006, 2007-2008 and 2009-2010) POPs were analysed in pooled serum samples, with exception for PFOS which was measured in individual serum samples at all time points. The differences in analysed samples (pooled or individual) and reported summary statistics make time trend observations difficult to interpret. In **Table 5.2.2d**, results based on the individual samples are given for all women, regardless of age or ethnicity, whereas results based on pooled serum samples are given for women in child-bearing age (20-39 years), divided into ethnicity groups. The results from 2003-2004 are given both as geometric mean for all women as well as arithmetic mean for women in child-bearing age categorized by ethnicity, to allow comparison with previous and later time points. The levels of several POPs increase with age, thus by excluding older and/or younger individuals, the results will differ. Several OCPs (i.e. aldrin, dieldrin, endrin, o,p'-DDT and heptachlor) were not analysed after 2004 since the levels in previous surveys had been lower than the LOD.

- ❖ *Aldrin and Dieldrin*: The levels of aldrin and dieldrin were only measured in NHANES 2001-2002 and 2003-2004. Aldrin and dieldrin have been banned for many years and any aldrin present would have degraded into dieldrin. The levels of dieldrin were below the limit of detection in most samples and the mean levels at the 95th percentile were 19.0-20.3 ng/g lipid. The levels of aldrin were below the limit of detection.
- ❖ *Chlordane*: *Oxychlordane*, a persistent metabolite of chlordane, and *trans-nonachlor*, a persistent by-product in technical chlordane, were measured in all NHANES surveys to evaluate the exposure to chlordane.
- ❖ *DDT/DDE*: The levels of o,p'-DDT and p,p'-DDT were below the limit of detection in most serum samples. The historic use of DDT can be reflected by measuring DDE, which is the main metabolite of DDT. In NHANES 1999-2000, 2001-2002 and 2003-2004, the geometric mean levels of p,p'-DDE in women of all age-groups ranged between 241 and 305 ng/g lipid, with no time trend observed. In the pooled serum samples from women in

childbearing age collected in 2005-2006 and 2007-2008 the mean levels of *p,p'*-DDE ranged between 91.8-895 ng/g lipid. There were no significant differences between the mean levels in the total study population in 2003-2004 compared to 2005-2006 and 2007-2008. The levels of DDE increased with age. For example, the levels of *p,p'*-DDE at the three latest time points were 530-720% higher in the ≥ 60 year age group compared to the 12-19 year olds (Sjodin et al., 2014).

- ❖ *Endrin*: In NHANES 2001-2002 and 2003-2004, the serum levels of endrin were below the limit of detection and no later measurements were made.
- ❖ *Heptachlor*: *Heptachlor epoxide*, a persistent metabolite of heptachlor, was measured in NHANES 1999-2000, 2001-2002 and 2003-2004. The serum levels were mostly below the limit of detection and the levels at the 95th percentile were 24.0, 21.8 and 18.9 ng/g lipid in respective survey period.
- ❖ *Hexachlorobenzene (HCB)*: The arithmetic mean levels of HCB were significantly lower in 2005-2006 and 2007-2008 compared to 2003-2004. The levels increased with age but there were no consistent differences between men and women (Sjodin et al., 2014). HCB was not detected in 1999-2000 and 2001-2002, probably due to higher detection limits.
- ❖ *Hexachlorocyclohexane (HCH)*: In NHANES, β -HCH and γ -HCH were measured to evaluate the HCH exposure. The levels of γ -HCH were below the limit of detection, whereas the levels of β -HCH were detected more frequently, but not in all samples.
- ❖ *Mirex*: The levels of mirex were measured at all NHANES time points and the levels were mostly below the limit of detection.
- ❖ *Polybrominated diphenyl ethers (PBDE) and Hexabromobiphenyl (HBB or BB-153)*: The levels of PBDEs and BB-153 were measured in 2003-2004, 2005-2006 and 2007-2008. Among the PBDEs, BDE-47 was found in the highest levels, three to four times higher than the levels of BDE-153. The arithmetic mean levels of PBDEs were generally lower in 2005-2006 and 2007-2008 compared to 2003-2004, although the decrease was not statistically significant for most PBDEs. Technical PentaBDE was phased-out in the U.S. in 2004. However, these compounds are present in products that are still in use, thus the decrease is not yet clearly visible in humans. In contrast to other POPs, the levels of PBDEs did not increase by age. This is probably due to assumed shorter biological half-life and a more recent exposure than other compounds banned for decades (Sjodin et al., 2014). It is well known that the levels of PBDEs are considerably higher in the U.S. population than in studied European populations (Sjodin et al., 2008).
- ❖ *Perfluorooctane sulfonate (PFOS)*: PFOS has been measured in individual samples from each survey period and the levels have been decreasing steadily in the whole study

population, from 30.4 µg/L in 1999 to 9.32 µg/L at the latest time point in 2009-2010 (Figure 5.2.2f).

- ❖ *Polychlorinated biphenyls (PCB)*: Pooled serum collected in 2005-2006 and 2007-2008 were analysed for 43 PCB congeners whereas individual serum samples from 2003-2004 were analysed for 35 PCB congeners. The levels of PCBs decreased during the survey period. The arithmetic mean concentration of PCB 153 in the age groups 12-19, 20-39 and 40-59 years were 37%, 32% and 24% lower, respectively, in 2007-2008 compared to 2003-2004. The levels increased by age, as ≥60 year olds had 920-1200% higher levels of PCB 153 than 12-19 year old adolescents (Sjodin et al., 2014).
- ❖ *Polychlorinated dibenzo-p-dioxins and furans (PCDD/F)*: PCDD/Fs were measured at the four first survey time points (1999-2006). The levels of these compounds are highly dependent on age, as the levels are higher in older people. It is therefore difficult to give a universal mean value. In the three first surveys, the mean concentrations of PCDD/Fs in serum from 20-39 year old women were 12.0, 10.8 and 7.4 pg TEQ/g lipid in 1999-2000, 2001-2002 and 2003-2004, respectively. The data from 1999-2004 indicate a decrease of PCDD/Fs in the younger age groups, whereas a slight increase was observed in the oldest age group (LaKind et al., 2009).

Table 5.2.2d Levels of persistent organic pollutants measured in individual serum samples from women >12 years of age (1999-2004) and in pooled serum samples from women 20-39 years of age divided into ethnicity groups (2005-2008). The results from 2003-2004 are also given for women 20-39 years of age, divided into ethnicity groups, for comparison of selected compounds. Geometric mean (GM) is given for individual samples and weighted arithmetic mean (AM) is given for pooled samples (as well as for ethnicity-divided results from 2003-2004) All levels are presented as ng/g lipid (CDC 2013; Sjodin et al., 2014).

	Year	Women >12 years GM	Non-hispanic white women 20-39 years AM	Non-hispanic black women 20-39 years AM	Mexican American women 20-39 years AM
Oxychlordan	99-00	*			
	01-02	11.7			
	03-04	9.63			
	05-06		5.64	5.56	4.39
	07-08		5.79	4.45	4.17
trans-Nonachlor	99-00	18.8			
	01-02	17.0			
	03-04	14.8			
	05-06		9.70	9.32	6.40
	07-08		8.95	9.42	7.55
p,p'-DDE	99-00	270			
	01-02	305			
	03-04	235	138	160	924
	05-06		102	237	895
	07-08		91.8	105	653
HCB	99-00/01-02	*			
	03-04	15.8	14.1	12.9	19.6
	05-06		7.1	5.9	9.8
	07-08		7.9	7.0	10.4
β-HCH	99-00	11.1			
	01-02	10.2			
	03-04	8.43			
	05-06		2.79	*	12.0
	07-08		*	*	5.65
PCB 153	99-00	*			
	01-02	26.1			
	03-04	19.7	14.4	15.3	6.6
	05-06		8.5	10.8	4.7
	07-08		9.4	9.0	5.6
BDE-47	03-04	19.6	40.7	53.5	39.6
	05-06		50.0	61.0	30.4
	07-08		32.2	32.2	31.2
BDE-153	03-04	4.78	17.5	8.4	6.0
	05-06		11.1	9.6	6.7
	07-08		11.8	11.0	11.1
BB-153	03-04	1.92			
	05-06		2.63	2.38	*
	07-08		1.81	*	*

*Not calculated: proportion of results below limit of detection was too high to provide a valid result or standard error >30% of mean.

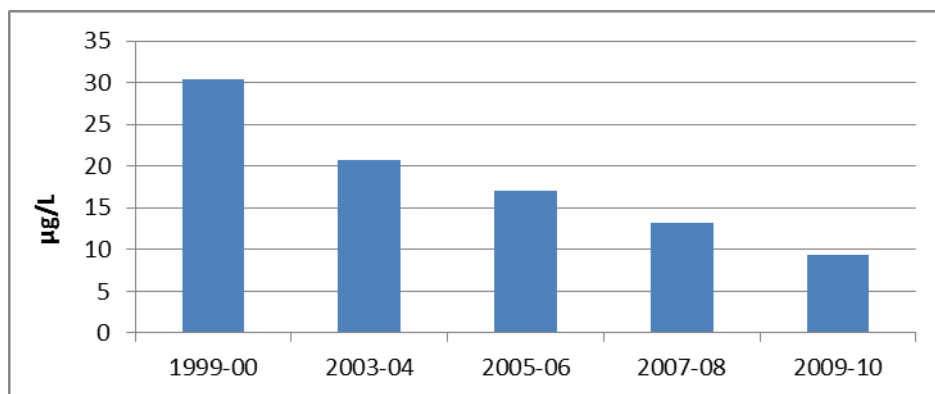


Figure 5.2.2f Levels of PFOS (µg/L) in the NHANES population between 1999 and 2010.

5.2.2.3.2 Canadian Health Measures Survey (CHMS) and the First Nations Biomonitoring Initiative (FNBI).

The Canadian Health Measures Survey (CHMS) is an on-going national survey conducted in two-year cycles. Two cycles (2007-2009 and 2009-2011) have been performed since the launch in 2007 (Health Canada 2010; Health Canada 2013). In cycle 1, several POPs included in the Stockholm Convention were measured in plasma from Canadians aged 20 to 79 years. In cycle 2, PFOS was the only POP included in the analysis. The results from these cycles are presented in **Table 5.2.2e**. The sample collection for cycle 3 will be completed in 2013 and the results were not available when writing this report.

The exposure to chemicals in the Canadian First Nation population living on reserves was measured in the First Nations Biomonitoring Initiative (FNBI). Blood samples were collected in 2011 from 503 adults and analysed for several POPs included in the Stockholm Convention (AFN 2013). Comparison to the CHMS data can be made, but the differences should be interpreted with caution since the target populations slightly differ. The levels of oxychlordane, trans-nonachlor, β -HCH, p,p'-DDT, PFOS and BDE-47 were statistically lower in FNBI compared to CHMS cycle 1. These differences can be explained by the time differences between the studies and/or differences between the study populations.

Table 5.2.2e Median levels ($\mu\text{g/kg lipid}$) of POPs in plasma measured in CHMS cycle 1 and FNBI. The levels of PFOS ($\mu\text{g/L}$) are also given for CHMS cycle 2.

Compound	CHMS		FNBI	
	%<LOD	Median	%<LOD	Median
Aldrin	100%	<LOD	100%	<LOD
Chlordane				
α -Chlordane	100%	<LOD	100%	<LOD
γ -Chlordane	99.8%	<LOD	100%	<LOD
<i>cis</i> -Nonachlor	49.1%	<LOD	51.6%	<LOD
<i>trans</i> -Nonachlor	6.0%	6.30	19.7%	0.03
Oxychlordane	2.6%	4.28	13.4%	2.35
p,p-DDT	90.6%	<LOD	96.8%	<LOD
p,p'-DDE	0.36%	126.78	4.0%	65.51
HCB	24.7%	9.31	41.5%	5.89
β -HCH	7.0%	5.19	35.5%	1.43
γ -HCH	99.5%	<LOD	100%	<LOD
Mirex	47.4%	<LOD	49.3%	1.40E
Toxaphene				
Parlar 26	73.7%	<LOD	81.5%	<LOD
Parlar 50	52.4%	<LOD	68.8%	<LOD
PCB				
Aroclor 1260	0.42%	153.30	7.6%	93.76E
PCB 153	2.5%	19.46	5.7%	12.06E
PBDE				
BDE 47	25.3%	9.71	32.7%	6.02E
BDE 153	58.7%	<LOD	47.3%	2.37
BB 153	96.6%	<LOD	94.1	<LOD
PFOS	0.14%	9.1 (cycle 1)	1.1	3.20
PFOS	0.39%	6.8 (cycle 2)		

*The survey estimates should be used with caution. Their associated coefficient of variation is between 16.6% and 33.3%

5.2.2.3.3 German Environmental Specimen Bank (ESB)

The German Environmental Specimen Bank (ESB) was established in 1985 as a permanent institution for the systematic collection, processing, characterisation and storage of environmental samples from marine, freshwater and terrestrial ecosystems as well as for human samples in Germany. Blood and other human specimens have been collected since 1981 from a group of about 100 persons in defined peripheral conditions (without known occupational / non dietary exposure) each year. The human media samples (blood, urine, and hair) are taken from individuals at selected sites and the aim of the sampling is to collect samples which represent the

general German population. It was decided to use voluntary students from the Universities of Münster, Halle, Greifswald, and Ulm as donors. With individuals and groups moving home frequently in a mobile society, it is assumed that almost the entire country is represented (Gies et al., 2007). Since samples are stored in a specimen bank retrospective studies can be performed. PCB 153 and HCB (**Figure 5.2.2g** and **Figure 5.2.2h**) have been analysed in pooled plasma samples from all sampling areas on a yearly basis. The data indicate a continuous decreasing trend. In addition, PFOS has been measured in plasma only from Münster students since 1982. The levels of PFOS doubled between 1982 and 1986 and then decreased gradually, reaching a level of 4 µg/L in 2010 (Schröter-Kermani et al., 2013) (**Figure 5.2.2i**).

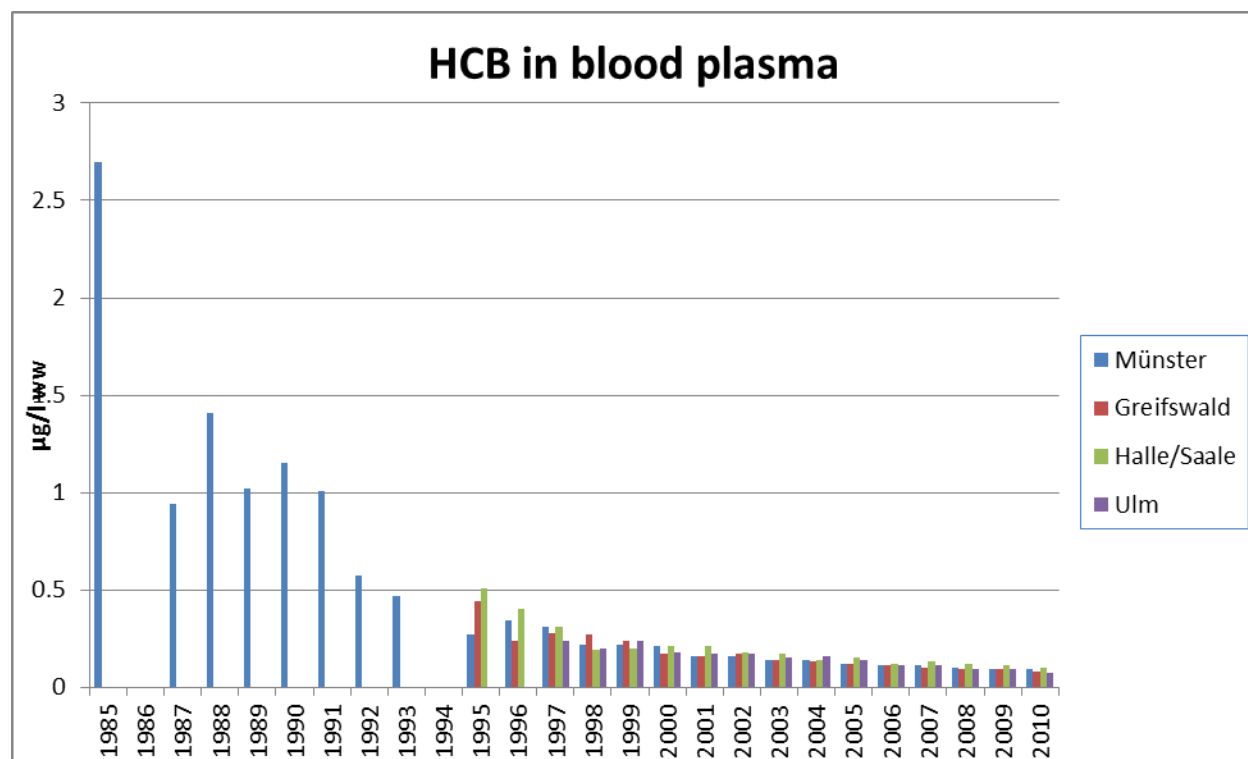


Figure 5.2.2g HCB in blood plasma (µg/L) from students in the German Environmental Specimen Bank (Umweltbundesamt 2013).

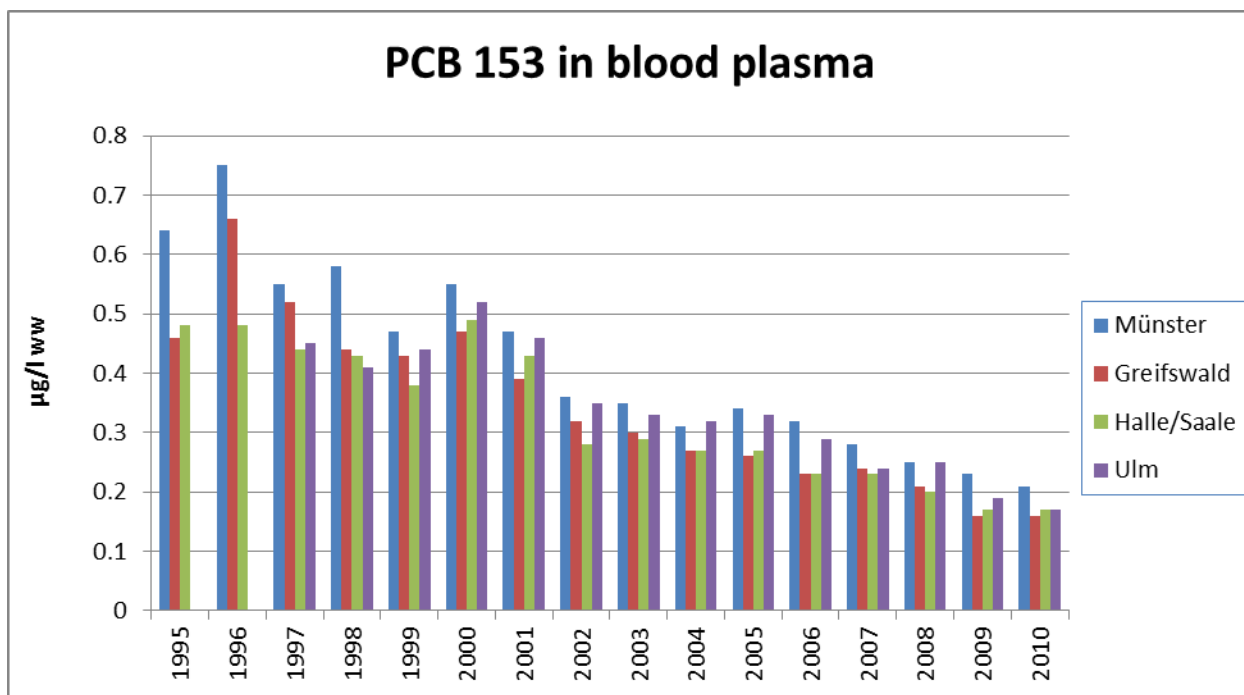


Figure 5.2.2h PCB 153 in blood plasma ($\mu\text{g/L}$) from students in the German Environmental Specimen Bank (Umweltbundesamt 2013).

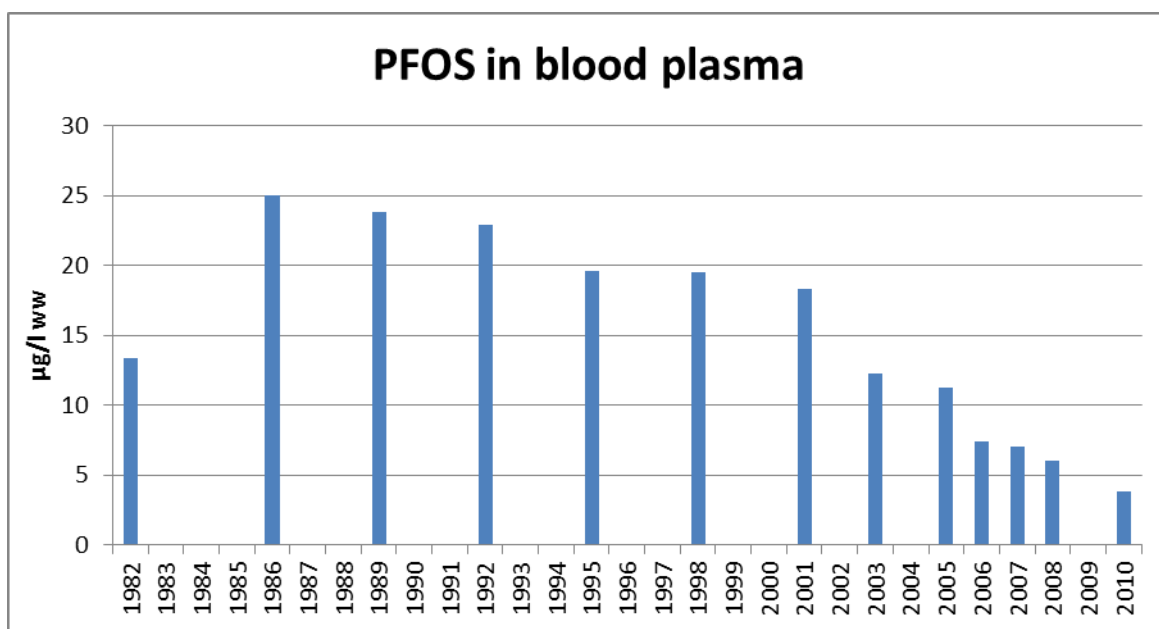


Figure 5.2.2i PFOS in blood plasma ($\mu\text{g/L}$) from students in the German Environmental Specimen Bank (Umweltbundesamt 2013).

5.2.2.3.4 German Environmental Survey (GerES)

The German Environmental Survey (GerES) is a representative population study aiming to determine the exposure of Germany's general population to environmental contaminants. The study has been conducted by the German Federal Environment Agency since the mid-1980s (Becker et al., 2008). Blood specimens from GerES III and GerES IV were analyzed for polychlorinated biphenyls (PCB), dichlorodiphenyldichloroethylene (DDE), hexachlorobenzene (HCB) and a number of other substances not a part of this evaluation. The number of samples taken has varied. For example, in GerES III a cross sectional sample was taken including 4822 adults aged 18 to 69 years from 120 sampling locations representative of the German population with regard to community size, age and gender. In GerES IV, 1790 children aged 3 to 14 years and living in 150 different sampling locations were examined (**Table 5.2.2f**). GerEs V, focusing on children and adolescents, is currently being prepared. However, no data was available from this round when writing this report.

Table 5.2.2f Levels of pollutants in whole blood of children (7-14 years) in the German Environmental Survey IV 2003/2006 (Becker et al., 2008).

Substance	Group	Mean estimated level (µg/L)
PCB (138, 153, 180)	Whole group	0.38
PCB (138, 153, 180)	Boys	0.39
PCB (138, 153, 180)	Girls	0.36
DDE	Whole group	0.30
DDE	Boys	0.31
DDE	Girls	0.30
HCB	Whole group	0.11
HCB	Boys	0.11
HCB	Girls	0.11

For the population not exposed at the workplace, the essential exposure pathway is through food consumption, particularly that of foods rich in fat of animal origin. Other social factors, length of breast feeding and gender will also determine the levels observed. Even if trends have not yet been reported from the German Environmental Survey, comparisons can be made with other German results. The data can be compared for example with the monitoring of organic pollutants in blood of children from Baden-Württemberg (Link et al., 2012b; see below) and data from North Rhine-Westphalia (Wilhelm et al., 2007). The observed levels of persistent organic pollutants can be dependent on a number of factors such as gender, age, place of living and length of breast feeding (Link et al., 2005; Link et al., 2012b; Wilhelm et al., 2007). The

available data do however indicate decreasing trends when comparisons are made within the same group at the same location.

Link and co-workers (Link et al., 2012b) measured DDE, HCB, PCBs and PCDD/PCDF in blood samples, collected at six sampling time points between 1996 and 2009, from 9-11 year old children living in Baden-Württemberg, Germany. The median levels of DDE, HCB and PCBs decreased by approximately one third over the study period (**Figure 5.2.2j**). PCDD/PCDF decreased to a lesser extent and did not decrease after 2002, which may be due to that many samples were in the range of the quantification limit. For all compounds, the levels were significantly higher in breastfed children than non-breastfed children. The blood samples collected between 2002 and 2009 were also analysed for PBDEs (Link et al., 2012a). The levels of PBDEs included in the Stockholm Convention decreased slightly or remained at consistent levels during the study period and no association with breast-feeding was found.

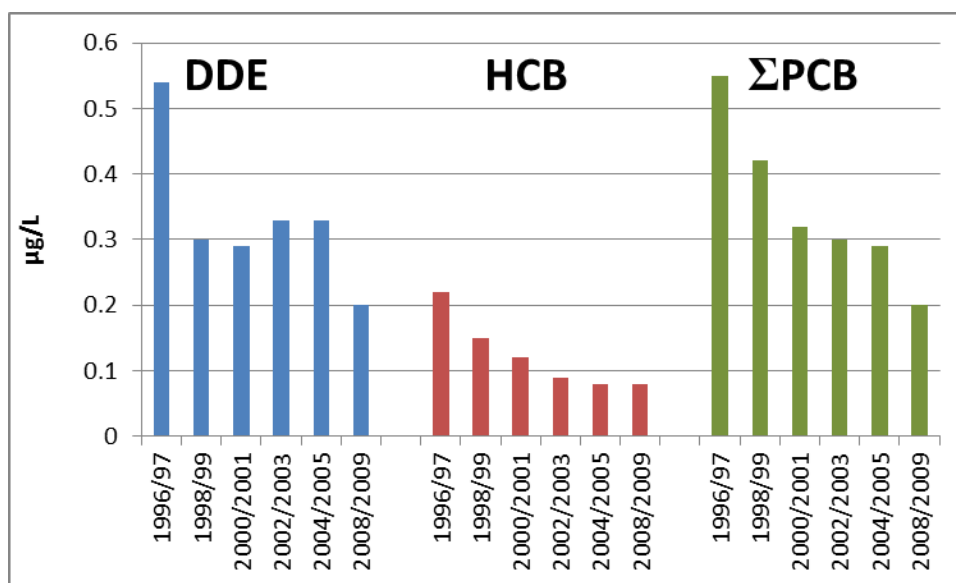


Figure 5.2.2j Concentrations (µg/L) of DDE, HCB and Sum PCB (PCB 138, 153 and 180) in blood samples from children living in Baden-Württemberg 1996-2009 (Link et al., 2012b).

5.2.2.3.5 Mother's milk and blood from Uppsala, Sweden

Temporal trends of PCBs, HCB, DDT-compounds, dioxins and PBDEs levels in breast milk are available from first-time mothers from the Uppsala area in Sweden. A large number of individual samples are measured within this programme which makes trend analyses possible.

PCB and *dioxins* were measured in mother's milk collected between 1996 and 2010. Multiple regression analysis showed that the adjusted mean decrease of PCB 28 was 4% per year while the levels of di-ortho PCB, mono-ortho PCB TEQ and non-ortho PCB TEQ decreased by 7-8% per year under the study period (**Table 5.2.2g**). Also the PCDD/F TEQ decreased by 7% per year (Lignell et al., 2012). During the same time period, the levels of p,p'-DDE and HCB in milk decreased by 8% and 7% per year, respectively.

The levels of *BDE-47*, *BDE-99* and *BDE-100* in milk decreased between 1996 and 2010 (**Table 5.2.2g**). The levels of *BDE-153* increased during the first half of the study period, but now seem to level out or even decrease. The levels of sum of PBDEs (*BDE-47*, -99, -100, -153 and -154) decreased by more than 5% per year during the survey period (Lignell et al., 2012). The trend of *HBCD* is uncertain, because many samples were below the LOQ. When only including the years when the LOQ was low, the levels of *HBCD* decreased by 4% per year from 2002 to 2010.

PBDEs, *HBCD* and *PFOS* were analysed in blood serum collected 3 weeks after delivery from the same women that provided milk samples. Linear regression analyses showed that the levels of *BDE-47*, *BDE-99* and *HBCD* significantly decreased between 1996 and 2010. After removal of a few outliers, also the levels of *BDE-100* significantly decreased, whereas the levels of *BDE-153* significantly increased during the study period (Lignell et al., 2011). The levels of *PFOS* in blood decreased with a mean rate of 8% per year (Glynn et al., 2012).

Table 5.2.2g Percent change in concentrations of POPs per year in mother's milk from primiparous women in Uppsala 1996-2010. Adjusted for age of the mother, pre-pregnancy BMI, weight gain during pregnancy and weight loss after delivery (*Lignell et al., 2012*).

Compound	Change/year (%)		half-time ^a (years)	R2 ^b	P
	Mean	SE			
PCB 28	-3.6	0.7	19	10	<0.001
di-ortho PCB ^c	-7.0	0.3	10	72	<0.001
mono-ortho PCB TEQ ^d	-6.8	0.3	10	67	<0.001
non-ortho PCB TEQ ^e	-7.4	0.4	9	63	<0.001
PCDD TEQ	-8.2	0.3	8	77	<0.001
PCDF TEQ	-5.4	0.4	12	58	<0.001
PCDD/F TEQ ^f	-7.3	0.3	9	74	<0.001
Total-TEQ ^g	-7.2	0.3	9	73	<0.001
BDE-47	-9.6	0.7	7	32	<0.001
BDE-99	-7.9	0.6	8	32	<0.001
BDE-100	-5.1	0.7	13	14	<0.001
BDE-153	+1.1	0.5	-64 ^h	22	0.021
BDE-153 (1996-2004)	+6.3	1.1	-11 ^h	30	<0.001
BDE-153 (2004-2010)	-7.0	1.5	9	34	<0.001
sumPBDE ⁱ	-5.5	0.5	12	24	<0.001
HBCD ^j	-4.4	1.7	15	7.6	0.011

^a the estimated time it takes for the concentrations to be halved in the population

^b coefficient of determination for the regression model

^c sum of PCB 153, 138 and 180

^d sum of PCB 105, 118, 156, 167 TEQs based on 2005 WHO TEFs

^e sum of PCB 77, 126, 169 TEQs based on 2005 WHO TEFs

^f sum of PCDD TEQ and PCDF TEQ

^g sum of mono-ortho PCB TEQ, non-ortho PCB TEQ, PCDD TEQ and PCDF TEQ

^h estimated time for the concentrations to be *doubled* in the population

ⁱ sum of BDE-47, -99, -100, -153 and -154

^j only results from 2002-03, 2004, 2009 and 2010 were included

5.2.2.3.6 Stockholm breast milk study

Probably the longest trend information available for POPs in mother's milk is the one initiated in Stockholm 1967. The studies have included measurements of DDTs, PCBs, PCDD/PCDFs, dieldrin, chlordane, HCB, BPDEs and PFOS in breast milk from women living in the Stockholm region.

Of the studied OCPs, 4,4'-DDE was measured in highest levels (Bergman et al., 2010; Noren and Meironyte 2000). The average level of 4,4'-DDE has decreased from 2000 ng/g lipid in the first measurement in 1967 to 75 and 160 ng/g lipid in 2008 and 2009, respectively (**Figure 5.2.2k**). The measured levels of 4,4'-DDT are less than 10% of the 4,4'-DDE levels. Also the

mean levels of PCBs have decreased. The mean level of PCB 153 was 25-35 ng/g lipid in 2009, corresponding to approximately 10% of the levels measured in the early 1970s (**Figure 5.2.2l**).

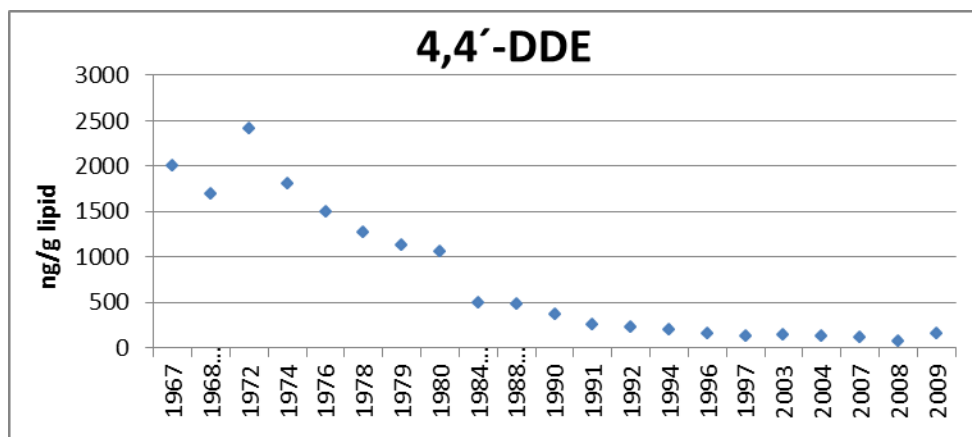


Figure 5.2.2k 4,4'-DDE in mother's milk from Swedish mothers (Bergman et al., 2010; Noren and Meironyte 2000).

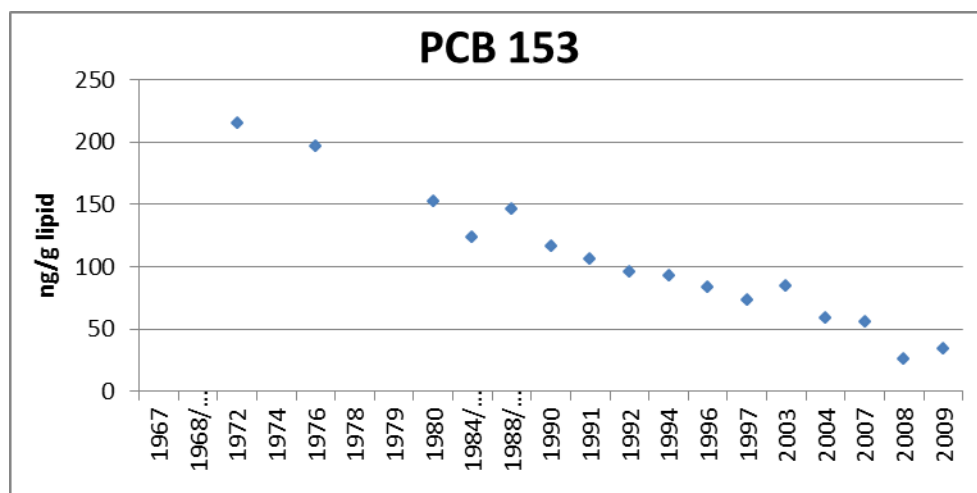


Figure 5.2.2l PCB 153 in mother's milk from Swedish mothers (Bergman et al., 2010; Noren and Meironyte 2000).

Dioxins and dioxin-like PCBs were analysed in samples from 1972-2011 by Fång et al (Fång et al., 2013). The relative annual decrease over the 40 year period was 6.1%, 6.1%, 6.9% and 6.5% for PCDDs, PCDFs, DL-PCBs and $\Sigma TEQs$, respectively. The decline during the last 10 years has been steeper than in previous decades, with relative annual decrease for PCDDs, PCDFs, DL-PCBs and $\Sigma TEQs$ of 10%, 7.3%, 12% and 10%, respectively (**Figure 5.2.2m** and **Figure 5.2.2n**).

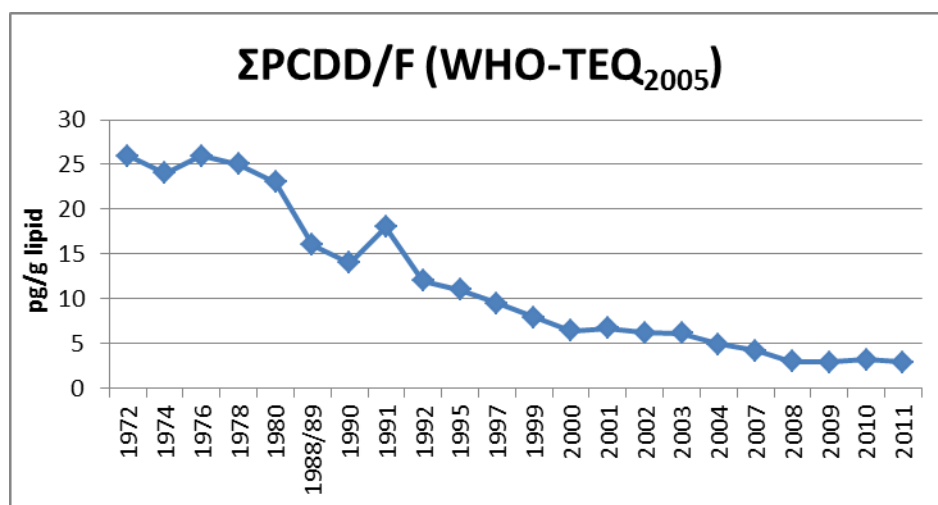


Figure 5.2.2m Temporal trend of TEQ(WHO-2005) for ΣPCDD/F in milk from Swedish mothers (Fång et al., 2013).

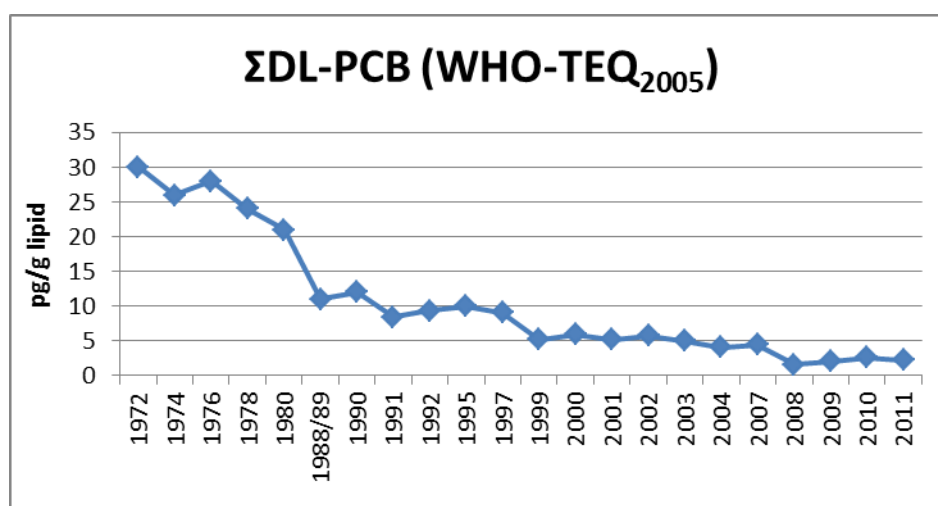


Figure 5.2.2n Temporal trend of TEQ(WHO-2005) for Σdioxin-like PCB in milk from Swedish mothers (Fång et al., 2013).

PFOS was analysed in samples collected between 1972 and 2008 (Sundström et al., 2011). The analysis showed that the levels increased until the late 1990s, levelled out and then decreased from 2001 until the end of the time series, reaching concentration of 75 pg/mL in 2008.

PBDEs were analysed in milk samples collected between 1972 and 2009 (Bergman et al., 2010; Fångström et al., 2008; Meironyte et al., 1999). The levels of BDE-47 peaked in the mid-1990s and then declined, whereas the levels of BDE-153 increased until the turn of the century and then seemed to decrease or level out. The reason for the relatively high mean levels of BDE-47, -99

and -100 in 2009 is unclear and these increased concentrations were not supported by measurements in another Swedish area at the same time. Differences over time may be affected by introducing a new clean-up method and analyse instrument in analyses after 2003.

The levels of *HBCD* were measured in mother's milk samples collected between 1980 and 2004. The levels increased by four to five times between 1980 and 2002, but seemed to level out in 2003 and 2004 (Fängström et al., 2008).

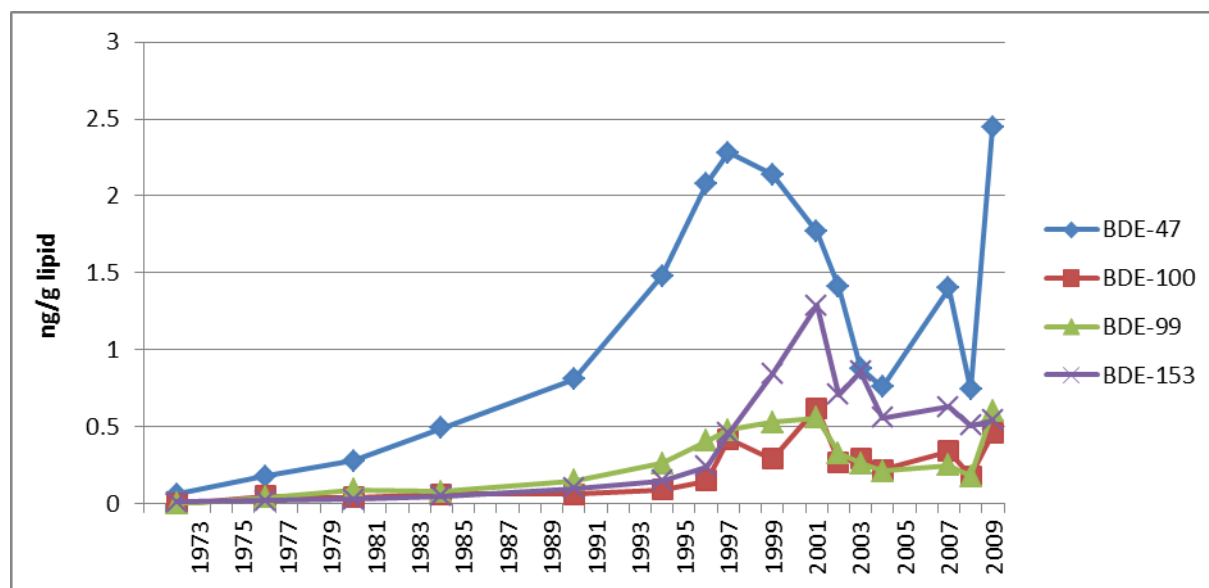


Figure 5.2.2o Temporal trend of PBDEs in milk from Swedish mothers (Bergman et al., 2010; Fängström et al., 2008; Meironyte et al., 1999).

5.2.2.3.7 Data from Australia and New Zealand

In Australasia and New Zealand national human biomonitoring programmes, such as the American NHANES or Canadian CHMS, are lacking. However, the levels of the POPs included in the Stockholm Convention have been measured in mother's milk and blood at several time points, allowing time trend evaluations. These data are presented here to give a full picture of the situation in the WEOG-region.

Time trends of dioxins, PCBs and OCPs in New Zealand breast milk

Three milk surveys, conducted in 1988 (Bates et al., 1990; Bates et al., 1994), 1998 (Bates et al., 2001) and 2008 (Mannetje et al., 2013), have been performed in New Zealand and can together

provide a time trend over the period. The time trend analysis showed that the concentrations of individual dioxins and furans declined by 60 to 76% between 1988 and 1998, and continued to decline by 20 to 72% between 1998 and 2008. The current concentrations are 10-20% of the initial concentrations. The levels of PCBs declined with 42 to 78% between 1988 and 2008 and are currently generally at 15% of the initial levels. In the study from 2008, the mean PCDD/F-TEQ was 3.54 pg/g lipid and the mean level of PCB-TEQ was 1.29 pg/g lipid. Also the concentrations of DDT, HCB and dieldrin were measured in all 3 studies and were shown to decline over the studied period. For example, the levels of DDT in milk declined more than 80% between 1998 and 2008.

Time trends of dioxins, PCBs and OCPs in Australian breast milk

In 2002/2003, PCBs and PCDD/Fs were analysed in pooled milk samples from 157 mothers living in different areas of Australia, as part of the Australian National Dioxin Programme (Harden et al., 2007). The mean level of PCDD/Fs was 5.8 pg TEQ₁₉₉₈/g lipid and the mean level of PCB was 3.1 pg TEQ₁₉₉₈/g lipid. In addition, 24 samples collected in 1993 were analysed as part of the programme. The comparison over time showed that the levels of PCBs and PCDD/Fs had decreased by approximately 40% between 1993 and 2002/2003. The levels of dioxins and dioxin-like PCBs in these studies were relatively low when compared to other WEOG countries participating in the WHO milk survey. The authors explained this observation with the lower industrialisation in Australia compared to Europe. The samples from 2002/2003 were also analysed for other POPs covered by the Stockholm Convention. For example, the mean levels of p,p'-DDE and p,p'-DDT were 310 and 8.8 ng/g lipid, respectively (Mueller et al., 2008). The levels of DDT did not decrease significantly between 1993 and 2002/2003, but longer time series of DDT in Australian milk samples have shown a great decrease since the early 1970s. Also other OCPs, such as dieldrin, have been shown to substantially decrease in mother's milk over the last decades. However, the data indicates that the decrease has slowed down in the last decade.

The protocol used for these studies was identical to the WHO milk survey protocol. Thus, comparisons can be made with the WHO Milk Surveys in Australia from 2001 and 2008/2009 (**Figure 5.2.2p**). However, these comparisons should be interpreted with caution due to difference in e.g. in the studied populations.

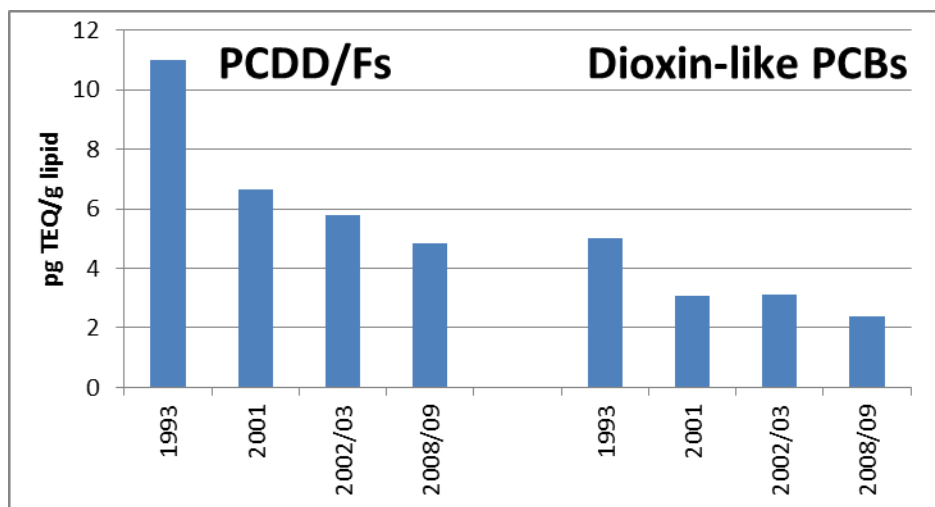


Figure 5.2.2p TEQ PCDD/F and TEQ Dioxin-like PCB in human milk from Australia analyzed in the WHO milk survey (2001 and 2008/09) and the Australian National Dioxin Programme (1993 and 2002/03). The results from 1993 and 2002/03 are presented as mean, from 2001 as median and from 2008/09 as the result of one pooled sample.

Time trends of PCBs and OCPs in Australian blood samples

PCBs and several OCPs have been analysed in pooled blood serum samples from the Australian population at several time points. At separate collections in 2008/2009 and 2010/2011, serum samples from South East Queensland were collected. In addition, serum samples were collected from five outspread Australian regions in 2002/2003. The mean levels of PCB 153 in the adult population (>16 years) were 15.3, 10.3 and 9.1 ng/g lipid in 2002/2003, 2008/2009 and 2010/2011, respectively. Among the OCPs, p,p'-DDE was found in the highest levels and seemed to decrease over the studied period. The mean levels of p,p'-DDE in the adult population were 610, 353 and 291 ng/g lipid in 2002/2003, 2008/2009 and 2010/2011, respectively (personal communication, Sara Broomhall 2013). These time trends should be interpreted with caution due to a slightly different age distribution in 2002/2003.

Time trends of PFOS in Australian blood samples

PFOS has been analysed in blood serum samples from Australians across a number of studies performed according to the same methodology (Toms et al., 2014). Levels of PFOS in pooled human sera from South East Queensland in 2002/2003, 2008/2009, and 2010/2011 were analysed and compared with samples from 2006/2007 previously analysed. A total of 9775 samples in 158 pools were available for the assessment. PFOS was detected in all pool samples in mean levels of 27, 20.5, 14.1 and 12 ng/ml for the adult population (>16 years) in 2002/2003, 2006/2007, 2008/2009 and 2010/2011, respectively. The mean concentration of PFOS in the

2010/2011 survey compared to 2002/2003 decreased by 56% in the adult population. For 5–15 year olds, the decrease in PFOS was 66% from 2002/2003 to 2010/2011, whereas for 0–4 year olds the decrease in PFOS from 2006/2007 (when data were first available for this age group) was 50%. The concentrations were higher in males than in females across all adult age groups, whereas no consistent age trend in blood PFOS levels was found.

Time trends of PBDEs and HBCD in the Australian population

Toms et al (2012) studied time trends of brominated flame retardants in breast milk samples from Australian women collected between 1993 and 2009, and in blood samples from the Australian population collected between 2002 and 2009. The levels of sum PBDEs (BDE-47, -99, -100 and -153) in pooled milk ranged between 2.5 and 15.8 ng/g lipid under the study period, with a mean value of 12.5 ± 6.4 ng/g lipid. The levels were highest in 2002–2006 and then decreased in 2007–2009 (**Figure 5.2.2q**). The levels of HBCD did not follow any obvious time trend between 1993 and 2009.

The levels of sum PBDEs (BDE-47, -99, -100 and -153) in pooled blood from Australian adults (>16 years) ranged between 5.6–30.3 ng/g lipid in 2002/2003, 4.0–12.2 ng/g lipid in 2004/2005, 5.5–14.5 ng/g lipid in 2006/2007 and 6.6–13.7 ng/g lipid in 2008/2009 (Toms et al., 2012). In additional samples from 2010/2011, the levels of sum PBDEs ranged from 5.0 to 13.5 ng/g lipid (personal communication, Sara Broomhall, 2013). No significant time trend for sum BPDEs in blood was found, however there was a decrease of BDE-47 in children. The levels of PBDEs were significantly higher in younger than in older age groups and higher in men than in women (Toms et al., 2012).

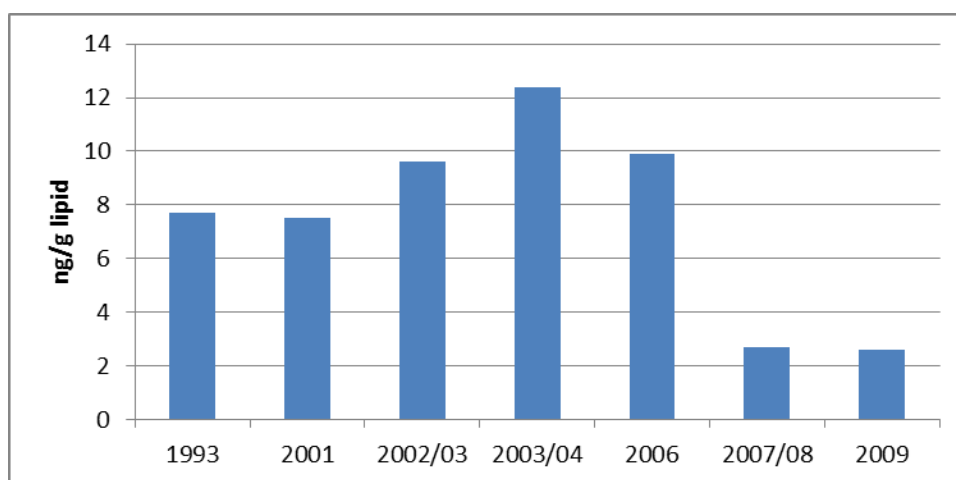


Figure 5.2.2q Levels (ng/g lipid) of sum PBDE (PBDE-47, -99, -100 and -153) in breast milk collected between 1993 and 2009 (Toms et al., 2012).

5.2.2.3.8 Data from Spain

Trend data from national biomonitoring programmes from Southern Europe are lacking. However, the Spanish Ministry of Agriculture, Food and Environment funded a national biomonitoring program (BIOAMBIENT.ES) to establish a national reference value for the Spanish working population (Pérez-Gómez et al., 2013). In 2009/2010, a nation-wide sample of 1880 blood samples from Spanish working adults was collected. The blood samples will be analysed for PCBs, PBDEs, and several organochlorine pesticides (DDT/DDE, HCH etc). The first data on PCB showed that the national geometric mean level of Σ PCB (PCB 138, 153 and 180) was 135 ng/g lipid. The levels increased with age and with higher fish consumption. Aiming to evaluate the trend of PCB levels in blood since the ban of PCBs, this nation-wide study was compared to previous studies from different regions of Spain. Generally, the levels of PCBs have decreased since the 1980s, however in some regions the levels have not markedly decreased over the last 5 years (Huetos et al., 2014).

5.2.2.4 Individual research studies

Numerous studies measuring persistent organic pollutants in blood samples or mother's milk in the WEOG region have been published and can add valuable information about the levels of these compounds. However, the study designs, populations, analytical methods and reported statistics vary, thus direct comparison between individual analyse data is not possible. These studies are presented mainly to provide data when other data are scarce.

A literature search covering data between 2000 and 2013 was performed. A comprehensive summary of the study findings is presented in Annex 2. The studies were rated by their use of external and internal quality controls and studies with insufficient quality information were not included in the summary. Note that the studies that applied external quality controls (e.g. AMAP ringtest or G-EQUAS) are indicated by asterisks. The results are reported as median and/or range unless stated otherwise by markings a-e. When the population is defined as adults, both men and women are included and when the population is defined as children, both girls and boys are included.

5.2.2.5 Discussion of results

5.2.2.5.1 Considerations

The levels of persistent pollutants observed in human matrices are mainly dependent on diet and age. The chief exposure route is via food, generally making up more than 90% of the total intake. Detailed statistical evaluations showed that the levels of POPs in human milk tend to increase with the age of the mother, and to decrease with the length of breast-feeding and the number of

breast-fed children. For the general population, food items are usually of widespread origin resulting in there being no distinct difference between exposure in urban and rural areas. Exposure pathways are possible resulting from for example, diet choice, and food production and processing practices that could lead to high concentrations in some population groups. The combination of local sources, different groups investigated, long range transport and other factors makes it however difficult to compare contaminant levels observed in different areas. The issue of age is well illustrated in the NHANES study showing that for the TEQ, as for most of the UNEP POPs, one cannot give a “universal” geometric mean, because the concentration is very much age dependent. This study also demonstrated the influence of ethnic patterns of dietary exposure. Therefore when seeking to detect changes in levels over time, the only really valid comparison is in one area and in the same group of people.

5.2.2.5.2 Levels

The amount of available information on levels of POPs in the WEOG region varies for different compounds and regions. International programmes such as the WHO milk survey and (to some extent) the AMAP programme generates comparable data that are essential to evaluate temporal and spatial trends in the diverse WEOG region. In addition, national programmes evaluating time trends of chemicals in blood and/or milk, such as NHANES and ESB, are important to assess local time trends but the levels are often not directly comparable to other regions due to different study designs and populations. Individual research studies that are not a part of any programme can indicate whether the levels of pollutants are of concern in a certain area, but cannot directly be used to evaluate differences between regions or over time.

The available human biomonitoring data mainly covers PCBs, dioxins, DDT/DDE, HCB, PBDEs and PFOS, whereas there is less information about the levels of the compounds which are generally not detectable in blood and milk, such as aldrin, endrin and mirex. Chlordecone was included in the Stockholm Convention in 2009, but no human biomonitoring data for this compound was found in neither national programmes or in the literature search. Also PeCB is a compound included in the Convention in 2009 with very scarce available biomonitoring information.

Compared to other regions within the WEOG region, the Inuit populations in the Arctic Canada and Greenland have the highest levels of most persistent organic pollutants in blood and milk. This is due to long-distance atmospheric transport with deposition of pollutants in the arctic region where they biomagnify in food chain and consequently are present in high levels in marine mammals which constitute the traditional Inuit diet.

The levels of PBDEs are known to be higher in North America compared to Europe, which has been shown in both human samples and house dust. This pattern probably reflects the historic high usage of pentaBDE preparations in North America. As a consequence of the recent ban of these compounds, a decrease is expected also in North America. However, the exposure to PBDEs will continue as long as PBDE containing products are still in use.

5.2.2.5.3 Trends

The trend studies covered in this report show that the levels of most persistent organic pollutants, such as PCBs, dioxins and DDE/DDT in human blood and milk, have been declining since the start of the trend studies, and are still decreasing. Some OCPs that have been banned for a long time, such as aldrin, endrin and mirex, are no longer present in human tissues in detectable levels.

However, the levels of PFOS and PBDEs show a slightly different temporal pattern. In the few available long term studies of PFOS, the levels increased in the 1980s and 1990s, reflecting the industrial production, and have then declined in most WEOG areas. While the phase-out of PFOS is reflected by declining levels in humans, some of the other PFAS still in use are now increasing in human tissues (Glynn et al., 2011; Lindstrom et al., 2011). Long time series of PBDEs have shown that the levels peaked around the late 1990s and early 2000s. For most PBDEs, the levels now seem to gradually decline, however it is unclear whether the level of BDE-153 is currently increasing or decreasing. Also, it is uncertain whether the levels of *HBCD* currently are decreasing.

5.2.2.5.4 Summary and conclusions

The levels of most persistent organic pollutants, such as PCBs, dioxins and DDE/DDT in human blood and milk, have been declining since the start of the trend studies, and are still decreasing. OCPs that have been banned for a long time, such as aldrin, endrin and mirex, are no longer present in human tissues in detectable levels.

The levels for PFOS increased in the 1980s and 1990s, reflecting the industrial production and use in different products. The levels in human matrices have however then declined and are still declining. The same holds for many PBDEs.

It is of importance that the national programmes evaluating time trends of chemicals in blood and/or milk will continue. They are important to assess local time trends noting that the levels are often not directly comparable to other regions due to different study designs and populations. Individual research studies that are not a part of any programme can indicate whether the levels of pollutants are of concern in a certain area, but cannot directly be used to evaluate differences between regions or over time. It is therefore impossible to set a “general” baseline concentration.

5.2.3 Water

5.2.3.1 Introduction

The objective of this chapter is to summarize the current state of knowledge of perfluoro-octane-sulfonate (PFOS) in water within the WEOG countries. With the addition of as PFOS to the Stockholm Convention, the need to have data for water has become important because of the hydrophilic properties of this chemical.

Water has not previously been included in the GMP. However, a significant amount of data has been published on POPs in surface waters (Muir and Lohmann, 2013). Water concentrations of persistent organic pollutants (POPs) in large lakes, coastal seas, and open oceans, reflect a dynamic balance of inputs via rivers and atmospheric deposition as well as re-release from sediments, and removal pathways such volatilization and sedimentation (Jurado et al., 2007; Stemmler and Lammel, 2009).

Long-term data on POPs in water thus can provide important information that can be used to assess the effectiveness of measures taken to reduce emissions. Concentrations of POPs in surface water are directly linked to their bioaccumulation in the food-chain; hence knowing dissolved concentrations in the water enables prediction of concentrations in aquatic species using bioaccumulation factors or lipid-water partitioning and food web biomagnification models (Gobas et al., 2009).

Unlike air or human and wildlife tissues, there are no robust temporal trend datasets yet available for PFOS in natural waters (nor for any other POPs for that matter). Therefore this chapter reviews the results available, focusing on PFOS and related chemicals, in rivers, lakes, estuaries and oceans within the WEOG area (Western Europe, North America, Australia/New Zealand and Antarctica). The focus is mainly on background sites. Therefore results from waste water effluents or from samples immediately downstream of wastewater outfalls were not included. Similarly studies from harbours and urban watersheds were not included.

All the available peer reviewed literature and government technical reports on PFOS and related per-fluoro and polyfluoroalkyl substances (PFAS) in water were reviewed. This literature is relatively recent with earliest reports for surface waters starting in 2002 (Hansen et al., 2002; Moody et al., 2002). As the use of mass labelled internal standards of PFAS along with high performance liquid chromatography-tandem mass spectrometry (LC-MS/MS) instrumentation method detection limits and performance (reproducibility, accuracy) improved significantly by

the mid-2000s (Taniyasu et al., 2005; Yamashita et al., 2004). Therefore this review includes data for studies published from about 2004 and utilizing LC-MS/MS with mass labelled standards in almost all cases.

5.2.3.2 Assessment Programmes and other sources of information

Regional monitoring and assessment programmes within the WEOG such as HELCOM, OSPAR, MEDPOL, AMAP, as well as national programmes in Norway, Sweden, Canada, Denmark, the USA and Australia, have generally not focused on measurements of PFOS or other PFAS in water. However, early measurements in lake and seawaters were made in Scandinavia under the Nordic Council of Ministers (Kallenborn et al., 2004) and the Joint Research Centre initiated a European wide surveillance of PFAS in the mid-2000s (Loos et al., 2008a). The International Council for Exploration of the Sea (ICES) database includes results for PFOS from the North Sea from 2005 only (ICES 2005). The majority of the available data for this assessment is from the peer reviewed scientific literature. These are from both independent university-led studies and from government laboratories that are involved in monitoring and surveillance of contaminants in water. Much of the monitoring effort has been focused on municipal waste waters and drinking waters. These were not considered for this assessment on the grounds that they would be too site-specific. However, sufficient information on samples from background or “far field” sites was available to permit assessment of the levels of PFAS in most WEOG countries and in nearby seas and ocean environments.

5.2.3.3 The analytes of interest

The main focus is on PFOS which present as an ionic species at prevailing pH. However there are many PFOS precursors (see air chapter) which are known to degrade to PFOS in water, especially during waste water treatment (Martin et al., 2010; Schultz et al., 2006). Several studies of PFAS in water have included perfluorooctane-sulfonamide (FOSA). Recently a series of perfluoro-sulfonamides and -sulfamidoethanols were also included in measurements of seawater (Xie et al., 2013). Thus this review also includes discussion of these precursors and documents levels of FOSA, the most widely measured PFOS precursor. PFOS isomers are also of interest as indicators of partitioning and transformation of precursors and are discussed briefly. Results for perfluorocarboxylate (PFOA) are also included in Annex 3 Table 1 because PFOA is a common co-contaminant with PFOS especially in surface waters and wastewaters, as well as a photolytic degradation product of perfluoro-sulfonamide and sulfamidoethanol precursors (Plumlee et al., 2009).

5.2.3.4 Summary of results for rivers, lakes, estuaries and oceans

Rivers

About 50 datasets for PFOS in background sites on rivers within Western Europe, Canada, USA and Australia were identified based on 27 peer reviewed papers and reports (Annex 3 Table 1). Concentrations range from 0.27 to 130 ng/L, however most concentrations are in the low part per trillion range (median 6.4 ng/L). The largest datasets are for the Rhine and the Elbe, where detailed studies have been conducted including estimates of loadings (Ahrens et al., 2009c; Paul et al., 2012).

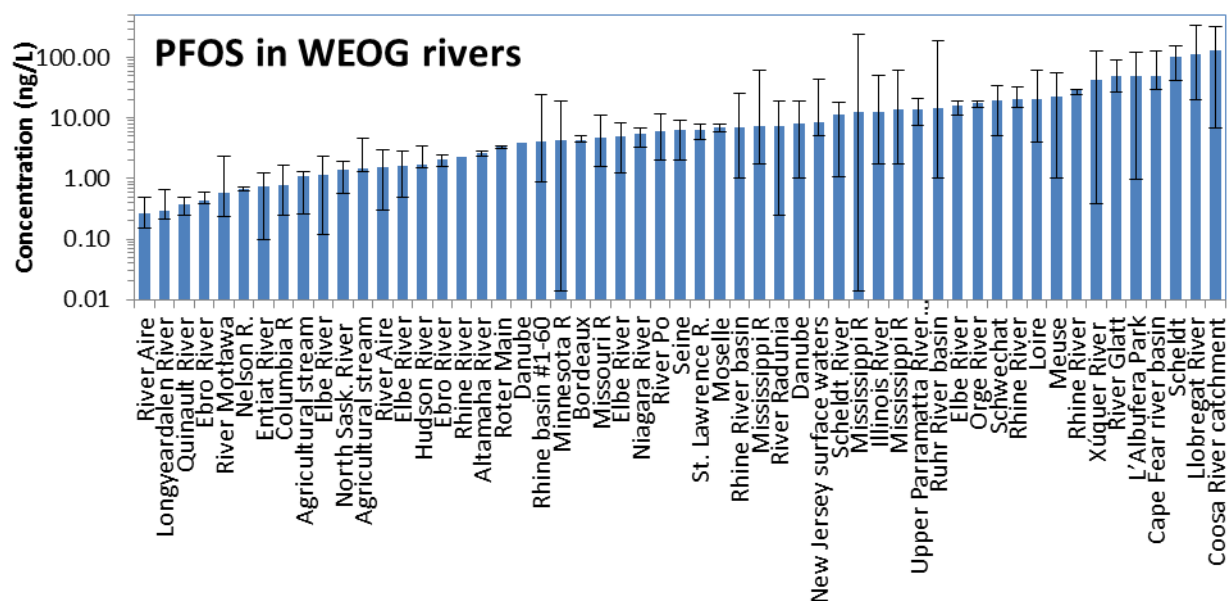


Figure 5.2.3a PFOS in river waters (ng/L). Vertical lines represent the range of reported concentrations.

In order to provide an estimate of the range of concentrations we used the following criteria for selection of results from the rivers: (1) studies with two or more sampling sites per river reach, (2) sites identified by the study authors as being upstream of waste water effluents, (3) only mainstream sampling sites were selected rather than tributaries. Inevitably due to the number of urban areas along major rivers in Europe and North America, sampling sites were downstream of known waste water effluents and an effort was made to identify and use far-field sites where possible. Also the potential for contamination from agricultural sources, i.e. from application of municipal and industrial wastes to agricultural lands as observed in the Moehne River (tributary of the Ruhr in Germany)(Skutlarek et al., 2006) and in the Conasauga River in Georgia (USA) (Konwick et al., 2008) means that upstream or background sites can also have elevated

concentrations. While data from the latter two studies were used, care was taken to use their less impacted sites.

The Elbe and Rhine rivers have had multiple detailed studies of PFOS and other PFAS (Ahrens et al., 2009b; Ahrens et al., 2009c) (Loos et al., 2008a; Möller et al., 2010; Quinete et al., 2009; Skutlarek et al., 2006). Sampling for the studies published as of June 2014 occurred between 2006 and 2008. Results for more recent sampling could not be found. Loos et al. (2008a) and Möller et al. (2010) sampled the same 7 sites on the Rhine River in autumn 2007 and 2008, respectively. Concentrations reported by Loos et al were 3 to 6-fold higher. This was unlikely to be due to declining emissions of PFOS but instead probably reflects differences in sampling design (see below). Earnshaw et al. (2014) found no change in PFOS concentrations in the Aire and Calder Rivers in northeast England between 2010 and 2013, based on similar profiles with distance downstream. These carefully designed studies, which include multiple sampling points along each river, and consideration of waste water and tributary inputs, will likely form the basis of future temporal trend studies.

Reports from contamination incidents in rivers as a result of accidental or deliberate release of PFOS. (De Solla et al., 2012; Moody et al., 2002; Rumsby et al., 2009) were also not included in this assessment. However, understanding the fate of PFOS following these events is important because these contamination incidents could influence prevailing concentrations in rivers and confound interpretation of loadings and of temporal trends.

Results for rivers can also be evaluated by country. This was done by Loos et al (2008a) in their pan-European study and it was extended with more recent data (Annex 3 Table 1) for countries in the European Union although there were multiple studies and multiple countries particularly in the case of the Rhine (**Figure 5.2.3b**). Available results were combined for regions within each country by averaging the mean concentrations and taking the minimum and maximum values reported. Results for small lakes were also included to expand the range of available data. A challenge of interpreting data by country is that the range of sites from truly remote background to near field sites varies among countries, with some having a larger proportion that are influenced by waste-water effluents, making valid comparisons difficult. The results showed that reported PFOS concentrations for background sites were highest in Belgium, Spain and Slovenia (means exceeding 100 ng/L). Mean results for four other countries (UK, Netherlands, Switzerland and USA) were between 10 and 100 ng/L (**Figure 5.2.3b**).

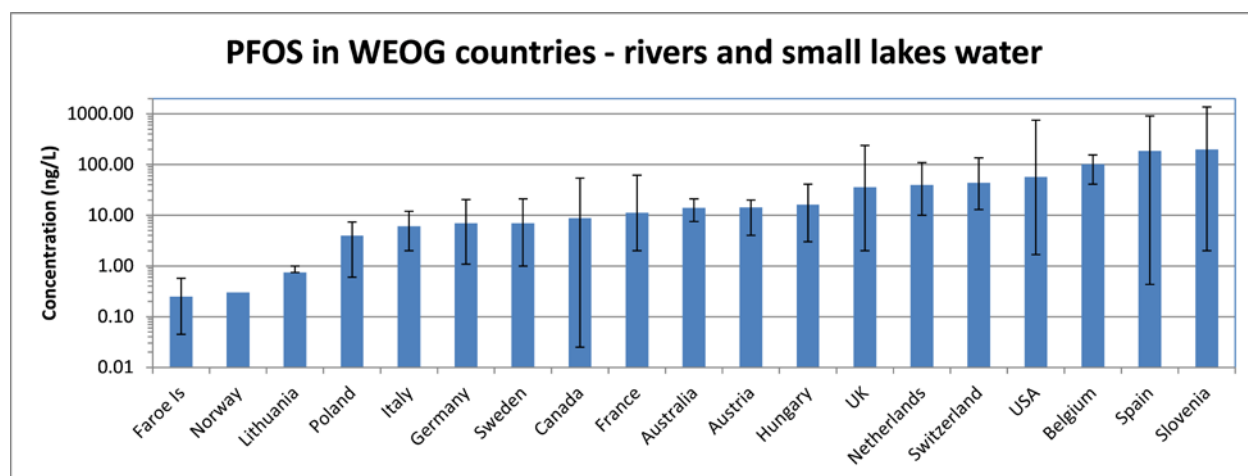


Figure 5.2.3b PFOS in waters of rivers and small lakes by country – based on combined datasets from each country from Annex 3 Table 1 and results Lithuania, Sweden, Hungary, UK, Netherlands, Switzerland and Slovenia from Loos et al (2008a). Vertical lines represent the range of reported concentrations from multiple studies.

Lakes

There have been fewer studies of PFOS in lakes within the WEOG region compared to rivers. As might be expected, small lakes (surface area <1000 km²), which are often included in studies of river basins, generally have higher PFOS concentrations than large lakes (Annex 3 Table 1). Very low concentrations (<0.03 ng/L) of PFOS have been in small remote lakes in the Arctic (Pingualuk in Northern Québec, Lake A and Lake Hazen, Ellesmere Is) and Antarctic (King George Is) (**Figure 5.2.3c**).

Detailed measurements have been made in open waters and coastal areas of the North American Great Lakes (De Silva et al., 2011; Furdui et al., 2008; Kim and Kannan, 2007; Scott et al., 2010). Lake Superior has the lowest concentrations of the five Great Lakes while Lakes Ontario and Erie had the highest (ranging from means of 2 to 6 ng/L; Annex 3 Table 1). PFOS concentrations were relatively uniform in surface waters within each lake (De Silva et al., 2011). Depth profiles in Lake Superior showed similar concentrations in bottom waters and at the surface (Scott et al., 2010). Lake wide sampling of Lake Ontario in 2004, 2005 and 2010 showed no change in mean concentrations over the 6 year period (De Silva et al., 2011; Furdui et al., 2008).

Highest concentrations are from lakes in or near urban areas, e.g. Lake Onondaga near Syracuse in upper NY State which is a Superfund site and also influenced by municipal waste water inputs (Kim and Kannan, 2007) (Annex 3 Table 1). Lake Niapenco near the Hamilton (ON) airport had PFOS concentrations averaging 76 ng/L. Lake Moehne, a rural lake in Germany, had elevated

concentrations of PFOS (17 ng/L) and other PFAS due to application of industrial wastes on agricultural lands within its watershed (Skutlarek et al., 2006). Merretta and Resolute Lakes in the Canadian arctic also had elevated PFOS (54 and 45 ng/L, respectively) due to historical contamination by wastewaters from a nearby airport (Stock et al., 2007). Because all of these lakes had PFOS levels exceeding 10 ng/L, they were essentially outliers among the results for all lakes so they omitted from the lake comparison (**Figure 5.2.3c**).

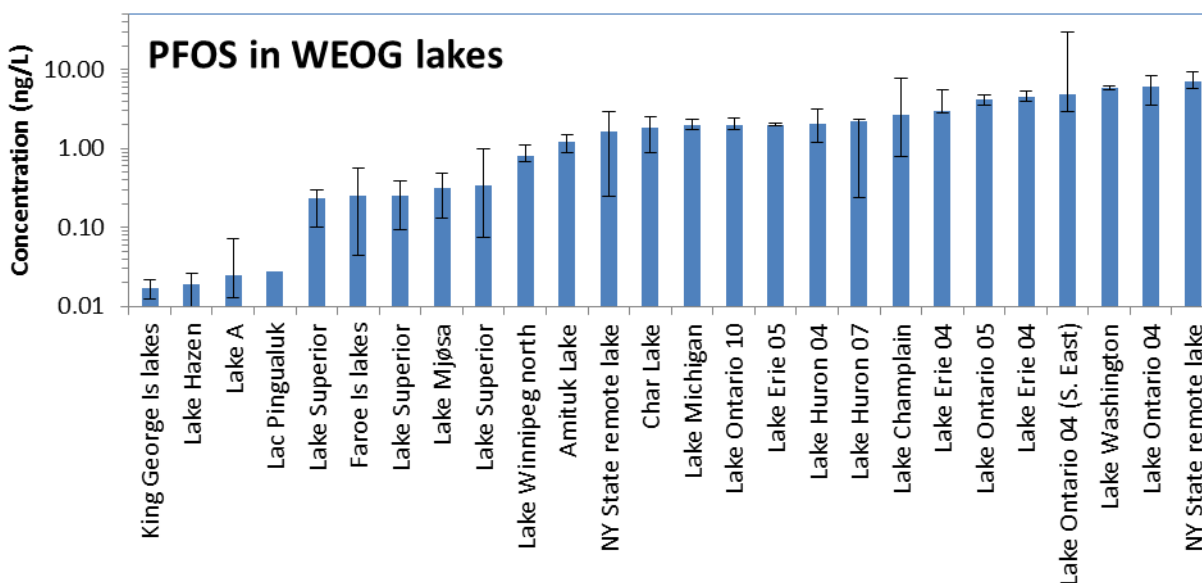


Figure 5.2.3c PFOS in WEOG lakes (ng/L). Vertical lines represent the range of reported concentrations.

Estuaries and coastal waters

Detailed measurements have been made for PFOS and other PFAS in the Baltic (Ahrens et al., 2010a; Kallenborn et al., 2004; Kirchgeorg et al., 2010) and the eastern North Seas in or near the Elbe estuary (Ahrens et al., 2010a; ICES, 2005; Theobald et al., 2007). Mean concentrations in the Elbe estuary ranged from 1-2 ng/L while in the open Baltic average concentrations ranged from 0.08 to 0.21 ng/L (Annex 3 Table 1) although concentrations close to Helsinki (Gulf of Finland) were 22 ng/L (HELCOM 2010). These studies will likely form the basis of future temporal trend monitoring conducted under HELCOM and OSPAR. Less spatially comprehensive results are available from a large number of other studies of estuaries and included coastal waters (Annex 3 Table 2). Lowest concentrations of PFOS were found in coastal waters of King Georg Is (Antarctica) and in several Arctic locations including Mackenzie Bay (S. Beaufort Sea), northwestern Spitzbergen, and coastal East Greenland (**Figure 5.2.3d**). Highest concentrations were found in urban influenced estuary and coastal waters e.g. in the

Scheldt (Rhine River delta), near the Elbe, in the northern Adriatic, Puget Sound, and San Francisco Bay (**Figure 5.2.3d**).

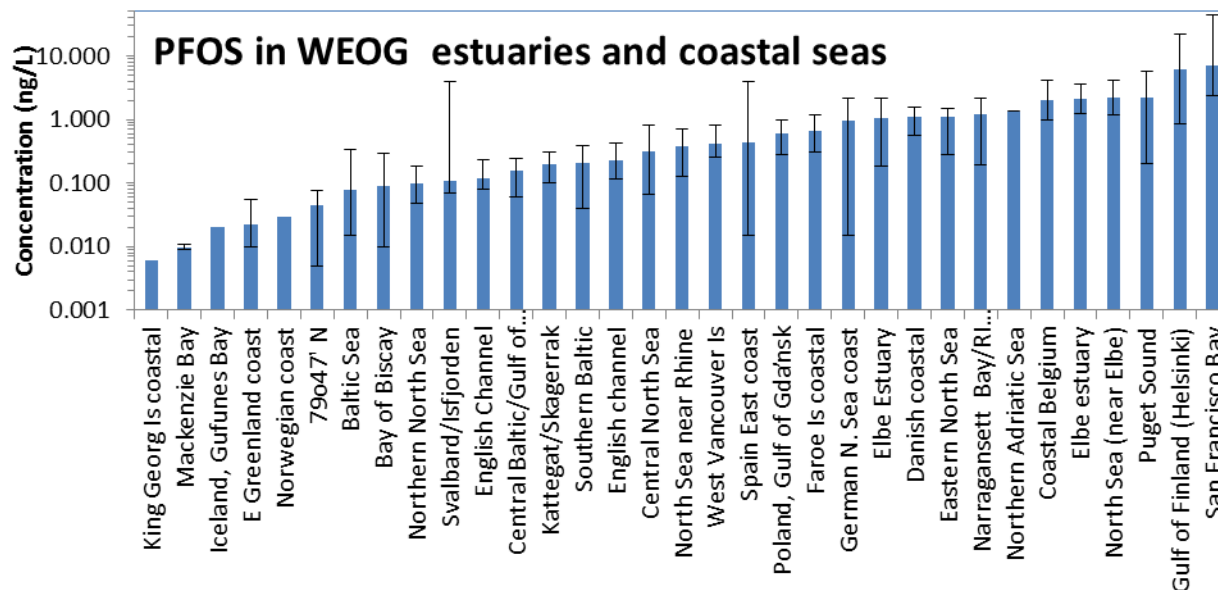


Figure 5.2.3d PFOS in WEOG coastal water and estuaries (ng/L). Vertical lines represent the range of reported concentrations.

Open ocean waters

Detailed dataset for PFOS are available for the North Atlantic, the Greenland and Norwegian seas, the Canadian Arctic archipelago, and the southern Ocean near Antarctica (Annex 3 Table 3). In **Figure 5.2.3e**, published data from all sampling sites reported by each study are presented. Results for the South Atlantic and Northwest Pacific area also included when they were part of a cruise in the WEOG region.

Compared to freshwaters and estuaries, open ocean concentrations are very low (median 24 pg/L). Lowest mean concentrations (<10-20 pg/L) are reported for the Greenland Sea and the Labrador Sea, as well as in the Southern Ocean. The transect from Western Europe (north western France) to West Africa is the most thoroughly studied with results from four separate cruises available (Annex 3 Table 3) (Ahrens et al., 2009a; Ahrens et al., 2010b; Benskin et al., 2012; Zhao et al., 2012). These studies are all in general agreement that the eastern Atlantic off of France and Portugal has the highest PFOS concentrations in the WEOG region oceans, and indeed in all open ocean waters analysed to date.



Figure 5.2.3e PFOS in open ocean waters of the North Atlantic, Arctic Ocean and the Southern Ocean near Antarctica (pg/L). Circles represent relative concentrations. Average concentrations and ranges are given in Annex 3 Table 3.

These waters are influenced by the south-flowing Canary Current which carries PFOS from continental Europe. No temporal trends are apparent in the current dataset which includes samples collected in the Eastern Atlantic from 2007 to 2010. However, the results from this region could serve a baseline for future temporal trend monitoring along the same cruise transect.

5.2.3.5 Discussion of study design and analytes

PFOS precursors. The majority of water measurements have been for total perfluorooctane sulfonic acid (usually analysed along with other perfluoroalkane sulfonates and PFCAs). However a limited number of studies have reported perfluorooctanesulfonamide ethanols (FOSEs) and perfluoro-octanesulfonamide (FOSA), the amide derivative of PFOS (Annex 3 Table 2). The FOSEs and FOSA have been shown to degrade abiotically (D'Eon and Mabury, 2007; Martin et al., 2006) to PFOS and PFOA as well as via biotic degradation (Tomy et al., 2004; Xu et al., 2004) to PFOS. Median concentrations of FOSA in seawater are about 60% of those for PFOS (15 pg/L vs 21 pg/L, respectively; **Table 5.2.3a**). However, fewer results are available (e.g. in seawater, n=17 reports for FOSA vs 31 for PFOS). There is also a much more variation in FOSA concentrations among studies along the same cruise transects. Ahrens et al (2009a) reported mean FOSA in the Eastern Atlantic in 2007 of 56 pg/L and PFOS < 10 pg/L in the same samples while a cruise along the same transect in 2008 concentrations averaged 18 pg/L (Ahrens et al., 2010b) (Annex 3 Table 1). The results for 2008 were in reasonable

agreement with Benskin et al (2012). In freshwater and estuarine environments, FOSA appears to represent a smaller proportion of PFOS-related substances, with median values that are about 5 (rivers) to 12% (estuary) of PFOS medians (Annex 3 Table 2).

Table 5.2.3a Comparison of median concentrations (ng/L) and number of reports of PFOS, FOSA, and PFOA¹.

	PFOS		FOSA		PFOA	
	N	Median	N	Median	N	Median
Rivers	55	6.33	15	0.500	55	5.23
Lakes	29	2.05	13	0.117	29	2.20
Estuaries	33	0.381	21	0.049	28	0.661
Open ocean	32	0.021	18	0.015	32	0.072

¹ Includes non-detects which were assumed to have ½ the concentration of the reported detection limit.

Xie et al (2013) determined concentrations of FOSA, other N-methyl and N-ethyl-perfluoroalkane sulfonamides (MeFOSA & EtFOSA), and N-methyl and N-ethyl perfluoroalkane sulfonamidoethanols (MeFOSE & EtFOSE) have in surface seawater and the atmosphere of the North Sea. Four PFOS precursors, MeFOSA, EtFOSA, MeFOSE, and EtFOSE were present at <0.1-2.6, <0.1-5.1, <0.1-35 and <0.2-17 pg/L, respectively. The highest concentrations were determined in the estuary of the Weser and Elbe rivers and a decreasing concentration profile was found towards the central part of the North Sea. Total concentrations of these PFOS precursors were, however, about 10-100 times lower than concentrations reported for FOSA and PFOS in the eastern North Sea near the Elbe (Annex 3 Table 1) and thus not very significant from a mass balance perspective. Möller et al. (2010) also determined MeFOSA, EtFOSA, MeFOSE, and EtFOSE in the Rhine River however concentrations were < 1 ng/L and not reported. Cai et al. (2012) also detected EtFOSA, MeFOSE, and EtFOSE in seawater in the Bering Sea at average concentrations ranging from 21-28 pg/L which were similar to PFOS concentrations although lower than FOSA (Annex 3 Table 3).

Many other PFOS precursors have been in commercial use such as the perfluoro-alkylsulfonamido-amines (Backe et al., 2013) and amino carboxylates (D'Agostino and Mabury, 2013). Analyses using total organic fluorine (Miyake et al., 2007) as well as ¹⁹F-NMR (Moody et

al., 2001) suggest that there could be other perfluorinated substances in surface waters, especially as a result of accidental or deliberate release of fire-fighting foams (Backe et al., 2013).

PFOS isomer specific analysis. The production of PFOS by electrochemical fluorination (ECF) results in both linear and branched C₈F₁₇-containing sulfonic acid isomers (Benskin et al., 2010a). Isomer profiling is particularly useful for perfluorocarboxylates because production of PFOA and related compounds has been both from ECF and telomerization processes. However for PFOS, only ECF has been used so isomer ratios are of less interest for source profiling, but do provide information on environmental fate of PFOS. Almost all monitoring and surveillance studies of PFOS in water have focused on total PFOS, i.e. combined measurement of the linear and branched isomers. In a survey of marine and freshwaters, Benskin et al (2010b) found PFOS isomer profiles were enriched in branched content (i.e., >50% branched) in the Mississippi River but marine waters, including harbours in Japan, China and The Netherlands, were similar or only slightly enriched in branched content relative to historical PFOS. Historically commercial PFOS reportedly had a consistent isomer composition of 70 ± 1.1% linear (L-PFOS) and 30 ± 0.8% branched (Reagen et al., 2007). In some cases linear and total PFOS have been reported together. In Great Lakes waters, linear (L)-PFOS represented from 28% (Michigan) to 62% (Superior) of total PFOS (De Silva et al., 2011), well below commercial PFOS. The enrichment in branched isomers in lakes may be indicative of greater sorption of L-PFOS, which is more hydrophobic than branched isomers, to sediments and sinking particles. Also biotransformation of PFOS precursor products proceeds more rapidly for branched isomers (Benskin et al., 2009), which could also lead to enrichment of branched PFOS content particularly near waste water treatment plants (WWTPs).

Study design and loading estimates for PFOS. Several studies have estimated mass flows of PFOS in rivers in the WEOG region as well as discharge to estuaries and seas (Ahrens et al., 2009b; Earnshaw et al., 2014; Huset et al., 2008; Loos et al., 2008b; Möller et al., 2010; Scott et al., 2009). Mass flows (kg/time (day, year)) are of interest for understanding the fate of PFOS and for assessing the influence of seasonal trends due to variations in river flow, or to discontinuous emissions by WWTPs. Combined with population density they can be used to infer per capita emissions. However, most studies performed sampling only once, annual river discharge can only be roughly estimated unless flows are constant. Loos et al (2008b) measured PFOS three times at the same location in the Po River and found a relatively narrow range of concentrations (7-12 ng/L) despite large differences in the hydrograph over the sampling period.

Sampling procedure (depth integrated, flow normalized, bridges vs boats) may affect measured concentrations. Two sampling programmes in the Rhine during 2007 and 2008 used different

procedures and got somewhat different results. Samples analysed by Loos et al.(2008a) were from the river bank or bridges, while Möller et al. (2010) sampled the mainly by boat, taking a greater number of samples. Loos et al. (2008a) reported PFOS concentrations ranging between 15 and 32 ng/L, while Möller et al. (2010) report lower values ranging from 1.7 and 13 ng/L. Paul et al. (2012) used both datasets to validate a transport model for PFOS in the Rhine and they concluded that the greater variation shown in the Möller et al. dataset could be due to localized sources and dilution, highlighted by the greater number of sampling points. Huset et al (2008) used time-proportional composites at two collection sites on the Glatt River in Switzerland a 24 h, flow-normalized composite sample at a point just before the Glatt River joins the Rhine River, to estimate discharge and assess the mass balance compared with inputs from WWTP effluents. This approach provided a better estimate of average PFOS concentrations and discharge.

Particles vs dissolved concentrations: Most studies of PFOS in surface waters have using unfiltered samples (Annex 3 Table 1). However, Ahrens et al (2009b; 2009c) filtered their Elbe River and estuary samples in a ship clean room They found that PFOS was entirely in the dissolved phase in the North Sea and 70-85% dissolved in the Elbe River. However, EtFOSE was exclusively found in the particulate phase. Using a fate and transport model, Paul et al. (2012) estimated that <20% of the total PFOS entering the Rhine was bound to sediments or suspended particles. Ahrens (2011) has noted that during filtration, PFAS can be adsorbed to the filtration equipment, while the dissolved phase can also adsorb to the filter material and equipment and to the walls of the receiving flask. The filter and equipment may also be a source for blank contamination. Thus it is not recommended except for samples with high suspended solids.

Effect of ice cover. Measurements of PFOS and other PFAS in the Arctic Ocean have shown that concentrations may be elevated in surface seawaters during ice melting (Muir et al., 2008). Bertrand et al. (2013) have shown that PFAS are higher in ice than in the seawater below by 1.7-3.7 fold for PFOS and 2.4 to 5.0 times for FOSA based on sampling in the Southeastern Beaufort Sea and the Barents Sea near Svalbard. Thus ice is a source for PFAS into surface waters during spring-summer in polar regions while sealing off surface waters from precipitation inputs during the winter months. This is yet another factor that may influence water concentrations in monitoring of PFOS in north temperate and polar environments.

5.2.3.6 Summary and Conclusions

- There are a large number of studies for PFOS in rivers, lakes, estuaries and ocean waters in the WEOG region
- The information available provides knowledge of spatial trends for PFOS across western Europe, the North Sea, the Baltic, and in the North Atlantic and Canadian Arctic archipelago
- Information is much more limited for North America and Australia. No information was found for New Zealand.
- In addition to environmental measurements, river discharges have been estimated and modelled (for the River Rhine and the Aire/Calder River system in northeast England)
- Ice and snow melt inputs of PFOS are likely to be important during spring melt events and need to be considered in timing of monitoring programmes
- The presence of PFOS in remote, uninhabited lakes in the Canadian Arctic and in the Antarctic illustrates the long range atmospheric transport of PFOS and/or precursors.
- The presence of PFOS in remote sectors of the southern Ocean, the Arctic Ocean and the mid-North Atlantic, including in deep waters (>1000 m), illustrates the long range ocean transport of PFOS.
- Temporal trend information is very limited. For rivers it consists of sampling of the same locations two or three times at the same location. For oceans results are available from four separate cruises from Western Europe (north western France) to West Africa. However, differences in sampling locations and in detection limits preclude any robust assessment of trends
- FOSA is an important PFOS related compound. Most studies of ocean and coastal seawater has included it. However, at present, FOSA data is much more limited for river water and thus its importance as a component of total PFOS in freshwater environments is uncertain
- A major knowledge gap is measurement of other neutral PFOS precursors (MeFOSA, EtFOSA, MeFOSE and EtFOSE) as well as less well known precursors recently identified in fire-fighting foams
- Understanding the current use or inventories and the fate of these PFOS precursors is important for being able predict future PFOS concentrations in water

5.2.4 Other media / non-core GMP media

5.2.4.1 Introduction

In 2007, the SC COP3 decided that for the GMP under article 16 the core media would be air and human tissue (milk, blood); the reasoning behind this choice still stands. The importance of other than core media to understand and assess changes over space and time of the risk posed by POPs to humans and the environment is indisputable. The choice of core media is based on strategic long term priorities in the context of a global exercise with very limited resources. Measurements in air and humans provide very valuable information that is globally comparable over space and time, if and only if, measurements are shown to follow agreed QA/QC procedures. Good quality measurements in other media are central and indispensable to gauge the importance over time of bio-geochemical and commercial pathways of POPs mixtures in the local environment and the consequent exposure routes to humans and ecosystems. The work delivered since 2009 by a number of long term international monitoring programmes in strategic partnership with the GMP will be briefly described. These programmes are measuring a number of POPs in aerosols, snow, ice, sea water, freshwater, sediments, soils, terrestrial and marine biota in the WEOG region and have been at work over the last few decades. We will focus in particular on information made available since the previous 2009 GMP report was released.

Much work has unfolded monitoring POPs in non-core media and reviewing the available data since 2009. A very significant share of it is explicitly attributed to the intention to contribute to the SC and in that sense is a strong indicator of the effectiveness of the convention and the GMP. We focus this summary on the work documented by a number of long term programmes that have been identified by GMP as strategic partners: AMAP, HELCOM, OSPAR, and MEDPOL. To a large extent the reports from these institutions include data from campaigns and sporadic data in their regions of interest.

The aim of this chapter is to review very briefly in a few pages the materials provided by these programmes about their work plans and published results. The intense activity over the past six years by thousands of motivated and competent scientist has contributed vast amounts of monitoring data over space and time concerning multiple POPs measured in very diverse environments. From microbial ecosystems in water, snow, ice, sediments and soil, to plankton, lichens and mosses, invertebrates, fish birds and mammals.

Samples have been taken of many different media, locations, species and time periods and analyzed for many different substances. The sampled organisms represent in some instances significant diet elements for sensitive groups in the WEOG region and indicate relevant

pathways to monitor progress in averting the negative effects of POPs. The focus of this document is the substances listed under the SC, and consequently the information is, to the extent possible, limited to them.

5.2.4.2 Programmes and relevant publications

The following sections are based on the most recent reports available for each program, a brief description of the programmes is presented in this chapter and summarized in a summary and highlights of the monitoring information reported on POPs since 2009 by AMAP and NCP, HELCOM, OSPAR MEDPOL, The Great Lakes and on Antarctica. More detailed information is cited in the Annex.

5.2.4.2.1 The Arctic: AMAP and NCP

POPs in the Arctic have been monitored in aerosols, snow, ice, sea and fresh water, soils and sediments, terrestrial and marine biota since the 1990s by The Arctic Monitoring and Assessment Programme (AMAP) and the Canadian Northern Contaminants Program (NCP). The following sections are based on the document prepared by AMAP for the GMP in 2014 and the NCP report published in 2013.

5.2.4.2.1.1 AMAP

The Arctic Monitoring and Assessment Programme (www.amap.no) is one of six Working Groups of the Arctic Council. The eight Arctic Council Member States are Canada, Denmark/Greenland/Faroe Islands, Finland, Iceland, Norway, Russian Federation, Sweden, the United States);

AMAP is mandated:

To monitor and assess the status of the Arctic region with respect to pollution and climate change issues.

To document levels and trends, pathways and processes, and effects on ecosystems and humans, and propose actions to reduce associated threats for consideration by governments.

To produce sound science-based, policy-relevant assessments and public outreach products to inform policy and decision-making processes.

AMAP's work is directed by the Ministers of the Arctic Council and their Senior Arctic Officials, who have requested AMAP to also support international processes that work to reduce the global threats from contaminants and climate change. These include the UN Framework Convention on Climate Change, UNEP's Stockholm Convention on Persistent Organic Pollutants and Minamata Convention on mercury, and the United Nation's Economic Commission for Europe (UNECE) Convention on Long-range Transboundary Air Pollution.

Since its establishment in 1991, AMAP has produced a series of high quality reports and related communication products that detail the status of the Arctic with respect to climate and pollution issues and that include policy-relevant science-based advice to the Arctic Council and governments.

AMAP is responsible for monitoring and assessing the status of the Arctic region with respect to pollution and climate change issues; documenting levels and trends, pathways and processes, and effects on ecosystems and humans, and proposing actions to reduce associated threats for consideration by governments; and producing sound science-based, policy-relevant assessments and public outreach products to inform policy and decision-making processes. Concerning methods and baseline levels of POPs in the Arctic extensive information can be found in de Wit et al 2004.

Letcher et al 2010 provide this informative overview on levels:

Generally, for all marine mammals, the general order (and similar to polar bears) of tissue concentrations are $\Sigma\text{PCB} > \Sigma\text{CHL} \approx \Sigma\text{DDT} \approx \Sigma\text{PFSA} > \Sigma\text{CBz} \approx \Sigma\text{HCH} \approx \Sigma\text{Toxaphene} \approx \Sigma\text{PFCA} > \Sigma\text{PBDE} > \text{HBCD}$. Extremely high levels of OHCs, i.e., ΣPCB , ΣCHL , ΣDDT , ΣCBz , $\Sigma\text{Toxaphene}$ and/or ΣPBDE have been reported for Alaskan and Northern Norway killer whales relative to other Arctic marine mammals and populations. In the case of Alaskan killer whales, ΣPCB , ΣCHL and ΣCBz levels in fat were >100 ppm (lw), and for Northern Norway animals levels of ΣPCB , ΣCHL and $\Sigma\text{Toxaphene}$ in fat were 27, 7 and 8 ppm (lw), respectively.

Generally, for all Arctic bird the general order of tissue (or egg) concentrations are $\Sigma\text{PCB} > \Sigma\text{CHL} \approx \Sigma\text{DDT} \approx \Sigma\text{Toxaphene} \approx \Sigma\text{CP}$ (chlorinated paraffins) $> \Sigma\text{CBz} \approx \Sigma\text{HCH} \approx \Sigma\text{PFSA} > \Sigma\text{PBDE} \approx \text{HBCD} > \Sigma\text{PFCA}$. Higher levels of ΣPCB of >1 ppm (lw or ww) have been reported for black-legged kittiwake, great (*Larus marinus*) and lesser (*Larus fuscus*) black-backed and herring (*Larus argentatus*) the general order of tissue concentrations $\Sigma\text{PCB} > \Sigma\text{CHL} \approx \Sigma\text{DDT} \approx \Sigma\text{Toxaphene} \approx \Sigma\text{CP}$. For the three bird species/populations, levels of ΣCHL and ΣDDT have also been reported to be >1 ppm (lw or ww).

Generally, for all fish reported, the order of tissue concentrations are $\Sigma\text{PCB} > \Sigma\text{CHL} \approx \Sigma\text{CP} > \Sigma\text{DDT} \approx \Sigma\text{Toxaphene} \approx \Sigma\text{CBz} \approx \Sigma\text{HCH} \approx \Sigma\text{PBDE} \approx \Sigma\text{PFSA} \approx \Sigma\text{PFCA} > \text{HBCD}$. High levels of ΣPCB of >1 ppm (lw or ww) have been reported in the muscle and/or liver for two species and populations of long-lived fish, Arctic charr (Bear Is.) and Greenland shark (Iceland and Southeastern Baffin Bay).

AMAP is currently preparing an assessment of POPs in the Arctic that will include a review of all available time-series datasets. Part of this work has been fast-tracked to provide the Stockholm Convention with information relevant to those POPs currently covered under the Stockholm Convention for inclusion in its 2015 GMP report.

For the purposes of the GMP 2015 report, AMAP biota monitoring datasets were selected that included data for the SC POPs and comprised at least 6 years of data. For ‘legacy’ POPs, an additional requirement was that the series include data from both before and after 2000. Previous AMAP temporal trend assessments have included both terrestrial and marine species. The current work included only marine species as no new data were available for the terrestrial components. Icelandic and Norwegian datasets include data reported to AMAP/OSPAR and archived at the AMAP marine TDC at the International Council for the Exploration of the Sea (ICES) in Denmark. Other AMAP data were collected from lead scientists responsible for relevant temporal trend monitoring studies in Canada, Denmark/Greenland/Faroe Islands, and the USA. The datasets/statistical analyses results presented in this report are a subset of the temporal trend data assessment that is being conducted for an updated AMAP Assessment of POPs in the Arctic that will be delivered in 2015. That assessment report will contain the publicly accessible data for time-series not yet available in AMAP TDCs.

Datasets and statistical analyses

Annex 5 shows the locations where long-time series monitoring of POPs in Arctic biota is conducted, together with the species monitored. Time-series were available from 7 countries for a total of almost 60 location-species-tissue combinations. The time-series include locations in Alaskan marine areas; Arctic Canada; East and West Greenland; marine areas around Iceland, the Faroe Islands and northern Norway; and lakes in Sweden. No long-time series biota datasets are currently available for the Arctic areas of Russia.

Statistical analyses were conducted using the PIA application on individual time-series concerning 22 compounds/compound groups (chlordanes (sum and *trans*-nonachlor), DDTs (sum and *p,p'*-DDE), dieldrin, heptachlor epoxide, hexachlorobenzene, hexachlorocyclohexanes

(α -, β - and γ -HCH), hexachlorobutadiene, mirex, pentachlorobenzene, perfluorooctanesulfonic acid (PFOS), polybrominated diphenyl ethers (PBDEs-47 and 99), polychlorinated biphenyls (sum and PCB-153), toxaphene (parlar-26 and -50)).

Over 1100 statistical analyses were performed, with datasets run for both time-series that start prior to the year 2000 (655 datasets) and for time-series that either begin after 2000, or with years prior to 2000 excluded (474 time-series), see **Figure 5.2.4a**.

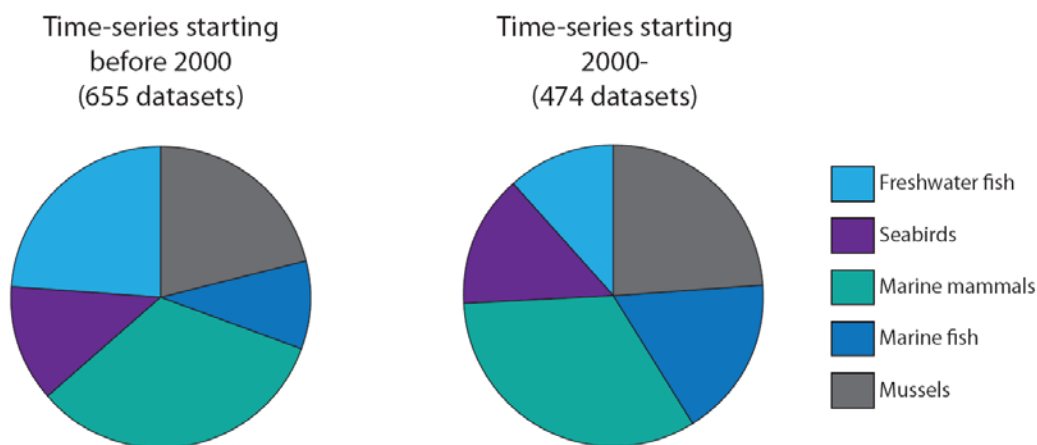


Figure 5.2.4a Overview of the breakdown of the available time-series by species (source: AMAP).

PIA provides a robust method for investigating trends in time-series data represented by annual index values (Nicholson et al., 1998). The method employed tests for the presence of (log-) linear trends and non-linear trend components in the time-series (at a significance level of 5%). Median concentrations were used as the annual index values to minimize the influence of outliers and less-than-detection-limit values. The method also evaluates the adequacy of the time-series to detect an annual change of 5% with a power of 80%.

Datasets were handled in a similar manner to previous similar evaluations (Rig  t et al., 2010), taking account of data originators recommendations for sub-setting animal groups and including covariates, etc. Many time-series were run in different configurations (for example, with and without covariate adjustment) to investigate the influence of factors such as age, sex, lipid content, etc. on the observed trends.

Time-series with a large number of values reported at less than detection limits were examined to consider the pattern of these (for example whether they were concentrated at the end of a time-series exhibiting declining trends). Time-series where <50% of values were reported as ‘less-than-detection-limit’ in two or more years were generally considered inappropriate for trend analyses, unless these years were concentrated at the start or end of the time-series. ‘Less-than’ qualified values were introduced at half the reported detection limit.

Trend results were classified into 7 classes as follows:

Increasing, a statistically significant increasing log-linear trend.

Increasing with non-linear trend component, increasing trend with a statistically significant non-linear component.

Decreasing, a statistically significant decreasing log-linear trend.

Decreasing with non-linear trend component, decreasing trend with a statistically significant non-linear component.

Non-linear component, a statistically significant non-linear (fluctuating) trend with no clear increasing or decreasing tendency.

No trend. The time-series did not exhibit a statistically significant trend.

Not evaluated. The time-series was unsuitable for trend analysis (e.g. it contained too many ‘below detection limit’ values).

Summary of results

The format of this report does not permit a detailed description of individual results. More information will be available in the AMAP update assessment of trends in POPs in the Arctic that is due to be published in 2015. Instead, simple summary graphics have been prepared (see **Figure 5.2.4c**, **Figure 5.2.4d** and **Figure 5.2.4e**) to provide an overview of the combined results – together with a few basic conclusions based on this meta-analysis. In addition, a few examples of individual time-series results are presented to illustrate the information that is available at a non-aggregated level.

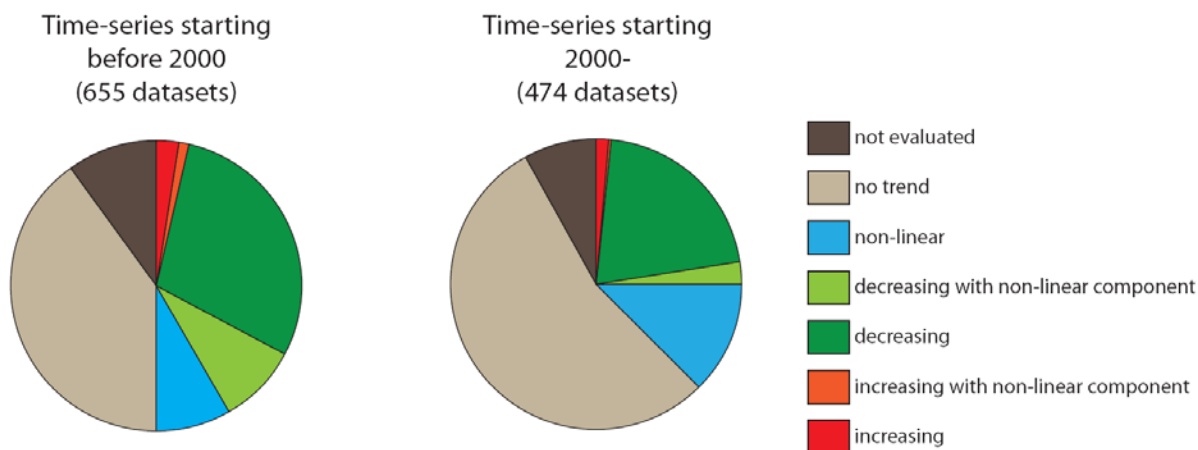


Figure 5.2.4b Overview of trend results for all datasets (source: AMAP).

Some observations on the aggregated results (summarized in Figure 5.2.4b – Figure 5.2.4d and Table 5.2.4a)

- ❖ Downward trends constitute the majority of statistically significant trends levels of (Stockholm Convention) POPs in Arctic biota.
- ❖ Many of the time-series begin decades before the Stockholm Convention entered into force. Downward trends therefore likely reflect the impact of control measures that were introduced at the national level, in the 1980s and 1990s in particular, both in Arctic countries and non-Arctic countries in neighbouring regions. This is apparent in exponential declines in concentrations of POPs such as PCBs and DDTs, as exemplified in **Figure 5.2.4e**.
- ❖ Comparing trends for the period after 2000 with those for time-series starting earlier than 2000 (**Figure 5.2.4c**), the proportion of significant (log) linear trends is lower and the number of time-series exhibiting fluctuating trends or no significant trends greater – as expected given that longer time-series are generally more powerful for trend detection.
- ❖ Considering results for specific compounds or compound groups (**Figure 5.2.4d** and **Figure 5.2.4e**), increasing trends are evident in the results PBDEs and HBCD and for PFOS. Controls on these substances at both the national and international level were not widely introduced before the late 1990s/2000s. For these substances, the increasing trends are no longer apparent if the time-series for the period after 2000 are considered and, for PBDE-47 and PFOS in particular the proportion of decreasing trends increases (see also example in **Figure 5.2.4e**)
- ❖ Other compounds/compound groups, including β -HCH (but not α - or γ -HCH) and trans-nonachlor show evidence of some increasing trends, as do a few datasets for

PCB/CB153, sumDDT (but not DDE) and HCB. Increasing trends are more evident in the (likely less powerful) post-2000 time-series.

- ❖ Differences in the way α -HCH and β -HCH partition between different environmental media provides a possible explanation for the differences between the observed trends in these two compounds in the Arctic. α -HCH is transported via the air whereas β -HCH partitions to a greater extent into water, and can therefore be transported via ocean currents. Reduction in use of technical HCH is therefore likely to be reflected sooner in (air transported) α -HCH-levels than in (slower, ocean transported) β -HCH levels at sites in the Arctic that are influenced primarily by long-range transport. It is also possible that loss of sea-ice and warming is resulting in a re-equilibration in the balance between HCH in the ocean and the atmosphere, with β -HCH entering the atmosphere from the ocean.
- ❖ It is often tempting to translate trends in levels in biota (or air or human media) to changes in emission levels. In the past, assessments of Arctic trend monitoring results have illustrated that interpreting trends in this over-simplistic fashion is inappropriate. Changes in food-web structure, and in feeding habits and diet can strongly affect levels in biota (including humans). Trends in levels in air and biota can reflect changes in environmental processes – a number of which can be associated with climate change and variability. A detailed examination of trends in individual datasets is necessary for reliable trend interpretation. Nonetheless, consistency in results from a large number of trend studies, over a large geographical extent, and involving different matrices may provide an indication that global controls on emissions or global processes are responsible for at least a part of the observed development.
- ❖ Tables summarizing trend results are included in Annex 5; these summaries show the annual percentage change (average and range) by species for the different contaminants/contaminant groups. Table 1 summarizes the trend results for all runs (for both series starting before 2000 and in or after 2000. Table 2 similarly summarizes the trends results for those series with either significant (log-) linear trends or that are considered of ‘adequate’ power (i.e., the ratio of the number of years in the series to the number of years required to detect a 5% annual change with a power of 80% is > 1).
- ❖ Of the more than 1100 statistical runs considered, approximately 25% were excluded, mainly due to the presence of ‘less than’ values. Of the non-excluded runs, approximately 12% of the time-series are currently of adequate length to detect a 5% annual change with a statistical power of 80%; this highlights the need to maintain monitoring effort to obtain sufficiently powerful time-series.

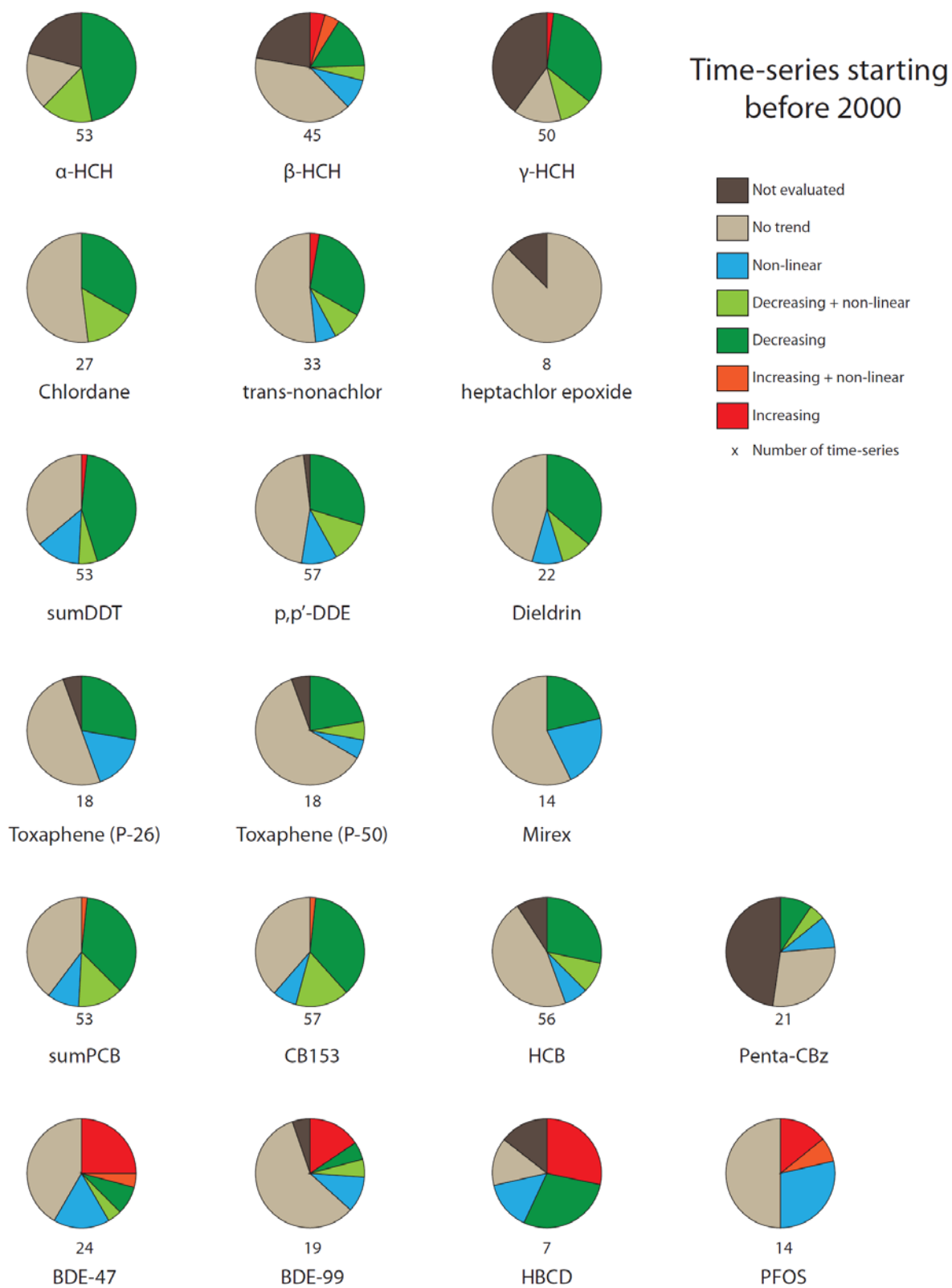


Figure 5.2.4c Overview of trend results by contaminant/contaminant group for entire time series (source: AMAP).

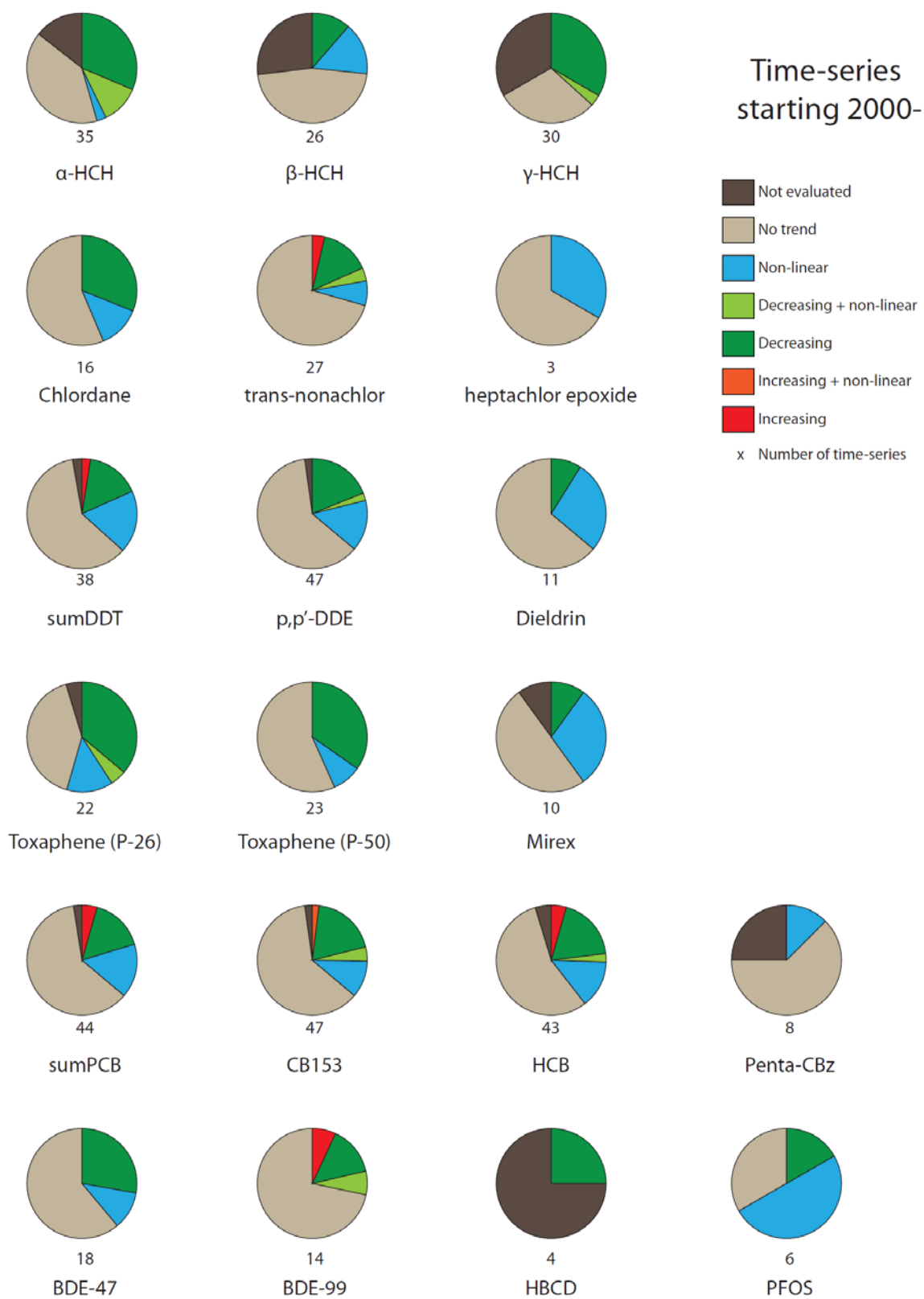


Figure 5.2.4d (Figure 4.5 of Annex 5) Overview of trend results by contaminant/contaminant group for the period 2000 - (source: AMAP).

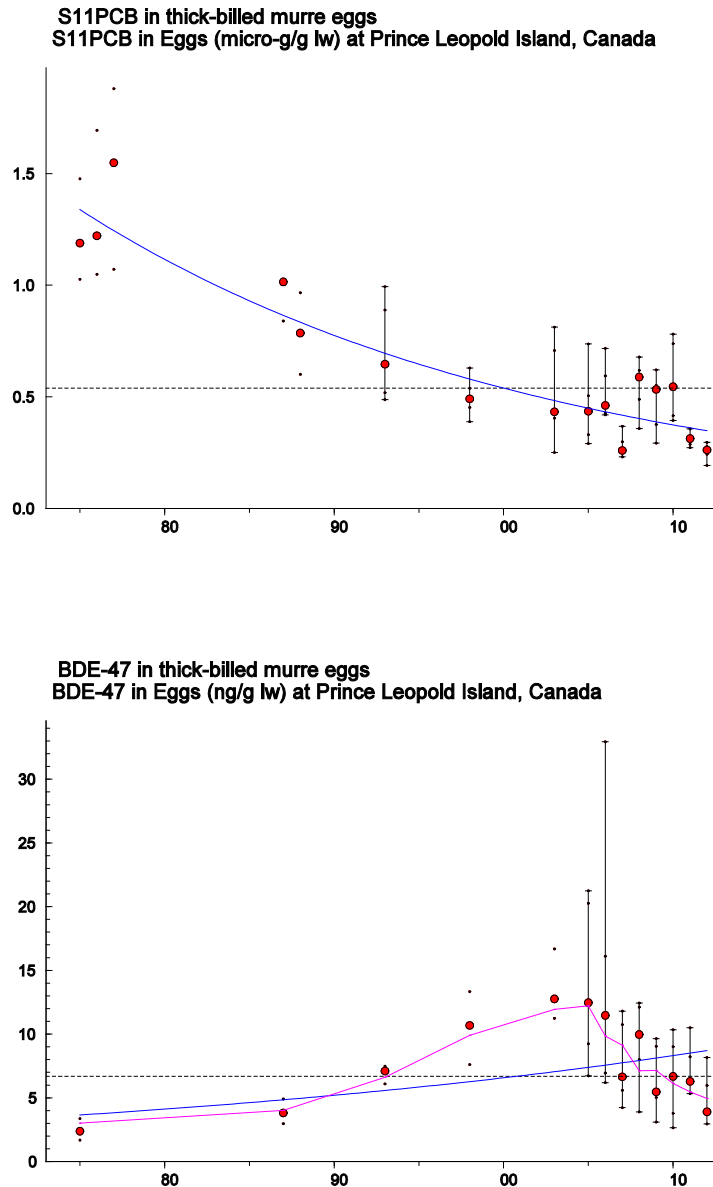


Figure 5.2.4e Example of trend results: PCBs (sum of 11 congeners) and PBDE-47 in thick-billed murre eggs collected at Prince Leopold Island, Canada (source: AMAP).

Future monitoring challenges

AMAP continues to face challenges to maintain the long-term monitoring that is essential for establishing temporal trends and to fill gaps in the circumArctic coverage. The emergence of new contaminants in the Arctic is placing additional pressures on monitoring programmes to provide information about an ever increasing suite of POPs. Some trend monitoring programmes

are reducing the frequency of sampling and/or analysis to reduce costs; in some cases this is to allow additional (new) contaminants to be added to the programme.

Reduction in sampling frequency can have serious negative impacts on the power of monitoring programmes to detect (temporal) trends. A possible compromise involves maintaining sampling frequency but reducing the frequency of analysis for contaminants that have exhibited declining trends and perhaps reached levels around detection limits. The resulting archived samples or sample extracts also provide a potential for reanalysis, including (re)analysis for newly emerging contaminants. Sample banks and other such archives are therefore likely to be increasingly important to future temporal trend studies, especially for emerging contaminants.

AMAP has contributed the material in this section and the full report (AMAP Update Report: Trends in Stockholm Convention Persistent Organic Pollutants (POPs) in Air, Human media and Biota) is attached to this document as Annex 5.

5.2.4.2.1.2 The Northern Contaminants Program (NCP)

The Northern Contaminants Program (NCP) was established in 1991 in response to concerns about human exposure to elevated levels of contaminants in wildlife species that are important to the traditional diets of northern Aboriginal peoples. The NCP was established in 1991 under the management and jurisdiction of the Department of Indian Affairs and Northern Development, the federal departments of Health, Environment, and Fisheries and Oceans, the Yukon, Northwest Territories and Nunavut territorial governments, and Northern Aboriginal organizations—Council of Yukon First Nations, Dene Nation, Inuit Circumpolar Conference, Inuit Tapirisat of Canada, and Métis Nation of the Northwest Territories.

The 2013 report (NCP 2013) is the third assessment of persistent organic pollutants (POPs) conducted by the NCP.

Previous assessments in 1997 and 2003 summarized results of Phase I (1991-1996) and Phase II (1997-2002) of the NCP and included both heavy metals and POPs. Under Phase III of the programme which began in 2003-04, environmental monitoring focused on fewer sampling sites for both air and biological samples. The biological sampling programmes were redesigned with the goal of being able to detect a 10% annual change in contaminant concentration over a period of 10-15 years with a power of 80% and confidence level of 95%.

The list of individual compounds analyzed was expanded in Phase III particularly for perfluorinated and polyfluorinated alkyl substances (PFAS), brominated flame retardants (BFRs) and current use pesticides (CUPs). About 35 chemicals or chemical groups that were not previously reported, or for which only very limited measurements were available in the previous assessment, have been detected particularly in arctic air, snow and biota.

(NCP 2013 p vii) executive summary:

The declining trend in concentrations in biota is most apparent for OC pesticides and less evident for PCBs and chlorobenzenes (ΣCBz). In marine species, percent annual declines of ΣDDT ranged from 2.5%/year in thick-billed murre eggs (Lancaster Sound) to 11%/year in polar bear fat (western Hudson Bay, WHB). Declines of chlordane-related compounds (ΣCHL) ranged from 1.2%/year in murre eggs to 7.4%/year in blubber of ringed seals in Hudson Bay, while polar bears (WHB) showed no decline.

Total HCHs (ΣHCH) declined in seals, beluga and polar bears due to rapid decline of the major isomer $\alpha\text{-HCH}$ (e.g. 12%/year in bears). However, $\beta\text{-HCH}$, the more bioaccumulative isomer, increased in the same species. This increase in $\beta\text{-HCH}$ in seals varied regionally, with large increases in South Beaufort Sea seals (16% at Ulukhaktok) and a decline in Hudson Bay (2.5%/year). The case of $\beta\text{-HCH}$ highlights the importance of ocean water moving through the Arctic archipelago from the Pacific Ocean via the Bering Sea and possibly Russian freshwater inputs. No other POPs shows this trend although declines of PCBs, ΣDDT , ΣCHL were lower or non-existent in beluga, ringed seals and polar bears in the South Beaufort compared to Hudson Bay and East Baffin regions.

Declines of legacy POPs have generally been more rapid in freshwater fish than in marine animals. For example, PCBs in landlocked arctic char declined by 6.4% and 7.6%/year in Amituk Lake and Lake Hazen, respectively, versus 3.8% and 4.0%/year in thick-billed murres and northern fulmars, respectively. Declines of $\geq 5\%$ /year were also seen for ΣHCH , ΣCHL , ΣDDT and toxaphene in lake trout from Lakes Laberge, Kusawa Lake and western basin of Great Slave Lake as well as in landlocked char in Lake Hazen, Char Lake and Amituk Lake. Declines for these OC pesticides were generally $<5\%$ /year in seabird eggs and marine mammals. A notable exception was the increase in concentrations of PCBs, ΣCHL , ΣDDTs , and toxaphene were over the period 2001 to 2009 in burbot liver sampled at Fort Good Hope on the Mackenzie River. However, as of 2010 concentrations of all four POPs had returned to levels found in the 1990s and early 2000s.

A major strength of the temporal trend programmes conducted under the NCP is the availability of archived samples from specimen banks. New POPs such as PBDEs and PFOS generally increased in seals, seabirds, beluga, and polar bear samples from the 1990s until the early 2000s and are now declining. Retrospective analysis of collections from specimen banks enabled measurements of the PBDEs, PFAS and other contaminants in samples from the 1970s, '80s and '90s, and annual sampling as of early 2000s enabled relatively rapid declines to be observed. For example, Σ PBDEs achieved maximum concentrations in northern fulmar and thick-billed murre eggs in 2005 and 2006, respectively and declined to levels similar to those in the early 1990s within 3 years.

Prominent, relatively new POPs are PBDEs and PFOS, which are detectable in all biota although generally at much lower concentrations than PCBs or toxaphene. An exception is PFOS, which is at the part per million level in polar bear liver and on par with several chlorinated POPs in polar bear adipose tissue. HBCD, has been reported in freshwater and marine fishes, beluga, seals, seabirds and polar bears. Perfluorinated compounds, PBDEs and HBCD are higher in ringed seals in Hudson Bay than other locations, reflecting the closer proximity to source regions in southern Canada and northern US. More detailed highlights concerning spatial and temporal trends of POPs monitored in biota presented in the NCP 2013 report can be found in Annex 5 to this chapter.

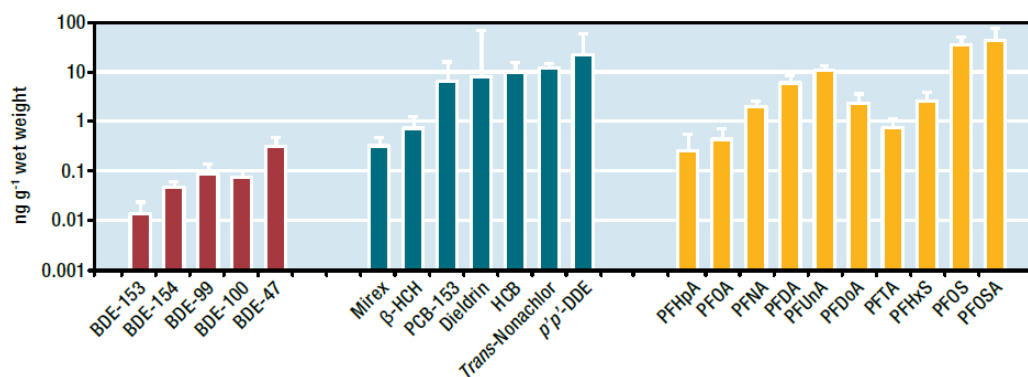


Figure 5.2.4f Concentrations ($\text{ng g}^{-1} \text{ ww}$) of selected PBDEs, PCBs, OCPs and PFAS in beluga whale liver from eastern Hudson Bay. Data are geometric means and standard deviations (from Kelly et al. 2008, Kelly et al. 2009).

Despite the decreasing trends in many legacy pollutants, the total burden is increasing due to new substances, and the persistence of the old ones. Figure 5.2.4f displays a case in point with a representation of the concentrations of PBDEs, PCBs, OCPs, and PFAS in beluga whale liver.

The Stockholm convention states under Article 3, Paragraph 3, that:

“Each party...shall take measures to regulate with the aim of preventing the production and use of new pesticides or new industrial chemicals which, ... exhibit the characteristics of persistent organic pollutants.”

Nevertheless, no such preventative measures seem to be undertaken sufficiently by the parties. To the contrary, many of the chemicals that were listed after banning the original 12 “legacy” POPs (4), have been introduced or scaled up in production and use to (at least partly) replace the ones that were banned (for example HBCD and other BFRs replaced PentaBDEs in many uses) (NCP2013 p13)

Between 2005 and 2012, six rounds of interlaboratory studies (ILS) were conducted to evaluate the analytical data provided to the Northern Contaminants Program (NCP). From 2007 laboratories that participated in the Arctic Monitoring and Assessment Programme (AMAP) were included and also evaluated to ensure that the pre-established NCP data quality objectives were met (Selliah et al. 2008).

The NCP 2013 report presents a summary of the study design, evaluation and statistical treatment of the results covering the period from 2005–2012 of NCP-III Phase 1 to Phase 6 (NCP-III 1-6) study. It presents the performance of NCP laboratories compared to the AMAP and all other laboratories that participated in the ILS (NCP2013 p463). Thirty-four organizations with forty-three laboratories from thirteen countries participated in NCP-III 1-6 for persistent organic pollutant (POPs) studies. The inter-laboratory studies demonstrated that the NCP laboratories are capable of producing excellent and satisfactory results for POPs analysis in the standards (72–89%) and satisfactory results for PCBs, OCPs, PCDDs analysis in certified natural-matrix materials (65–71%) (NCP2013 p463).

5.2.4.2.2 HELCOM

HELCOM (Baltic Marine Environment Protection Commission - Helsinki Commission) (www.helcom.fi) is the governing body of the Convention on the Protection of the Marine Environment of the Baltic Sea Area, known as the Helsinki Convention. The Contracting Parties are Denmark, Estonia, the European Union, Finland, Germany, Latvia, Lithuania, Poland, Russia and Sweden. HELCOM was established about four decades ago to protect the marine environment of the Baltic Sea from all sources of pollution through intergovernmental

cooperation. Monitoring programmes are based on HELCOM Monitoring and Assessment Strategy. They are under review during 2013-2014.

The HELCOM assessment products, based on quality assured data, are needed to make sound decisions for how to restore the Baltic Sea ecosystem, to support the implementation of the HELCOM objectives and actions and to identify emerging environmental problems. For this reason a procedure to harmonize the monitoring at the regional Baltic Sea level has been agreed upon.

Monitoring is since long a well-established function of the Helsinki Convention. Monitoring of inputs of nutrients and hazardous substances started in 1998. Monitoring of physical, chemical and biological variables of the open sea started in 1979; monitoring of radioactive substances in the Baltic Sea started in 1984.

The HELCOM monitoring system consists of several complementary programmes:

- ❖ The Pollution Load Compilation programmes (PLC-Air and PLC-Water) quantify emissions of nutrients and hazardous substances to the air, discharges and losses to inland surface waters, and the resulting air and waterborne inputs to the sea.
- ❖ The COMBINE programme quantifies the impacts of nutrients and hazardous substances in the marine environment, also examining trends in the various compartments of the marine environment (water, biota, sediment). The programme also assesses physical forcing.
- ❖ COMBINE monitoring data can be downloaded from ICES Oceanographic database. Monitoring data can be also visualized and downloaded in the ICES EcoSystemData map service.
- ❖ Monitoring of radioactive substances (MORS) quantifies the sources and inputs of artificial radionuclides, as well as the resulting trends in the various compartments of the marine environment (water, biota, sediment).

HELCOM also coordinates the surveillance of deliberate illegal oil spills around the Baltic Sea, and assesses the numbers and distribution of such spills on an annual basis.

Despite the declining trends of POPs, their concentrations in the marine environment are still of concern. PCBs are clearly the most widespread and problematic group of pollutants in the Baltic

Sea (HELCOM 2010a). The concentrations of dioxins and furans also still exceed the safety criteria for seafood in the northern and northeastern parts of the Baltic Sea, although the levels in the more southern areas were classified as being ‘good’ according to environmental standards. Exceedances of the threshold values for cadmium and mercury concentrations in fish and mussels were found in almost all areas of the Baltic Sea (HELCOM 2010a).

There are positive signals of decreasing trends of persistent organic pollutants (POPs) in the Baltic Sea. In many cases, the declines can be directly related to bans or restrictions on the production or use of the substances. Dioxins, measured as TCDD-equivalents in common guillemot (*Uria aalge*) eggs from Stora Karlsö in the Western Gotland Basin since the end of the 1960s, are decreasing. The temporal trend of DDE, a degradation product of DDT, measured in herring muscle has been declining since the end of the 1970s. PCBs show significant declining trends for herring, perch and blue mussels in several regions in the Baltic Sea, which has entered the marine environment primarily due to its use in anti-fouling paints on ship hulls, has declined at least in Danish and German waters (HELCOM 2010a)

HELCOM core indicators form the critical set of indicators that are needed to regularly assess the status of the Baltic Sea marine environment against targets that reflect good environmental status. The need for a Baltic Sea-wide, coherent assessment of the state of the marine environment triggered HELCOM to launch the CORESET project (2010- 2013), which was given a clear objective to develop the core indicators for biodiversity and hazardous substances, and set up a web-based follow-up system for the state of the marine environment. The CORESET project was set under the supervision of the HELCOM Monitoring and Assessment Group.

Core indicator substances are: Polybrominated biphenyl ethers (PBDE), Hexabromocyclododecane (HBCD), Perfluorooctane sulphonate (PFOS), PCBs, and dioxins and furans. Although DDTs, HCHs and HCB were not proposed as core indicators, monitoring their levels in the Baltic Sea should be continued with regular assessments. This may be relatively easy to achieve as their chemical analysis can be done together with the analysis of PCBs - a core indicator.

The set of hazardous substances selected as core indicators is a tiny fraction of all anthropogenic substances present in the marine environment. Although the selected substances are considered representative in terms of their PBT properties and known concentrations in the Baltic Sea, environmental monitoring should cover other substances as well. For a detailed list

organism/tissue/substances monitored in open sea by HELCOM and what group is reporting them see the table in Law et al 2010 p100.

5.2.4.2.2 OSPAR

The Convention for the Protection of the Marine Environment of the North-East Atlantic (the “OSPAR Convention”, www.ospar.org) was opened for signature at the Ministerial Meeting of the former Oslo and Paris Commissions in Paris on 22 September 1992. The Convention entered into force on 25 March 1998. The Contracting Parties are: Belgium, Denmark, the European Union, Finland, France, Germany, Iceland, Ireland, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

The 2012 assessment of data collected under the OSPAR Coordinated Environmental Monitoring Programme (CEMP) (OSPAR 2013c) was prepared by the OSPAR Working Group on Monitoring and Trends and Effects of Substances in the Marine Environment (MIME) at, and following, its meeting in December 2012 and is based upon data reported by Contracting Parties to ICES and held in the ICES Environmental databases.

The CEMP is the monitoring under the OSPAR Joint Assessment and Monitoring Programme where the national contributions overlap and are coordinated through adherence to commonly agreed monitoring guidelines, quality assurance tools and assessment tools. It covers temporal trend and spatial monitoring programmes for concentrations of selected chemicals and nutrients, and for biological effects. Monitoring under the CEMP aims to indicate the extent of contamination of fish, shellfish and sediments with hazardous substances and the intensity of their biological effects". The purpose of CEMP is to support OSPAR assessments of the effectiveness of measures to reduce releases of hazardous substances to the environment.

The OSPAR assessment for 2013 covers in excess of 25000 measurements with more than 50 parameters and 7500 time trends in sediment, biota and for biological effects (Annexes 1-3). Assessment products are presented in the Web assessment tool at <http://dome.ices.dk/osparmime/main.html>, assessment data are also available at this location, together with supporting tables, plots, help files, and methodological information.

The contaminants covered by the CEMP are metals (cadmium (Cd), mercury (Hg), lead (Pb), nickel (Ni), copper (Cu), zinc (Zn), chromium (Cr), arsenic (As) and the organic contaminants PCBs (congeners 28, 52, 101, 105, 118, 126, 138, 153, 156, 169, 180) and PAHs (naphthalene,

phenanthrene, anthracene, dibenzothiophene, fluoranthene, pyrene, thiphenylene, benzo[a]anthracene, benzo[a]pyrene, benzo[ghi]perylene, and indeno[123-cd]pyrene).

The 2013 assessment covers the concentrations of a selection of hazardous substances from the CEMP in marine sediment, fish tissue (muscle and liver) and shellfish tissues. A downward trend was observed for 95% of the dioxins-furans and PCBs. A number of UK stations and Spanish stations are nonetheless showing increasing trends for CBs and some samples were above the Ecological Assessment Criteria (EAC).

Analyzed substances having significant time trends in biota (OSPAR 2013c, p21.)

PCB 101,105,118,126,138,153,156,169,180,28,52

PBDE47

DDE (p,p') (DDEPP)

1,2,5,6,9,10-hexabromocyclododecane (HBCD)

Hexachlorobenzene (HCB)

alpha-HCH (alpha-hexachlorocyclohexane)

gamma-HCH (gamma-hexachlorocyclohexane)

OSPAR environmental monitoring has concentrated on a set of 7 PCB congeners, which cover the range of toxicological properties of the group (CB congeners 28, 52, 101, 118, 138, 153, 180). CB153 is generally present in the highest concentration and correlates well with other analyzed PCBs. CB118 is representative of the more toxicologically relevant mono-ortho/planar PCBs.

Contamination from PCBs is widespread and there are few areas where concentrations are close to zero. Concentrations are lowest along the northern coast of Norway (Region I). PCBs are however among the most prevalent pollutants in the Arctic and are widely distributed by long-range atmospheric transport. At most locations in Regions II, III and IV, concentrations of at least one PCB congener in fish and shellfish pose a risk of causing pollution effects. PCB 118 is the congener most often above EAC, Concentrations are decreasing at a high proportion of the fish/shellfish stations, particularly along the continental coast of the North Sea, the west of the UK, and Ireland. A small number of stations showed increasing trends (OSPAR 2013c).

A general reduction in concentrations of lindane (γ -HCH) in fish and shellfish has been achieved across the OSPAR area as a result of the phase out and banning of its use. Concentrations are close to zero in some areas, for example western and northern Norway, and parts of Ireland, France and Iceland. However, concentrations in some other areas are still at levels with a risk of pollution effects. Particular examples are the Brittany coast, the German Bight, and some northern UK estuaries (Humber, Clyde, Forth, Tay). The localized nature of these hotspots, which may persist for years to come, may reflect historic use nearby (OSPAR 2009a).

Data on the concentrations of lindane in sediment are relatively sparse compared to the data for metals, CBs, or PAHs. Where data exist, concentrations are generally not close to background. Concentrations in northern France and the Netherlands are less than the upper assessment criterion (ERL). Some concentrations around Denmark are above the ERL implying some potential for adverse environmental effects. There are insufficient time series of data to make any statements on temporal trends on lindane in sediments in the OSPAR area. The monitoring data show a wide range of concentrations of lindane in biota. In some areas, for example western and northern Norway, parts of Ireland, France and Iceland, concentrations are close to zero (i.e. close to background). The scattered occurrence of concentrations above the upper assessment criterion (EAC), for example in western Brittany, parts of Germany, Denmark, the UK and Ireland, may reflect localized historical use (OSPAR 2009a). Measuring lindane (γ -HCH) in precipitation is mandatory under CAMP (OSPAR 2009c). Four stations (Belgium, Germany, Iceland, Norway) reported data in precipitation for 2010. Some countries are no longer reporting lindane because it has been undetectable /unquantifiable for several years (OSPAR 2012c).

The OSPAR Commission has ensured a high level of information sharing and joint assessment in the North-East Atlantic, following on from repeated integrated environmental assessments in order to enhance regional coordination for the Initial Assessment (MSFD Article 8). The OSPAR Quality Status Report 2010, together with its underlying assessment reports, provides the primary basis for coordination of national initial assessments across those North-East Atlantic OSPAR Contracting Parties which are also EU Member States.

With a view to achieving common goals, OSPAR commits to strengthen cooperation with other Regional Sea Conventions involved in facilitating the implementation of the Directive, in particular the Helsinki and the Barcelona Conventions, to which some OSPAR Contracting Parties are also parties. Furthermore, considering that concentrations of nutrients and hazardous substances are related to atmospheric depositions and loads from rivers in the catchment area, we will reinforce cooperation with land-locked States, using established cooperation structures, such

as International River Basin Commissions. OSPAR is preparing to revise its Joint Monitoring and Assessment Programme over 2013-2014 in order to support countries' MSFD needs, in particular the 2014 MSFD monitoring programmes and the 2018 update of the initial assessment. Monitoring programmes would need to be designed to allow tracing back chemicals from the environment via their pathways to the sources in order to allow the appropriate development of programmes of measures to achieve good environmental status and assess progress being made.

5.2.4.2.3 MEDPOL

The Convention for the Protection of the Marine Environment and the Coastal Region of the Mediterranean (Barcelona Convention, www.unepmap.org) was adopted in 1976 and came into force in 1978. The Programme for the Assessment and Control of Marine Pollution in the Mediterranean region (MED POL) is the environmental assessment component of the Mediterranean Action Plan (MAP). It was initiated in 1975 and is now in Phase IV. It is responsible for the implementation of the Land-Based Sources, Dumping, and Hazardous Wastes Protocols. It assists Mediterranean countries in the formulation and implementation of pollution monitoring programmes (trend, compliance and biological effects monitoring) and pollution control measures, and in the drafting of action plans aiming to eliminate pollution from land-based sources (Law et al. 2010).

UNEP/MAP 2011 reviews the progress made in the implementation of the marine monitoring programme of MED POL Phase IV and presents a spatial and temporal assessment of the hazardous substances in sediment and biota in the Mediterranean, based on the MED POL marine monitoring database. The document reviews the progress in the following activities:

- I. Marine monitoring and data collection
- II. II. Data Quality Assurance
- III. III. Status and pollution trends monitoring of the Mediterranean marine environment IV. Development of a harmonized integrated MAP monitoring programme to assess the quality status of the Mediterranean.

Some highlights of this report are detailed in Annex 5 and provide the basis for Table 2.

The Reference Methods for the analysis of pollutants in water, sediment and biota, in the framework of the UNEP/MAP-MEDPOL, can be found in www.unepmap.org (Document and publications/ Library Resources/ Reference Methods)

5.2.4.3 Other processes in WEOG relevant for monitoring POPs baselines and changes over time in non-core media

5.2.4.3.1 The Great Lakes of North America

Since the mid-1970s, Environment Canada and the US EPA have implemented an extraordinary monitoring effort in the Great Lakes of North America that has provided some very valuable high quality long term data to investigate the presence, fate and impact of POPs. This effort has had a significant effect in developing global strategies to deal with the risks associated with POPs. It can be argued that this work has not only monitored changes and trends over time but has been effective in steering those trends to decline achieving environmental and public health benefits. The monitoring information has been reported through a suite of science-based ecosystem indicators as part of the State of the Lakes Ecosystem Conferences (SOLEC).

From (http://binational.net/solec/intro_e.html, accessed April 2014):

The State of the Lakes Ecosystem Conferences (SOLEC) are hosted by the U.S. Environmental Protection Agency and Environment Canada on behalf of the two countries. These conferences are held every two years in response to a reporting requirement of the binational Great Lakes Water Quality Agreement (GLWQA). The goal of SOLEC is to achieve the overall purpose of the GLWQA “to restore and maintain the physical, chemical and biological integrity of the Great Lakes Basin”. The conferences are intended to report on the state of the Great Lakes ecosystem and the major factors impacting it, and to provide a forum for exchange of this information amongst Great Lakes decision-makers. These conferences are not intended to discuss the status of programmes needed for protection and restoration of the Great Lakes basin, but to evaluate the effectiveness of these programmes through analysis of the state of the ecosystem.

These conferences are a culmination of information gathered from a wide variety of sources and engage a variety of organizations. In the year following each conference, the Governments prepare a report on the state of the Great Lakes based in large part upon the conference process.

The first conference, held in 1994, addressed the entire system with particular emphasis on aquatic community health, human health, aquatic habitat, toxic contaminants and nutrients in the water, and the changing Great Lakes economy.

The most recent State of the Lakes Ecosystem Conference (SOLEC) was held in Erie, Pennsylvania, October 26-27, 2011 and it assembled, with involvement from more than 125 scientists and experts from the Great Lakes community within Canada and the United States, the

information published in the State of the Great Lakes 2011 report (Environment Canada and US EPA 2011). See Annex for a more detailed citation of this report.

Environmental Specimen Banks containing tissue samples are a key component of both the U.S. and Canadian monitoring programmes, allowing for retrospective analyses of newly identified chemicals of concern to develop long- term trends in the short-term. Fostering collaboration between U.S. and Canadian monitoring programmes for various media will be beneficial, especially in times of fiscal restraint. In 2009, an ad-hoc binational group was formed to bring together government representatives and researchers working on identifying new chemicals in the Great Lakes ecosystem with the objective to facilitate best management practices and sharing of information and resources. The group provides a forum for agencies and researchers to seek and provide information on emerging contaminant surveillance, monitoring, chemical methods development, and provides a place to collaborate on similar chemicals, or classes of chemicals, in different media. Collaboration among research in differing media also provides an excellent opportunity for cost sharing, an accelerated rate of discovery, and a validation of results among the Great Lakes research and monitoring community (p209).

5.2.4.3.2 Antarctica

Antarctica and the adjacent islands and ocean (area delimited by the Antarctic Convergence) have a very small human population. There is no industrial activity and no agriculture. Human presence in the region is concerned largely with scientific investigations and the logistics operations in support of these. Locally the greatest impact can be expected where research is carried out at long-term stations. The number of people conducting and supporting scientific research and other work on the continent and its nearby islands varies from about 1,000 in winter to about 5,000 in the summer. Pelagic fisheries are an important operation in some parts of the region, and tourism is also an increasingly important activity. Both of these may account for slight increases in emissions of some POPs, but these will normally be highly dispersed (UNEP, 2002).

The Standing Scientific Group on Physical Sciences of SCAR, which is very much involved in the issue of environmental contamination, accepted a proposal from the Polar Chemistry Project of the Italian Research Program in Antarctica (PNRA) and established the Action Group “Environmental Contamination in Antarctica (ECA)” at XXIX SCAR in Hobart (July 2006). The main aims of the ECA action group are as follows:

- ❖ to understand the mechanisms and processes controlling distribution and transport of micro- components in polar environments, and their environmental effects;

- ❖ to assess the effects of global climatic changes on processes controlling the dispersion and transport of micro-components and to estimate the contribution of micro-components on climate and environmental changes in polar regions;
- ❖ to monitor the environmental characteristics in Antarctica and set up a data base of environmental parameters to follow the environmental evolution in polar regions.

A handful of only five research studies have monitored the occurrence of PFOS, PFOA and PFAS in aquatic organisms and fauna in Antarctica, contributing to this last aim of the ECA action group. Two of those studies have included 8 and 16 other PFAS congeners, respectively. Evidence of PFOS permeation into the Southern Ocean food-web comes from algae, superficial soil and vertebrate predators foraging in the western Antarctic Peninsula area or sub-Antarctic latitudes of this sector (Figure 5.2.4g). PFOS was further detected in migratory seabird species of the eastern sector spending the winter season outside the Antarctic region. These seabirds can be found in the Ross Sea region and Heard and McDonald Island. However, more studies are necessary to monitor biological samples and to better understand the influences of long range environmental transport: by atmospheric and oceanic transport and migratory species and also the bioaccumulation and consequent biomagnification through the food chain. The available information for PFOS in Antarctica, in biota and superficial soil, is summarized in Annex 4.

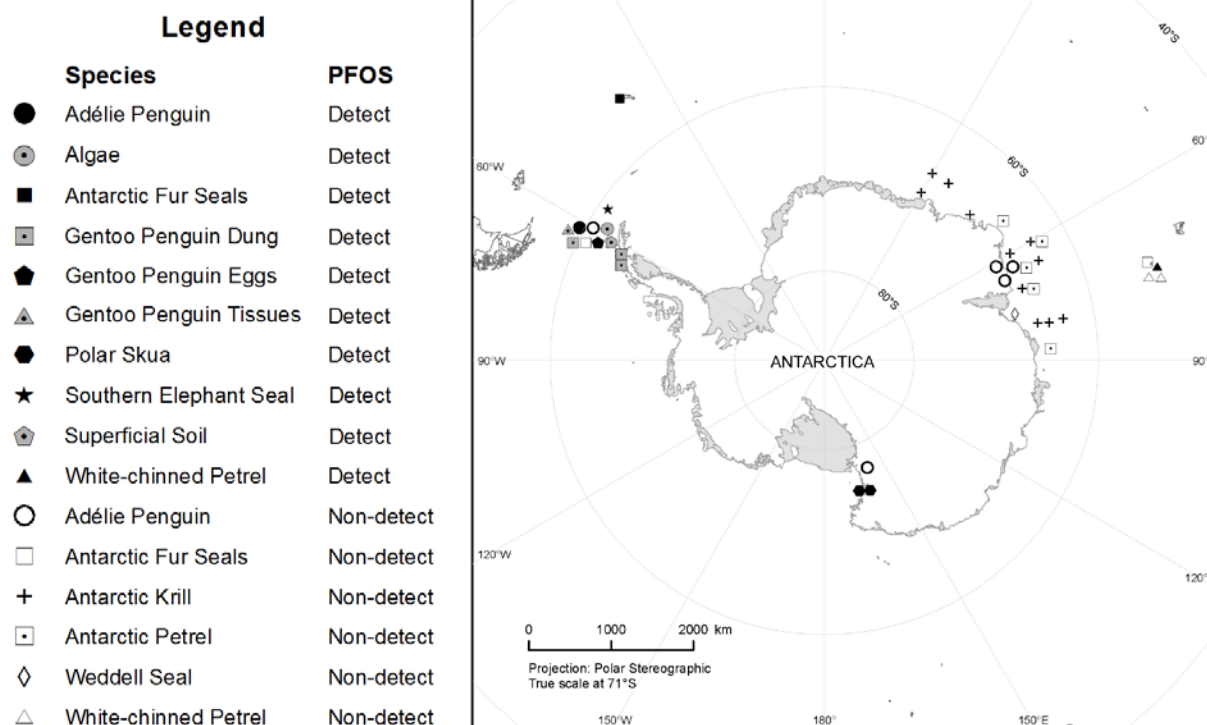


Figure 5.2.4g PFOS in biota of Antarctica from five research studies (Bengtson Nash et al., 2010; Giesy and Kannan, 2001; Llorca et al., 2012; Schiavone et al., 2009; Tao et al., 2006). Filled icons reflect positive detects. Average concentrations and ranges are given in Annex 4. There is a cluster of points at the tip of the Antarctic Peninsula. The true location of the points shown in two rows of four on the map is where the points at the right end of each row are situated. The map is courtesy of the Australian Antarctic Data Centre. The coastline of Antarctica is from the Antarctic Digital Database version 6 © 1993-2014 Scientific Committee on Antarctic Research.

5.2.4.3.3 USA

CCMA Center for Coastal Monitoring and Assessment addresses pollution through the National Status and Trends Program (NS&T), through which long-term monitoring of toxic chemicals and environmental conditions is conducted at more than 350 sites along U.S. coasts. The programme also documents the nature and severity of the biological effects associated with toxic chemicals in 25 coastal ecosystems. The programme was begun in 1984 and is the only nationwide source of long-term data on toxic contaminants in U.S. coastal waters and estuaries. Outcomes include a status of contaminant concentrations around the U.S. including Alaska, Hawaii, the Great Lakes, and Puerto Rico. The programme's data information products are available to the public via publications and the Internet. The NS&T is comprised of two programmes, Mussel Watch and Bioeffects. Parameters monitored in the Mussel Watch Program include sediment and bivalve

tissue chemistry for over 100 organic and inorganic contaminants; bivalve histology; and *Clostridium perfringens* (pathogen) concentrations. This project regularly quantifies PAHs, PCBs, DDTs and its metabolites, TBT and its metabolites, chlorinated pesticides and toxic trace elements. Bioeffects Assessment Program identifies and assesses biological effects associated with contaminant exposure. Over forty intensive regional studies have been conducted since 1986 using the Sediment Quality Triad approach which utilizes a stratified random sampling method to determine the areal extent of contaminated sediments. The data include: sediment chemistry, toxicity, and species diversity and quantity for the same suite of organic contaminants and trace metals as the Mussel Watch Program (from Law et al 2010).

A number of data repositories that include large collections of POPs measurements in other media are available in the USA (personal communication with Dr. John Kucklick, National Institute of Standards and Technology, Hollings Marine Lab Charleston). These include:

- ❖ NOAA mussel watch data: <http://ccma.nos.noaa.gov/about/coast/nsandt/download.aspx>
- ❖ San Francisco Estuary Institute data: <http://www.sfei.org/sfeidata.htm>
- ❖ Southern California Coastal Water Research Program data:
<http://www.sccwrp.org/Data.aspx>
- ❖ USGS's NAWQA data: http://cida.usgs.gov/nawqa_public/apex/f?p=136:1:0
- ❖ EPA's air data: <http://www.epa.gov/airdata/>
- ❖ EPA's water data: <http://water.epa.gov/scitech/datait/tools/waters/data/index.cfm>

5.2.4.4 Summary and Conclusions

On levels and trends

Trends for legacy POPs indicate significant decreases from the mid-1970s to the mid-1990, and much smaller changes since then. DDTs, HCHs HCB and most significantly PCBs still present levels of concern in the WEOG region, the attribution of these changes is more related to LRT, circulation of POPs between media and changes in climate than to changes in primary sources. Several POPs listed more recently (PBDE, PFOS, HBCD) show recent or ongoing increasing trends. This is probably attributable to current sources, and thus will constitute important indicators of the effectiveness of the SC in the future.

On monitoring/reporting strategies in the future

Best efforts should be made to maintain and extend coverage of monitoring of biotic and abiotic media, with particular emphasis on establishing and maintaining common QA/QC methods, and making best use of available data by making them available in shared depositories and databases. Particular emphasis should be placed on the constitution, maintenance and coordination of sample collections for future analysis.

Monitoring and modeling in the context of GMP >2015

The significant increase, since the GMP 2009 report, in scientific publications reporting monitoring data on POPs that are explicitly linked to the SC is an important indicator of the effectiveness of the Convention in enhancing knowledge on POPs

In the future, the number of substances considered by monitoring programmes will continue to increase, and the resources will always be limited. A very valuable and positive outcome of the efforts deployed is the vast corpus of information obtained since the 1970s through long term regular and stable monitoring programmes, briefly described in this chapter. This corpus provides invaluable insight and indispensable data to understand spatial and temporal characteristics of sources and pathways of POPs. All efforts should be made to make best use of this information to improve models and define future monitoring strategies.

It would be essential to develop a POPs modeling community of a practice in cooperation with other international initiatives such as the Task Force on Hemispheric Transport of Air Pollution (HTAP), under LRTAP, EBAS/NILU, the Global Atmospheric Watch GAW under WMO and the Global Earth Observation Systems GEOS.

Table 5.2.4a Summary and highlights of the monitoring information reported on POPs in non-core media since 2009 by AMAP, NCP, HELCOM, OSPAR, MEDPOL, The Great Lakes and on Antarctica. The shading (Green – low level of concern; Yellow – some relevant issues; Red – deserves special attention; Grey – insufficient data) is based on expert review and summary of the programme reports and not by the programmes themselves.

Chemical	AMAP (Arctic) average and range of annual % change in biota time series starting <2000	NCP (Arctic)	HELCOM (Baltic Sea region)	OSPAR (North-East Atlantic Sea region)	MEDPOL (Mediterranean Sea region)	Great Lakes (North America)	Antarctica
aldrin		Strong decrease since 1980 < 50ng/g lw in biota	Low levels in all matrices		Strong decrease since 1970s concentrations in <i>Mytilus galloprovincialis</i> in the low ng/g ww. range	Levels in whole trout average annual decline 2- 18% (measured as dieldrin) ¹ . Levels in 2009 <30ng/g ww	
chlordane	-4.5 (-19.9 to 0.8) N=28	Declines of 1.2%/year in murre eggs to 7.4%/year in blubber of ringed seals in Hudson Bay, while polar bears showed no decline.				Declined in whole trout since 1988, no change in recent years , levels <18ng/g ww	
sDDT	-4.0 (-10.7 to 5.6) N=54	Annual declines range from 2.5%/year in thick-billed murre eggs (Lancaster Sound) to 11%/year in polar bear fat (western Hudson Bay) Still of concern in marine mammals	DDE level has decreased by 4-11% annually from late 1970s to the early 1990s in most matrices, slower or no trend since then	Substantial decreases until late 1990s, not much later and still some local issues	Decreasing trends (factor of 5 in 15 years) from 1970s to late 1990s not later, and still some problem areas and new sources. Levels in mussels in the 10s of ng/g ww	Concentration in whole trout average annual decline 4-7 % since 1972. Levels of DDE not declining in birds since 2000.	2008-2011 Increasing burden in adult males of <i>Megaptera Novanglie</i> . ΣDDT measured in fat of Adelaide penguins in 2006 was significantly higher than 1964

1 Dielldrin is used as a surrogate as Aldrin and Endrin are converted to dielldrin once released into the environment

Chemical	AMAP (Arctic) average and range of annual % change in biota time series starting <2000	NCP (Arctic)	HELCOM (Baltic Sea region)	OSPAR (North-East Atlantic Sea region)	MEDPOL (Mediterranean Sea region)	Great Lakes (North America)	Antarctica
dieldrin	-3.1 (-9.6 to 0.9) N=22	Decline since the 1970s currently higher levels in marine mammals from the eastern Arctic	Low levels in all matrices		Strong decrease since 1970s concentrations in <i>Mytilus galloprovincialis</i> in the low ng/g ww. range	Detected in water throughout the lakes. Levels in whole trout average annual decline 2-18%. Levels in 2009 <30ng/g ww.	
endosulfan		Increases from the late 1990 in several lakes 0.1 ng/g ww in trout also detected in cod, salmon lichens, caribou and wolf	Endosulfan sulphate found at low levels in almost all fish samples			Atmospheric deposition decreasing with a slow halving rate of 11-14 years.	
endrin		At or below 1 ng / g ww levels in ptarmigan and hares, caribou, lamb and muskox.	Low levels in all matrices		Strong decrease since 1970s concentrations in <i>Mytilus galloprovincialis</i> in the low ng/g ww. range	Levels in whole trout average annual decline 2-18% (measured as dieldrin). Levels in 2009 <30ng/g ww.	
Heptachlor	-9.7 (-39.3 to 1.5) N=9	Primary metabolites of heptachlor (heptachlor epoxide), were present in fish, seaducks and marine mammals				No recent decline in concentrations in off shore water.	
HCB	-2.5 (-14.7 to 5.2) N=57	No significant east-west gradient about 5pg/L in ocean water, 0.8 ng/g ww in cod, no decline in fish 1993-2011. Found in lichens, caribou and wolf	Significant decreasing trends in almost all matrices until 1995 but not later		No significant decrease since 2000 and some hotspots	No significant changes in concentrations in water and fish since 2000.	2008-2011 Increasing burden in adult males of <i>Megaptera Novanglie</i>
α HCH	-8.7 (-20.6 to 1.2) N=54	Declined in beluga, seals and polar bear (12% year)	Strong decreasing trend since the 1980s in all matrices			Decreasing with halving time of 3-4 years (by 2009) in all media.	Significant decline in plankton
β HCH	-0.3 (-23.2 to 15.8) N=46	Increasing in polar bear and in seals 16% year at Ulukhaktok					
γ HCH	-7.2 (-18.5 to 3.0) N=51	In ocean water 1999 (310 pg / L) and 2008 (129-200 pg /L). (1999-2012) 4-fold decline in burbot in Mackenzie river. Found in lichens caribou and wolf	Strong decreasing trend since the 1980s in all matrices	General reduction achieved across the region. Concentrations in some areas are still at levels with a risk of effects	Found in significant amounts in some areas	Decreasing with halving time of 3-4 years (by 2009) in all media.	Significant decline in plankton

Chemical	AMAP (Arctic) average and range of annual % change in biota time series starting <2000	NCP (Arctic)	HELCOM (Baltic Sea region)	OSPAR (North-East Atlantic Sea region)	MEDPOL (Mediterranean Sea region)	Great Lakes (North America)	Antarctica
mirex	-6.7 (-28.0 to 5.1) N=15	In ptarmigan from the Canadian Arctic, levels ranged from 1–5 ng g ⁻¹ ww (1998) <1 ng/g ww in beluga from Hudson bay 2008				Detected only in L Ontario whole trout, average annual decline 4-12%. Levels in 2009 < 60 ng/g ww.	
toxaphene	Toxa 26 -3.9 (-20.9 to 11.3) Toxa 50 -5.9 (-14.5 to 1.8) N=18	Among the most abundant POPs in Canadian arctic biota. In 2009 Sea-run char in 15.1± 8.3 ng /g ww. In walrus from Hall Beach and Igloodik (NU) 370 ng /g lw . No significant decreases in biota since 2009.				Decreases in whole trout since the mid-1980s until 2007, levels in 2010 in 50 - 500 n/g ww range.	
PBDEs	PBDE 47 4.0 (-6.3 to 22.5) N=24 PBDE 99 3.8 (-7.2 to 25.1) N=19	Detected in all biota Concentrations Increased in seals, seabirds, beluga, and polar bear samples from the 1990s until the early 2000s and are now declining. Local sources can be relevant. ΣPBDE 5.4 ng/g lw in bivalves, 9.8 ng/g in arctic cod and 72.8 ng/g in sculpin, 10-50 ng/g lw in beluga blubber	In marine top predators PBDE levels are a cause of concern	2000-2005 found in all compartments of the marine ecosystem	Levels of concern in some matrices and locations	Sediment accumulation has recently peaked or continues to increase. Concentrations in whole Trout and Walleye rose from 1970s to the early 2000s and the average annual decline is 3-6% L.Ontario, 17-19% L.Michigan. Not decreasing in birds	Present near stations
HBCD	4.7 (-4.1 to 13.3) N=5	Increasing concentrations in all media. In blubber of ringed seals concentrations were about 10-fold lower than the ΣPBDEs. Polar bears in Svalbard (44.4 ng/g lw) and East Greenland (44.5 ng/g lw) greater than in Bering-Chukchi (0.40 ng/g lw).	Ongoing Increases of 3% a year since 1970s in common guillemot eggs	2000-2005 found in all compartments of the marine ecosystem		Concentrations in sediment cores indicate that inputs are doubling every 8 to 24 years. Surface concentrations decrease with increasing latitude. ¹	

1 Source: Yang et al. ES&T 2012

Chemical	AMAP (Arctic) average and range of annual % change in biota time series starting <2000	NCP (Arctic)	HELCOM (Baltic Sea region)	OSPAR (North-East Atlantic Sea region)	MEDPOL (Mediterranean Sea region)	Great Lakes (North America)	Antarctica
PFOS	3.0 (-3.4 to 8.5) N=13	Concentrations reached maxima in ringed seal livers in 1999-2003 in Hudson Bay, Lancaster Sound and East Baffin. In caribou and moose, PFAS were the major POPs with concentrations in liver ranking ahead of PFOS, PCBs and PBDEs	PFOS are the predominant PFOA in biota, increasing trends of 7-10% per year since the 1970s in common guillemot (<i>uria aalge</i>)			Sediment accumulation has recently peaked or continues to increase.	A few research studies have shown the occurrence of PFOS, PFOA and PFCs in Antarctic biota
PeCB	-4.2 (-27.9 to 1.6) N=22	Among the dominant OCPs detected in East Hudson Bay sediment and near shore biota. For fish, seaducks and marine mammals, OCP levels were in the 10 ng g ⁻¹ lw to 1,000 ng g ⁻¹ lw range, with a rank order of ΣDDT > ΣCHL > ΣCBz > ΣHCH, and are comparable to other studies of POPs in arctic fish, seabirds and marine mammals					
ΣPCBs	ΣPCB ₁₀ -3.7 (-17.9 to 20.7) N=54 PCB 153 -3.8 (-19.2 to 19.6) N=58	Overall trends (1993-2009) show a decline, the rates have slowed and some more highly chlorinated congeners have increased slightly in recent years. Declines were lower or non-existent in beluga, ringed seals and polar bears in the South Beaufort compared to Hudson Bay and East Baffin regions. Dietary shift might lead to higher concentrations.	Declining in fish and mussels at 5-10%/yr since the 1970s until the late 1990s, levels in some matrices and locations still a matter of concern	Significant decreases since the 1970s. Concentrations of at least one PCB congener in fish and shellfish pose a risk. PCB118 is the congener most often above EAC	Different congener profiles in different areas. No trends since 2000 still significant hotspots	Average annual decline in whole trout 3-7% 1970 - 2009. Levels (2009) still above the 100 ng/g ww target. Consumption advisories occur in all Lakes	2008-2011 Increasing burden in adult males of <i>Megaptera Novanglie</i>
PCDD/Fs		Concentrations in Lake DV09 core peaked in the 1970s with a maximum TEQ value of 0.07 ng/g dw detected in 1978. Concentrations in the blubber of ringed seals from Ulukhaktok. 8.6–14.6 pg/g did not change between 1981 and 2000.	Although top sediments show lower concentrations compared to deep sediments, trends have not declined in fish over the period 1990-2005.		Significant decreases 1970s to 2000 Significant levels in some matrices and in some areas near population and industry	Declined in waterbirds 1970s – 2009 in all Lakes. Consumption advisories in all lakes.	Levels of concern in 2002 in Adelaide Penguins and South polar skua eggs.

5.3 Long-range transport

5.3.1 Background

The potential to undergo long-range transport (LRT) in the environment is one of the defining characteristics of a POP, and it is one of the screening criteria defined in Annex D of the Stockholm Convention. For substances that are nominated for addition to the Convention, the purpose of the risk profiles compiled under Annex E is to evaluate whether a substance is likely, as a result of LRT, to lead to significant adverse human health and/or environmental effects, and therefore warrants global action.

Compelling evidence of LRT is available for many POPs in the form of observations of their presence in regions of the world that are remote from sources, and results of monitoring programmes that report such information are summarized in other chapters of this report. Chemical fate and transport models can be used in combination with monitoring data to assess and understand LRT of identified POPs and in the assessment of POP candidate substances. This chapter focuses on the contributions of contaminant fate and transport modeling toward the implementation and effectiveness evaluation of the Convention, with a particular focus on the WEOG region.

5.3.2 Motivations and challenges for assessing LRT using models

There are two key motivations for assessing and studying the LRT of chemical substances using fate and transport models. First, for identified POPs, models provide a conceptual basis to understand the levels and trends that are observed at monitoring stations. Models link the concentrations of POPs in the environment to emissions that have occurred at specific locations and times. Thus, models provide a basis to assess the effectiveness of actions that have been taken to reduce the production, use and emissions of POPs. Models can also be applied to isolate the effect of emission reductions from other factors that may affect levels and trends of POPs observed at monitoring stations, such as variability in local conditions, and long-term changes in climate. The second key motivation for developing, evaluating, and refining chemical fate and transport models is to improve the scientific basis for screening POP candidates for LRT potential. Models provide scientific support for screening chemicals for POP-like characteristics, and in compiling risk profiles.

Models can be evaluated using monitoring and emission data for current POPs. When there are disagreements between the model and observations, alternative model scenarios can be used to support iterative improvements to the models, chemical property data, and emission estimates. The value of the so-called “integrated approach” of combining emissions inventories, models

and measurement data to compose a complete and quantitative picture of environmental contamination by POPs is increasingly recognized. Integrating information about emissions and environmental concentrations using models allows inconsistencies in available information to be identified, and helps set priorities for further research that will support decision-making (UNECE, 2010). When used as part of an integrated approach, models can be viewed as a framework for assembling a repository of knowledge and conceptual understanding about POPs in the environment (**Figure 5.3a**, MacLeod et al. 2010).

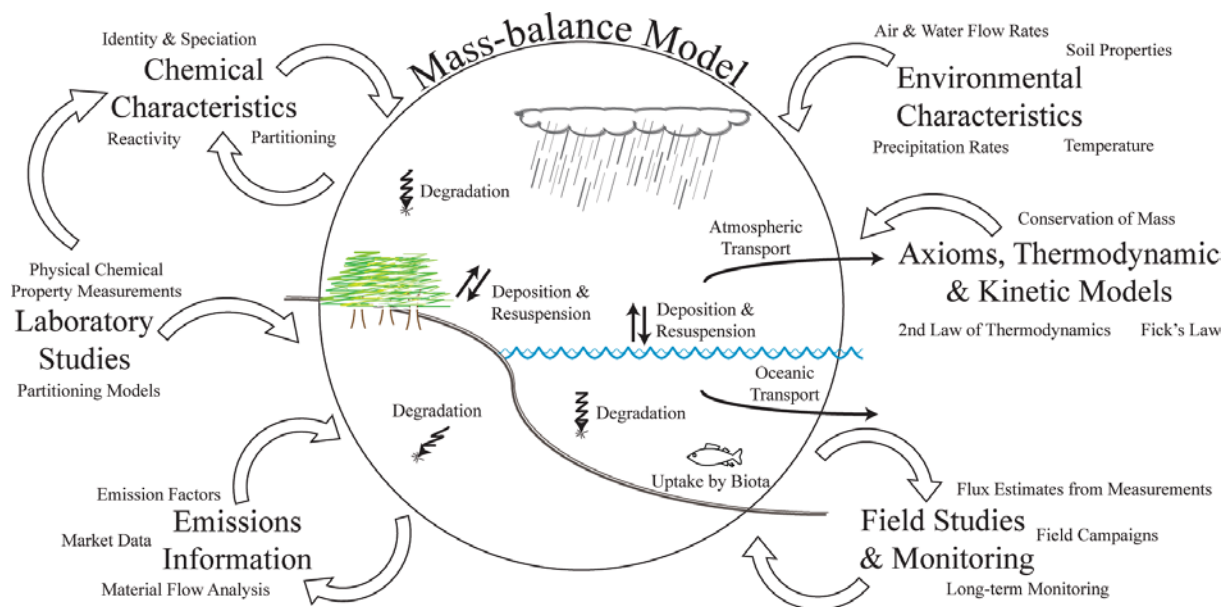


Figure 5.3a Mass-balance chemical fate and transport models play a central role in integrating information and understanding about the behavior of POPs in the environment. The curved arrows illustrate the flow of information about chemical and environmental properties that determine the behavior of POPs in the environment, laboratory and field studies, and an integrative mass balance model. The framework provided by the model allows disparate aspects of the system to be assembled into an integrated picture, and compared for internal consistency. (Figure reproduced with permission from MacLeod et al. 2010).

Models are particularly useful when they can be interrogated for information that can be used to form hypotheses or to inform decision making (MacLeod et al. 2010). Models designed for screening and assessing potential risks as a result of LRT are specifically designed to provide decision-relevant information, and they are based on the same formulations and principles that are used in models that are evaluated against field data. Thus, there are synergies between modeling existing POPs and applying models to screen for new POPs and compile risk profiles.

Several international working groups have been formed in recent years to explore and evaluate fate and transport modeling capabilities, to identify knowledge and data gaps, and to make recommendations for research priorities. Notable efforts include the 2010 Assessment Report of the Task Force on Hemispheric Transport of Air Pollutants (UNECE, 2010, Gusev et al. 2012), which was formed under the Convention on Long-range Transboundary Air Pollution in 2010, the Saltsjöbaden V workshop (Grennfelt et al. 2013), the workshop on Next Generation Air Quality Monitoring (Hung et al. 2013), and the final report of the ArcRisk EU FP7 Collaborative Project (ArcRisk, 2014). Reports from these working groups have generally agreed that important research priorities for applying models to understand the levels and trends of POPs that are observed at long-term monitoring stations include:

1. Improving emission inventories;
2. Improving understanding of mechanisms and rates of degradation of POPs in air, water, soil and sediments;
3. Enhancing modeling capabilities, especially for describing air-surface exchange;
4. Understanding and quantifying climate-related effects on POPs in air that might obscure or modulate trends

In the following sections we summarize highlights of recent POPs research that aims to use models as part of an integrated approach to understand emissions, fate and transport pathways, and levels in the environment, and in scenario analyses aimed at identifying new POPs and evaluating alternative policy decisions. The examples given below are not intended to be an exhaustive review of research in these areas, but rather to illustrate the benefits and insights that can be gained from modeling POPs.

5.3.3 Understanding LRT of POPs and potential POPs by integrating emission estimates, modeling and measurements

Lack of information about emissions of POPs and potential POPs is often the limiting factor that determines uncertainties in model-based assessments (Arnot et al. 2012). Parties to the Stockholm Convention and the UNECE LRTAP convention are required to compile emission inventories for identified POPs. However, the usefulness of official emission data for scientific purposes, such as modeling source–receptor relationships on a European or global scale, is limited because there is insufficient information on spatial and temporal variability, and official inventories do not cover POP candidate substances (Breivik et al. 2006). Research aimed at estimating emissions of POPs and candidate POPs that can provide a basis for contaminant fate and transport modeling has proceeded on two fronts: “Bottom-up” studies of production, inventories and emission factors for POPs, and, more recently, “top-down” studies that measure

levels of POPs near potential source areas and use inverse modeling to calculate area or per-capita normalized emissions.

“Bottom-up” emission estimates that can be used in global and regional scale integrated assessments of POPs have been published for a few identified POPs, notably PCBs (Breivik et al. 2007), the mixture of technical HCHs (Li 1999, Wöhrnschimmel et al. 2012) and DDT (Semeena & Lammel 2003, Schenker et al. 2008). Emission inventories have also been compiled for perfluorinated alkyl substances (including PFOS) based on production and use information for perfluorooctane sulfonyl fluoride and fluorotelomer alcohols, and related substances with different chain lengths (Prevedouros et al. 2005, Paul et al. 2009, Cousins et al. 2011, Wang et al. 2014a, Wang et al. 2014b).

Recently, “top-down” methods to estimate emissions based on a combination of measurements and modeling applied at local scales in suspected source areas have been increasingly applied. These methods rely on measuring the levels and fluctuations of chemicals in the atmosphere during stable weather conditions and applying a local- or regional-scale model to calculate emission rates that can account for the observed levels (MacLeod et al. 2007). The top-down emission estimation method has been extensively applied in the urban area of Zurich, Switzerland to provide per-capita emission estimates for PCBs (Gasic et al. 2009, Bogdal et al. 2014), PCDD/Fs (Bogdal et al. 2014), PBDEs (Moeckel et al. 2010), poly- and perfluorinated alkyl substances (Wang et al. 2012) and cyclic volatile methyl siloxanes (Buser et al. 2013). The modeling approach has also been combined with measurement data from the city of Chicago, USA to estimate emissions of PCBs (Gasic et al. 2010) and decamethylcyclopentasiloxane (Buser et al. 2014). And, a similar approach that combines measurements with modeling and information about chemical inventories has been applied to estimate emissions of PCBs and PBDEs to the atmosphere from the city of Toronto, Canada (Diamond et al. 2010; Zhang et al. 2011).

For POPs and POP candidates where global-scale emission estimates are available, Eulerian contaminant fate and transport models can be applied to calculate concentrations at long-term monitoring sites and thus evaluate our understanding of sources, fate and transport. A recent example is the global mass budgets of α - and β -HCH reported by Wöhrnschimmel et al. (2012). They used an emission inventory that specifies annual primary emissions to air and soil from usage of technical HCH between 1945 and 2012 on a $15^\circ \times 15^\circ$ global-scale model grid. Secondary emissions to air from soil, water and vegetation are calculated by the model they employed, BETR Research, as a function of relative concentrations in air and the surface media, chemical properties and temperature. Modeling with this emission inventory indicates that

primary emissions of both HCH isomers are lower than secondary sources to the atmosphere after the year 2000, and have been completely phased out since 2012 (**Figure 5.3b**).

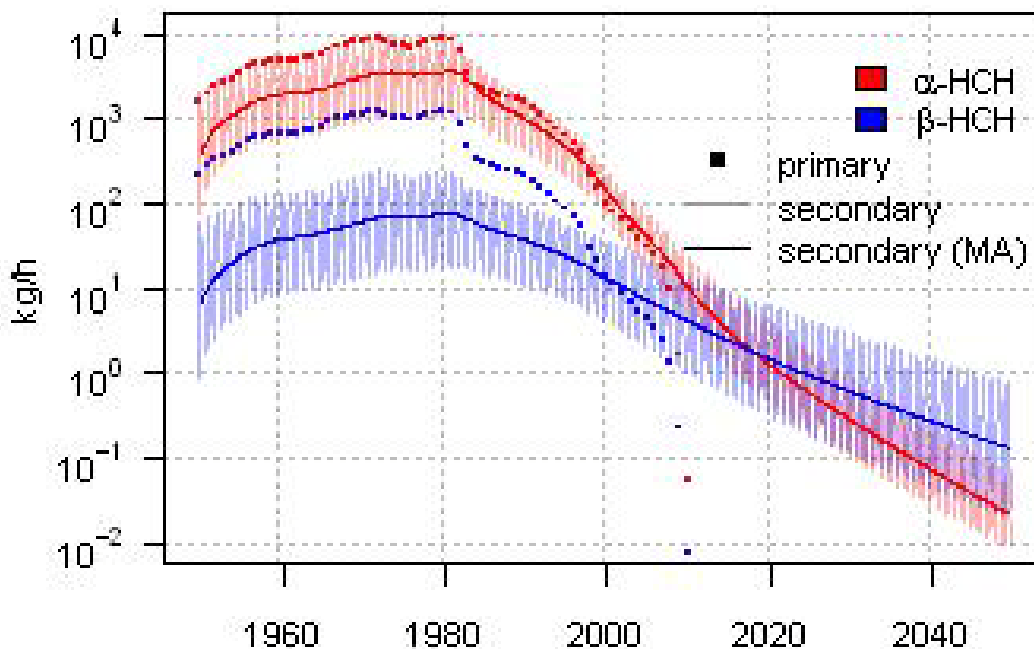


Figure 5.3b Primary emissions to the atmosphere from the use of α -HCH and β -HCH compared to secondary emissions from soil, vegetation, fresh water and oceans calculated in the modeling scenario of Wöhrnschimmel et al. (2012). MA = 12 month moving geometric average.

Driven by the emission scenario in **Figure 5.3b**, the BETR Research model reproduces over 70% of concentrations of α - and β -HCH measured in air at long-term monitoring sites within a factor of 3 and 8, respectively (**Figure 5.3c**). In ocean water, more than 70% of the modeled α - and β -HCH concentrations agree with measured values collected from data reported in the scientific literature within a factor of 5 and 20, respectively (data not shown). Comparing the model to measurements provides guidance about research needs to improve our understanding of the current mass balance of the HCHs, and to improve the model's description of fate and transport processes for POPs in general (Wöhrnschimmel et al. 2012).

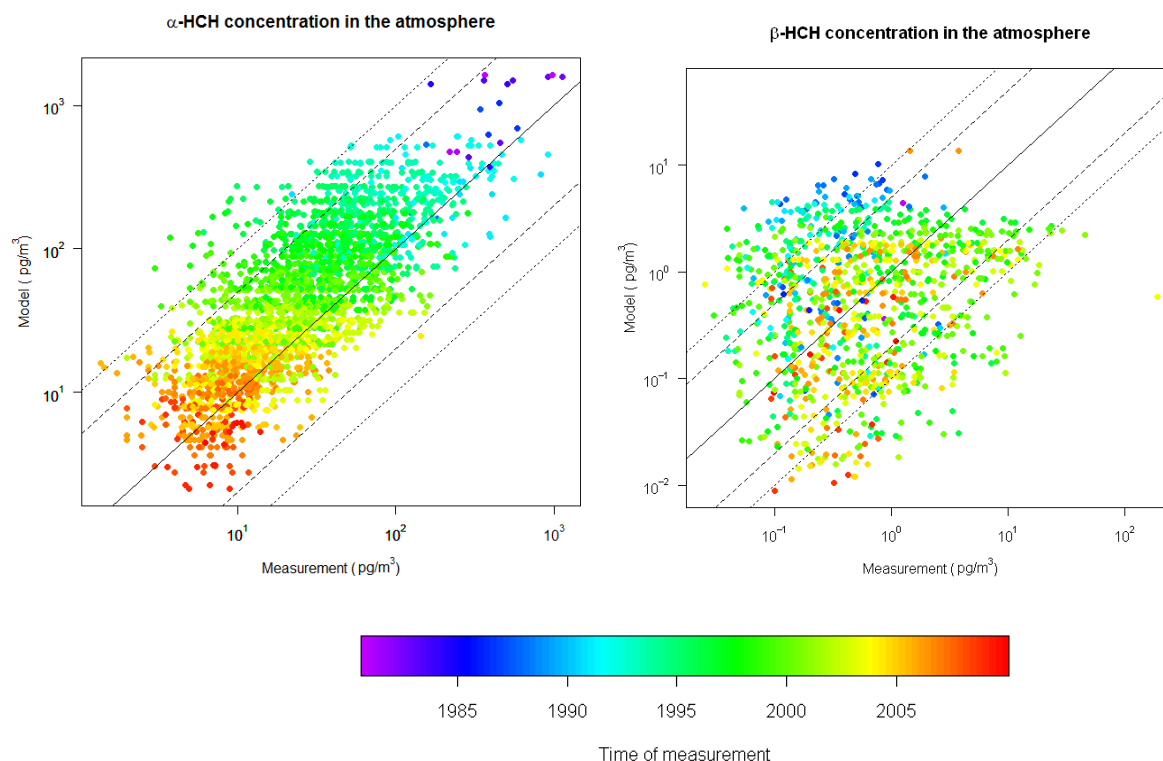


Figure 5.3c Comparison of modeled and measured concentrations of α -HCH and β -HCH in the atmosphere. The solid line shows perfect agreement; dotted lines indicate ratios of 5 and 10. Measured concentrations are from long term monitoring stations that are described in detail in Chapter 5.2.1.

In addition to HCHs, global-scale modeling studies that integrate emissions estimates with monitoring data have been carried out for other POPs where emission inventories and monitoring data are available. These include PCBs (Lamon et al. 2009; Malanichev et al. 2004; Gusev et al. 2012), DDT (Stemmler and Lammel, 2009; Schenker et al. 2008) and PFOS (Armitage et al. 2009). A notable example of the integrated approach applied at the global scale is the emission estimates, modeling and analysis of long-range transport and persistence in the context of the Stockholm Convention that contributed to the discussion of the risk profile for endosulfan (Becker et al. 2011). Global-scale modeling studies have also been carried out for a few persistent organic substances that are not identified as POPs, including perfluoroalkyl acids (Stemmler and Lammel, 2010; Armitage et al. 2006) and decamethylcyclopentasiloxane (McLachlan et al. 2010; MacLeod et al. 2011; Genualdi et al. 2011).

Another useful and complementary modeling approach is the application of Lagrangian atmospheric trajectory models in combination with measurements from long-term monitoring

stations. Combining trajectory models with emission estimates provides a basis to evaluate the emission estimates, and can be used to identify and characterize poorly-constrained sources of POPs. Notable examples of this approach are an analysis of source regions impacting levels of γ -HCH and PCB-28 at the monitoring station at Birkenes, Norway (Eckhardt et al. 2009) and an analysis of re-mobilization of PCBs from forest soils during forest fires (Eckhardt et al. 2007).

5.3.4 Hypothesis generation, screening-level assessment and scenario analysis using POPs models

As repositories of knowledge and understanding about POPs, chemical fate and transport models can be applied to explore processes that control levels of POPs in the environment, hypothetical scenarios for new chemicals, and how alternative scenarios for future changes in emissions and climate will affect POPs. Contaminant fate and transport models are now well-established as useful tools for conducting screening-level hazard classification of chemicals according to metrics of overall persistence and long-range transport potential. A notable example is the Organization for Economic Cooperation and Development's overall persistence and long-range transport potential screening tool (OECD, 2014), which was applied to provide input for the risk profiles prepared for Stockholm Convention POP candidate substances in 2006 and 2007 (ETHZ, 2014).

In recent years, models have increasingly been applied to survey the “chemical space” of chemical properties that spans the plausible range of combinations of volatility, hydrophobicity, and degradability of non-ionizing organic chemicals. Explorative modeling exercises that survey the chemical space provide insights into the behavior of existing POPs, and help to identify real chemicals with combinations of properties that may lead to POP-like behavior in the global environment. Based on modeling simulations of the chemical space, Gouin and Wania (2007) proposed that POPs and potential POPs could be grouped by their mode of global transport as fliers that travel in the atmosphere, single hoppers that are emitted to air and deposit to the surface only once, multi-hoppers that undergo cycles of exchange between the atmosphere and the Earth's surface, and swimmers that are transported in the oceans (**Figure 5.3d**). They demonstrated that the mode of transport and persistence of chemicals conspire to determine how quickly the effects of emission reductions could be observed at monitoring stations in remote regions such as the Arctic. A subsequent modeling study linked a foodweb bioaccumulation model to the global chemical fate model and identified time-scales for persistent chemicals with different combinations of properties to accumulate in humans living in the Arctic (Czub et al. 2008).

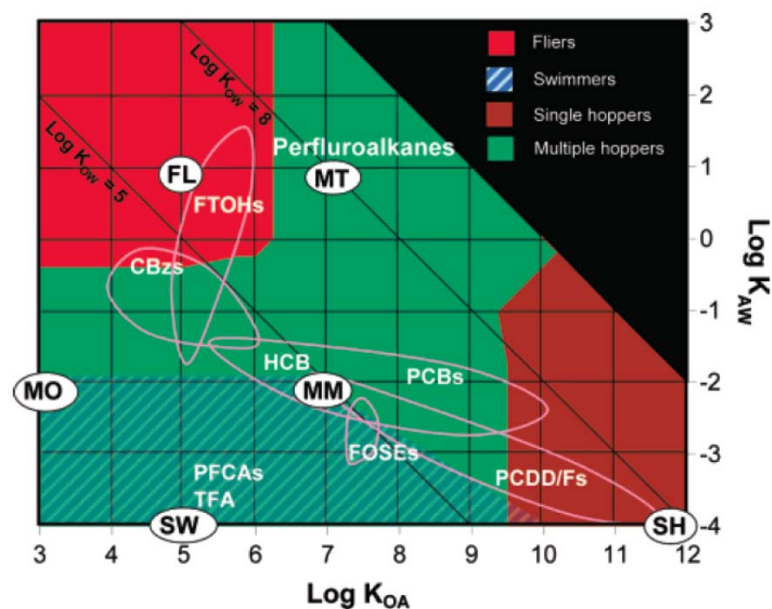


Figure 5.3d A chemical space plot showing the dominant mode of transport of persistent organic chemicals with a wide range of volatility and hydrophobicity, and properties of selected POPs or potential candidate POPs. ($\text{Log } K_{OA}$: $\text{Log octanol:air partition coefficient}$, $\text{Log } K_{AW}$: $\text{Log air:water partition coefficient}$, $\text{Log } K_{OW}$: $\text{Log octanol:water partition coefficient}$, FTOHs: fluorotelomer alcohols, CBzs: chlorobenzenes, FOSEs: perfluorosulfonamides, PFCAs and TFA: perfluorocarboxylic acids and trifluoroacetic acid). (Figure reproduced with permission from Gouin & Wania, 2007).

Insights gained from measuring and modeling existing POPs and modeling the relationship between chemical properties and environmental behavior have made it possible to conduct high-throughput screening assessments for chemicals that are used in commerce or that are included in databases of existing substances (Muir and Howard, 2006). Screening exercises aimed at identifying potential POPs typically start with only chemical structure as input, and use quantitative structure-property relationship (QSPR) models to estimate chemical properties, which are in turn used to estimate environmental fate profiles. Howard and Muir (2010, 2011, 2013) conducted a series of screening exercises using QSPR models and expert judgment to identify chemicals in commerce that might be persistent and bioaccumulative. Several of the chemicals they identified in their screening were subsequently confirmed to be present in the environment (Howard and Muir, 2010). In a screening study of more than 100 000 industrial chemicals, Brown and Wania (2008) identified 120 high production volume chemicals that are structurally similar to known Arctic contaminants and have properties that suggest they are potential POPs. And, starting from a list of 93 144 organic chemicals, Scheringer et al. (2012) identified between 190 and 1200 chemicals that are potential POPs. One limitation of these chemical screening exercises is that the QSPR models must be extrapolated to substances that

likely fall outside of the domain of applicability of the models, which is defined by the structures of chemicals in the model's training set. Recently, the use of more fundamental methods to estimate environmentally-relevant properties of chemicals from quantum mechanics and statistical thermodynamics has been demonstrated (Wittekindt and Goss, 2009). These approaches have the potential to lessen the "streetlight effect" observational bias (Wikipedia, 2014) that is introduced by searching for unrecognized POPs among chemicals in commerce while relying on professional judgment and QSPR models trained with data for relatively well-studied chemicals.

Models, especially those that have been evaluated against current information about emissions and levels in the environment, can be applied to forecast changes in concentrations of POPs under alternative future scenarios. In particular, climate change is expected to alter patterns of human economic activity and the associated emissions of chemicals, and also to affect the transport and fate of persistent organic pollutants (POPs). Wöhrnschimmel et al. (2013) used a global-scale chemical fate model to analyze and quantify the impact of climate change on emissions and fate of POPs, and their transport to the Arctic. They analyzed the impact of the IPCC's SRES-A2 climate scenario on two well-characterized POPs, PCB153 and α -HCH, and modeled the combined impact of altered emission patterns and climatic conditions on environmental concentrations of potential future use substances represented by the chemical space. Their alternative emission scenarios postulated two types of changes in emission patterns in response to climate change: enhanced use and release of industrial chemicals in an ice-free Arctic, and intensified application of agrochemicals due to higher demands on crop production and poleward expansion of potential arable land. They found that both increases and decreases in concentrations of POP-like chemicals in the Arctic were possible under the climate change scenario compared to the base-case climate. Increases in POP concentrations in the Arctic were up to a factor of 2 in air and 4 in water under the climate change scenario, and were mostly attributable to changes in transport and fate of chemicals rather than changes in emission rates and patterns.

Other modeling studies at global (Gouin et al. 2012) and regional (Kong et al. 2014, Lamon et al. 2012) scales have also reported approximately a factor of 2 change in concentrations of POPs under climate change scenarios. A factor of 2 is small compared to uncertainties in the forecasts for POP concentrations in the modeling scenarios, especially the uncertainties due to emissions and degradation rates of POPs. Many of the recent studies examining climate scenarios for POPs were conducted as part of the ArcRisk European Union research project. The final report of ArcRisk concluded that the largest likely impacts of climate change on environmental and human exposure to POPs in the Arctic would arise from increased exploitation of natural

resources, and possibly from alterations in foodweb structures, but not from direct effects of climate change on global transport patterns of POPs (ArcRisk, 2014).

5.3.5 Summary and outlook

A summary of current modeling approaches that support effectiveness evaluation of the Stockholm Convention by providing information about emissions, long-range transport and fate, and levels and trends of POPs in the environment is given in **Table 5.3a**, and a summary of modeling approaches for identification and risk profiling of new POPs is given in **Table 5.3b**.

Table 5.3a Summary of modeling approaches for integrated assessment of emission estimates, environmental fate and long-range transport and levels and trends of POPs in the environment.

Modeling approach	Resource requirements	Added value and limitations
“Bottom-up” inventories and emission factors	Information about production of POPs and emissions models	Provide emissions information that is independent of field observations Labor intensive and information is often lacking, incomplete or highly uncertain
“Top-down” urban or local-scale measurement campaigns and modeling	Campaign-based field measurements and process-based models parameterized for local conditions	Provide information about emissions from poorly characterized diffuse sources No information about specific source locations or categories
Trajectory modeling combined with measurements to identify episodic sources or source areas	Can exploit existing air monitoring data for POPs at remote locations	Provide qualitative or semi-quantitative information about emission source strength and location
Global or hemispheric integration of emission estimates with measurement data using fate and transport modeling	Exploits existing air monitoring data from both active and passive samplers. Models with varying levels of fidelity to the real environment can be applied to address different types of questions or confront high uncertainties	Provide process-level explanations for the presence of POPs at remote locations and identify research priorities to improve understanding Data and labor intensive, and may be subject to high and/or unquantified uncertainties

Table 5.3b *Summary of modeling approaches for identification and risk profiling of new POPs.*

Modeling approach	Resource requirement	Added value and limitations
High-throughput screening of chemicals in commerce	QSAR models and generic fate and transport models or heuristic prioritization rules	Provide early-stage information about potentially problematic chemical substances and help to set research priorities Uncertainties are high and results are potentially biased by prior experience
Screening-level modeling of overall persistence and potential for long-range transport	Physico-chemical properties and degradability estimates for POPs and publically-available models	Provide a comparative assessment of candidate POPs against known POPs

Many of the models and case studies that have contributed to effectiveness evaluation and implementation of the Stockholm Convention have also provided scientific input to the Convention on Long Range Transboundary Air Pollution (CLRTAP). Through the Task Force on Measurement and Modeling and the Task Force on Hemispheric Transport of Air Pollution, CLRTAP has placed a strong focus on emissions estimation and modeling of POPs that compliments the Stockholm Convention's focus on monitoring. However, in recent years work on POPs under the CLRTAP has not been prioritized relative to work on other air pollutants covered by that convention. There are certainly unrealized synergies that can be achieved through cooperation and collaboration between the CLRTAP and the Stockholm Convention on issues related to POPs and chemical pollution in general, some of which are outlined in a recent report that made recommendations for future policies to address international air pollution (Grennfelt et al. 2013).

The development, application and continued refinement of contaminant fate and transport models is crucial to the implementation and effectiveness evaluation of the Stockholm Convention. Models provide key scientific input for identifying potential new POPs, and in the risk profiling process. For existing POPs, models provide a framework to describe and explain the levels and trends that are measured at various monitoring sites over time. It is not always the case that the response to emission reduction efforts for POPs will be monotonic decreasing trends in concentrations at all monitoring sites at all times. Interpreting and integrating information about properties of POPs, emission estimates and monitoring data within the framework of contaminant fate models provides insights about processes and unrecognized sources of POPs, and thus provides policy makers with information that supports policies to ensure that the goals of the Stockholm Convention are realized.

6 CONCLUSIONS AND RECOMMENDATIONS

6.1 Findings and Conclusions

This section provides a brief synopsis of the major findings of the WEOG report and key messages for the Conference of the Parties.

6.1.1 Summary of the baseline concentrations

The concept of ‘baseline’ in this report does not represent a number or value but rather has more to do with the description of the state of knowledge for a particular substance. The geographic coverage of this information, across the WEOG region, is also an important of establishing an ‘adequate’ baseline. Many of the original POPs listed under the Stockholm Convention were already regulated or banned by countries long before 2004. Consequently the ‘baseline’ period for the GMP, may represent concentrations that have already decreased substantially from peak levels or concentrations that are now levelling off. In some cases secondary sources have begun to dominate emissions (e.g. emissions from POP reservoirs such as oceans and soils; see Figure 5.3b). Therefore, for the ultimate purpose of attributing reductions in environmental levels of POPs to the ‘effectiveness’ of the Convention, it is more appropriate to consider baseline data and trends associated with the newer POPs. **Table 6.1a** summarizes the availability of ‘baseline’ information on POPs across the WEOG region.

Much of the WEOG region data for POPs in blood and/or human milk comes from national programmes such as NHANES and ESB (or the Australian Pilot Monitoring Programme). Such programmes are important for assessing country-scale time trends however the levels are often not directly comparable to other countries/regions due to different study designs and populations. Similarly, individual research studies that are not a part of any programme can indicate whether the levels of pollutants are of concern in a certain area but cannot directly be used to evaluate differences between regions or over time. It is therefore impossible to set a “general” baseline concentration for the WEOG region for POPs in human blood and/or milk.

Table 6.1a Summary of available baseline information on POPs in different media in the WEOG region.

Chemical	Air	Human Tissues	Other Media
aldrin			
chlordane			
chlordecone			
DDT			
dieldrin			
endosulfan			
endrin			
HBB			
HBCD			
HCB			
α HCH			
β HCH			
γ HCH			
Heptachlor			
mirex			
PBDEs			
Σ PCBs			
PCDD/Fs			
PFOS			
PeCB			
toxaphene			

	Adequate information on baselines
	Limited information on baselines
	No information on baselines

Likewise for air, while air monitoring programmes provide the opportunity to derive time trends and region-specific spatial comparisons (e.g. the Arctic, the Great Lakes, the Alps and the UK), concentrations reported by different air monitoring programmes are not directly comparable because of the differences in sampling methods (active versus passive sampling methods), analytical procedures, sampling frequencies, target compounds and programme QA/QC protocols. So it is also not possible to provide baseline concentrations of POPs in air that would apply to the entire WEOG region.

New air monitoring networks have been established to provide better spatial coverage of POPs, notably the establishment of an Australian Pilot Monitoring Programme and stations in Australia and Antarctica.

Water monitoring data is available for PFOS and some of its precursors over the period 2003-2013, with most results from studies conducted between 2005 and 2010. As almost no measurements of PFOS in water existed prior to 2003, these studies have effectively established a baseline for the specific study locations. Also the sampling and analytical methodology used for PFOS in water is quite similar in all studies. However the water concentrations of PFOS vary widely across the WEOG region (e.g. by more than 200-fold in the case of river water) and thus no general baseline exists.

There are a large number of studies for PFOS in rivers, lakes, estuaries and ocean waters in the WEOG region, especially over the period 2005-2010. The information available provides knowledge of spatial trends for PFOS across Western Europe, the North Sea, the Baltic, and in the North Atlantic and Canadian Arctic archipelago. Information is much more limited for North America and Australia. No information was found for New Zealand. In addition to environmental measurements, river discharges have been estimated and modelled (for the River Rhine and the Aire/Calder River system in northeast England). Ice and snow melt inputs of PFOS are likely to be important during spring melt events and need to be considered in timing of monitoring programmes. For oceans, results are available from four separate cruises from Western Europe (north western France) to West Africa.

Current levels in non-core media for legacy POPs such as Dieldrin, Mirex, DDT, PCB, HCB, HCH are substantially below the levels in the 1970s, and now in the low ng/g range, and have not significantly decreased since 2000. Even when there are no new sources, the existing pool of pollutant can be of concern in some areas for decades. Levels of Endosulfan, PFOS, PBDE, and HBCD have increased over the past decades and are similar to the current levels of legacy pollutants. Although the levels in most biota are below the expected levels of effect (with the exception of 'hot spots'), the increasing load and increasing number of substances (including some newly listed POPs, POP candidates, and POP-like chemicals that have not yet been assessed) present reasons for concern and sustained attention.

6.1.2 Summary of evidence of temporal trends

In the first GMP report of the WEOG region, temporal trends were already available for many of the original POPs listed under the Convention. These trends established a baseline trend against which future trends could be compared. Many of the existing WEOG monitoring programmes and some of the new programmes have already included newly listed POPs in their target lists. In some cases, temporal information is already becoming available however, in most cases, the

time series is not yet sufficient for assessing trends. **Table 6.1b** summarizes the availability of trend information on POPs in the different media.

Table 6.1b Summary of available temporal trend information on POPs in different media in the WEOG region.

Chemical	Air	Human Tissues	Other Media
aldrin		ND	
chlordane		ND	
chlordecone			
DDT			
dieldrin			
endosulfan			
endrin		ND	
HBB			
HBCD			
HCB			
α HCH			
β HCH			
γ HCH			
Heptachlor			
mirex		ND	
PBDEs			
Σ PCBs			
PCDD/Fs			
PFOS			
PeCB			
toxaphene			

ND = "non detect". Low levels, often below detection limit.

	Adequate information on temporal trends
	Limited information on temporal trends
	No information on temporal trends

The trend studies covered in this report show that the levels of most persistent organic pollutants, such as PCBs, dioxins and DDE/DDT in human blood and milk, have been declining since the start of the trend studies, and are still decreasing. Some OCPs that have been banned for a long time, such as aldrin, endrin and mirex, are no longer present in human tissues in detectable levels. However, the levels of PFOS and PBDEs show a slightly different temporal pattern. In the few available long term studies of PFOS, the levels increased in the 1980s and 1990s, reflecting the industrial production, and have then declined in most WEOG areas in human matrices. The levels of most PBDEs are currently decreasing, whereas the levels of some PBDEs (e.g. BDE-153) in human matrices are not decreasing in some parts of the WEOG region.

National and international long-term monitoring programmes continued to provide time trends of POPs in air during this review period. Temporal trends for older POPs that were previously banned continue to decline or have levelled off in air. There are some exceptions, for instance, HCB and PCBs in Arctic air are showing increasing and varying trends at specific locations that may be related to recent warming. This warming has led to enhanced revolatilization from oceans and other reservoirs of POPs (e.g. due to reduced sea-ice and melting glaciers). Some of the recently listed POPs (e.g. PBDEs, PFOS and precursors) show more variable temporal tendencies across the WEOG region. For instance, while PBDEs are declining in air in many parts of Europe, such declines are not observed in North American background sites in the Great Lakes and the Arctic, possibly reflecting the greater historical consumption of PBDEs in North America. PFOS precursors MeFOSE and EtFOSE showed non-changing and declining trends in Arctic air respectively, reflecting the phaseout of the production of PFOS, PFOA, and PFOS-related products. Temporal data are lacking for many of the newer POPs (e.g. PFOS, HBB and HBCD). Toxaphene and chlordecone were not included in any recent air monitoring programme (toxaphene was monitored in air during the 1990s) so there are no levels or time trends to report. Both compound classes present analytical challenges and attempts to monitor these compounds have resulted in poor detection success, as their concentrations in air are quite low.

Temporal trend information is very limited for PFOS and its precursors in river, lake or ocean water. For rivers it consists of sampling of the same locations two or three times at the same location. Rivers in Europe, especially the Elbe and the Rhine, offer the best opportunity for assessing temporal trends assuming sampling continues at the same locations. For oceans results are available from four separate cruises from Western Europe (north western France) to West Africa. Differences in sampling times, locations, and in detection limits preclude any robust assessment of trends.

The AMAP extensive study on trends in biota notes that downward trends constitute the majority of statistically significant trends levels of Stockholm Convention POPs in Arctic biota. **Table 6.1c** is a summary of the results and show trends for biota as in % change per year. The concentration of most POPs decreased between the 1970s and 2000. However, some substances, such as endosulfan, β -HCH, PBDE, HBCD and PFOS, present frequent increasing trends.

Table 6.1c Summary table taken from AMAP trend study (AMAP 2014) showing temporal trends in Arctic biota for different POPs. Trends are expressed as average % change per year for over 1100 statistical analyses, with datasets run for both time-series that start prior to the year 2000 (655 datasets) and for time-series that either begin after 2000, or with years prior to 2000 excluded (474 time-series). Negative values indicate declining trends (shaded green if larger

than 5% per year) while positive values (indicated with red shading) indicate an average increasing trend.

	Average % change per year	
	Before 2000	After 2000
α -HCH	-8.7	-9.5
β -HCH	-0.3	0.8
CHL	-4.5	-5.8
DDE PP	-4.2	-4.6
Dieldrin	-3.1	-0.7
γ -HCH	-7.2	-5.6
HBCD	4.7	-5.7
HCB	-2.5	-0.5
HEPOX	-9.7	-1.6
Mirex	-6.7	-3.3
PBDE-47	4.0	-4.7
PBDE-99	3.8	7.1
ΣPCBs	-3.7	-1.0
PCB-153	-3.8	-2.7
PFOS	3.0	-7.6
ΣDDT	-4.0	-23.9
Toxa-26	-3.9	-3
Toxa-50	-5.9	-7.2

	Reducing at rate of ≥ 5 % per year
	Reducing at rate of ≤ 5 % per year
	Increasing rate

6.1.3 Summary of evidence of long range transport and the effects of climate change

People living in the Arctic and consuming a diet composed of local foods have higher exposure to certain POPs than people living in temperate regions. The presence of POPs in regions of the world that are remote from sources, such as the Arctic, is compelling evidence of their long-range transport. A complete and quantitative picture of the location and strength of sources of POPs, their fate and long-range transport in the environment, and the levels that are present in remote regions can be assembled using mass balance chemical fate models as a unifying framework. Case studies that integrate emission inventories and monitoring data at the global scale have been carried out for a few POPs, including PCBs, HCHs, DDT and PFOS. Uncertainties in the description of the global fate and long-range transport of POPs in these case studies are frequently driven by uncertainties in emissions inventories and in the rates of degradation of POPs in air, water, soil and sediments.

The level of cooperation between scientists studying the sources of POPs, those engaged in monitoring and campaign-based measurements of POPs in the environment, and the contaminant fate and transport modeling community is growing. A notable example is the development of “top-down” methods to estimate emissions of POPs from suspected source areas based on a combination of measurements and modeling. It is important to encourage and strengthen such collaborations. More effective methods to identify and characterize emissions of POPs are also needed to assess the impact of transport of goods and waste, in particular e-waste, all over the world. Measurements in West Africa and South East Asia show evidence of sources of POPs from e-waste recycling.

The long-range transport of PFOS presents a new set of challenges relative to other POPs because of its distinct properties and potential for formation in the environment from precursor substances. Clear evidence for long-range transport in the atmosphere and deposition of PFOS and/or its precursors to remote waters can be seen from detectable levels in remote, uninhabited lakes in northern Canada and in Antarctica. Long-range transport in the oceans is also evident from detectable levels of PFOS thousands of kilometers from emission sources in surface and deep ocean waters. Modeling approaches have recently been developed to describe the fate and long-range transport of PFOS, and these should enable more effective assessment of similar substances.

Improved modeling capabilities will enable the vast corpus of environmental monitoring data that has been established over the past decades to be leveraged to achieve a more quantitative and predictive understanding of the levels and trends of POPs and POP candidates in the environment. For example, total HCHs (Σ HCH) have been observed to decline in seals, beluga and polar bears due to rapid decline of the major isomer α -HCH (e.g. 12%/year in bears). However, β -HCH, the more bioaccumulative isomer, increased in the same species. This increase in β -HCH in seals varied regionally, with large increases in South Beaufort Sea seals (16% at Ulukhaktok) and a decline in Hudson Bay (2.5%/ year). The case of β -HCH highlights the importance of ocean water moving through the Arctic archipelago from the Pacific Ocean via the Bering Sea (NCP 2013). The relative trends that are observed for α - and β -HCH in Arctic mammals are consistent with results of global-scale modeling which identify β -HCH to be more persistent and less rapidly transported to remote regions than α -HCH, and which forecast that β -HCH will eventually become the dominant HCH isomer in the environment (Wöhrnschimmel et al. 2013).

Enhancing modelling capabilities, especially for describing air-surface exchange will also help to reduce uncertainties about the extent of long-range transport of POPs and POP candidates. For example, measurements of POPs in soil and spruce needles in the European Alps showed higher concentrations in peripheral regions of the Alps compared to more shielded central regions. These observations demonstrate the potential for preferential deposition of POPs in cool, high-altitude forested regions, but the influence of this effect in global-scale models is so far poorly constrained.

Levels of HCB and PCBs at certain monitoring stations in the Arctic have shown increasing time trends in recent years, which may be related to local revolatilization due to a warming environment. Global and regional-scale model scenarios that forecast the impact of climate change on levels of POPs generally find that changes of up to a factor of 2 in air and a factor of 4 in water are possible relative to base-case climate scenarios. However, in the same modeling scenarios, reductions in emission rates of POPs that are expected to occur simultaneously with climate change can reduce levels by orders of magnitude. Therefore, in the long term (i.e., decadal time scales) climate change is not expected to obscure or counteract reductions in levels of POPs that are possible due to phase-out of production, use and emissions. Levels and trends of POPs at remote locations can also be affected by sources from materials used at the monitoring stations. For example, stations in Antarctica have measured BDEs in local air that is attributable to materials used at the station.

There is clear evidence that transport of POPs into remote regions occurs in the atmosphere, oceans and rivers, through biovectors, and in the technosphere by transport of materials. Models can be used to integrate information from emission inventories and monitoring programmes to quantitatively assess the relative weight of these routes in explaining the concentration for each pollutant, location and point in time. This is of great importance to interpret trends and ascertain the effectiveness of actions that have been undertaken, and to forecast impacts of current action or lack of it.

6.1.4 Summary of gaps in data coverage

Table 6.1a and **Table 6.1b** reflect the availability of baseline monitoring and trend information for POPs in the WEOG region. While baseline data are becoming available for newer POPs, time trends are yet unavailable for most. Continued monitoring of these substances in a consistent manner is needed to provide temporal assessments in the future. A new Australian Pilot Monitoring Programme for air has been established in Australia and in Antarctica where additional data will become available soon, but monitoring in New Zealand is lacking. While the

urban environment is a major source of new POPs that are associated with consumer products and household items, current urban air monitoring of POPs is limited. Better spatial coverage can be achieved through the use of passive air samplers.

Temporal and spatial trend evaluations in the current report for POPs in human milk and/or blood are based on a small number of on-going international and national programmes, whereas results from individual research studies were considered unsuitable for the trend evaluation. Available information indicates that the levels of substances included in the Stockholm Convention, where comparable data is available, are generally decreasing in most cases. It is noteworthy that although concentrations of some individual POPs are declining in some parts of the region (but not others), the number of POP-like chemicals to which humans and the environment are exposed are increasing.

6.1.5 Summary of new developments in POPs monitoring

A review of the work carried out monitoring POPs in other media since 2009 in WEOG shows that the use of long time monitoring series has had an important role in shaping policy in the Arctic, the Great lakes and the Baltic, North Atlantic and Mediterranean—and that the actions undertaken have worked. The environmental concentrations of the POP substances that were regulated decades ago and monitored since then have significantly decreased, and the majority of primary sources have stopped in these regions. There is a large corpus of high quality monitoring information on POPs in air, water, soil and organisms such as plankton, fish, birds and mammals, in multiple sites regularly sampled over decades. The available data from these efforts should be studied in detail and in an integrated and interdisciplinary framework to develop better understanding of the rates of change in the environment and the time delays and modulations in concentration changes in different media. Improving the models of POPs pathways and fate is central to gauge the potential impact of action or inaction on a given process or substance.

Marine and freshwater ecosystems are relatively well documented; there is a notable gap of information on terrestrial ecosystems, beyond mosses, lichens and a few large animals. It is somehow surprising how little information is available on POPs in terrestrial ecosystems that are relatively easy to sample and would be informative.

The practice of sample archiving is increasingly being adopted by long-term monitoring programmes for POPs. Sample banks allow retrospective analysis of environmental samples for determining concentrations of priority chemicals, candidate POPs and newly listed POPs. Retrospective analysis can be triggered by the availability of analytical standards, adequate and

sensitive analytical methods being developed and by the demand for monitoring data for conducting risk assessments (e.g. needs of the POPRC or national risk assessments) and/or risk management.

6.2 Recommendations for the future

To complement the conclusions presented above, the following recommendations are offered to the COP to enhance future effectiveness evaluations.

Human Media: Given the lack of comparable monitoring data for POPs, it is highly important that existing programmes are continued in a consistent way in the future. Hopefully we will see a continuation of newly started measuring series, such as CHMS, FNBI and the Australian Pilot Monitoring Programme. Also, new harmonized and sustainable human biomonitoring initiatives should be encouraged. To better evaluate trends over time and in different regions, human monitoring programmes should be initiated in regions, such as Southern Europe and New Zealand, which are currently lacking such programmes. Fat soluble substances can be monitored in mother's milk and blood as long as adequate Quality Assurance / Quality Control programs are in place. The levels of more polar substances such as PFOS are higher in blood. For other substances that may be considered in the future for inclusion in the Convention, other media such as urine may be worthwhile exploring for monitoring of levels (depending on the substance).

Air monitoring: As many of the legacy POPs are declining in air, and resources (funding and expertise) are becoming limited, programmes should consider strategically adapting their monitoring efforts for legacy compounds, as needed (e.g. reducing analytical frequencies and, in some cases, target chemical lists). These efficiencies will help to ensure that resources can be available for addressing the monitoring needs of newer POPs. Passive air samplers should continue to be implemented as a cost-effective approach for improving spatial information for POPs in air.

One of the most relevant parameters that can be used to evaluate effectiveness of the Convention is the changes in emissions of POPs, regionally and globally. However, assembling emission inventories for POPs (bottom-up approach; see Ch. 5.3) is challenging due to lack of information on use. Furthermore, many commercial products contain unknown quantities and types of POPs and this information is not adequately tracked. One way around this problem is through top-down approaches, where emissions are assessed from monitoring information and special studies.

With many of the newer POPs and candidate POPs being associated with commercial products and emissions from indoor air, urban areas may become more important as both sources and receptors of POPs; i.e. indoor to outdoor fate pathway. It may be advantageous to include urban background sites (e.g. urban parks) and indoor surveys as part of air monitoring efforts as these sites are likely to respond relatively quickly to changes in the predominant emissions/usage of some 'newer' POPs that are used in commercial products (e.g. PBDEs, HBCD and PFOS precursors).

There is growing impetus to make better connections between POPs monitoring and toxicity and long term effects of mixtures in air. Although the burden of individual POPs may be on the decline in some regions, the number of POPs present in air is increasing. Sensitive in vitro methods are currently available and could be explored for assessing toxicity of POP mixtures in air and linking with monitoring data on POPs. Concepts such as a 'health index' for air, based on POPs, could be explored. Because these topics are beyond the mandate of the GMP and typically not incorporated into existing monitoring programmes for air, it is recommended that these issues be considered through partnerships with appropriate experts and institutions such as the World Health Organisation.

Water: Systematic temporal trend studies at a few key sites could build on past measurements. Results for rivers offer perhaps the best opportunity to assess temporal trends provided that sources e.g. waste water treatment plants (WWTPs), tributaries, accidental spills etc, are well documented. For oceans, collaborative monitoring programmes along key cruise transects sites should be encouraged. Models for this include the Joint Global Ocean Flux Study (JGOFS; 1987-2003). Scientific Committee of Oceanic Research (SCOR) and JGOFS developed fieldwork for several Process Studies which included sampling for POPs (North Atlantic, Equatorial Pacific, Indian Ocean, Southern Ocean and North Pacific). Oceans are expected to have a long lag time before concentrations of PFOS will begin to decline in response to emissions reductions. As a PFOS precursor, FOSA is an important PFOS related compound, particularly in ocean water, where it has been found at concentrations similar to PFOS in some studies, and should be included in all future analyses. At present FOSA data is available for only about a third of river water analyses. A major knowledge gap is measurement of other neutral PFOS precursors (MeFOSA, EtFOSA, MeFOSE and EtFOSE) as well as less well known precursors recently identified in fire-fighting foams. Understanding the current use or inventories and the fate of these PFOS precursors is important for being able predict future PFOS concentrations in water.

Other Media: There is a vast corpus of information that has been obtained since the 1970s on POPs in numerous environmental media. These data provide invaluable insight and indispensable information for understanding spatial and temporal characteristics of sources and pathways of POPs. All efforts should be made to make best use of this information to improve models and to define effective future monitoring strategies. Existing data series for POPs in other media should continue to contribute to the regional and global monitoring reports.

It would be certainly productive to further develop the POPs modeling community of a practice in cooperation with other international initiatives such as the Task Force on Hemispheric Transport of Air Pollution (HTAP), under LRTAP, EMEP/EBAS/NILU, the Global Atmospheric Watch GAW under WMO and the Global Earth Observation Systems GEOSS.

Long range transport and effects of climate change and climate variability:

Integrated assessments that use models to link emissions inventories with environmental monitoring data are the most effective way to quantify the extent of long range transport of POPs. Research priorities for improving integrated assessment of POPs are; (i) improving emission inventories; (ii) reducing uncertainties about rates of degradation of POPs in air, water, soil and sediments; and, (iii) enhancing modeling capabilities, especially for describing air-surface exchange.

Experience with modeling existing POPs has beneficial synergies with applying models for identification and risk profiling of candidate POPs. Key research needs in this area are improved models for estimating properties of chemicals from molecular structure, and better information about uses and emission of industrial chemicals and especially candidate POP substances.

Climate-related effects can impact the emissions and cycling of POPs in the environment, and have the potential to obscure or modulate trends of POPs that are observed in air and other media. The European research project ArcRisk concluded that the influence of climate change on levels and trends of POPs in the global environment on the time-scale of decades is likely much smaller than the influence of policies that would reduce emissions. However, shorter-term effects of climate change and climate variability that vary by region and subregion and by chemical and should be taken into consideration when interpreting measurements of POPs in environmental media.

Sample Archiving / Sample Banks: Sample archiving is an important practice for all media and provides an opportunity to develop comparable data for spatial and temporal trends analysis. Sample banks are also useful for conducting retrospective analysis for screening studies and for assessing new POPs as these priorities are identified and/or as analytical methods become available. Long term monitoring programmes should invest resources to ensure the integrity and sustainability of sample banks.

Data archiving and accessibility: Databases play an important role in identifying, documenting and making accessible reliable and comparable data sets on POPs. Scientists should be encouraged to share information on databases in a timely manner and should be given credit for datasets that have not yet been published through the peer review process. These data are needed for assessing environmental levels and trends for POPs and for developing and validating transport models. Effort should be invested to make databases easily accessible (e.g. data downloadable) and integrating databases where appropriate and possible. Further development of simple visualization tools such as those implemented under the GMP database is useful.

Challenges with new POPs: The growing number of listed POPs and candidate substances presents a resource pressure for existing monitoring programmes. Furthermore, some new POPs require modified sampling methods and/or new and sometimes complex analytical methods. Some new POPs do not behave in the conventional manner and may involve precursor chemicals (e.g. PFOS) or may generate stable degradation products which may also exhibit POP-like properties.

Research studies are needed as existing models are often not adequate for assessing new compounds that behave differently in the environment. Studies of partitioning to particles and particle-associated transport and fate are needed for high molecular weight POPs and polar/ionizable chemicals that exist in air primarily on the particle-phase. It was previously thought that chemicals that tend to attach to particles would deposit faster and are not subjected to atmospheric long-range transport. However, more recent studies have shown that such chemicals can be transported very far from sources because they tend to attach to very fine particles that do not deposit quickly. The chemicals may be protected from photodegradation and transformation during particle transport. It is thus important to better understand this transport process.

Emissions of POPs have shifted from mainly industrial / combustion / agricultural sources to a wide range of indoor sources associated with commercial products, where human exposure can

be a significant concern. Emissions from the waste sector (e.g. waste water treatment plants and landfills) to water, air, and soil (e.g. through sludge application) is also relevant for the newer POPs, as a result of their commercial uses and waste disposal fate pathways. Monitoring strategies include assessment of these sources and attempts to link emissions of these chemicals to human and environmental burdens. Monitoring programmes need to be flexible and adaptable to deal with the challenges presented by new POPs.

Efficiencies for Monitoring Programmes: In order to deal with added analysis pressures of new POPs, monitoring programmes may need to adjust their protocols and resources to better align with new priorities. Possible strategies include reduced sampling frequency for legacy POPs for which long-term data series exhibiting declining trends already exist. Reducing or focusing analyte lists is also an option for complex technical mixtures (e.g. PCBs, Toxaphene and PBDEs). In some cases analytical methods can be improved or combined so that numerous target analytes can be determined in the same run.

Partnerships among labs and programmes at the regional and even international scale could be explored as an option for dealing with analytical challenges for some classes of new and candidate POPs. It is not feasible for every lab to be an expert for every class of POPs.

Improved integration between monitoring programmes and modelers may help to identify gaps in information and optimize future study designs and ongoing monitoring efforts.

Lastly, passive air samplers should continue to be implemented for air as a cost-effective approach for improving spatial resolution and for carrying out screening and source identification studies on new and candidate POPs. Opportunities should also be explored for using passive air samplers and monitoring sites for complementary activities such as assessing the air burden or health risk. Numerous bioassay methods have been developed with high sensitivity to assess toxicity of mixtures for a range of toxicity endpoints (e.g. androgenic, anti-androgenic, estrogenic, anti-estrogenic, mutagenicity, DNA damage etc).

Comparability of data: Each of the existing programmes that contributed information for the WEOG review has their own procedures for maintaining intra-programme comparability of information. However, in general, different programmes do not use the same analytical laboratories. Although there are procedures to evaluate variance between laboratories (such as blind interlaboratory comparisons), the use of different analytical laboratories remains a potential major source of variance between programmes. Due to the large number of existing programmes used as information sources for the WEOG report, it was concluded that it would be unrealistic

to expect comparability between programmes now and in the future. Therefore it is recommended that future efforts are focused to promote internal comparability within programmes over time. While this conclusion generally means that there will be very limited direct comparability between regions, significant exceptions are evident, such as the WHO coordinated human milk programme and the GAPS Network which use a single laboratory. The extensive use of such measures as utilization of common analytical laboratories and data centers has demonstrated the possibility of achieving adequate comparability between well established programmes in the WEOG region. An example is the collaborative practices of AMAP, EMEP, OSPAR, and HELCOM.

Mediterranean rim: The review found a significant improvement in the information on the Mediterranean rim since 2009. It is recommended that steps be explored for enhancing long term cooperation in POPs monitoring in the Mediterranean region to improve the information base for future effectiveness evaluations of the Convention.

Longevity of monitoring arrangements: Finally, this review has relied on information provided by a relatively small number of existing national and international monitoring programmes. The ability to compare POPs levels over time within these programmes makes their long term viability of utmost importance for future trend analysis to evaluate the effectiveness of the Convention. It is also important that such programmes do not alter their procedures in ways that compromises the data comparability that is necessary for the examination of temporal trends. The existing programmes should be commended for their outstanding work.

7 REFERENCES

Ambient Air (5.2.1)

Bossi, R., Skjøth, C. A. and Skov, H. (2013) Three years (2008–2010) of measurements of atmospheric concentrations of organochlorine pesticides (OCPs) at Station Nord, North-East Greenland. *Environ. Sci.: Processes Impacts*, 15: 2213-2219.

Castro-Jiménez, J., Berrojalbiz, N., Mejanelle, L. and Dachs, J. (2013) “Sources, transport and deposition of atmospheric organic pollutants in the Mediterranean Sea” in *Occurrence, Fate and Impact of Atmospheric Pollutants on Environmental and Human Health*; McConnell, L., et al; ACS Symposium Series; American Chemical Society: Washington, DC. p. 231- 260.

Covaci, A., Gerecke, A.C., Law, R.J., Voorspoels, S., Kohler, M., Heeb, N.V., Leslie, H., Allchin, C.R., and De Boer, J. 2006. Hexabromocyclododecanes (HBCDs) in the Environment and Humans: A Review. *Environ. Sci. Technol.* 40, 3679-3688.

Dreyer, A., Weinberg, I., Temme, C., Ebinghaus, R. (2009) Polyfluorinated compounds in the atmosphere of the Atlantic and Southern Oceans: Evidence for a global distribution. *Environ. Sci. Technol.* 43, 6507-6514.

Gawor, A., Shunthirasingham, C., Hayward, S. J., Lei, Y. D., Gouin, T., Mmereki, B. T. , Masamba, W., Ruepert, C., Castillo, L. E., Shoeib, M., Lee, S. C., Harner, T. and Wania, F. (2014) Neutral polyfluoroalkyl substances in the global atmosphere. *Environ. Sci.: Processes Impacts*, 16, 404-413.

Hung, H., Halsall, C. J., Blanchard, P., Li, H. H., Fellin, P., Stern, G. and Rosenberg, B. (2002). Temporal trends of organochlorine pesticides in the Canadian Arctic atmosphere. *Environ. Sci. Technol.*, 36: 862-868.

Hung, H., Kallenborn, R., Breivik, K., Su, Y., Brorstrøm-Lunden, E., Olafsdottir, K., Thorlacius, J. M., Leppanen, S., Bossi, R., Skov, H., Manø, S., Stern, G., Sverko, E., Fellin, P. (2010) Atmospheric monitoring of organic pollutants in the Arctic under the Arctic Monitoring and Assessment Programme (AMAP): 1993-2006. *Sci. Tot. Environ.* 408: 2854–2873.

Kallenborn, R., K. Breivik, S. Eckhardt, C. R. Lunder, S. Manø, M. Schlabach, and A. Stohl. Long-term monitoring of persistent organic pollutants (POPs) at the Norwegian Troll station in Dronning Maud Land, Antarctica. *Atmos. Chem. Phys.*, 13, 6983–6992, 2013

Piekarz, A. M., Primbs, T., Field, J. A., Barofsky, D. F., Simonich, S. (2007) Semivolatile fluorinated organic compounds in Asian and Western U. S. air masses. *Environ. Sci. Technol.* 41: 8248-8255.

Schenker, U., Scheringer, M., MacLeod, M., Martin, J. W., Cousins, I. T. and Hungerbühler (2008). Contribution of volatile precursor substances to the flux of perfluorooctanoate to the Arctic. *Environ. Sci. Technol.*, 42: 3710-3716.

Shoeib, M., Harner, T. and Vlahos, P. (2006) Perfluorinated chemicals in the arctic atmosphere. *Environ Sci Technol.* 40(24):7577-83.

Shunthirasingham, C., Oyiliagu, C.E., Cao, X.S., Gouin, T., Wania, F., Lee, S.-C., Pozo, K., Harner, T., Muir, D.C.G. (2010) Spatial and temporal pattern of pesticides in the global atmosphere. *J. Environ. Monitor.*, 12, 1650-1657.

Venier, M. and Hites, R. A. Regression model of partial pressures of PCBs, PAHs, and organochlorine pesticides in the Great Lakes' atmosphere. *Environ. Sci. Technol.* 2010, 44, 618–623.

Venier, M., Hung, H., Tych, W., Hites, R. A. (2012) Temporal trends of persistent organic pollutants: A comparison of different time series models. *Environ. Sci. Technol.*, 46(7): 3928-34.

Human Tissue (5.2.2)

AFN. First Nations Biomonitoring Initiative - National Results (2011). Ottawa, Ontario: Assembly of the First Nations 2013

Airaksinen, R.; Rantakokko, P.; Eriksson, J.G.; Blomstedt, P.; Kajantie, E.; Kiviranta, H. Association between type 2 diabetes and exposure to persistent organic pollutants. *Diabetes Care*. 34:1972-1979; 2011

AMAP. Assessment Report: Arctic Pollution Issues. Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway; 1998

AMAP. AMAP Assessment 2002: Human Health in the Arctic. Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway; 2003

AMAP. AMAP Assessment 2009: Human Health in the Arctic. Arctic Monitoring and Assessment Program (AMAP), Oslo, Norway; 2009

Antignac, J.P.; Cariou, R.; Zalko, D.; Berrebi, A.; Cravedi, J.P.; Maume, D.; Marchand, P.; Monteau, F.; Riu, A.; Andre, F.; Le Bizec, B. Exposure assessment of French women and their newborn to brominated flame retardants: determination of tri- to deca-polybromodiphenylethers (PBDE) in maternal adipose tissue, serum, breast milk and cord serum. *Environ Pollut*. 157:164-173; 2009

Antignac, J.P.; Veyrand, B.; Kadar, H.; Marchand, P.; Oleko, A.; Le Bizec, B.; Vandentorren, S. Occurrence of perfluorinated alkylated substances in breast milk of French women and relation with socio-demographical and clinical parameters: results of the ELFE pilot study. *Chemosphere*. 91:802-808; 2013

Barbarossa, A.; Masetti, R.; Gazzotti, T.; Zama, D.; Astolfi, A.; Veyrand, B.; Pession, A.; Pagliuca, G. Perfluoroalkyl substances in human milk: a first survey in Italy. *Environ Int*. 51:27-30; 2013

- Bates, M.N.; Buckland, S.J.; Hannah, D.J.; Taucher, J.A.; van Maanen, T. Organochlorine Residues in the Breast Milk of New Zealand Women. A Report to the Department of Health; 1990
- Bates, M.N.; Garrett, N.; Thomson, B. Investigation of organochlorine contaminants in the milk of New Zealand Women. Client Report FW00104 April 2001 from the Institute of Environmental Science and Research to the Ministry of Health, Wellington, New Zealand; 2001
- Bates, M.N.; Hannah, D.J.; Buckland, S.J.; Taucher, J.A.; van Maanen, T. Chlorinated organic contaminants in breast milk of New Zealand women. *Environ Health Perspect.* 102 Suppl 1:211-217; 1994
- Becker, K.; Müssig-Zufika, M.; Conrad, A.; Lüdecke, A.; Schulz, C.; Seiwert, M.; Kolossa-Gehring, M. German Environmental Survey for Children 2003/06 GerES IV. Berlin: Umweltbundesamt; 2008
- Bergman, Å.; Hovander, L.; Sundström, M.; Athanassiadis, I.; Athanasiadou, M.; Sällsten, G.; Bignert, A.; Nyberg, E. Insamling och kemisk analys av miljöföroreningar i svensk modersmjölk - Resultat från 2008-2010 Rapport till Naturvårdsverket 2010
- Bergonzi, R.; Specchia, C.; Dinolfo, M.; Tomasi, C.; De Palma, G.; Frusca, T.; Apostoli, P. Distribution of persistent organochlorine pollutants in maternal and foetal tissues: data from an Italian polluted urban area. *Chemosphere.* 76:747-754; 2009
- Bjermo, H.; Darnerud, P.O.; Lignell, S.; Pearson, M.; Rantakokko, P.; Nalsen, C.; Enghardt Barbieri, H.; Kiviranta, H.; Lindroos, A.K.; Glynn, A. Fish intake and breastfeeding time are associated with serum concentrations of organochlorines in a Swedish population. *Environ Int.* 51:88-96; 2013
- Buttke, D.E.; Wolkin, A.; Stapleton, H.M.; Miranda, M.L. Associations between serum levels of polybrominated diphenyl ether (PBDE) flame retardants and environmental and behavioral factors in pregnant women. *J Expo Sci Environ Epidemiol.* 23:176-182; 2013

Carignan, C.C.; Abdallah, M.A.; Wu, N.; Heiger-Bernays, W.; McClean, M.D.; Harrad, S.; Webster, T.F. Predictors of tetrabromobisphenol-A (TBBP-A) and hexabromocyclododecanes (HBCD) in milk from Boston mothers. *Environ Sci Technol.* 46:12146-12153; 2012

CDC. Fourth National Report on Human Exposure to Environmental Chemicals. Centers for Disease Control and Prevention; 2009

CDC. Fourth National Report on Human Exposure to Environmental Chemicals - Updated Tables, September 2013. Centers for Disease Control and Prevention; 2013

Cok, I.; Mazmanci, B.; Mazmanci, M.A.; Turgut, C.; Henkelmann, B.; Schramm, K.W. Analysis of human milk to assess exposure to PAHs, PCBs and organochlorine pesticides in the vicinity Mediterranean city Mersin, Turkey. *Environ Int.* 40:63-69; 2012

Colles, A.; Koppen, G.; Hanot, V.; Nelen, V.; Dewolf, M.C.; Noel, E.; Malisch, R.; Kotz, A.; Kypke, K.; Biot, P.; Vinkx, C.; Schoeters, G. Fourth WHO-coordinated survey of human milk for persistent organic pollutants (POPs): Belgian results. *Chemosphere.* 73:907-914; 2008

Croes, K.; Colles, A.; Koppen, G.; Govarts, E.; Bruckers, L.; Van de Mieroop, E.; Nelen, V.; Covaci, A.; Dirtu, A.C.; Thomsen, C.; Haug, L.S.; Becher, G.; Mampaey, M.; Schoeters, G.; Van Larebeke, N.; Baeyens, W. Persistent organic pollutants (POPs) in human milk: a biomonitoring study in rural areas of Flanders (Belgium). *Chemosphere.* 89:988-994; 2012

Dallaire, R.; Ayotte, P.; Pereg, D.; Dery, S.; Dumas, P.; Langlois, E.; Dewailly, E. Determinants of plasma concentrations of perfluorooctanesulfonate and brominated organic compounds in Nunavik Inuit adults (Canada). *Environ Sci Technol.* 43:5130-5136; 2009

Daniels, J.L.; Pan, I.J.; Jones, R.; Anderson, S.; Patterson, D.G., Jr.; Needham, L.L.; Sjodin, A. Individual characteristics associated with PBDE levels in U.S. human milk samples. *Environ Health Perspect.* 118:155-160; 2010

Environmental Health in Europe No 3. Levels of PCBs, PCDDs, PCDFs and PCBs in human milk. 2nd round of WHO coordinated exposure survey. Copenhagen, Denmark: Regional Office for Europe; 1996

Environmental Health Series No 43. Levels of PCBs, PCDDs and PCDFs in breast milk. Copenhagen, Denmark: WHO Regional Office for Europe; 1989

Fei, C.; McLaughlin, J.K.; Tarone, R.E.; Olsen, J. Perfluorinated chemicals and fetal growth: a study within the Danish National Birth Cohort. *Environ Health Perspect.* 115:1677-1682; 2007

Focant, J.F.; Frery, N.; Bidondo, M.L.; Eppe, G.; Scholl, G.; Saoudi, A.; Oleko, A.; Vandentorren, S. Levels of polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and polychlorinated biphenyls in human milk from different regions of France. *Sci Total Environ.* 452-453:155-162; 2013

Foster, W.G.; Cheung, A.P.; Davis, K.; Graves, G.; Jarrell, J.; Leblanc, A.; Liang, C.L.; Leech, T.; Walker, M.; Weber, J.P.; Van Oostdam, J. Circulating metals and persistent organic pollutant concentrations in Canadian and non-Canadian born primiparous women from five Canadian centres: results of a pilot biomonitoring study. *Sci Total Environ.* 435-436:326-336; 2012

Foster, W.G.; Gregorovich, S.; Morrison, K.M.; Atkinson, S.A.; Kubwabo, C.; Stewart, B.; Teo, K. Human maternal and umbilical cord blood concentrations of polybrominated diphenyl ethers. *Chemosphere.* 84:1301-1309; 2011

Frederiksen, M.; Thomsen, C.; Froshaug, M.; Vorkamp, K.; Thomsen, M.; Becher, G.; Knudsen, L.E. Polybrominated diphenyl ethers in paired samples of maternal and umbilical cord blood plasma and associations with house dust in a Danish cohort. *Int J Hyg Environ Health.* 213:233-242; 2010

Fromme, H.; Midasch, O.; Twardella, D.; Angerer, J.; Boehmer, S.; Liebl, B. Occurrence of perfluorinated substances in an adult German population in southern Bavaria. *Int Arch Occup Environ Health.* 80:313-319; 2007

- Fång, J.; Nyberg, E.; Bignert, A.; Bergman, A. Temporal trends of polychlorinated dibenzo-p-dioxins and dibenzofurans and dioxin-like polychlorinated biphenyls in mothers' milk from Sweden, 1972-2011. *Environ Int.* 60:224-231; 2013
- Fängström, B.; Athanassiadis, I.; Odsjö, T.; Noren, K.; Bergman, Å. Temporal trends of polybrominated diphenyl ethers and hexabromocyclododecane in milk from Stockholm mothers, 1980-2004. *Mol Nutr Food Res.* 52:187-193; 2008
- Gari, M.; Grimalt, J.O. Inverse age-dependent accumulation of decabromodiphenyl ether and other PBDEs in serum from a general adult population. *Environ Int.* 54:119-127; 2013
- Gies, A.; Schröter-Kermani, C.; Rüdell, H.; Paulus, M.; Wiesmüller, G.A. Frozen Environmental History: The German Environmental Specimen Bank. *Organohalogen Compounds.* 69:504-507; 2007
- Glynn, A.; Berger, U.; Bignert, A.; S., U.; Lignell, S.; Aune, M.; Darnerud, P. Perfluorerade organiska ämnen i serum från förstföderskor i Uppsala - tidstrend 1996-2010 Sakrapport till Naturvårdsverkets Miljöövervakning: Livsmedelsverket; 2011
- Glynn, A.; Berger, U.; Bignert, A.; Ullah, S.; Aune, M.; Lignell, S.; Darnerud, P.O. Perfluorinated alkyl acids in blood serum from primiparous women in Sweden: serial sampling during pregnancy and nursing, and temporal trends 1996-2010. *Environ Sci Technol.* 46:9071-9079; 2012
- Gomara, B.; Herrero, L.; Ramos, J.J.; Mateo, J.R.; Fernandez, M.A.; Garcia, J.F.; Gonzalez, M.J. Distribution of polybrominated diphenyl ethers in human umbilical cord serum, paternal serum, maternal serum, placentas, and breast milk from Madrid population, Spain. *Environ Sci Technol.* 41:6961-6968; 2007
- Harden, F.A.; Toms, L.M.; Symons, R.; Furst, P.; Berry, Y.; Muller, J.F. Evaluation of dioxin-like chemicals in pooled human milk samples collected in Australia. *Chemosphere.* 67:S325-333; 2007

- Harley, K.G.; Marks, A.R.; Chevrier, J.; Bradman, A.; Sjodin, A.; Eskenazi, B. PBDE concentrations in women's serum and fecundability. *Environ Health Perspect.* 118:699-704; 2010
- Harrad, S.; Porter, L. Concentrations of polybrominated diphenyl ethers in blood serum from New Zealand. *Chemosphere.* 66:2019-2023; 2007
- Haug, L.S.; Huber, S.; Becher, G.; Thomsen, C. Characterisation of human exposure pathways to perfluorinated compounds--comparing exposure estimates with biomarkers of exposure. *Environ Int.* 37:687-693; 2011
- Health Canada. Report on Human Biomonitoring of Environmental Chemicals in Canada - Results of the Canadian Health Measures Survey Cycle 1 (2007–2009). Ottawa: Health Canada; 2010
- Health Canada. Second Report on Human Biomonitoring of Environmental Chemicals in Canada. Results of the Canadian Health Measures Survey Cycle 2 (2009-2011). Ottawa: Health Canada; 2013
- Hoopmann, M.; Albrecht, U.V.; Gierden, E.; Huppmann, R.; Suchenwirth, R. Time trends and individual characteristics associated with polybrominated diphenyl ethers in breast milk samples 2006-2009 in Lower Saxony, Germany. *Int J Hyg Environ Health.* 215:352-359; 2012
- Horton, M.K.; Bousleiman, S.; Jones, R.; Sjodin, A.; Liu, X.; Whyatt, R.; Wapner, R.; Factor-Litvak, P. Predictors of serum concentrations of polybrominated flame retardants among healthy pregnant women in an urban environment: a cross-sectional study. *Environ Health.* 12:23; 2013
- Huetos O, Bartolomé M, Aragonés N, Cervantes-Amat M, Esteban M, Ruiz-Moraga M, Pérez-Gómez B, Calvo E, Vila M; BIOAMBIENT.ES, Castaño A. Serum PCB levels in a representative sample of the SPANISH adult population: the BIOAMBIENT.ES project. *Sci Total Environ.* 493:834-844; 2014.

Hulek R., Boruvkova J., Gregor J., Kalina J., Bednarova Z., Sebkova K., Melkes O., Salko M., Novak R., Jarkovsky J., Dusek L., Klanova J. Global Monitoring Plan of the Stockholm Convention on Persistent Organic Pollutants: visualisation and on-line analysis of global levels of chemicals in air, water, breast milk and blood [online]. Masaryk University, 2014. Available from: <http://www.pops-gmp.org/visualization-2014>.

Humblet, O.; Williams, P.L.; Korrick, S.A.; Sergeyev, O.; Emond, C.; Birnbaum, L.S.; Burns, J.S.; Altshul, L.; Patterson, D.G.; Turner, W.E.; Lee, M.M.; Revich, B.; Hauser, R. Predictors of serum dioxin, furan, and PCB concentrations among women from Chapaevsk, Russia. *Environ Sci Technol.* 44:5633-5640; 2010

Ibarluzea, J.; Alvarez-Pedrerol, M.; Guxens, M.; Marina, L.S.; Basterrechea, M.; Lertxundi, A.; Etxeandia, A.; Goni, F.; Vioque, J.; Ballester, F.; Sunyer, J. Sociodemographic, reproductive and dietary predictors of organochlorine compounds levels in pregnant women in Spain. *Chemosphere.* 82:114-120; 2011

Ingelido, A.M.; Marra, V.; Abballe, A.; Valentini, S.; Iacovella, N.; Barbieri, P.; Porpora, M.G.; Domenico, A.; De Felip, E. Perfluorooctanesulfonate and perfluorooctanoic acid exposures of the Italian general population. *Chemosphere.* 80:1125-1130; 2010

Kalantzi, O.I.; Geens, T.; Covaci, A.; Siskos, P.A. Distribution of polybrominated diphenyl ethers (PBDEs) and other persistent organic pollutants in human serum from Greece. *Environ Int.* 37:349-353; 2011

Kalantzi, O.I.; Martin, F.L.; Thomas, G.O.; Alcock, R.E.; Tang, H.R.; Drury, S.C.; Carmichael, P.L.; Nicholson, J.K.; Jones, K.C. Different levels of polybrominated diphenyl ethers (PBDEs) and chlorinated compounds in breast milk from two U.K. Regions. *Environ Health Perspect.* 112:1085-1091; 2004

Kannan, K.; Corsolini, S.; Falandysz, J.; Fillmann, G.; Kumar, K.S.; Loganathan, B.G.; Mohd, M.A.; Olivero, J.; Van Wouwe, N.; Yang, J.H.; Aldoust, K.M. Perfluorooctanesulfonate and related fluorochemicals in human blood from several countries. *Environ Sci Technol.* 38:4489-4495; 2004

- Karlsson, M.; Julander, A.; van Bavel, B.; Hardell, L. Levels of brominated flame retardants in blood in relation to levels in household air and dust. *Environ Int.* 33:62-69; 2007
- Karrman, A.; Ericson, I.; van Bavel, B.; Darnerud, P.O.; Aune, M.; Glynn, A.; Lignell, S.; Lindstrom, G. Exposure of perfluorinated chemicals through lactation: levels of matched human milk and serum and a temporal trend, 1996-2004, in Sweden. *Environ Health Perspect.* 115:226-230; 2007
- Knutsen, H.K.; Kvalem, H.E.; Haugen, M.; Meltzer, H.M.; Brantsaeter, A.L.; Alexander, J.; Papke, O.; Liane, V.H.; Becher, G.; Thomsen, C. Sex, BMI and age in addition to dietary intakes influence blood concentrations and congener profiles of dioxins and PCBs. *Mol Nutr Food Res.* 55:772-782; 2011
- Knutsen, H.K.; Kvalem, H.E.; Thomsen, C.; Froshaug, M.; Haugen, M.; Becher, G.; Alexander, J.; Meltzer, H.M. Dietary exposure to brominated flame retardants correlates with male blood levels in a selected group of Norwegians with a wide range of seafood consumption. *Mol Nutr Food Res.* 52:217-227; 2008
- Kubwabo, C.; Vais, N.; Benoit, F.M. A pilot study on the determination of perfluorooctanesulfonate and other perfluorinated compounds in blood of Canadians. *J Environ Monit.* 6:540-545; 2004
- Kärman, A.; Mueller, J.F.; van Bavel, B.; Harden, F.; Toms, L.M.; Lindström, G. Levels of 12 perfluorinated chemicals in pooled Australian serum, collected 2002-2003, in relation to age, gender, and region. *Environ Sci Technol.* 40:3742-3748; 2006
- Laird, B.D.; Goncharov, A.B.; Chan, H.M. Body burden of metals and persistent organic pollutants among Inuit in the Canadian Arctic. *Environ Int.* 59:33-40; 2013
- LaKind, J.; Hays, S.; Aylward, L.; Naiman, D. Perspective on serum dioxin levels in the United States: an evaluation of the NHANES data *J Expo Sci Environ Epidemiol*; 2009

- Lignell, S.; Aune, M.; Glynn, A.; Cantillana, T.; Fridén, U. Levels of persistent halogenated organic pollutants (POP) in mother's milk from first-time mothers in Uppsala, Sweden - results from 2008/2010 and temporal trends 1996-2010 in: Program) R.t.t.S.E.t.H.-R.E.M., ed: Livsmedelsverket; 2012
- Lignell, S.; Aune, M.; Isaksson, M.; Redeby, J.; Darnerud, P.; Glynn, A. BDE-209 i blodserum från förstföderskor i Uppsala – tidstrend 1996-2010. Sakrapport till Naturvårdsverkets Miljöövervakning: Livsmedelsverket; 2011
- Lindh, C.H.; Rylander, L.; Toft, G.; Axmon, A.; Rignell-Hydbom, A.; Giwercman, A.; Pedersen, H.S.; Goalczyk, K.; Ludwicki, J.K.; Zvezday, V.; Vermeulen, R.; Lenters, V.; Heederik, D.; Bonde, J.P.; Jonsson, B.A. Blood serum concentrations of perfluorinated compounds in men from Greenlandic Inuit and European populations. *Chemosphere*. 88:1269-1275; 2012
- Lindstrom, A.B.; Strynar, M.J.; Libelo, E.L. Polyfluorinated compounds: past, present, and future. *Environ Sci Technol*. 45:7954-7961; 2011
- Link, B.; Gabrio, T.; Mann, V.; Schilling, B.; Maisner, V.; Konig, M.; Flicker-Klein, A.; Zollner, I.; Fischer, G. Polybrominated diphenyl ethers (PBDE) in blood of children in Baden-Wurttemberg between 2002/03 and 2008/09. *Int J Hyg Environ Health*. 215:224-228; 2012a
- Link, B.; Gabrio, T.; Zoellner, I.; Piechotowski, I.; Paepke, O.; Herrmann, T.; Felder-Kennel, A.; Maisner, V.; Schick, K.H.; Schrimpf, M.; Schwenk, M.; Wuthe, J. Biomonitoring of persistent organochlorine pesticides, PCDD/PCDFs and dioxin-like PCBs in blood of children from South West Germany (Baden-Wuerttemberg) from 1993 to 2003. *Chemosphere*. 58:1185-1201; 2005
- Link, B.; Gabrio, T.; Zollner, I.; Jaroni, H.; Piechotowski, I.; Schilling, B.; Felder-Kennel, A.; Flicker-Klein, A.; Konig, M.; Maisner, V.; Schick, K.H.; Fischer, G. Decrease of internal exposure to chlororganic compounds and heavy metals in children in Baden-Wurttemberg between 1996/1997 and 2008/2009. *Int J Hyg Environ Health*. 215:196-201; 2012b

- Llop, S.; Ballester, F.; Vizcaino, E.; Murcia, M.; Lopez-Espinosa, M.J.; Rebagliato, M.; Vioque, J.; Marco, A.; Grimalt, J.O. Concentrations and determinants of organochlorine levels among pregnant women in Eastern Spain. *Sci Total Environ.* 408:5758-5767; 2010
- Mannetje, A.; Coakley, J.; Bridgen, P.; Brooks, C.; Harrad, S.; Smith, A.H.; Pearce, N.; Douwes, J. Current concentrations, temporal trends and determinants of persistent organic pollutants in breast milk of New Zealand women. *Sci Total Environ.* 458-460:399-407; 2013
- Meijer, L.; Weiss, J.; Van Velzen, M.; Brouwer, A.; Bergman, A.; Sauer, P.J. Serum concentrations of neutral and phenolic organohalogenes in pregnant women and some of their infants in The Netherlands. *Environ Sci Technol.* 42:3428-3433; 2008
- Meironyte, D.; Noren, K.; Bergman, A. Analysis of polybrominated diphenyl ethers in Swedish human milk. A time-related trend study, 1972-1997. *J Toxicol Environ Health A.* 58:329-341; 1999
- Midasch, O.; Schettgen, T.; Angerer, J. Pilot study on the perfluorooctanesulfonate and perfluorooctanoate exposure of the German general population. *Int J Hyg Environ Health.* 209:489-496; 2006
- Monroy, R.; Morrison, K.; Teo, K.; Atkinson, S.; Kubwabo, C.; Stewart, B.; Foster, W.G. Serum levels of perfluoroalkyl compounds in human maternal and umbilical cord blood samples. *Environ Res.* 108:56-62; 2008
- Mueller, J.F.; Harden, F.; Toms, L.M.; Symons, R.; Furst, P. Persistent organochlorine pesticides in human milk samples from Australia. *Chemosphere.* 70:712-720; 2008
- Noren, K.; Meironyte, D. Certain organochlorine and organobromine contaminants in Swedish human milk in perspective of past 20-30 years. *Chemosphere.* 40:1111-1123; 2000
- Olsen, G.W.; Mair, D.C.; Church, T.R.; Ellefson, M.E.; Reagen, W.K.; Boyd, T.M.; Herron, R.M.; Medhdizadehkashi, Z.; Nobiletti, J.B.; Rios, J.A.; Butenhoff, J.L.; Zobel, L.R.

Decline in perfluorooctanesulfonate and other polyfluoroalkyl chemicals in American Red Cross adult blood donors, 2000-2006. *Environ Sci Technol.* 42:4989-4995; 2008

Porta, M.; Gasull, M.; Puigdomenech, E.; Gari, M.; Bosch de Basea, M.; Guillen, M.; Lopez, T.; Bigas, E.; Pumarega, J.; Llebaria, X.; Grimalt, J.O.; Tresserras, R. Distribution of blood concentrations of persistent organic pollutants in a representative sample of the population of Catalonia. *Environ Int.* 36:655-664; 2010

Pérez-Gómez B, Pastor-Barriuso R, Cervantes-Amat M, Esteban M, Ruiz-Moraga M, Aragonés N, Pollán M, Navarro C, Calvo E, Román J, López-Abente G, Castaño A; BIOAMBIENT.ES. BIOAMBIENT.ES study protocol: rationale and design of a cross-sectional human biomonitoring survey in Spain. *Environ Sci Pollut Res Int.* 20(2):1193-1202; 2013

Porta, M.; Lopez, T.; Gasull, M.; Rodriguez-Sanz, M.; Gari, M.; Pumarega, J.; Borrell, C.; Grimalt, J.O. Distribution of blood concentrations of persistent organic pollutants in a representative sample of the population of Barcelona in 2006, and comparison with levels in 2002. *Sci Total Environ.* 423:151-161; 2012

Pratt, I.; Anderson, W.; Crowley, D.; Daly, S.; Evans, R.; Fernandes, A.; Fitzgerald, M.; Geary, M.; Keane, D.; Morrison, J.J.; Reilly, A.; Tlustos, C. Brominated and fluorinated organic pollutants in the breast milk of first-time Irish mothers: is there a relationship to levels in food? *Food Addit Contam Part A Chem Anal Control Expo Risk Assess.* 30:1788-1798; 2013

Pratt, I.S.; Anderson, W.A.; Crowley, D.; Daly, S.F.; Evans, R.I.; Fernandes, A.R.; Fitzgerald, M.; Geary, M.P.; Keane, D.P.; Malisch, R.; McBride, J.; Morrison, J.J.; Reilly, A.; Tlustos, C. Polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) in breast milk of first-time Irish mothers: impact of the 2008 dioxin incident in Ireland. *Chemosphere.* 88:865-872; 2012

Raab, U.; Albrecht, M.; Preiss, U.; Volkel, W.; Schwegler, U.; Fromme, H. Organochlorine compounds, nitro musks and perfluorinated substances in breast milk - results from Bavarian Monitoring of Breast Milk 2007/8. *Chemosphere.* 93:461-467; 2013

- Raab, U.; Preiss, U.; Albrecht, M.; Shahin, N.; Parlar, H.; Fromme, H. Concentrations of polybrominated diphenyl ethers, organochlorine compounds and nitro musks in mother's milk from Germany (Bavaria). *Chemosphere*. 72:87-94; 2008
- Roosens, L.; D'Hollander, W.; Bervoets, L.; Reynders, H.; Van Campenhout, K.; Cornelis, C.; Van Den Heuvel, R.; Koppen, G.; Covaci, A. Brominated flame retardants and perfluorinated chemicals, two groups of persistent contaminants in Belgian human blood and milk. *Environ Pollut*. 158:2546-2552; 2010
- Rylander, C.; Lund, E.; Froyland, L.; Sandanger, T.M. Predictors of PCP, OH-PCBs, PCBs and chlorinated pesticides in a general female Norwegian population. *Environ Int*. 43:13-20; 2012
- Rylander, C.; Sandanger, T.M.; Froyland, L.; Lund, E. Dietary patterns and plasma concentrations of perfluorinated compounds in 315 Norwegian women: the NOWAC Postgenome Study. *Environ Sci Technol*. 44:5225-5232; 2010
- Rylander, C.; Sandanger, T.M.; Petrenya, N.; Konoplev, A.; Bojko, E.; Odland, J.O. Indications of decreasing human PTS concentrations in North West Russia. *Glob Health Action*. 4; 2011
- Salihovic, S.; Lampa, E.; Lindstrom, G.; Lind, L.; Lind, P.M.; van Bavel, B. Circulating levels of persistent organic pollutants (POPs) among elderly men and women from Sweden: results from the Prospective Investigation of the Vasculature in Uppsala Seniors (PIVUS). *Environ Int*. 44:59-67; 2012
- Schröter-Kermani, C.; Muller, J.; Jurling, H.; Conrad, A.; Schulte, C. Retrospective monitoring of perfluorocarboxylates and perfluorosulfonates in human plasma archived by the German Environmental Specimen Bank. *Int J Hyg Environ Health*. 216:633-640; 2013
- Siddique, S.; Xian, Q.; Abdelouahab, N.; Takser, L.; Phillips, S.P.; Feng, Y.L.; Wang, B.; Zhu, J. Levels of dechlorane plus and polybrominated diphenylethers in human milk in two Canadian cities. *Environ Int*. 39:50-55; 2012

Sjodin, A.; Jones, R.S.; Caudill, S.P.; Wong, L.Y.; Turner, W.E.; Calafat, A.M. Polybrominated diphenyl ethers, polychlorinated biphenyls, and persistent pesticides in serum from the national health and nutrition examination survey: 2003-2008. *Environ Sci Technol.* 48:753-760; 2014

Sjodin, A.; Wong, L.Y.; Jones, R.S.; Park, A.; Zhang, Y.; Hodge, C.; Dipietro, E.; McClure, C.; Turner, W.; Needham, L.L.; Patterson, D.G., Jr. Serum concentrations of polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyl (PBB) in the United States population: 2003-2004. *Environ Sci Technol.* 42:1377-1384; 2008

Smith, D. Worldwide trends in DDT levels in human breast milk. *Int J Epidemiol.* 28:179-188; 1999

Sundström, M.; Ehresman, D.J.; Bignert, A.; Butenhoff, J.L.; Olsen, G.W.; Chang, S.C.; Bergman, Å. A temporal trend study (1972-2008) of perfluorooctanesulfonate, perfluorohexanesulfonate, and perfluorooctanoate in pooled human milk samples from Stockholm, Sweden. *Environ Int.* 37:178-183; 2011

Thomas, G.O.; Wilkinson, M.; Hodson, S.; Jones, K.C. Organohalogen chemicals in human blood from the United Kingdom. *Environ Pollut.* 141:30-41; 2006

Thomsen, C.; Knutsen, H.K.; Liane, V.H.; Froshaug, M.; Kvalem, H.E.; Haugen, M.; Meltzer, H.M.; Alexander, J.; Becher, G. Consumption of fish from a contaminated lake strongly affects the concentrations of polybrominated diphenyl ethers and hexabromocyclododecane in serum. *Mol Nutr Food Res.* 52:228-237; 2008

Thomsen, C.; Stigum, H.; Froshaug, M.; Broadwell, S.L.; Becher, G.; Eggesbo, M. Determinants of brominated flame retardants in breast milk from a large scale Norwegian study. *Environ Int.* 36:68-74; 2010

- Thuresson, K.; Bergman, K.; Rothenbacher, K.; Herrmann, T.; Sjolín, S.; Hagmar, L.; Papke, O.; Jakobsson, K. Polybrominated diphenyl ether exposure to electronics recycling workers--a follow up study. *Chemosphere*. 64:1855-1861; 2006
- Toms, L.M.; Calafat, A.M.; Kato, K.; Thompson, J.; Harden, F.; Hobson, P.; Sjolín, A.; Mueller, J.F. Polyfluoroalkyl chemicals in pooled blood serum from infants, children, and adults in Australia. *Environ Sci Technol*. 43:4194-4199; 2009
- Toms, L.M.; Guerra, P.; Eljarrat, E.; Barcelo, D.; Harden, F.A.; Hobson, P.; Sjolín, A.; Ryan, E.; Mueller, J.F. Brominated flame retardants in the Australian population: 1993-2009. *Chemosphere*. 89:398-403; 2012
- Toms, L.M.; Harden, F.A.; Symons, R.K.; Burniston, D.; Furst, P.; Muller, J.F. Polybrominated diphenyl ethers (PBDEs) in human milk from Australia. *Chemosphere*. 68:797-803; 2007
- Toms LM, Thompson J, Rotander A, Hobson P, Calafat AM, Kato K, Ye X, Broomhall S, Harden F, Mueller JF. Decline in perfluorooctane sulfonate and perfluorooctanoate serum concentrations in an Australian population from 2002 to 2011. *Environ Int*. 71:74-80; 2014
- Turgeon O'Brien, H.; Blanchet, R.; Gagne, D.; Lauziere, J.; Vezina, C.; Vaissiere, E.; Ayotte, P.; Dery, S. Exposure to toxic metals and persistent organic pollutants in Inuit children attending childcare centers in Nunavik, Canada. *Environ Sci Technol*. 46:4614-4623; 2012
- Umweltbundesamt. German Environmental Specimen Bank. 2013. Available at: <http://www.umweltbundesamt.de/en/portal/german-environmental-specimen-bank>
- UNEP. Results of the global survey on concentrations in human milk of persistent organic pollutants by the United Nations Environment Programme and the World Health Organization. UNEP/POPS/COP.6/INF/33. Geneva, 2013.

- Valera, B.; Jorgensen, M.E.; Jeppesen, C.; Bjerregaard, P. Exposure to persistent organic pollutants and risk of hypertension among Inuit from Greenland. *Environ Res.* 122:65-73; 2013
- Van Leeuwen, R.; Malisch, R. Results of the third round of the WHO coordinated exposure study on the levels of PCBs, PCDDs, and PCDFs in human milk. *Organohalogen Compounds* 56:311-316; 2002
- Vassiliadou, I.; Costopoulou, D.; Ferderigou, A.; Leondiadis, L. Levels of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) in blood samples from different groups of adults living in Greece. *Chemosphere.* 80:1199-1206; 2010
- Weihe, P.; Kato, K.; Calafat, A.M.; Nielsen, F.; Wanigatunga, A.A.; Needham, L.L.; Grandjean, P. Serum concentrations of polyfluoroalkyl compounds in Faroese whale meat consumers. *Environ Sci Technol.* 42:6291-6295; 2008
- Wilhelm, M.; Ewers, U.; Wittsiepe, J.; Furst, P.; Holzer, J.; Eberwein, G.; Angerer, J.; Marczyński, B.; Ranft, U. Human biomonitoring studies in North Rhine-Westphalia, Germany. *Int J Hyg Environ Health.* 210:307-318; 2007
- Windham, G.C.; Pinney, S.M.; Sjodin, A.; Lum, R.; Jones, R.S.; Needham, L.L.; Biro, F.M.; Hiatt, R.A.; Kushi, L.H. Body burdens of brominated flame retardants and other persistent organo-halogenated compounds and their descriptors in US girls. *Environ Res.* 110:251-257; 2010
- Wittsiepe, J.; Schrey, P.; Lemm, F.; Eberwein, G.; Wilhelm, M. Polychlorinated dibenzo-p-dioxins/polychlorinated dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), and organochlorine pesticides in human blood of pregnant women from Germany. *J Toxicol Environ Health A.* 71:703-709; 2008
- Vizcaino, E.; Grimalt, J.O.; Lopez-Espinosa, M.J.; Llop, S.; Rebagliato, M.; Ballester, F. Polybromodiphenyl ethers in mothers and their newborns from a non-occupationally exposed population (Valencia, Spain). *Environ Int.* 37:152-157; 2011

Water (5.2.3)

Ahrens, L. (2011). "Polyfluoroalkyl compounds in the aquatic environment: A review of their occurrence and fate." Journal of Environmental Monitoring **13**(1): 20-31.

Ahrens, L., et al. (2009). "Longitudinal and latitudinal distribution of perfluoroalkyl compounds in the surface water of the Atlantic Ocean." Environmental Science and Technology **43**(9): 3122-3127.

Ahrens, L., et al. (2009). "Polyfluorinated compounds in waste water treatment plant effluents and surface waters along the River Elbe, Germany." Marine Pollution Bulletin **58**(9): 1326-1333.

Ahrens, L., et al. (2010). "Sources of polyfluoroalkyl compounds in the North Sea, Baltic Sea and Norwegian Sea: Evidence from their spatial distribution in surface water." Marine Pollution Bulletin **60**(2): 255-260.

Ahrens, L., et al. (2009). "Determination of polyfluoroalkyl compounds in water and suspended particulate matter in the river Elbe and North Sea, Germany." Frontiers of Environmental Science and Engineering in China **3**(2): 152-170.

Ahrens, L., et al. (2010). "Distribution of perfluoroalkyl compounds in seawater from Northern Europe, Atlantic Ocean, and Southern Ocean." Chemosphere **78**(8): 1011-1016.

Backe, W. J., et al. (2013). "Zwitterionic, Cationic, and Anionic Fluorinated Chemicals in Aqueous Film Forming Foam Formulations and Groundwater from U.S. Military Bases by Nonaqueous Large-Volume Injection HPLC-MS/MS." Environmental Science & Technology **47**(10): 5226-5234.

Benskin, J. P., et al. (2010). "Isomer profiling of perfluorinated substances as a tool for source tracking: A review of early findings and future applications." Reviews of Environmental Contamination and Toxicology **208**: 111-160.

Benskin, J. P., et al. (2009). "Isomer-specific biotransformation rates of a perfluorooctane sulfonate (PFOS)-precursor by cytochrome P450 isozymes and human liver microsomes."

Environmental Science and Technology **43**(22): 8566-8572.

Benskin, J. P., et al. (2012). "Perfluorinated compounds in the Arctic and Atlantic Oceans." Environ. Sci. Technol.

Benskin, J. P., et al. (2010). "Perfluorinated acid isomer profiling in water and quantitative assessment of manufacturing source." Environmental Science and Technology **44**(23): 9049-9054.

Bertrand, O. R. A., et al. (2013). Enrichment of perfluoroalkyl substances (PFAS) in Arctic sea ice. Poster presentation at the 23rd Annual Meeting of SETAC Europe, Glasgow, UK. May 12-16

Cai, M., et al. (2012). " Occurrence of perfluoroalkyl compounds in surface waters from the North Pacific to the Arctic Ocean." Environ. Sci. Technol. **46**: 661–668.

D'Eon, J. C. and S. A. Mabury (2007). "Production of perfluorinated carboxylic acids (PFCAs) from the biotransformation of polyfluoroalkyl phosphate surfactants (PAPS): Exploring routes of human contamination." Environmental Science and Technology **41**(13): 4799-4805.

D'Agostino, L. A. and S. A. Mabury (2013). "Identification of Novel Fluorinated Surfactants in Aqueous Film Forming Foams and Commercial Surfactant Concentrates." Environmental Science & Technology **48**(1): 121-129.

De Silva, A. O., et al. (2011). "Detection of a cyclic perfluorinated acid, perfluoroethylcyclohexane sulfonate, in the great lakes of North America." Environmental Science and Technology **45**(19): 8060-8066.

De Solla, S. R., et al. (2012). "Highly elevated levels of perfluorooctane sulfonate and other perfluorinated acids found in biota and surface water downstream of an international airport, Hamilton, Ontario, Canada." Environment International **39**(1): 19-26.

Earnshaw, M. R., et al. (2014). "Comparing measured and modelled PFOS concentrations in a

UK freshwater catchment and estimating emission rates." Environment International **70**(0): 25-31.

Furdui, V. I., et al. (2008). "Trace level determination of perfluorinated compounds in water by direct injection." Chemosphere **73**(1 SUPPL.): S24–S30.

Gobas, F., et al. (2009). "Revisiting Bioaccumulation Criteria For POPs and PBT Assessments." Integ. Environ. Assess. Manag. **5**(4): 624-637.

Hansen, K. J., et al. (2002). "Quantitative characterization of trace levels of PFOS and PFOA in the Tennessee river." Environmental Science and Technology **36**(8): 1681-1685.

Huset, C. A., et al. (2008). "Occurrence and mass flows of fluorochemicals in the Glatt Valley Watershed, Switzerland." Environmental Science and Technology **42**(17): 6369-6377.

ICES (2005). Results for perfluorooctane sulfonate in seawater from the North Sea. Copenhagen, DK, International Council for Exploration of the Sea.

Jurado, E., et al. (2007). "Fate of persistent organic pollutants in the water column: does turbulent mixing matter?" Mar. Poll. Bull. **54**: 441-451.

Kallenborn, R., et al. (2004). Perfluorinated Alkylated Substances (PFAS) in the Nordic Environment, Nordic Council of Ministers: 107 pp.

Kim, S. K. and K. Kannan (2007). "Perfluorinated acids in air, rain, snow, surface runoff, and lakes: Relative importance of pathways to contamination of urban lakes." Environmental Science and Technology **41**(24): 8328-8334.

Kirchgeorg, T., et al. (2010). "Perfluorinated compounds in marine surface waters: Data from the Baltic Sea and methodological challenges for future studies." Environmental Chemistry **7**(5): 429-434.

Konwick, B. J., et al. (2008). "Concentrations and patterns of perfluoroalkyl acids in Georgia, USA surface waters near and distant to a major use source." Environmental Toxicology and Chemistry **27**(10): 2011-2018.

Loos, R., et al. (2008). EU Wide Monitoring Survey of Polar Persistent Pollutants in European River Waters, European Commission, Joint Research Centre, Institute for Environment and Sustainability: 51 pp.

Loos, R., et al. (2008). "Analysis of perfluorooctanoate (PFOA) and other perfluorinated compounds (PFCs) in the River Po watershed in N-Italy." Chemosphere **71**(2): 306-313.

Martin, J. W., et al. (2010). "PFOS or PreFOS? Are perfluorooctane sulfonate precursors (PreFOS) important determinants of human and environmental perfluorooctane sulfonate (PFOS) exposure?" Journal of Environmental Monitoring **12**(11): 1979-2004.

Martin, J. W., et al. (2006). "Atmospheric chemistry of perfluoroalkanesulfonamides: Kinetic and product studies of the OH radical and Cl atom initiated oxidation of N-ethyl perfluorobutanesulfonamide." Environmental Science and Technology **40**(3): 864-872.

Miyake, Y., et al. (2007). "Determination of trace levels of total fluorine in water using combustion ion chromatography for fluorine: A mass balance approach to determine individual perfluorinated chemicals in water." Journal of Chromatography A **1143**(1-2): 98-104.

Möller, A., et al. (2010). "Distribution and sources of polyfluoroalkyl substances (PFAS) in the River Rhine watershed." Environmental Pollution **158**(10): 3243-3250.

Moody, C. A., et al. (2001). "Determination of perfluorinated surfactants in surface water samples by two independent analytical techniques: liquid chromatography/tandem mass spectrometry and ¹⁹F NMR." Anal Chem **73**(10): 2200-2206.

Moody, C. A., et al. (2002). "Monitoring perfluorinated surfactants in biota and surface water samples following an accidental release of fire-fighting foam into Etobicoke Creek." Environmental Science and Technology **36**(4): 545-551.

Muir, D. and R. Lohmann (2013). "Water as a new matrix for global assessment of hydrophilic POPs." TrAC - Trends in Analytical Chemistry **46**: 162-172.

Muir, D. C. G., et al. (2008). Perfluoroalkyl acids in waters of the Canadian archipelago and Arctic Ocean. Presented at the SETAC Europe Annual Meeting, Warsaw, Poland May 23-26 2008. MO 240.

Paul, A. G., et al. (2012). "Estimating the aquatic emissions and fate of perfluorooctane sulfonate (PFOS) into the river Rhine." Journal of Environmental Monitoring **14**(2): 524-530.

Plumlee, M. H., et al. (2009). "Indirect Photolysis of Perfluorochemicals: Hydroxyl Radical-Initiated Oxidation of N-Ethyl Perfluorooctane Sulfonamido Acetate (N-EtFOSAA) and Other Perfluoroalkanesulfonamides." Environmental Science & Technology **43**(10): 3662-3668.

Quinete, N., et al. (2009). "Determination of perfluorooctane sulfonate and perfluorooctanoic acid in the rhine river, Germany." Fresenius Environmental Bulletin **18**(7 B): 1356-1362.

Reagen, W. K., et al. (2007). Environmental characterization of 3M electrochemical fluorination derived perfluorooctanoate and perfluorooctanesulfonate. Society of Environmental Toxicology and Chemistry 28th North American meeting, 11-15 Nov, 2007. Milwaukee, WI, USA.

Rumsby, P. C., et al. (2009). "Perfluorooctane sulphonate and perfluorooctanoic acid in drinking and environmental waters." Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences **367**(1904): 4119-4136.

Schultz, M. M., et al. (2006). "Fluorochemical Mass Flows in a Municipal Wastewater Treatment Facility." Environ. Sci. Technol. **40**(23): 7350-7357.

Scott, B. F., et al. (2010). "Perfluoroalkyl acids in Lake Superior water: Trends and sources." Journal of Great Lakes Research **36**(2): 277-284.

Scott, B. F., et al. (2009). "Perfluorinated alkyl acid concentrations in Canadian rivers and

creeks." Water Quality Research Journal of Canada **44**(3): 263-277.

Skutlarek, D., et al. (2006). "Perfluorinated surfactants in surface and drinking waters." Environmental Science and Pollution Research **13**(5): 299-307.

Stemmler, I. and G. Lammel (2009). "Cycling of DDT in the global environment 1950-2002: World ocean returns the pollutant." Geophysical Research Letters **36**(24).

Stock, N. L., et al. (2007). "Perfluoroalkyl contaminants in the Canadian Arctic: Evidence of atmospheric transport and local contamination." Environ. Sci. Technol. **41**: 3529-3536.

Taniyasu, S., et al. (2005). "Analysis of fluorotelomer alcohols, fluorotelomer acids, and short- and long-chain perfluorinated acids in water and biota." Journal of Chromatography A **1093**(1-2): 89-97.

Theobald, N., et al. (2007). Development and validation of a method for the determination of polyfluorinated organic substances in sea water, sediments and biota. Occurrence of these compound in the North and Baltic Seas. Executive summary. Hamburg, Germany, German Federal Maritime and Hydrographic Agency: 9 pp.

Tomy, G. T., et al. (2004). "Biotransformation of N-Ethyl Perfluorooctanesulfonamide by Rainbow Trout (*Onchorhynchus mykiss*) Liver Microsomes." Environmental Science and Technology **38**(3): 758-762.

Xie, Z., et al. (2013). "Neutral poly- and perfluoroalkyl substances in air and seawater of the North Sea." Environ. Sci. Pollut. Res. **20**: 7988-8000.

Xu, L., et al. (2004). "Biotransformation of N-Ethyl-N-(2-hydroxyethyl)perfluorooctanesulfonamide by rat liver microsomes, cytosol, and slices and by expressed rat and human cytochromes P450." Chemical Research in Toxicology **17**(6): 767-775.

Yamashita, N., et al. (2004). "Analysis of perfluorinated acids at parts-per-quadrillion levels in

seawater using liquid chromatography-tandem mass spectrometry." Environmental Science and Technology **38**(21): 5522-5528.

Zhao, Z., et al. (2012). "Distribution and long-range transport of polyfluoroalkyl substances in the Arctic, Atlantic Ocean and Antarctic coast." Environmental Pollution **170**: 71-77.

Other Media (5.2.4)

Note: More detailed references are presented in Annex 4. The following list includes the reports that have provided the main base for this summary.

AMAP, 2014. Trends in Stockholm Convention Persistent Organic Pollutants (POPs) in Arctic Air, Human media and Biota. AMAP Technical Report to the Stockholm Convention. AMAP Technical Report No. 7 (2014), Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway.

de Wit, C.A. , A.T. Fisk, K.E. Hobbs, D.C.G. Muir, G.W. Gabrielsen, R. Kallenborn et al. (2004) AMAP Assessment 2002. Persistent Organic Pollutants in the Arctic, AMAP, Oslo, 2004 Norway xvi+310pp.

ECA report (2009). Persistent Organic Pollutants (POPs) in the Antarctic environment A Review of Findings by The SCAR Action Group on Environmental Contamination in Antarctica. R. Fuoco, G. Capodaglio, B Muscatello and M. Radaelli a Department of Chemistry and Industrial Chemistry, University of Pisa (Italy), Department of Environmental Sciences, University of Venice (Italy) February 2009 .

Environment Canada and the U.S. Environmental Protection Agency. 2014. State of the Great Lakes 2011. Cat No. En161-3/1-2011E-PDF. EPA 950-R-13-002. Available at <http://binational.net>

HELCOM 2010 Hazardous substances in the Baltic Sea – An integrated thematic assessment of hazardous substances in the Baltic Sea. Balt. Sea Environ. Proc. No. 120B.

Kelly BC, Ikonomou MG, Blair JD, Gobas FA. 2008. Bioaccumulation behaviour of polybrominated diphenyl ethers (PBDEs) in a Canadian Arctic marine food web. *Sci. Total. Environ.* 401: 60-72.

Kelly BC, Ikonomou MG, Blair JD, Surridge B, Hoover D, Grace R, Gobas FAPC. 2009. Perfluoroalkyl contaminants in an arctic marine food web: Trophic magnification and wildlife exposure. *Environ. Sci. Technol.* 43: 4037-4043.

Law, R., Hanke, G., Angelidis, M., Batty, J., Bignert, A., Dachs, J., Davies, I., Denga, A., Duffek, B., Herut, H., Hylland, K., Lepom, P., Leonards, P., Mehtonen, J., Piha, M., Roose, P., Tronczynski, J., Velikova, V. and Vethaak, D. (2010). Marine Strategy Framework Directive - Task Group 8 Report Contaminants and pollution effects. EUR 24335 EN - Joint Research Centre Scientific and Technical Reports. Luxembourg: Office for official Publications of the European Communities, 2010. 161pp. Scientific and Technical Research series, ISSN 978-92-79-15648-9. DOI 10.2788/85887

Letcher, R.J., J.O. Bustnes, R. Dietz, B.M. Jenssen, E.H. Jørgensen, C. Sonne, J. Verreault, M.M. Vijayan, G.W. Gabrielsen (2010). Exposure and effects assessment of persistent organohalogen contaminants in arctic wildlife and fish. *Science of the Total Environment* 408 (2010) 2995-3043

NCP 2013. Canadian Arctic Contaminants Assessment Report On Persistent Organic Pollutants – 2013.

Muir D, Kurt-Karakus P, Stow J. (Eds). Northern Contaminants Program, Aboriginal Affairs and Northern Development Canada, Ottawa ON. xxiii k+ 487 pp + Annex

OSPAR 2009a. CEMP assessment report: 2008/2009 Assessment of trends and concentrations of selected hazardous substances in sediments and biota, OSPAR Commission, 2009. OSPAR Publication 390/2009. ISBN 978-1-906840-30-3.

OSPAR 2009b. Background Document on Assessment Criteria used for assessing CEMP Monitoring Data for the Concentrations of Hazardous Substances in Marine Sediments and Biota in the Context of QSR 2010. OSPAR Publication 461/2009. ISBN 978-1-907390-08-1.

OSPAR 2012a. Finding common ground Towards regional coherence in implementing the Marine Strategy Framework Directive in the North-East Atlantic region through the work of the OSPAR Commission. OSPAR publication 578/2012 ISBN 978-1-909159-12-9"

OSPAR 2012b. MSFD Advice document on Good environmental status - Descriptor 8:Contaminants.Version of 2 March 2012 Prepared by the OSPAR Committee of Hazardous Substances and Eutrophication (HASEC). OSPAR publication 584/2012. ISBN 978-1-909159-17-4

OSPAR 2012c. Comprehensive Atmospheric Monitoring Programme. Deposition of air pollutants around the North Sea and the North-East Atlantic in 2010. OSPAR publication 564/2012. ISBN 978-1-907390-79-1

OSPAR 2013a.. Comprehensive Atmospheric Monitoring Programme in 2011, OSPAR Publication 597/2013. ISBN 978-1-909159-30-3

OSPAR 2013b. Riverine Inputs and Direct Discharges to Convention Waters - OSPAR Contracting Parties' RID 2011 Data Report. OSPAR. Publication 598/2013, ISBN 978-1-909159-31-0.

OSPAR 2013c. Levels and trends in marine contaminants and their biological effects – CEMP Assessment report 2012. OSPAR. Publication 596/2013, ISBN 978-1-909159-29-7.

Selliah S. Reiner E, Toner D, Dawood R, Farag R, Ali B. 2008. Northern Contaminants Quality Assurance Program: Synopsis of Research Conducted under the 2007-2008 Northern Contaminants Program. Indian and Northern Affairs Canada, Ottawa ON. p. 176-181.

UNEP/MAP-MED POL 2009. Hazardous substances in the Mediterranean an assessment of the MEDPOL Database (J.Pon , C. Murciano, J. Albaigés) final report 91 p.

LRT (5.3)

Arnot J, Brown TN, Wania F, Breivik K, McLachlan MS. Prioritizing chemicals and data requirements for screening-level exposure and risk assessment. *Environmental Health Perspectives* 2012, 120, 11, 1565-1570.

Bogdal C, Mueller CE, Buser AM, Wang Z, Scheringer M, Gerecke AC, Schmid P, Zennegg M, MacLeod M, Hungerbuhler K. Emissions of polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins, and polychlorinated dibenzofurans during 2010 and 2011 in Zurich, Switzerland. *Environmental Science & Technology* 2014, 48, 482-490.

Breivik K, Bestreng V, Rozovskay O, Pacyna JM. Atmospheric emissions of some POPs in Europe: A discussion of existing inventories and data needs. *Environmental Science & Policy* 2006 9, 7-8, 663-674.

Breivik K, Sweetman A, Pacyna JM, Jones KC. Towards a global historical emission inventory for selected PCB congeners – a mass balance approach. 3. An update. *Science of the Total Environment* 2007, 377 (2-3), 296-307.

Buser AM, Kierkegaard A, Bogdal C, MacLeod M, Scheringer M, Hungerbuhler K. Concentrations in ambient air and emissions of cyclic volatile methylsiloxanes in Zurich, Switzerland. *Environmental Science & Technology* 2013, 47 (13), 7045–7051.

Buser AM, Bogdal C, MacLeod M, Scheringer M. Emissions of decamethylcyclopentasiloxane from Chicago. *Chemosphere* 2014, 107, 473-475.

Cousins IT, Kong D, Vestergren R. Reconciling measurement and modelling studies of the sources and fate of perfluorinated carboxylates. *Environmental Chemistry* 2010, 8 (4), 339-354.

Diamond ML, Melymuk L, Csiszar SA, Robson M. Estimation of PCB stocks, emissions, and urban fate: Will our policies reduce concentrations and exposure? *Environmental Science & Technology* 2010, 44 (8), 2777-2783.

Gasic B, Moeckel C, MacLeod M, Brunner J, Scheringer M, Jones KC, Hungerbuhler K. Measuring and modeling short-term variability of PCBs in air and characterization of urban source strength in Zurich, Switzerland. *Environmental Science & Technology* 2009, 43 (3), 769–776.

Gasic B, MacLeod M, Klanova J, Scheringer M, Illic P, Lammel G, Pajovic A, Breivik K, Holoubek I, Hungerbuhler K. Quantification of sources of PCBs to the atmosphere in urban areas: A comparison of cities in North America, Western Europe and former Yugoslavia. *Environmental Pollution* 2010, 10, 3230-3235.

Gusev A, MacLeod M, Bartlett P. Intercontinental transport of persistent organic pollutants: A review of key findings and recommendations of the Task Force on Hemispheric Transport of Air Pollutants and directions for future research. *Atmospheric Pollution Research* 2012, 3, 463-465.

Grennfelt P, Engleryd A, Munthe J, and Håård U. Saltsjöbaden V – Taking international air pollution policies into the future. Nordic Council of Ministers 2013, <http://dx.doi.org/10.6027/TN2013-571>.

Hung H, MacLeod M, Guardans R, Scheringer M, Barra R, Harner T, Zhang G. Toward the next generation of air quality monitoring: Persistent organic pollutants. *Atmospheric Environment* 2013, 80, 591-598.

Li YF. Global technical hexachlorocyclohexane usage and its contamination consequences in the environment: From 1948 to 1997. *Science of the Total Environment* 1999, 232 (3), 121–158.

MacLeod M, Scheringer M, Podey H, Jones KC, Hungerbuhler K. The origin and significance of short-term variability of semivolatile contaminants in air. *Environmental Science & Technology* 2007, 41 (9), 3249-3253.

Moeckel C, Gasic B, MacLeod M, Scheringer M, Jones KC, Hungerbuhler K. Estimation of the source strength of polybrominated diphenyl ethers based on their diel variability in air in Zurich, Switzerland. *Environmental Science & Technology* 2010, 44 (11), 4225–4231.

Paul AG, Jones KC, Sweetman AJ. A first global production, emission and environmental inventory for perfluorooctane sulfonate. *Environmental Science & Technology* 2009, 43 (2), 386-392.

Prevedouros K, Cousins, IT, Buck R, Korzeniowski SH. Sources, fate and transport of perfluorocarboxylates. *Environmental Science & Technology* 2006, 40 (1), 32-44.

Schenker U, Scheringer M, Hungerbuhler K. Investigating the global fate of DDT: Model evaluation and estimation of future trends. *Environmental Science & Technology* 2008, 42 (4), 1178-1184.

Semeena S, Lammel G. Effects of various scenarios of entry of DDT and gamma-HCH on the global environmental fate as predicted by a multicompartment chemistry-transport model. *Fresenius Environmental Bulletin* 2003, 12 (8), 925-939.

UNECE (United Nations Economic Commission for Europe). Hemispheric Transport of Air Pollutants 2010, Part C: Persistent Organic Pollutants. Air Pollution Studies No. 19, Edited by S Dutchak and A Zuber. EC/EB.AIR/102, United Nations Publication, New York.
<http://www.htap.org/>

Wang Z, Scheringer M, MacLeod M, Bogdal C, Mueller CE, Gerecke AC, Hungerbuhler K. Atmospheric fate of poly- and perfluorinated alkyl substances (PFAS): II. Emission source strength in summer in Zurich, Switzerland. *Environmental Pollution* 2012, 169, 204–209.

Wang Z, Cousins IT, Scheringer M, Buck RC, Hungerbuhle K. Global emission inventories for C4–C14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, Part I: Production and emissions from quantifiable sources. *Environment International* 2014, 69 (in press).

Wang Z, Cousins IT, Scheringer M, Buck RC, Hungerbuhle K. Global emission inventories for C4–C14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, Part II: The remaining pieces of the puzzle. *Environment International* 2014, 69, 166-176.

Wöhrnschimmel H, Tay P, von Waldow H, Hung H, Li, YF, MacLeod M, Hungerbühler K. Comparative assessment of the global fate of alpha- and beta-hexachlorocyclohexane before and after phase-out. *Environmental Science and Technology* 2012, 46, 4, 2047-2054.

Zhang X, Diamond ML, Robson M, Harrad S. Sources, emissions and fate of polybrominated diphenyl ethers and polychlorinated biphenyls indoors in Toronto, Canada. *Environmental Science & Technology* 2011 45 (8) 3268-3274.

8 ANNEX

The following annexes to the WEOG report contain supplementary information and data. These annexes are available as separate documents.

8.1 Ambient Air

8.2 Human Tissues

8.3 Water

8.4 Other Media

8.5 AMAP Trends Report - <http://www.amap.no/documents/doc/Trends-in-Stockholm-Convention-Persistent-Organic-Pollutants-POPs-in-Arctic-Air-Human-media-and-Biota/1081>