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on Persistent Organic
Pollutants**

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Item 5 (i) of the provisional agenda*

**Matters related to the implementation of the
Convention: effectiveness evaluation**

Second global monitoring report

Note by the Secretariat

As referred to in the note by the Secretariat on the global monitoring plan for effectiveness evaluation (UNEP/POPS/COP.8/21), the second global monitoring report prepared by the global coordination group is set out in the annex to the present note. The executive summary of the report, including the conclusions and recommendations of the global coordination group, is also reproduced in the six official languages of the United Nations in document UNEP/POPS/COP.8/21/Add.1. The present note, including its annex, has not been formally edited.

* UNEP/POPS/COP.8/1.

Annex

Second global monitoring report

JANUARY 2017

SECOND GLOBAL MONITORING REPORT



**GLOBAL MONITORING PLAN
FOR PERSISTENT ORGANIC POLLUTANTS**

UNDER THE STOCKHOLM CONVENTION ARTICLE 16 ON EFFECTIVENESS EVALUATION

UN 
environment


Stockholm Convention

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Air monitoring activities are implemented in the five UN regions in cooperation with strategic partners: the Arctic Monitoring and Assessment Programme (AMAP), the Global Atmospheric Passive Sampling (GAPS) Network, the East Asia Air Monitoring Programme, the European Monitoring and Evaluation Programme (EMEP), the Integrated Atmospheric Deposition Network (IADN), the Great Lakes Basin Monitoring programme, and the MONET Programme of the Research Centre for Toxic Compounds in the Environment (RECETOX). Thanks are also extended to those involved in maintaining the sampling sites and collecting the samples at the national level.

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The human milk survey draws on the collaboration between the Secretariat of the Stockholm Convention, the United Nations Environment Programme (UNEP) Division of Technology, Industry and Economics (DTIE) Chemicals Branch and the World Health Organization (WHO). The State Institute for Chemical and Veterinary Analysis of Food (CVUA), Freiburg, Germany, is acknowledged for the analytical work related to human milk samples. The MTM Research Centre, Örebro University, Sweden, is acknowledged for the analysis and provision of data on perfluorinated chemicals in human milk. Thanks are also expressed to the national coordinators of the joint WHO/UNEP exposure study for the work to collect and process the human milk samples.

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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 national 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 or public health 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 one asterisk in footnotes 1-3). Two additional chemicals were listed in 2011 and in 2013 (two or three asterisks in footnotes 1-3, respectively). POPs listed at the seventh meeting of the Conference of the Parties in 2015 are not yet addressed in this report.

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 POPs. This evaluation is to be based on comparable and consistent monitoring data on the presence of POPs in the environment and in humans, as well as on 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 identify changes in concentrations of POPs over time, as well as information on their regional and global environmental transport.

The present global monitoring report synthesizes information from the first (2000-2008) and second (2009-2015) phase of the global monitoring plan and presents the current findings on POPs concentrations at the global scale. 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 initial POPs, this second global monitoring report 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. The report also addresses aspects relevant to long range transport of POPs and climate effects from a global perspective, and includes new information on both legacy POP compounds and new POPs from the newly implemented programmes in the second phase. Finally, an extensive global assessment of perfluorooctane sulfonic acid (PFOS) concentrations in water has been conducted in the second phase of the global monitoring plan and is included for the first time in the global monitoring report.

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 (PeCBz)*, **polychlorinated biphenyls (PCB)**.

³ **hexachlorobenzene (HCB)**, pentachlorobenzene (PeCB)*, **polychlorinated biphenyls (PCB)** and **polychlorinated dibenzo-*p*-dioxins (PCDD)** and **dibenzofurans (PCDF)**.

ABBREVIATIONS AND ACRONYMS

ACP	Arctic Contamination Potential
AMAP	Arctic Monitoring and Assessment Programme
BCF	Bioconcentration Factor
CEE	Central and Eastern Europe
COP	Conference of the Parties
CTD	Characteristic Travel Distance
CV	Coefficient of Variation
DDD /DDE	Metabolites of DDT
DDT	Dichlorodiphenyltrichloroethane
dl-PCB	Dioxin-like PCB
EDCs	Endocrine Disrupting Chemicals
EMAN	Ecological Monitoring and Assessment Network
EMEP	Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe
EPER	European Pollutant Emission Register
ERL	Effects Range Low
ERM	Effects Range Median
EROD	7-ethoxyresorufin-O-deethylase
EtFOSA	N-ethyl-perfluoroalkane sulfonamide
EtFOSE	N-ethyl perfluoroalkanesulfonamidoethanol
EUSES	European Union System for the Evaluation of Substances
FAO	Food and Agriculture Organization of the United Nations
GAPS	Global Atmospheric Passive Sampling
GEF	Global Environment Facility
GEMS	Global Environment Monitoring System
GLB	Environment Canada's Air Monitoring in the Great Lakes Basin
GLBTS	Great Lakes Bi-national Toxics Strategy
GMP	Global Monitoring Plan
FOSA	Perfluorooctane sulfonamide
HBCD	Hexabromocyclododecane
HCB	Hexachlorobenzene
HCBD	Hexachlorobutadiene
HELCOM	Helsinki Commission/The Baltic Marine Environment Protection Commission
HCHs	Hexachlorocyclohexanes
HIPS	High Impact Polystyrene
HPLC	High Performance Liquid Chromatography
HRGC	High Resolution Gas Chromatograph(y) (capillary column)
HRMS	High Resolution Mass Spectrometer/-metry
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
IMO	International Maritime Organization

INSPQ	Centre de Toxicologie du Québec
INFOCAP	Information Exchange Network on Capacity Building for the Sound Management of Chemicals
IPPC	Integrated Pollution Prevention and Control
I-TEQ	International Toxicity Equivalence
K _{AW}	Air/Water Partition Coefficient
K _{OA}	Octanol/Air Partition Coefficient
K _{OW}	Octanol/Water Partition Coefficient
LC ₅₀	Median Lethal Concentration
LD ₅₀	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
L RTP	Long Range Transport Potential
MDL	Minimum Detectable Level
MEDPOL	Mediterranean Pollution Monitoring and Research Programme
MEA	Multilateral Environmental Agreements
MeFOSA	N-methyl perfluoroalkane sulfonamide
MeFOSE	N-methyl perfluoroalkane sulfonamidoethanol
MRL	Maximum Residue Limit
MSCE-East	Meteorological Synthesizing Centre-East
NAFTA	North American Free Trade Agreement
NARAPs	North American Regional Action Plans
NDAMN	U.S. Environmental Protection Agency's National Dioxin Air Monitoring Network
ND	Not Detected
NGOs	Non-Governmental Organizations
NHATS	National Human Adipose Tissue Survey
NIS	Newly Independent States
NOAA	National Oceanic and Atmospheric Administration
NOAEL	No Observable Adverse Effect Level
NOEL	No Observable Effect Level
NWT	Northwest Territories
OCs	Organochlorines
OCPs	Organochlorine Pesticides
OECD	Organization for Economic Co-operation and Development
OPs	Organophosphates
OSPAR	Commission for the Protection of the Marine Environment of the North-East Atlantic
PAHs	Polycyclic aromatic hydrocarbons
PBDEs	Polybrominated diphenyl ethers
PCB	Polychlorinated biphenyls
PCDD	Polychlorinated dibenzo- <i>p</i> -dioxins
PCDF	Polychlorinated dibenzofurans

PCP	Pentachlorophenol
PeCBz	Pentachlorobenzene
PFOA	Perfluorooctanoate
PFOS	Perfluorooctane sulfonic acid
PIC	Prior Informed Consent
POPs	Persistent Organic Pollutants
PRTRs	Pollutant Release and Transfer Registers
PTS	Persistent Toxic Substances
PUF	Polyurethane Foam
PVC	Polyvinylchloride
QA/QC	Quality Assurance and Quality Control Regimes
QUASIMEME	Quality Assurance of Information for Marine Environmental Monitoring in Europe
REACH	Registration, Evaluation and Authorization of Chemicals
RECETOX	Research Centre for Environmental Chemistry and Ecotoxicology
RENAP	Regional Network on Pesticide Production in Asia and Pacific
ROGs	Regional Organization Groups for the Global Monitoring Plan
ROPME	Regional Organization for the Protection of the Marine Environment
ROWA	Regional Office for West Asia
SAICM	Strategic Approach to International Chemicals Management
SCCPs	Short-chain Chlorinated Paraffins
SOP	Standard Operating Procedure
SPM	Suspended Particulate Matter
SPREP	South Pacific Regional Environment Programme
t	Tonne(s)
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 Organization
WFD	Water Framework Directive
WHO	World Health Organization
WMO	World Meteorological Organization
WWTPs	Waste Water Treatment Plants
XAD	Styrene/divinylbenzene-co-polymer Resin

GLOSSARY OF TERMS

Activity	Any programme, project or activity that generates data or information on the concentrations of POPs in the environment or in humans that can contribute to the effectiveness evaluation under Article 16 of the Stockholm Convention
Core matrices	The sample types identified by the Conference of the Parties to the Stockholm Convention at its second meeting as recommended/essential for the first evaluation: A = ambient air; M = human (mothers') milk and / or B = human blood
CTD	The characteristic travel distance– defined as the “half-distance” for a substance present in a mobile phase
I L-1	Instrumentation level1 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)
I L-	Instrumentation level capable to analyze perfluorinated compounds at ultra-trace concentrations: liquid chromatography combined with two mass spectrometers or MS-TOF
Intercomparisons	Participation in national and international intercalibration activities such as ring-tests, proficiency tests or laboratory performance testing schemes
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 concentrations 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 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 conducted by the Conference of the Parties at its seventh meeting, information collected between 2009 and 2013.

EXECUTIVE SUMMARY

Introduction and background

The second phase of the global monitoring plan (GMP) was conducted in compliance with the amended global monitoring plan for persistent organic pollutants,⁴ the amended implementation plan for the global monitoring plan for persistent organic pollutants,⁵ and the updated guidance on the global monitoring plan.⁶

The second global monitoring report has been developed on the basis of the five regional monitoring reports⁷ by the GMP coordination group, with the assistance of invited experts. The report synthesizes information from the first (2000-2008) and second (2009-2015) phases of the GMP and presents the current findings on persistent organic pollutants (POPs) concentrations at the global scale.

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 initial POPs, the second global monitoring report provides first indications as to the changes over time in concentrations of the chemicals initially listed in the Convention, as well as baseline information on the newly listed POPs.

The report also addresses aspects relevant to long-range transport of POPs and climate effects from a global perspective, and includes new information on all POPs from the newly implemented programmes in the second phase.

An extensive global assessment of perfluorooctane sulfonic acid (PFOS) concentrations in water has been conducted in the second phase of the GMP and is included for the first time in the global monitoring report (see Chapter 6.3 and the annex).

Major achievements

Since its entry into force, the Stockholm Convention has catalyzed POPs monitoring activities and research worldwide and triggered increased awareness and knowledge about these chemicals.

These developments have been underpinned by increased POPs monitoring data availability and coverage at the global scale, most notably due to the capacity-building activities carried out in the regions, strategic partnerships in place between emerging and well-established monitoring programmes, increased national commitment and sustained donor support.

Long term viability of existing monitoring programmes (air and human bio-monitoring) was and continues to be essential to ensure that changes in concentrations over time can be investigated to support the evaluation of the effectiveness of the Convention.

The implementation of the GMP under the Convention channelled the development of harmonized guidance for monitoring activities worldwide, leading to enhanced comparability within and across monitoring programmes to evaluate changes in levels over time. Quality assurance/quality control practices (QA/QC) have been and continue to be essential for ensuring comparability, along with inter-laboratory comparison assessments.

A major focus of the second phase of the GMP has been to provide support to the regional organization groups (ROGs) with enhanced harmonized data handling for the collection, processing, storing and presentation of their data. A GMP data warehouse currently supports data handling and assists the regional organization groups and the global coordination group in

⁴ UNEP/POPS/COP.6/INF/31/Add.1.

⁵ UNEP/POPS/COP.6/INF/31/Add.2.

⁶ UNEP/POPS/COP.6/INF/31.

⁷ UNEP/POPS/COP.7/INF/38.

producing the regional and global monitoring reports. All monitoring data obtained in the frame of the GMP are publically available and represent a valuable resource for both policy makers and researchers worldwide.

Major findings

Long time series monitoring data of legacy POPs⁸ in air, human matrices and other media are available from Asia and the Pacific, Central and Eastern Europe (CEE) and Western Europe and Others Group (WEOG), while information on changes in concentrations over time is very limited in Africa and in Latin American and Caribbean Group (GRULAC). Information on changes over time in concentrations of the newly listed POPs⁹ is still limited.

The trend information available from Asia-Pacific, CEE and WEOG indicates that, overall, concentrations of POPs measured in air have largely decreased; a steep decrease in air concentrations of legacy POPs (organochlorine pesticides, polychlorinated biphenyls - PCB, polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans - PCDD/PCDF) seems to have followed their early regulation in the 1980s. By 2000, the majority of primary sources had been controlled and the relatively low levels that are currently measured do not show significant changes and are driven by secondary sources and, for some compounds, emissions from stockpiles/waste management practices.

In general, air concentrations of the newly listed POPs (such as polybrominated diphenyl ethers - PBDEs, PFOS, hexabromocyclododecane - HBCD, pentachlorobenzene - PeCBz) seem to show increases over the 1990s, then leveling off and decreasing in the early 2000s. Among these, hexachlorocyclohexanes (HCHs) are the only group of compounds that has sufficiently resolved monitoring data to assess time trends.

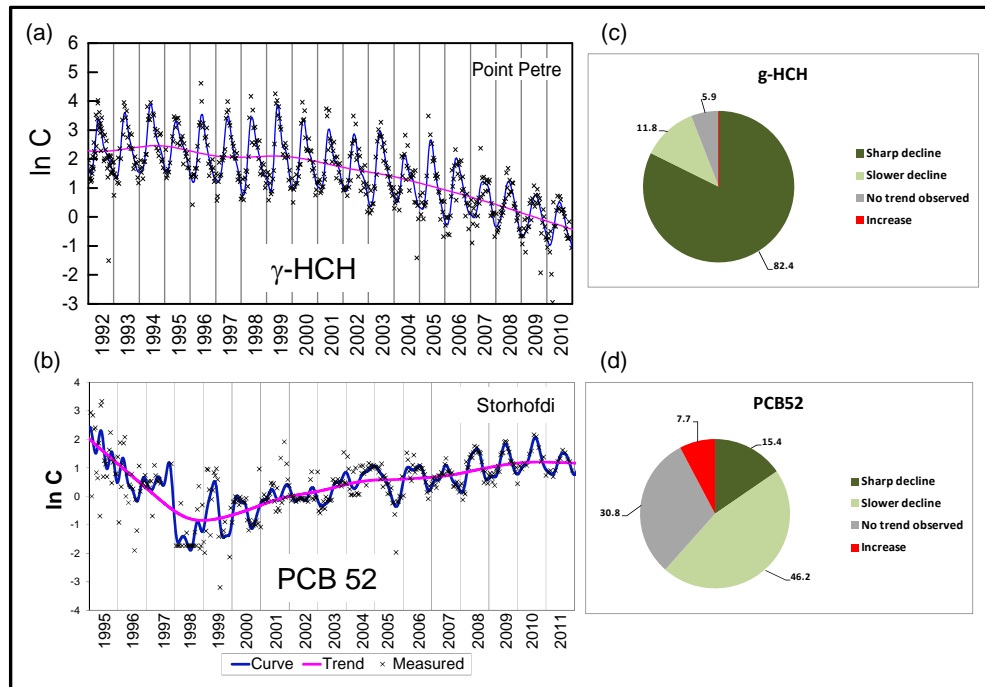
Changes over time in human exposure to these POPs show a similar pattern, but the decrease in some POPs seems to be more sustained than in air and is significant after 2000. Similar trends are observed for concentrations of POPs measured in other media.

Temporal trend information for PFOS in water is currently very limited. Differences in sampling locations and in detection limits currently preclude any robust assessment of trends of PFOS concentrations in water.

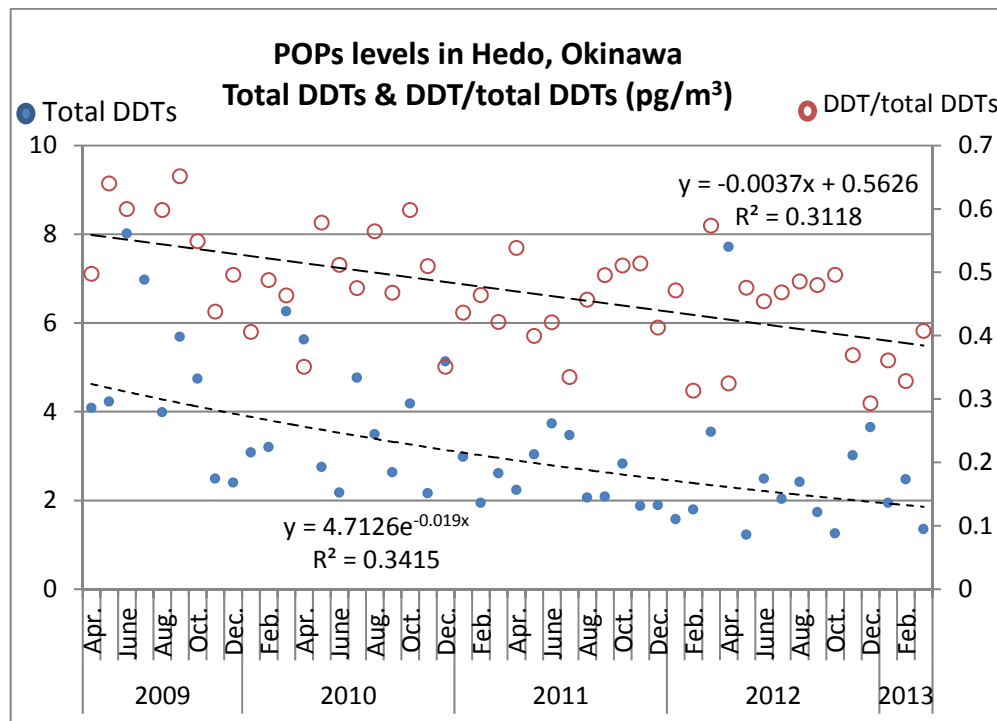
⁸ Those 12 chemicals listed when the Convention entered into force in 2004.

⁹ Those chemicals listed in the annexes to the Convention after 2004.

Time trends of (a) γ -HCH measured in air at the Canadian Great Lake site of Point Petre and (b) PCB 52 at the arctic station of Stórhöfði in Iceland. Also shown are the general summary pie charts of time trends observed in the WEOG region for (c) γ -HCH and (d) PCB 52. (Source: Western Europe and Others Group Region Report)



Changes in monthly total DDT levels in air and the ratios between DDT and total DDTs in Hedo, Okinawa. Total DDTs: sum of six isomers, i.e., *p,p'*- and *o,p'*-DDTs, DDEs and DDDs. DDT: sum of *p,p'*-DDT and *o,p'*-DDT



Changes over time in POPs concentrations measured in air and human matrices. Shadings indicates: **green** – generally decreasing trends; **red** – increasing trends; **blue** – no change or cannot establish trend; white – no trend data; **★** - warning to indicate limited data

Chemical	Air					Human matrices					
	Africa	Asia and the Pacific	Central and Eastern Europe	Latin American & Caribbean States	Western Europe and Other Groups	Africa	Asia and the Pacific	Central and Eastern Europe	Latin American & Caribbean States	Western Europe and Other Groups	
aldrin	Baseline data available	Mostly below LOD or poor recovery	Baseline data available at 2 sites	Baseline data available.	Decline in Great Lakes; no trend in Arctic ★	Below LOQ	Below LOD or <LOQ	Below LOQ	Below LOQ	Below LOD	
chlordanes	Baseline data available	Decreasing in Japan. Mostly below LOD in China ★	Baseline data available at 6 sites	Baseline data available.	Mostly declining trends	degradation product oxychlordan e detected	No decrease since 1998 in Japan; Oxychlordan e detected with decreasing levels over time in Fiji ★	degradation product oxychlordan e detected	degradation product oxychlordan e detected	degradation product oxychlordan e detected	
chlordecone	Bdl at all sites.	Below LOD in Japan.	Monitored at 1 site all below LOD.	Baseline data available.		-	-	-	-	-	
DDT and transformation products	No discernable trends	Decrease in Japan ★	Mostly no trend	Declining at 8 sites	Baseline data available.	Mostly declining trends	Baseline data available.	Decrease from 1972 to the first half of 1990s, then leveling off in Japan; Decreasing concentrations over time measured in Fiji ★	No detectable trend.	Declining concentrations in Haiti, no change in Chile ★	Declining trend in human milk (Swedish mothers), or below LOD
dieldrin	No discernable trends	No trend in Japan; Mostly below LOD in China; Baseline data available in other countries ★	Baseline data available at 4 sites	Baseline data available.	Decline in Great Lakes; no trend in Arctic	Baseline data available.	Declining trend in Japan; Decreasing concentrations over time measured in Fiji ★	Baseline data available	Declining concentrations measured over time in Haiti, Chile ★	Measured at low levels	

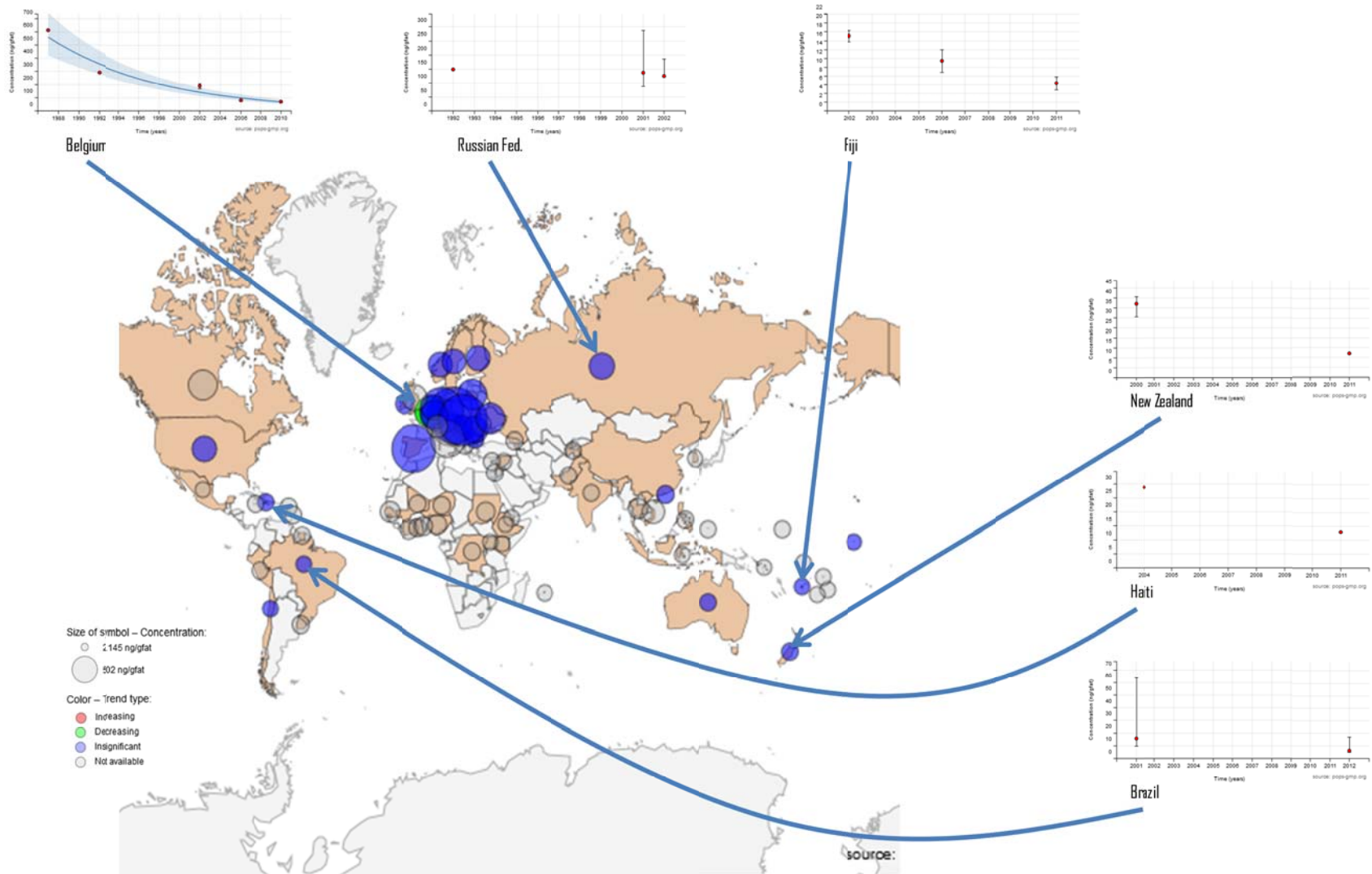
Chemical	Air					Human matrices						
	Africa	Asia and the Pacific	Central and Eastern Europe	Latin American & Caribbean States	Western Europe and Other Groups	Africa	Asia and the Pacific	Central and Eastern Europe	Latin American & Caribbean States	Western Europe and Other Groups		
endosulfan	Decreasing tendencies at 3 sites, not changing at others ★	Baseline data available in Fiji (below LOD) and Japan	Baseline data available at 4 sites	Baseline data available.	Decline in Europe and Great Lakes	No change in Arctic	alpha-endosulfan detected in one sample ; beta-endosulfan <LOQ; endosulfan sulphate measured in two samples	Baseline data available	Below LOQ	Below LOQ	Below LOD	
endrin	Baseline data available	No trend in Japan; Mostly below LOD in China; Baseline data available in other countries ★	Baseline data available at 2 sites	Baseline data available.	No discernable trend in the Arctic ★		Below LOQ	Below LOD or <LOQ	Below LOQ	Below LOQ	Below LOD	
HBB	Variable trends at different sites	Baseline data available in Fiji and Japan (below LOD)		Baseline data available.			Levels below LOQ but in one country	Baseline data available	Below LOQ	Below LOQ	Concentrations are low and mostly undetected	
HBCD	No discernable trends	Baseline data available in Fiji (below LOD) and Japan		Baseline data available.	Decreasing at 1 Arctic site. No trend in urban Great Lakes. Mostly below LOD at other sites ★		Baseline data available	Increasing concentrations measured over 1974-2006 in Japan	Baseline data available	Baseline data available	Increasing till 2002, then leveling off in 2003-2004 in Sweden	
HCB	Variable trends at different sites	No trend in Japan. Baseline data available in	Mostly no trend	Decreasing at 1 site	Baseline data available.	Very slow decline at most	Increasing in 2 Arctic	Baseline data available.	Decrease from 1980 to the first half of 1990s, then leveling	Significant decrease in concentrations from two	Decreasing concentrations over time measured in	Declining trend from German ESB data

Chemical	Air						Human matrices					
	Africa	Asia and the Pacific	Central and Eastern Europe		Latin American & Caribbean States	Western Europe and Other Groups		Africa	Asia and the Pacific	Central and Eastern Europe	Latin American & Caribbean States	Western Europe and Other Groups
		other countries ★		Increasing at 1 site		sites	sites		off in Japan; No change in levels in Fiji ★	consecutive years in the Czech Rep ★	Brazil, Haiti ★	
α-HCH	Decreasing tendency at all sites	Baseline data available.	Mostly no trend	Decreasing at 12 sites	Baseline data available.	Sharp decreases at most sites		Below LOQ		Baseline data available	Below LOQ	Below LOD
β-HCH	Baseline data available	Baseline data available	Mostly no trend	Decreasing at 6 sites	Baseline data available.	Concentrations very low and mostly below LOD ★		Baseline data available.	Decrease from 1972 to the first half of 1990s in Japan, then leveling off	Baseline data available	Decreasing concentrations over time measured in Brazil, Chile ★	levels of β-HCH detected, but not in all samples
γ-HCH	Variable trends at different sites	Baseline data available.	Mostly no trend	Decreasing at 20 sites	Baseline data available.	Sharp decreases at most sites		Baseline data available	Baseline data available	Baseline data available	Baseline data available	Measured at low levels
heptachlor	Baseline data available	Decreasing in Japan; Mostly below LOD in China; Baseline data available in other countries ★	Baseline data available at 4 sites		Baseline data available.	Decline in Great Lakes	No trend in Arctic	Baseline data available	Declining trend in Japan. Below LOD in Pacific islands and China	Below LOD for heptachlor and trans-heptachlorepoixide; decrease for cis-heptachlor suggested from two data points in the Czech Rep. ★	Baseline data available for trans-heptachlorepoixide	Metabolite detected
mirex	Baseline data available	No trend in Japan. Mostly below LOD in China. Baseline data available in other countries	Baseline data available at 2 sites		Baseline data available.	Declining in the Great Lakes ★		Below LOQ	Mostly below LOQ, measured at low levels in China	Below LOQ	Below LOQ	Below LOD

Chemical	Air					Human matrices						
	Africa	Asia and the Pacific	Central and Eastern Europe	Latin American & Caribbean States	Western Europe and Other Groups	Africa	Asia and the Pacific	Central and Eastern Europe	Latin American & Caribbean States	Western Europe and Other Groups		
PBDEs	No discernable trends	Baseline data available in Fiji and Japan	Baseline data available at 3 sites	Baseline data available.	Decreasing in Europe and some Great Lakes sites ★	No trend in Arctic Canada	Baseline data available.	Baseline data available.	Baseline data available.	Baseline data available.	Increasing concentrations in Nunavik (Canada); Concentrations reported to be leveling off or decreasing in Sweden and Norway; No significant time trend in Australia	
PCB	No discernable trends	Decreased in Japan 1974-1988 and remained at similar level since then. ★	Mostly no trend	Declining at 14 sites	Baseline data available.	Mostly declining. Slow decline in Great Lakes	Increasing at 1 Arctic site.	Baseline data available.	Decreasing trend from 1972 to 1990s in Japan, then leveling off; Decreasing concentrations in Fiji ★	Significant decrease in CEE countries that used PCB in paints ★	Declining concentrations measured over time in Haiti and Chile ★	Declining concentrations over time in human milk and blood
PCDD/PCDF	Variable trends at different sites	General reduction tendency	Baseline data available at 1 site	Baseline data available	Declining in the Alps and UK urban sites. No change at US sites and UK rural sites.	Baseline data available.	Declining trend in Japan till 1998, then leveling off	Decrease observed in several countries in the region	Declining concentrations measured over time in Haiti and Chile ★	Declining concentrations over time in human milk and blood		
PFOS		Baseline data available in Fiji and Japan	Baseline data available at 1 site	Only Uruguay reported air data	In Arctic air, PFOS shows no trend. PFOS precursors show no trend or are decreasing ★	Baseline data available	Two studies from Japan indicate: 1. concentrations have increased over the past 25 years; 2. concentrations in blood have decreased from 2003 to 2011	Baseline data available	Baseline data available	Declining trend in NHANES, declining as of 2000 in German ESB data, declining in Australia		

Chemical	Air					Human matrices				
	Africa	Asia and the Pacific	Central and Eastern Europe	Latin American & Caribbean States	Western Europe and Other Groups	Africa	Asia and the Pacific	Central and Eastern Europe	Latin American & Caribbean States	Western Europe and Other Groups
PeCBz	Variable trends at different sites	Baseline data available.	Decreasing at 1 site ★	Baseline data available.		Levels below LOQ but in one country	Baseline data available	Baseline data available	Baseline data available.	Below LOD
toxaphene		Baseline data available				Baseline data available	Mostly <LOQ, measured at low levels in China and Pacific Isl.	No significant change in concentrations from two data points in the Czech Rep. ★	Baseline data available	Measured at low levels

Trends in concentrations of indicator PCB in human milk (Sum 6 PCB; ng/g fat)



Conclusions and recommendations toward the third GMP phase

General considerations

Progress in the second phase of the Global Monitoring Plan (GMP)

1. The second phase of the GMP was conducted in compliance with the amended global monitoring plan for persistent organic pollutants,¹⁰ the amended implementation plan for the global monitoring plan for persistent organic pollutants,¹¹ and the updated guidance on the global monitoring plan.¹² These documents provided an appropriate framework and sufficient guidance to perform the required activities.

Recommendation: *Third phase of the global monitoring plan should continue to use the amended global monitoring plan, implementation plan and guidance document as its foundation.*

2. Since its entry into force the Stockholm Convention has triggered new POPs research and monitoring activities worldwide, and brought together research findings from around the world. Data availability and coverage has significantly increased at the global scale in the second phase of the GMP as compared with the first phase. In the first GMP report, temporal trends were available from a few regions with long time series monitoring data for some of the initial POPs listed under the Convention. Through sustained monitoring since the first phase of the GMP as of 2004, information on temporal trends is now becoming available globally. Furthermore, long-term monitoring programmes have enlarged the scope of their activities to cover newly listed POPs in addition to legacy POPs, and new programmes have emerged. Activities for sampling of PFOS in water have also been initiated as part of the second phase. In most cases, monitoring data show clear decreasing trends for legacy POPs, suggesting that, when regulations are established and implemented, they can successfully address global environmental contamination problems.

Recommendation: *Ensure sustainability of ongoing monitoring activities in the long term in developed and developing countries to provide the important information required to support the effectiveness evaluation of the Stockholm Convention. Intensify and diversify efforts as required to address remaining gaps in data coverage and to monitor new POPs as they are added to the Convention.*

3. Enhanced comparability within and across monitoring programmes, to evaluate changes in concentrations over time and the regional and global transport of POPs, was an important milestone in the second phase of the GMP. QA/QC practices have been and continue to be essential for ensuring comparability, along with inter-laboratory comparison exercises and intercalibration studies. A major focus of the work in the second phase of the GMP was to develop a GMP data warehouse to enhance data harmonization, accessibility and to support data handling by the regional organization groups and the global coordination group, and aiding in the production of regional and global monitoring reports.

Recommendation: *Efforts towards ensuring comparability and consistency in monitoring data at the global level should continue. The regional and global monitoring reports should be broadly shared and GMP data warehouse should be serviced and supported to support data handling in the frame of the GMP and to provide access to up-to-date POPs monitoring data.*

4. The GMP guidance document provides essential information supporting implementation of the Convention in the five UN regions. The guidance is continuously

¹⁰ UNEP/POPS/COP.6/INF/31/Add.1.

¹¹ UNEP/POPS/COP.6/INF/31/Add.2.

¹² UNEP/POPS/COP.6/INF/31.

updated to include the most recent technical and scientific information and to address monitoring needs for new chemicals (sampling and analysis), as they are listed in the Convention.

Recommendation: *The latest version of the guidance should always be used as the reference document.*

5. Sample archiving and sample banks have proven to be useful to address data needs for listed POPs to support the GMP and effectiveness evaluation and for screening studies on chemicals under consideration for listing.

Recommendation: *Monitoring programmes should be encouraged to maintain long-term sample archives for retrospective analysis.*

Capacity building

6. Systematic capacity building activities have been carried out in developing countries, including strategic partnerships with well-established monitoring programmes. Despite these efforts, several regions still have limited capacity to monitor POPs. The addition of new POPs to the Convention creates additional demand for training to implement and sustain POPs monitoring activities.

Recommendation: *There is need for further capacity building and training for sample collection and analysis, for data analysis, and for assessment of long-range transport. Regions maintaining or seeking to build capacity should be encouraged and supported to form and /or maintain strategic partnerships with existing monitoring programmes.*

7. ROGs in some regions have experienced challenges in coordination due to limitation in communication and access to information exchange infrastructure.

Recommendation: *There is need to strengthen regional communication and information exchange structures to enhance information sharing among the regional organization groups and to strengthen regional coordination. Parties should maintain updated lists of contact points internally and with the Secretariat.*

8. Limitations in sustained financial resources for existing monitoring programmes and new financial resources for programmes addressing data gaps are a major constraint in ensuring the sustainability of the GMP.

Recommendation: *Global monitoring of POPs, should be sustained in the long term to confirm decreasing concentrations of legacy POPs in the environment and in humans and to identify trends in the concentrations of the newly listed POPs. Continued support to monitoring programmes is required to ensure continuity of the monitoring activities including sampling, analysis and data QA/QC and storage, in order to provide adequate data to assess temporal trends and long-range transport of POPs, for existing and new monitoring activities.*

9. Data quality, consistency and comparability is key to assess temporal trends and evaluate effectiveness of measures that have been undertaken.

Recommendation: *Laboratories in programmes contributing monitoring data to the GMP should participate in international interlaboratory assessments.*

10. There is an abundance of untapped capacity in regions that could be used to enhance future work under the GMP.

Recommendation: *The ROGs and the regional centers should strive to improve intra-regional coordination among experts (including academia) to address GMP data requirements.*

Challenges

11. The growing list of POPs and chemicals proposed for listing adds pressure on monitoring programmes and analytical laboratories.

Recommendation: *Additional funding and resources will be needed to respond to pressures for analysis of new POPs. In addition, monitoring programmes may need to adjust their protocols and resources to better align with new priorities. Some pressure can be relieved by reducing analysis frequency for legacy POPs (e.g. PCB, organochlorine pesticides) where declining trends have been established, optimizing analytical methods, and establishing partnerships among laboratories to address specialized analytical needs. It is not necessary for every laboratory to be an expert for every class of POPs.*

12. In addition, alternatives to the listed POPs are being used without a sufficient evaluation of their potential POPs properties. Increased concentrations of some of these alternatives were monitored in some regions.

Recommendation: *To establish an effective link between the POPRC and the GMP on the issue of alternatives and make best use of the available monitoring data.*

13. Although the burden of individual POPs may be on the decline in some regions, the overall number of man-made chemicals present in environmental samples is increasing. Sensitive in vitro methods to assess some toxicity endpoints of mixtures in the environment are currently available and further developed. They are explored by some programmes to assess environmental impacts and health effects indicators.

Recommendation: *Strategies should be considered for making better connections between POPs monitoring and toxicity tests for the assessment of long term effects of mixtures in the environment.*

Monitoring activities to evaluate changes in POPs levels over time

Ambient Air

14. Significant improvements in global coverage in air monitoring data and new capacity for POPs monitoring have been realized in all regions as a result of the Stockholm Convention. These improvements are largely attributed to adoption of passive sampling techniques, the development of successful partnerships with existing passive monitoring programmes such as the Global Atmospheric Passive Sampling (GAPS), the MONitoring NETwork for POPs (MONET), the Latin American Passive Atmosphere Monitoring Network (LAPAN) and through the implementation of Global Environment Facility (GEF) and Strategic Approach to International Chemicals Management (SAICM) projects.

Recommendation: *Continue passive air sampling and capacity building in a sustainable manner to enhance information on temporal trends and to improve spatial coverage.*

15. Monitoring data for POPs in air are reported for all five UN regions. Some geographic regions (e.g. Europe) have very good spatial coverage while improvements in reporting/coverage is needed in some other regions.

Recommendation: *Spatial coverage of monitoring activities should improve in Central and Northern Africa, Russia, and large parts of Asia. Improved coordination and partnership with established programmes (e.g. the Arctic Monitoring and Assessment Programme - AMAP, the European Monitoring and Evaluation Programme - EMEP, GAPS, MONET, POPs Monitoring Programme in East Asian countries) is recommended as a means towards addressing data needs and to fill technical and data gaps in future GMP reporting.*

16. Long-term monitoring data are available for most legacy POPs from active air sampling programmes that predated the Stockholm Convention (e.g. AMAP, EMEP, the

Northern Contaminants Program - NCP, the Integrated Atmospheric Deposition Network - IADN/GLB). Several air monitoring programmes using active samplers have also been newly implemented to address the needs of the GMP (e.g. in China, Australia, East Asia and Africa). The GRULAC region is the only region that has not reported active air sampling results.

Recommendation: *Continue air monitoring using active samplers according to programme QA/QC protocols to ensure data consistency for trend development. The GRULAC region should strive to implement such air monitoring and deliver results from at least one station during the next phase of the GMP.*

17. For legacy POPs, baseline data are available for all regions. Among the newly listed POPs, HCHs are the only group of compounds that has adequately resolved time trends, largely due to their listing in various multilateral agreements predating the Stockholm Convention. Data are becoming available for the other newly listed POPs. However, for some of the newly listed POPs (e.g. HBCD, PFOS and its precursors) data are only available from a few monitoring programmes.

Recommendation: *Air monitoring for newly listed POPs should be continued and expanded to provide representative baselines and trends.*

18. There is a low reporting rate for some legacy POPs such as toxaphene and mirex. This is largely attributed to low abundance in air due to limited past uses (e.g. mirex), declining air concentrations coupled with the low volatility of these compounds and, in some cases, relatively high analytical costs (e.g. toxaphene).

Recommendation: *Regional experts should define monitoring priorities based on available resources and information on concentrations in air and emissions, while considering the GMP guidance document.*

19. In addition to the regional and global monitoring reports, international and global databases such as EBAS (<http://ebas.nilu.no/>) and the GMP data warehouse (<http://www.pops-gmp.org/visualization-2014/>) are important in compiling and making monitoring data accessible to international and national policy makers, to modelers for assessing fate and transport, and to the general public. These databases provide a long-term, publicly-available repository for these data.

Recommendation: *Databases need to be maintained and updated to ensure data quality, consistency and compatibility among databases, data continuity, and ease of access.*

20. Temporal trend data on POPs are available mainly from the long-term active air monitoring programmes. The Stockholm Convention triggered the implementation of passive air monitoring programmes to deliver additional information for assessing temporal trends.

Recommendation: *Continue air monitoring with both active and passive sampling methods to allow further development of long-term temporal trends.*

21. For most legacy POPs, concentrations in air have declined and continue to decline or remain at low levels due to restrictions on POPs that predated the Stockholm Convention. Primary emissions are believed to be the main driver for POPs levels in air, however secondary emissions (of previously deposited POPs) and climate factors can also influence temporal trends for POPs. For some chemicals, e.g. PCB, PBDEs and other new POPs, emissions continue from stockpiles, continued product usage and waste disposal/dismantling/ recycling practices.

Recommendation: *Factors that determine concentrations of POPs in air, including changes in primary and secondary emission sources and climate effects must be considered, e.g. with the help of models, in order to properly interpret observed trends.*

22. For many newer POPs (e.g. HBCD, endosulfan, PBDEs) concentrations in air are beginning to show declining tendencies although in a few instances, increasing and/or unchanging concentrations over time are observed.

Recommendation: *Continue air monitoring of newer POPs to develop trends.*

Human tissues (milk and blood)

23. Monitoring data for POPs in human matrices are reported with good geographical coverage. Since the entry into force of the Stockholm Convention, many countries have implemented harmonized protocols to generate consistent and comparable POPs monitoring data in human matrices, especially a large number of developing countries being included in the global UNEP/WHO human milk survey. Furthermore, valuable baseline and trend information on POPs concentrations in human blood from the Arctic region is contributed by the Arctic Monitoring and Assessment Programme.

Recommendation: *POPs monitoring in human matrices needs to be sustained in the long term in view of generating information on changes in concentrations over time to support effectiveness evaluation, and further efforts will be needed to fill remaining gaps.*

24. The global assessment of POPs concentrations in human matrices is made possible through the long term implementation of the UNEP/WHO milk survey that generate comparable data to evaluate changes over time. In addition, national and international long-term programmes (e.g. AMAP) monitoring chemicals in milk and/or blood are important for assessing time trends. The levels are often not directly comparable across regions or programmes due to different study designs and populations.

Recommendation: *Opportunities should be explored with incipient or planned human monitoring activities in regions to complement existing data sets under the GMP.*

25. Since the 1980s, PCDD/PCDF have been monitored in human milk, and PCB to a lesser extent. As of 2000, the full spectrum of the POPs listed in the Stockholm Convention and their transformation products have been analyzed in the frame of the UNEP/WHO human milk survey. Quantifiable concentrations are detected for all POPs with the exception of aldrin, chlordecone and endrin, although levels vary by orders of magnitude.

Recommendation: *Monitoring should be continued and expanded for newly listed POPs to provide the information needed to assess changes over time.*

26. In regions with sufficient data to evaluate changes over time, levels of legacy POPs including their transformation products, such as PCDD/PCDF, PCB, and DDT/DDE, have generally declined.

For newly listed POPs in the Stockholm Convention, information regarding changes over time in their concentrations in human matrices is very limited. Based on studies available from WEOG and Asia Pacific, the levels of PFOS and PBDEs seem to gradually decline.

Recommendation: *Monitoring should continue at the global level to further develop trends of legacy POPs and to evaluate trends for newly listed POPs.*

27. Although PFOS is measured at low concentrations in human milk and better detected in human blood, there is good correlation between measurement results in these two matrices.

Recommendation: Results for PFOS in both human milk and human blood can be used for assessing changes over time.

28. According to the GMP guidance and for the purpose of the effectiveness evaluation, pooled samples are analyzed to generate one data point per country in the frame of the UNEP/WHO human milk survey. The human milk surveys are scheduled to take place every five years. For the initial campaigns that have produced several pools or individual samples per country, the median concentration from all national samples is used.

Recommendation: This approach should continue to be used for consistency purposes.

29. Monitoring of human matrices cannot be implemented without the involvement of public health sector and ethical clearance. These arrangements often lead to delays in implementation at the national level.

Recommendation: Participating countries should facilitate communication between the environment and health sectors for smooth implementation of human monitoring programmes at the national level.

30. Sample archiving proved to be a useful tool for conducting retrospective analysis of the newly listed POPs.

Recommendation: Archiving of human samples should be encouraged as a cost effective means to generate a consistent set of baseline data for the POPs newly added to the Convention.

31. The most important criterion in the implementation of the global UNEP/WHO human milk survey is the selection of donors, who must be first-time mothers. This is the major criterion enabling comparison among data at the global scale and between years.

Recommendation: To enable comparison among different programmes/studies, the main criterion to be considered is the selection of first-time mothers as donors.

32. The partnerships with the WHO and AMAP are important for assessing levels and trends in human tissues and to address any human health risk related aspect, among others.

Recommendation: Continue cooperation with strategic partners on issues relevant to human health risks of POPs.

Water

33. According to the regional monitoring reports, a large number of studies is available in the WEOG region on PFOS in rivers, lakes, estuaries and ocean waters; in the Asia and the Pacific PFOS has been analysed in water collected from China (including Hong Kong Special Administrative Region and Macao Special Administrative Region), Japan, Republic of Korea, Philippines and Thailand; monitoring of PFOS in water has been initiated on pilot basis in the Africa and CEE regions; no PFOS monitoring data in water are currently available from GRULAC. Despite of compiling complementary information on PFOS concentrations in water from other information sources, analysis of temporal trends is currently not possible due to insufficient data.

Recommendation: All regions should strive to implement sustainable programmes for monitoring PFOS in water.

34. The approach for water sampling and PFOS analysis varies among studies and has not yet been harmonized, but a guidance document for PFOS analysis in water for the GMP has been published (2015). Progress has also been made via international projects on PFOS in water conducted in the frame of the MONET project, the UNEP pilot projects in Africa,

Asia-Pacific, GRULAC and WEOG funded by the GEF, and the United Nations University project.

Recommendation: *With progress having been made on capacity-building for determination of PFOS in water, laboratories should be encouraged to participate in inter-laboratory studies organized with the help of UNEP or by other organizations (e.g. Quality Assurance of Information for Marine Environmental Monitoring in Europe - QUASIMEME, AMAP)..*

35. Spatial trends of PFOS in ocean waters are relatively well studied with measurements of surface waters in all oceans as well as in some deep basins. The transect from Western Europe (North Western France) to West Africa is the most thoroughly studied with results from four separate cruises available. Open ocean concentrations of PFOS are typically two orders of magnitude lower than for freshwaters and estuaries.

Recommendation: *Collaborative monitoring programmes along key cruise transects sites should be encouraged for monitoring of the oceans. Models for this include the Joint Global Ocean Flux Study (JGOFS; 1987-2003). SCOR (Scientific Committee of Oceanic Research) and JGOFS developed fieldwork for several process studies which included sampling for POPs in the North Atlantic, Equatorial Pacific, Indian Ocean, Southern Ocean and North Pacific.*

36. Most studies of PFOS in surface waters have analyzed unfiltered samples. Several studies have shown that PFOS is entirely in the dissolved phase in ocean waters and mainly (>80% dissolved) in river waters. However, some PFOS precursors have been found in the particulate phase.

Recommendation: *While most studies to date have recommended analysis of unfiltered water samples, except for those with high suspended solids, further study is needed to develop more precise guidance for filtering of water samples with high suspended solids in order to consider PFOS and precursors.*

37. Almost all monitoring and surveillance studies of PFOS in water have focused on total PFOS anions, i.e. combined measurement of the linear and branched isomers. The limited information available suggests that PFOS isomer profiles are enriched in branched content, especially in river waters. L-PFOS is more hydrophobic than branched isomers, and L-PFOS is thus removed more readily by sinking particles and sediment sorption.

Recommendation: *Future monitoring of water should report both total PFOS isomers and linear PFOS.*

38. In addition to environmental measurements, river discharges have been estimated and modeled for a small number of rivers. The River Rhine outflow and the Aire/Calder River system in northeast England have had relatively detailed studies.

Recommendation: *The design of water monitoring programmes for PFOS should include the capacity to estimate mass flows (kg/time (day, year)). These 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, as well as estimating per capita emissions.*

39. A major gap in knowledge of PFOS in water is the relative importance of neutral PFOS precursors including perfluorooctane-sulfonamide (FOSA), N-methyl perfluoroalkane sulfonamide (MeFOSA), N-ethyl-perfluoroalkane sulfonamide (EtFOSA), N-methyl perfluoroalkanesulfonamidoethanol (MeFOSE) and N-ethyl perfluoroalkanesulfonamidoethanol (EtFOSE), as well as less well-known precursors identified in fire-fighting foams. FOSA is known to be an important PFOS related

compound, particularly in ocean water. At present FOSA data is available for most ocean cruises but for only about 1/3 of river water analyses.

Recommendation: *Future monitoring should include investigation of precursor compounds in water in order to assess their relative importance to total "PFOS related" substances.*

40. Temporal trend information for PFOS in water is very limited. For rivers it consists of sampling 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.

Recommendation: *River water monitoring offers the best opportunity to assess temporal trends provided that sources e.g. waste water treatment plants, tributaries, accidental spills etc, are well documented. Systematic temporal trend studies at a few key riverine sites within each UN Region should be considered which can build on past measurements. As noted above, ocean monitoring along key cruise transects sites would enable future temporal trend assessment.*

Other media

41. Large collections of good quality data in biotic and abiotic media have been reported that include POP concentrations which are available for areas such as the North American Great Lakes, the Arctic, the Baltic and in Japan. Some data were reported for Africa; whereas the CEE and GRULAC Regional Reports did not include data on other media.

Recommendation: *Data sets on the presence and changes of POP levels over time can be used to identify contaminant pathways and to support effectiveness evaluation.*

42. Data show clear declines for legacy POPs from the 1970s until 2000 and little changes thereafter. This observation may reflect the effectiveness of measures taken earlier. Primary emissions (e.g. from stockpiles/waste/recycling) and secondary emissions (e.g. reemission from environmental sinks) may sustain levels in biotic and abiotic environments long after the implementation of regulations. More recently listed POPs (such as PBDEs, HBCD, PFOS and endosulfan) show increasing trends over the past decade, the increases in some cases (PFOS) seem to slow down or have stabilized.

Recommendation: *Make best efforts to decrease the timeline for implementing control measures for POPs to avoid building up of unaccountable repositories that may continue emissions long after control.*

43. There is no systematic compilation of guidance for the sampling and analysis of POPs in other media under the GMP.

Recommendation: *Refer to guidance and QA/QC documentations from established monitoring programmes, e.g. AMAP/NCP, the Helsinki Commission (HELCOM), the Commission for the Protection of the Marine Environment of the North-East Atlantic (OSPAR), in order to obtain comparable data.*

44. Natural archives (e.g. sediment and ice cores, tree rings, etc.) and sample banks have shown to be useful for retrospective analysis for the occurrence and changes over time of POPs, in particular for newly listed substances, as well as to increase spatial coverage in regions with limited data.

Recommendation: *Encourage information exchange through collaboration with existing monitoring programmes and sample banks in other media to support GMP data needs.*

Long range transport

45. Models enable the integrated approach (i.e. combining emission, transport models and measurements) to understand concentrations and trends of POPs in the global environment, and can be applied to explore alternative emission reduction scenarios that inform effectiveness evaluation.

Recommendation: *Reporting under the GMP organized by the ROGs should exploit models as tools to synthesize and interpret monitoring data.*

46. The integrated approach has benefited from increased data availability and accessibility from new and existing monitoring programmes and data sharing through international and global databases including the GMP data warehouse.

Recommendation: *Maintain and expand efforts to monitor levels of POPs in all 5 UN regions, and make data available in openly accessible databases.*

47. Models can help to determine if changes over time in monitoring data are attributable to changes in emissions or other factors such as climate variability or remobilization of POPs that were deposited in the past.

Recommendation: *Expand the use of models to interpret monitoring data and identify and quantify the key factors that drive temporal changes in concentrations of POPs.*

48. Combining models with monitoring data has been shown to be useful in the GMP to understand the long-range transport of POPs.

Recommendation: *Modeling tools should be further explored, applied and compared to support interpretation of monitoring data and for risk evaluation under Article 8.*

49. Models have contributed to interpretation of environmental monitoring data and evaluation of regional and global transport of POPs in scientific activities organized by both the Convention on Long-Range Transboundary Air Pollution (CLRTAP) and the Stockholm Convention.

Recommendation: *Improve the co-ordination of scientific activities undertaken under the CLRTAP and the Stockholm Convention to realize synergies.*

50. One of the key limitations on modeling POPs at the global level is a lack of complete and reliable emission inventories. A study confirmed that modelling of global dispersion of PCDD/PCDF using a global inventory of emissions compiled under the Stockholm Convention using the Toolkit for Identification and Quantification of Releases of Dioxins, Furans and Other Unintentional POPs under Article 5 of the Stockholm Convention on POPs reasonably reproduces observed levels of air concentrations.

Recommendation: *Parties should pay more attention to issues related to QA/QC of POPs release inventories and consistency and comparability of data reported for various reference years. The process for updating release estimates in order to reveal trends over time should be considered in conjunction with the revision (recalculation or correction) of previous release estimates. The Toolkit for Identification and Quantification of Releases of Dioxins, Furans and Other Unintentional POPs under Article 5 of the Stockholm Convention on POPs should be used for this purpose. Alternative approaches to estimate emissions, for example, using inverse modeling that leverages monitoring data and campaign-based field studies to derive emission estimates for POPs, should be explored, and could benefit effectiveness evaluation.*

1 Introduction

The present global monitoring report synthesizes information from the first and second phases of the GMP and presents current findings on POPs concentrations at the global level. 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 global monitoring report provides first indications as to the changes in concentrations of the chemicals initially listed in the Convention (commonly referred to as the legacy POPs), as well as baseline information on the newly listed POPs.

The report has been developed on the base of the five regional monitoring reports (UNEP/POPS/COP.7/INF/38) by the GMP coordination group, with the assistance of invited experts in areas where particular expertise was required, such as monitoring of POPs in air and in human matrices, modeling of long range transport and the global assessment of PFOS concentrations in water. The report synthesizes regional findings and assesses levels and trends in monitoring data from a global perspective. Namely, while the regional reports include information on the regional environmental transport of POPs where such information was available, the assessment of monitoring data and long-range transport considerations are addressed from a global perspective in the present report.

The Conference of the Parties to the Stockholm Convention, 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 GMP, as well as for harmonized data collection, storage and handling. The guidance document is continuously updated to include the most recent scientific information and provides up-to-date guidance for sampling and analysis of all POPs listed in the Convention. The latest version of the guidance is included in document UNEP/POPS/COP.7/INF/39.

The global coordination group met five times over the period 2011-2015 in order to oversee and guide implementation of the second phase of the GMP, 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 to support the evaluation of the effectiveness of the Convention. National air monitoring activities having contributed data to the first monitoring reports continued during the second phase, and new programmes have been identified to contribute data to and 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 GMP, providing useful long-term results showing how human exposure to POPs changed over time as measures are implemented to enforce the Convention at the global level.

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 additional POPs in the Convention brought additional challenges in the implementation of the GMP. Perfluorooctane sulfonic acid (PFOS) and its related chemicals listed in the Convention 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 presents, for the first time in the frame of the GMP, results as to the concentrations of such chemicals in water. An extensive global assessment of PFOS concentrations in water has therefore been conducted and is included for the first time in the global monitoring report.

During the second phase of the GMP, harmonized data handling was enhanced and some regions could benefit of support in the processing, storing and presentation of monitoring data. A GMP data warehouse supports data compilation and handling along with data analysis and visualization, and assists the regional organization groups and the global coordination group in producing the regional and global monitoring reports, and ultimately the effectiveness evaluation. The GMP 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 Data availability at the global level

Since its entry into force, the Stockholm Convention has catalyzed POPs research and monitoring activities worldwide. Bringing together research findings from around the world, the Convention triggered increased awareness and knowledge about POPs. This is demonstrated, for instance, through a significant increase in the number of scientific articles on the topic over the last three decades. In the period 1980-2014, the number of articles relevant to "levels" of "persistent organic pollutants", increased significantly in the mid-1990s further to the adoption of two major treaties to protect human health and the environment from these chemicals: CLRTAP and the Stockholm Convention:

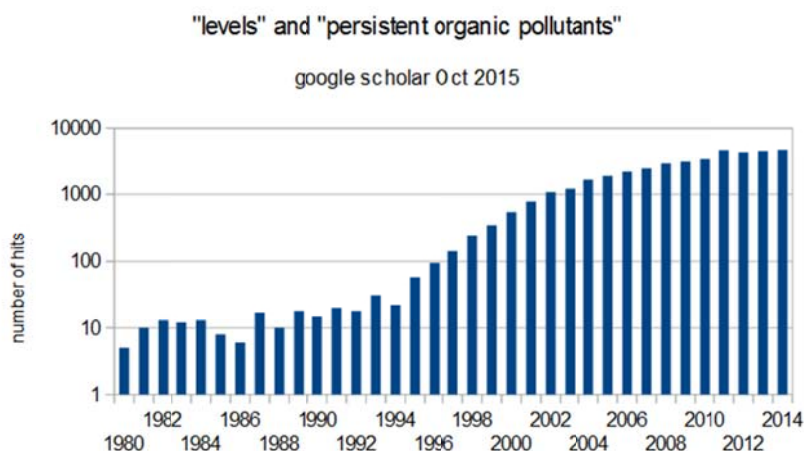


Figure 2.1. Number of articles relevant to "levels" of "persistent organic pollutants" over the period 1980-2014

Data availability and coverage has significantly increased at the global scale as compared with the first phase of the GMP. Long-term monitoring programmes have enlarged the scope of their activities to cover newly listed POPs in addition to legacy POPs, and new programmes have emerged. **Table 2.1** provides an overview of the contributing monitoring programmes in each UN region.

Table 2.1. Monitoring programmes contributing data to the GMP (Source: Second regional monitoring reports under the global monitoring plan, UNEP/POPS/COP.7/INF/38)

Region	Air	Human matrices	Water	Other media
Africa	Global Atmospheric Passive Sampling Network (GAPS) MONET Africa UNEP GEF GMP1 project	UNEP/WHO human milk survey UNEP GEF GMP1 project	MONET Africa pilot project UNEP GEF pilot project	Limited monitoring dealing with the contamination of water, soil, sediments and food by POP pesticides
Asia Pacific	POPs Monitoring Programme in East Asian Countries China national POPs monitoring programme Japan national monitoring programme MONET Fiji UNEP GEF GMP1 project	China monitoring programme on human milk Japan POPs monitoring programme on human milk Japan monitoring programme on human blood UNEP/WHO human milk survey	United Nations University program "Environmental Monitoring and Governance in the Asian Coastal Hydrosphere" National water monitoring programmes: China, Japan	Japan national programme on water, ground water, bottom sediments, soil, biota, food

CEE	<p>APOPSBAL Arctic Monitoring and Assessment Programme (AMAP) GAPS European Monitoring and Evaluation Programme (EMEP) MONET - Europe MONET - CEE MONET - CZ</p>	<p>UNEP/WHO human milk survey</p>	<p>Joint Danube Survey (2009) MONET-Europe NORMAN - NORMAN Association</p>	<p>National programmes on e.g.soil, sediments and biota are available in the region but rather variable, episodic</p>
GRULAC	<p>GAPS Latin Passive Air Monitoring Network (LAPAN) UNEP GEF GMP1 project</p>	<p>UNEP/WHO human milk survey UNEP GEF GMP1 project</p>		
WEOG	<p>AMAP Australian Pilot Monitoring Programme –air (AGAM) EMEP GAPS Integrated Atmospheric Deposition Network (IADN)/ Environment Canada’s Air Monitoring in the Great Lakes Basin (GLB) Northern Contaminants Programme (NCP) Norwegian Troll Station Monitoring Network in the Alpine Region for Persistent and other Organic Pollutants (MONARPOP) MONET - Europe U.S. EPA’s National Dioxin Air Monitoring Network (NDAMN) UK-Norwegian Transect The UK Toxic Organic Micro Pollutants (TOMPs) program</p>	<p>AMAP Australia “snap shot” surveys (under the Australian pilot monitoring programme) CDC/CCEHIP/-NCEH CHMS and FNBI ESB Germany GerES New Zealand “snap shot” surveys Sweden national programmes: Uppsala, Stockholm UNEP/WHO human milk survey</p>	<p>Australian Pilot Monitoring Programme International Council for Exploration of the Sea (ICES) database</p>	<p>AMAP Australian Pilot Monitoring Programme Great Lakes HELCOM OSPAR MEDPOL NCP</p>

Through the existing air monitoring network including newly initiated programmes, the ongoing human exposure studies, and the initial water sampling activities under the GMP, better spatial coverage of POPs concentrations in the environment and in human populations has been achieved since the first phase. The scope of the plan has also been enlarged to cover more analytes including the newly listed POPs. 23 POPs are currently monitored. **Figure 2.2.a-d** shows data availability worldwide according to the matrix. More detailed information on data availability per compound and per region is provided in the following sections.

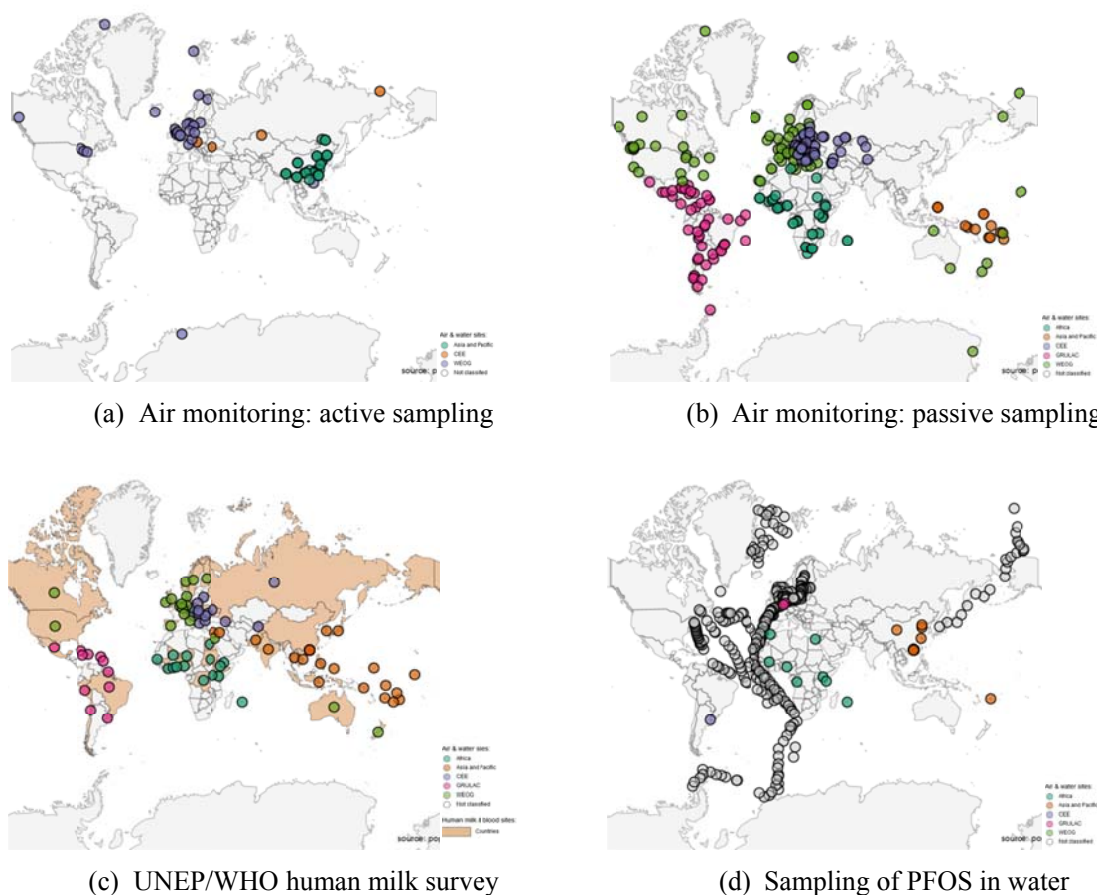


Figure 2.2. Data availability in the second phase of the GMP: (a) air - active sampling; (b) air – passive sampling; (c) human milk; (d) water

2.1 Baseline information

The first global monitoring report (UNEP/POPS/COP.4/33) set a baseline for information on levels of POPs in humans and the environment. The data available for each region vary greatly, with some regions having considerable historical data. Under the effectiveness evaluation the global progress achieved under the Convention will be evaluated. For that reason, in most cases the status quo as of the date on which the Convention or its amendments entered into force¹³ will be used as the baseline to evaluate its effectiveness on the global level. If such information is not available (e.g., monitoring data) the first relevant information which becomes available is considered as the baseline against which changes over time will be evaluated.

¹³ The Stockholm Convention entered into force on 17 May 2004. For amendments, there is no general entry into force date because pursuant to Article 22.4, parties can elect to be bound by amendments adopted within one year of their circulation by the depositary unless they object, or to be subject to a ratification procedure. Because most parties have chosen to be bound by the former process, while recognizing there is no single entry into force date, that date will be used.

With the Stockholm Convention into force, providing for regulatory measures being taken worldwide, concentrations of the POPs listed in the Convention are expected to show consistent decrease worldwide. A limited number of observations show increase in environmental levels. Nevertheless, such local increases do not prevent concluding on the effectiveness of the Convention as a global regulatory mechanism, as measures taken by countries to implement the Convention show their effects in terms of declining concentrations globally, in both the environment and in human populations.

Table 2.1.1 summarizes, based on expert judgment, the availability of baseline information on POPs by region.

2.2 Temporal trend information / Information regarding changes in levels over time

In the first GMP report, temporal trends were available from few regions with long monitoring time series for a number of the POPs initially listed under the Convention. These trends established a baseline trend against which future trends could be compared. Many of the existing 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 are not yet sufficient for assessing trends.

Table 2.2.1 summarizes, based on expert judgment, the availability of trend information on POPs in the different media.

Table 2.1.1. Summary of available baseline information on POPs in different media by region.








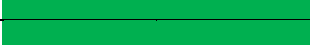



























Legend				
		Adequate information on baselines		
		Limited information on baselines		
		No information on baselines		
Chemical	Region	Air	Human Tissues	Water and Other Media
Aldrin	Africa	Limited information on baselines		
	Asia Pacific	Adequate information on baselines	Limited information on baselines	
	CEE	Limited information on baselines	Adequate information on baselines	No information on baselines
	GRULAC	Adequate information on baselines		
	WEOG	Limited information on baselines	Adequate information on baselines	
Chlordanes	Africa	Limited information on baselines		
	Asia Pacific	Adequate information on baselines	Limited information on baselines	
	CEE	Adequate information on baselines		
	GRULAC	Adequate information on baselines		
	WEOG	Adequate information on baselines		
Chlordecone	Africa	No information on baselines		
	Asia Pacific	Limited information on baselines		
	CEE	Limited information on baselines	No information on baselines	
	GRULAC	No information on baselines		
	WEOG	No information on baselines		
DDT	Africa	Limited information on baselines		
	Asia Pacific	Adequate information on baselines	Limited information on baselines	
	CEE	Adequate information on baselines		
	GRULAC	Adequate information on baselines		
























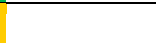




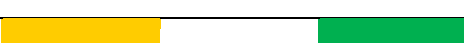

Table 2.2.1. Summary of available temporal trend information on POPs in different media by region.



































Legend				
		Adequate information on temporal trends		
		Limited information on temporal trends		
		No information on temporal trends		
Chemical	Region	Air	Human Tissues	Water and Other Media
Aldrin	Africa	Limited information on temporal trends	No information on temporal trends	
	Asia Pacific	Limited information on temporal trends	Limited information on temporal trends	
	CEE	Limited information on temporal trends		
	GRULAC	No information on temporal trends		
	WEOG	Limited information on temporal trends	Adequate information on temporal trends	
Chlordanes	Africa	Limited information on temporal trends	No information on temporal trends	
	Asia Pacific	Limited information on temporal trends		
	CEE	Limited information on temporal trends		
	GRULAC	No information on temporal trends		
	WEOG	Adequate information on temporal trends	Adequate information on temporal trends	
Chlordecone	Africa	No information on temporal trends		
	Asia Pacific	No information on temporal trends		
	CEE	Limited information on temporal trends	No information on temporal trends	
	GRULAC	Limited information on temporal trends		No information on temporal trends
	WEOG	No information on temporal trends		
DDT	Africa	Limited information on temporal trends	No information on temporal trends	
	Asia Pacific	Limited information on temporal trends		
	CEE	Adequate information on temporal trends	Limited information on temporal trends	No information on temporal trends
	GRULAC	Limited information on temporal trends		



























	WEOG	
Dieldrin	Africa	
	Asia Pacific	
	CEE	
	GRULAC	
	WEOG	
Endosulfan	Africa	
	Asia Pacific	
	CEE	
	GRULAC	
	WEOG	
Endrin	Africa	
	Asia Pacific	
	CEE	
	GRULAC	
	WEOG	
HBB	Africa	
	Asia Pacific	
	CEE	
	GRULAC	
	WEOG	
HBCD	Africa	
	Asia Pacific	
	CEE	
	GRULAC	











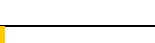



	WEOG	
Dieldrin	Africa	
	Asia Pacific	
	CEE	
	GRULAC	
	WEOG	
	WEOG	
Endosulfan	Africa	
	Asia Pacific	
	CEE	
	GRULAC	
	WEOG	
	WEOG	
Endrin	Africa	
	Asia Pacific	
	CEE	
	GRULAC	
	WEOG	
	WEOG	
HBB	Africa	
	Asia Pacific	
	CEE	
	GRULAC	
	WEOG	
	WEOG	
HBCD	Africa	
	Asia Pacific	
	CEE	
	GRULAC	





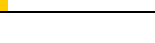


	WEOG			
HCB	Africa			
	Asia Pacific			
	CEE			
	GRULAC			
	WEOG			
α HCH	Africa			
	Asia Pacific			
	CEE			
	GRULAC			
	WEOG			
β HCH	Africa			
	Asia Pacific			
	CEE			
	GRULAC			
	WEOG			
γ HCH	Africa			
	Asia Pacific			
	CEE			
	GRULAC			
	WEOG			
Heptachlors	Africa			
	Asia Pacific			
	CEE			
	GRULAC			

	WEOG			
HCB	Africa			
	Asia Pacific			
	CEE			
	GRULAC			
	WEOG			
α HCH	Africa			
	Asia Pacific			
	CEE			
	GRULAC			
	WEOG			
β HCH	Africa			
	Asia Pacific			
	CEE			
	GRULAC			
	WEOG			
γ HCH	Africa			
	Asia Pacific			
	CEE			
	GRULAC			
	WEOG			
Heptachlors	Africa			
	Asia Pacific			
	CEE			
	GRULAC			

	WEOG		
Mirex	Africa		
	Asia Pacific		
	CEE		
	GRULAC		
	WEOG		
PBDEs	Africa		
	Asia Pacific		
	CEE		
	GRULAC		
	WEOG		
PCB	Africa		
	Asia Pacific		
	CEE		
	GRULAC		
	WEOG		
PCDD/PCDF	Africa		
	Asia Pacific		
	CEE		
	GRULAC		
	WEOG		
PFOS	Africa		
	Asia Pacific		
	CEE		
	GRULAC		

	WEOG			
Mirex	Africa			
	Asia Pacific			
	CEE			
	GRULAC			
	WEOG			
	PBDEs	Africa		
PBDEs	Asia Pacific			
	CEE			
	GRULAC			
	WEOG			
	PCB	Africa		
	PCB	Asia Pacific		
CEE				
GRULAC				
WEOG				
PCDD/PCDF		Africa		
PCDD/PCDF		Asia Pacific		
	CEE			
	GRULAC			
	WEOG			
	PFOS	Africa		
	PFOS	Asia Pacific		
CEE				
GRULAC				

	WEOG		
PeCBz	Africa		
	Asia Pacific		
	CEE		
	GRULAC		
	WEOG		
Toxaphene	Africa		
	Asia Pacific		
	CEE		
	GRULAC		
	WEOG		

	WEOG		
PeCBz	Africa		
	Asia Pacific		
	CEE		
	GRULAC		
	WEOG		
Toxaphene	Africa		
	Asia Pacific		
	CEE		
	GRULAC		
	WEOG		

3 Data consistency and comparability

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

Inter-programme comparability is useful for investigations of regional and global transport of POPs and in the context of model application and evaluation. Inter-programme comparability has been assessed through intercalibration exercises and co-location of samplers among programmes. Some overlap of monitoring network sites is already occurring and could be further exploited to evaluate this issue. Data comparability from different sampling approaches (e.g. passive vs. active; gas-phase, particle-phase or total concentrations) and strategies (e.g. time-integrated sampling or intermittent sampling such as 1 day in 10) has been a key area of work during the second phase. Long-term comparisons of PUF disks and high volume air samplers have been for instance established for several classes of POPs at the Kosetice site in the Czech Republic.

In the early stages of the GMP, air concentration data from passive sampling were reported either on a mass basis (pg/filter) or on a concentration basis (pg/m³). Air data are now uniformly reported in units of concentration in air, according to the frequency of sampling (e.g. weekly, monthly, seasonally-every 3 months, annually). In support of comparability at the global level, these data are aggregated as the yearly mean (arithmetic mean) air concentrations for given sampling sites, in units of pg/m³.

Comparable human exposure data are generated at the global level through the UNEP-WHO human breastmilk monitoring programme which operates in all UN regions and that has maintained a centralized analytical facility servicing all regions. The UNEP-WHO coordinated human milk programme, utilizing common methodology, analytical laboratories and data centre, has demonstrated the possibility of achieving excellent data comparability globally. Similarly, in the Arctic region, AMAP ring test for blood sampling is organized according to a consistent set of methods. The most important criterion enabling comparison among human data at the global scale and between years is the selection of donors, who must be first-time mothers.

In the case of water sampling for PFOS, the use of filtered vs. non-filtered samples is likewise an important parameter to be considered when comparing data.

A number of other useful parameters are reported together with the analytical results, such as the blank values. Further, metadata are also included with the datasets, providing useful details for the analysis and interpretation of results.

Compounds found at levels between LOD and LOQ are reported as present, or possibly as being present at an estimated concentration, but in the latter case the result is marked as being below LOQ. Results below the detection limit are reported as <"LOD". Additional details on reporting monitoring data under the GMP are available in the guidance document (UNEP/POPS/COP.6/INF/31).

4 Data handling

A major focus of the work in the second phase of the GMP has been to provide support to the ROGs with enhanced harmonized data handling for the compilation, processing, storing and presentation of their data. A GMP data warehouse supports data handling and assists the regional organization groups and the global coordination group in producing the regional and global monitoring report. It includes an interactive on-line data capture system, handling, and a presentation module. The compiled information is available to the ROGs for the development of the monitoring reports and to other scientists to work with the data in statistical analysis and mathematical models.

The data evaluation procedure including their validation by the regional organization groups supports comparability of the different samples, especially from the point of view of the type of site, matrix, sampling method, time span and sampling frequency. The data warehouse also includes data visualization tools and means for statistical and trend analysis. Details on statistical considerations and their implementation in the second phase of the GMP are available in the guidance document (UNEP/POPS/COP.6/INF/31). Several figures used in this report are graphical outputs of the data warehouse.

Long term monitoring programmes with already established data handling and analysis protocols exist in some regions. These programmes have been operating for more than a decade and exercise well established QA/QC protocols for sample collection and analysis, which are consistent with the standards outlined in the GMP guidance document. The majority of these programmes have existing data handling procedures and their own databases, and deliver their results to the GMP data warehouse as well. Efforts to ensure compatibility among the GMP at a warehouse and ongoing or emerging information systems on POPs, such as the Korean information warehouse, are also ongoing.

Furthermore, data that have undergone validation by the regional organization groups but have not been reported to the GMP data warehouse can only be found in the regional monitoring reports and are not available in electronic form. However, it should be noted that such instances are limited.

The GMP data warehouse constitutes a publicly available repository of valuable information that can serve as a useful resource for policy makers, modelers and researchers worldwide. The tool is available at www.pops-gmp.org.

5 Challenges to the implementation of the global monitoring plan

Key Messages

The growing number of newly listed POPs chemicals is increasing pressure on monitoring programmes and analytical laboratories.

Some regions still lack adequate technical and analytical capacities to monitor most POPs in core media.

Limitations in communication and information exchange infrastructure were a major impediment to some ROGs in coordinating regional activities.

Limited financial resources are a major constraint in ensuring continuity and sustainability of the POPs monitoring activities for future evaluations.

The goal of the GMP is to provide comparable data from all five UN regions to allow evaluation of the effectiveness of the SC by assessing temporal trends and long-range transport of POPs in the Global environment. The original strategy included two core media namely: human milk or blood and ambient air. However, with addition of new POPs such as PFOS and its precursors, water has been included as an additional core-medium for polar POPs. By 2015, two phases of the GMP had been implemented. The experiences gathered in these two phases have revealed a number of challenging issues that need to be systematically addressed to improve future implementation of the GMP. These challenges are discussed below:

1. Increasing number of new POPs. The Stockholm Convention has a mechanism for review and addition of new POPs to the initial list of the twelve legacy compounds. Through this mechanism, potential POPs are continually reviewed and the chemicals that meet the criteria for POPs listing are added to the Convention annexes A, B or C. Once listed, the chemicals are included in the GMP POPs monitoring programmes to provide data on their global trends and long range transport over time. By the end of 2014, the list of POPs had grown from the initial 12 to 23 chemicals/groups and this number will continue to increase in the future. When the emission, environmental fate and environmental partitioning of new POPs differ from their legacy counterparts, this requires modification of the monitoring strategies in terms of matrices, sampling techniques and analytical methodologies. For instance, PFOS and its precursors are more hydrophilic and are more suitable to be monitored in water rather than in air and in human blood rather than in human milk. As a consequence, the growing number of POPs and candidate substances presents a resource challenge for existing monitoring programmes. In addition, there is need to understand the transport and fate of these chemicals to adequately interpret environmental levels and trends.
2. Lack of technical capacity for POPs monitoring: Whereas the GMP calls for production of comparable POPs monitoring data from all the five UN regions, the existing human resource capacities to monitor POPs across the regions are different. In addition, the inclusion of new POPs in the monitoring programmes demands for further training in their sampling and analysis.
3. Need for analytical capacities for POPs analysis. The GMP calls for monitoring POPs levels at background sites in order to detect changes in concentrations over time. However, the environmental levels at remote sites are very low and require the use of high resolution analytical equipment for their detection. In addition, laboratories with state of the art facilities capable of analyzing all groups of POPs are limited in some regions. Whereas most of the regional laboratories, especially in developing regions, possess HRGC/ECD and HRGC/LRMS, this equipment may not be suitable for analyzing POPs that require more advanced analytical procedures such as PCDD/PCDF and PFOS. As a consequence, several developing regions depend on strategic partnerships with existing monitoring programmes for supporting analysis of POPs in their monitoring samples. Whereas this has successfully provided the required results in

the initial phases of GMP, the number of POPs compounds and matrices are increasing pressure on the existing programmes, hence the need to build regional capacities and cooperation between regions to ensure long-term sustainability for POPs monitoring in core media and other media.

4. A survey conducted through UNEP DTIE coordinated two inter-laboratory assessments in 2010/2011 and in 2012/2013 to evaluate capacities and performances of the laboratories to analyze the major groups of POPs established that:

- a. A number of laboratories performed poorly with the analysis of ‘real’ matrices such as fish and human milk.
- b. Most laboratories were biased for certain matrices only, and sometimes for one or two groups of POPs contaminants.
- c. GC-ECD was the most commonly used analytical instrumentation in most countries for detection of OCPs, however, labs utilizing GC-MS demonstrated better performance. Compared to GC-MS, GC-ECD is less specific and thus more prone to errors due to interferences.

Overall, 101 laboratories participated in 2010-2011 and 106 in 2012-2013, as reflected in figure 5.1 below:

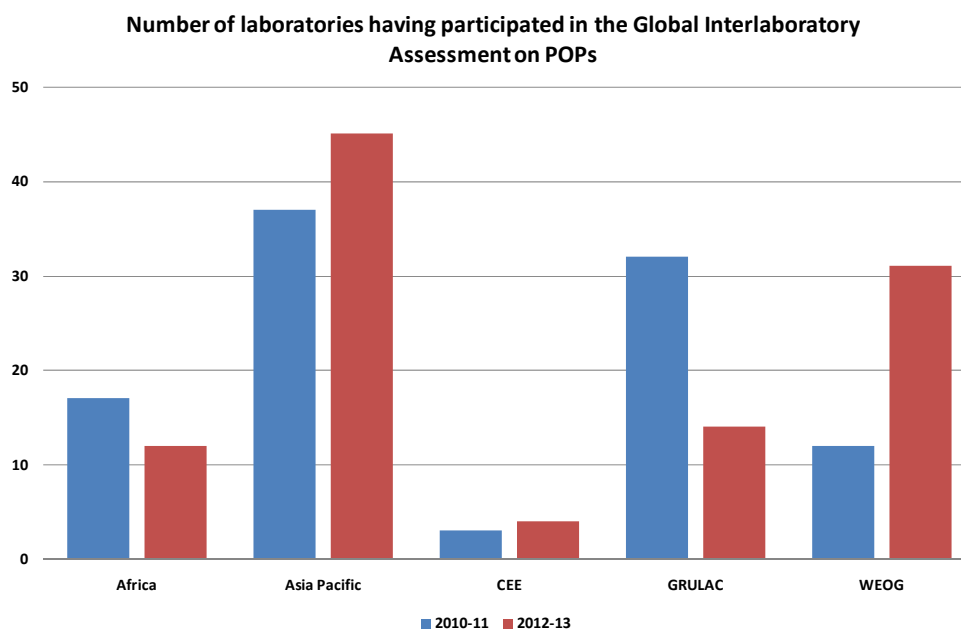


Figure 5.1. Number of laboratories participating in the Global Interlaboratory Assessment on POPs

5. Challenges with communication and information exchange. The implementation of GMP has been successful through the established regional structures such as the regional organization groups and the Global coordination group. However, ROGs experienced various challenges at regional levels that if resolved will enhance the implementation of future GMP activities. The impediments included: high turnover rates of the Stockholm Convention national contacts and lack of updated contact details; lack of responsiveness from the national SC contacts; inadequate information exchange infrastructure in some regions to facilitate communication and dissemination of information on POPs, and unreliable internet connection.

6. Sample specimen banking needs: Whereas a large amount of POPs data have been produced through the GMP activities, the addition of new compounds to the Convention Annexes A, B and C or the need for data verification may require or benefit from retrospective analysis of samples to determine baseline concentrations and temporal trends. Currently WHO provides

specimen banking for human milk samples, however similar specimen banks are not common for other core media.

7. Financial constraints for POPs monitoring: Whereas the goal of the GMP is to provide comparable and representative data from all regions, it is noteworthy that monitoring activities are finance-intensive and the information gathered so far is mainly from a relatively small number of existing international programmes. In some cases the long-term sustainability of these programmes relies on the support of contributing national programmes. The long-term viability of these programmes is of utmost importance to the GMP in order to ensure the integrity and comparability of long term data.

8. Data handling, archiving and retrieval: The collections of reliable and comparable data that the ROGs have identified and compiled have been made available to policy makers, modelers and researchers worldwide in a harmonized database that documents the data and presents them in user friendly interfaces. This POPs database is a useful resource that can be continually updated and improved to allow ease of access to information for assessing levels and trends of POPs in different media. It can also serve as a resource to modelers in conducting integrated assessments of environmental levels, sources, fate and transport of POPs. Currently, the GMP data is produced by different international programmes with their established protocols with differences in data collection, handling and archiving procedures. This presents some challenges for ensuring data comparability and for linking data and databases from different programmes with the GMP database.

9. Dealing with low detection in future monitoring: From the results of the second phase of the GMP, there is emerging evidence that some POPs have declined to levels that are difficult to measure in core media. The question on whether to reduce the frequency of monitoring of these compounds needs to be explored further to provide guidance to future monitoring activities.

6 Evaluation and assessment of changes in persistent organic pollutant levels over time

6.1 Ambient air

Key messages

Spatial coverage of air monitoring has improved due to introduction of passive air sampling methods.

Baseline data for older POPs are available for most regions; temporal trend data are lacking in Africa and GRULAC regions.

Baseline data and temporal trend data for most newly listed POPs are lacking.

Levels of POPs in air are controlled by primary and secondary emissions, climate effects and meteorology; models are useful for assessing these inputs/influences, relative contributions and to interpret trends.

Overview

Air was selected as a core medium for the GMP because it is important in the transport of POPs and it is a medium that responds relatively quickly (i.e. chemical concentrations will increase or decrease) to changes in emissions. Thus by making measurements in air at the global scale and over time, we can inform Article 16 on effectiveness evaluation through: i.) information on the long-range transport of POPs and ii.) monitoring data that reveals temporal trends.

The presence of POPs in air is complex and reflects numerous contributions that may have their own variabilities. These include changes in primary emissions (e.g. due to control strategies on POPs), changes in secondary emissions (e.g. revolatilization from soil or water of previously emitted and deposited chemicals), and various other confounding factors such as meteorology, climate, and other changes to the environment. The chapter on modeling that is included in this GMP report, complements this chapter on air by addressing these issues and providing insight and context for interpreting temporal trend data for POPs.

This air chapter provides a global overview based on information that was reported in the five regional GMP reports submitted in May 2015 at COP 7. These regional reports reflect progress that has been made over the past 10 years to supplement a few existing long term monitoring programmes for POPs that were already measuring POPs in air. Further incentive to implement new air monitoring activities came from the first GMP report (2009) that identified areas lacking data on POPs. These new monitoring activities have benefited from GEF-funding and partnerships and consultation with existing international air monitoring programmes such as AMAP, MONET, GAPS and the East Asia Air Monitoring Programme. Spain has developed a national monitoring plan since 2008. Progress in improving spatial coverage of POPs monitoring data for air has followed the guidance provided in the GMP Guidance document and has resulted in new high volume sampling programmes and a large number of passive sampling stations. Passive sampling devices have been especially effective in meeting the challenges of regional air monitoring because they are simple to use, inexpensive, and do not require electricity. Figure 6.1.1 shows the current global scale coverage and trend information for PCB-52 based on both high volume and passive sampling-based air monitoring programmes. The results for PCB-52 reflect the level of data availability for an older POP that is abundant in air and has well established analytical methods.

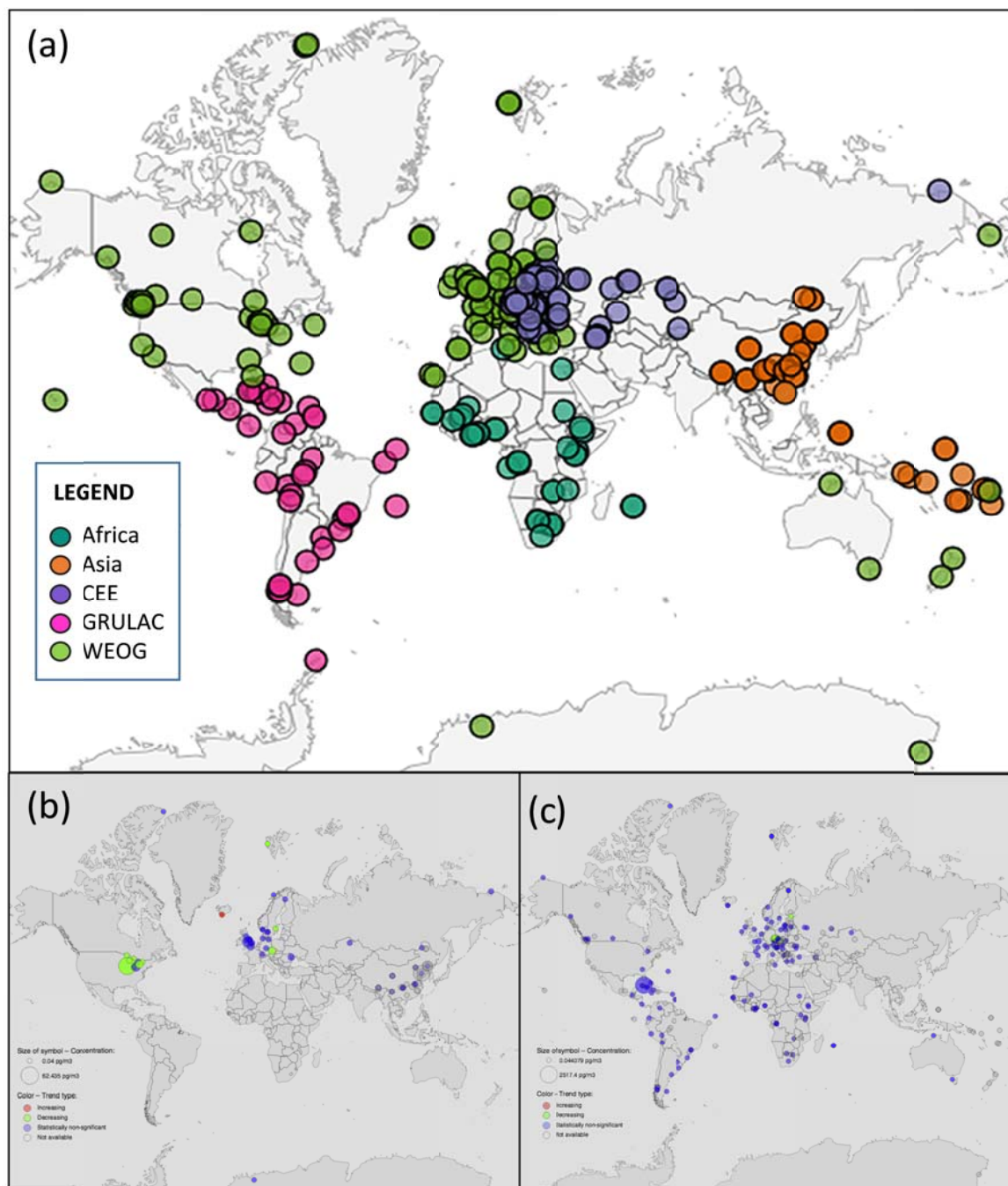


Figure 6.1.1. Global air monitoring of PCB 52 (a) All air monitoring stations reporting PCB air monitoring results. Color of marker indicates the five regions. (b) Temporal trends in air concentration derived from active air sampling sites. (c) Temporal trends in air concentration derived from passive air sampling sites. For (b) and (c), decreasing trend is shown in green, increasing trend in red, statistically non-significant trend in blue, and no trend in grey. The diameter of the sampling site circle marker is related to the concentration level (mean) of PCB 52 observed at that site. Maps generated with the GMP data warehouse – Data Visualization http://www.pops-gmp.org/visualization-2014/GMP_DWH. Data sources are identified in the Regional Reports and in the GMP DWH.

Regional Summaries

The following summaries are based on the content of regional reports that were adopted at COP7. They reflect the current status on: i.) availability of air monitoring data for POPs, ii.) progress to address data gaps, and iii.) availability and status of temporal trend data for POPs. In addition, the summaries cover some specific issues for each region and one visual highlight from

each region is presented. Table 6.1.1. summarizes the global picture of availability of time trend information for the different POPs.

Table 6.1.1. Temporal trend and data summary of air monitoring results on POPs for the five UN Regions. Shadings indicates: green – generally decreasing trends; red – increasing trends; blue – no change (statistically insignificant trend) or cannot establish regional trend; white – no trend data; ★ - warning to indicate that trend assessment is based on limited data. Notes specific to each region are given on the last row.

Chemical	Africa	Asia and the Pacific	Central and Eastern Europe		Latin American & Caribbean States	Western Europe and Other Groups	
aldrin	Baseline data available.	Mostly below LOD or poor recovery	Baseline data available at 2 sites.		Baseline data available.	Decline in Great Lakes; no trend in Arctic ★	
chlordanes	Baseline data available.	Decreasing in Japan. Mostly below LOD in China. ★	Baseline data available at 6 sites.		Baseline data available.	Mostly declining trends	
chlordecone	Below LOD at all sites.	Below LOD in Japan.	Monitored at 1 site all below LOD.		Baseline data available.		
DDTs^a	No discernable trends	Decrease in Japan ★	Mostly no trend	Declining at 8 sites.	Baseline data available.	Mostly declining trends	
dieldrin	No discernable trends	No trend in Japan. Mostly below LOD in China. Baseline data available in other countries. ★	Baseline data available at 4 sites		Baseline data available.	Decline in Great Lakes; no trend in Arctic	
endosulfan	Decreasing tendencies at 3 sites, not changing at others ★	Baseline data available in Fiji (below LOD) and Japan.	Baseline data available at 4 sites.		Baseline data available.	Decline in Europe and Great Lakes.	No change in Arctic.
endrin	Baseline data available.	No trend in Japan. Mostly below LOD in China. Baseline data available in other countries. ★	Baseline data available at 2 sites.		Baseline data available.	No discernable trend in the Arctic ★	
HBB	Variable trends at different sites	Baseline data available in Fiji and Japan (below LOD).			Baseline data available.		
HBCD	No discernable trends	Baseline data available in Fiji (below LOD) and Japan.			Baseline data available.	Decreasing at 1 Arctic site. No trend in urban Great Lakes. Mostly below LOD at other sites. ★	
HCB	Variable trends at different sites	No trend in Japan. Baseline data available in other countries. ★	Mostly no trend	Decreasing at 1 site Increasing at 1 site	Baseline data available.	Very slow decline at most sites.	Increasing in 2 Arctic sites attributed to warming.
α-HCH	Decreasing tendency at all sites	Baseline data available.	Mostly no trend	Decreasing at 12 sites	Baseline data available.	Sharp decreases at most sites	
β-HCH	Baseline data available.	Baseline data available.	Mostly no trend	Decreasing at 6 sites	Baseline data available.	Concentrations very low and mostly below LOD ★	
γ-HCH	Variable trends at different sites	Baseline data available.	Mostly no trend	Decreasing at 20 sites	Baseline data available.	Sharp decreases at most sites	
heptachlor	Baseline data available.	Decreasing in Japan. Mostly below LOD in China. Baseline data available in other countries. ★	Baseline data available at 4 sites		Baseline data available.	Decline in Great Lakes	No trend in Arctic
mirex	Baseline data available.	No trend in Japan. Mostly below LOD	Baseline data available at 2 sites		Baseline data available.	Declining in the Great Lakes ★	

Chemical	Africa	Asia and the Pacific	Central and Eastern Europe		Latin American & Caribbean States	Western Europe and Other Groups	
		in China. Baseline data available in other countries.					
PBDEs	No discernable trends	Baseline data available in Fiji and Japan.	Baseline data available at 3 sites		Baseline data available.	Decreasing in Europe and some Great Lakes sites. ★	No trend in Arctic Canada. Increasing at 3 Great Lakes sites
PCB	No discernable trends	Decreased in Japan 1974-1988 and remained at similar level since then. ★	Mostly no trend	Declining at 14 sites	Baseline data available.	Mostly declining. Slow decline in Great Lakes related to urban stockpile.	Increasing at 1 Arctic site attributed to warming.
PCDD/ PCDF	Variable trends at different sites	General reduction tendency	Baseline data available at 1 site		Baseline data available.	Declining in the Alps and UK urban sites. No change at US sites and UK rural sites.	
PFOS		Baseline data available in Fiji and Japan.	Baseline data available at 1 site		Only Uruguay reported air data.	In Arctic air, PFOS shows no trend. PFOS precursors show no trend or are decreasing ★	
PeCBz	Variable trends at different sites	Baseline data available.	Decreasing at 1 site ★		Baseline data available.		
toxaphene		Baseline data available.					
Notes	Good spatial coverage of region. Monitoring period too short to confirm trends. Baseline data available for future trend development.	Longer term monitoring data are available in China, Japan and 1 site in Korea. Baseline data are available in a limited number of other countries.	One EMEP site, namely Košice, generated time trend data for >20 years. Passive air sampling increased spatial coverage since 2006. Most sites showed no trends in POPs due to short monitoring periods.		Good spatial coverage of region. Monitoring period too short to confirm temporal trends. Baseline data available for future trend development.	Long term monitoring data for older POPs available from several programmes. New POPs are being reported by existing programmes. AMAP results for the arctic region are reported through the WEOG region report.	

^a This table summarizes results for sums of DDTs (combinations of *p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDE, *o,p'*-DDE, *p,p'*-DDD, *o,p'*-DDD) and trends of individual isomers reported for the group.

Africa

The Africa region consists of 6 sub-regions with 54 countries. In Africa, air monitoring is primarily carried out using passive air sampling that started in 2005 through partnerships with the GAPS Network. Then, in 2008, the MONET programme initiated two campaigns (2008 and 2010-2012) at more than 20 sites that resulted in greatly improved spatial and temporal resolution. Assessment of POPs short-term temporal variations in air are already reported for the Africa region. It is expected that a more comprehensive analysis of longer term trends will be possible for the third GMP report.

Among all POPs, pesticides were found to be the highest in ambient air in this region. DDTs, HCHs and endosulfan were the most dominant POPs detected in air. The presence of pesticides such as DDTs could be attributed to the widespread agricultural and public health uses in the past throughout the region. Contamination may also have originated from obsolete stockpiles or

contaminated sites/soils. The concentrations of indicator PCB were generally higher than the levels of dioxin-like PCB in air. The relative advancement of PCB management varies among countries. PCDD/PCDF are widely detected in air in this region which could be attributed to releases from uncontrolled combustion of wastes including municipal wastes, medical wastes incineration, biomass burning of agricultural fields, industrial power generation activities and related thermal processes. PBDEs were generally low in air concentrations compared to other industrial POPs. The most abundant PBDEs were PBDE 47 and PBDE 99. Their probable origin is the crude recycling practices of e-wastes and end-of-life vehicles. PFOS and related compounds were only measured in two samples and levels were generally low.

The use of numerous passive air sites in the Africa region has enabled spatial assessment of POP concentrations in air and an investigation of short-term temporal variations over the period 2010-2012, as shown in Figure 6.1.2.

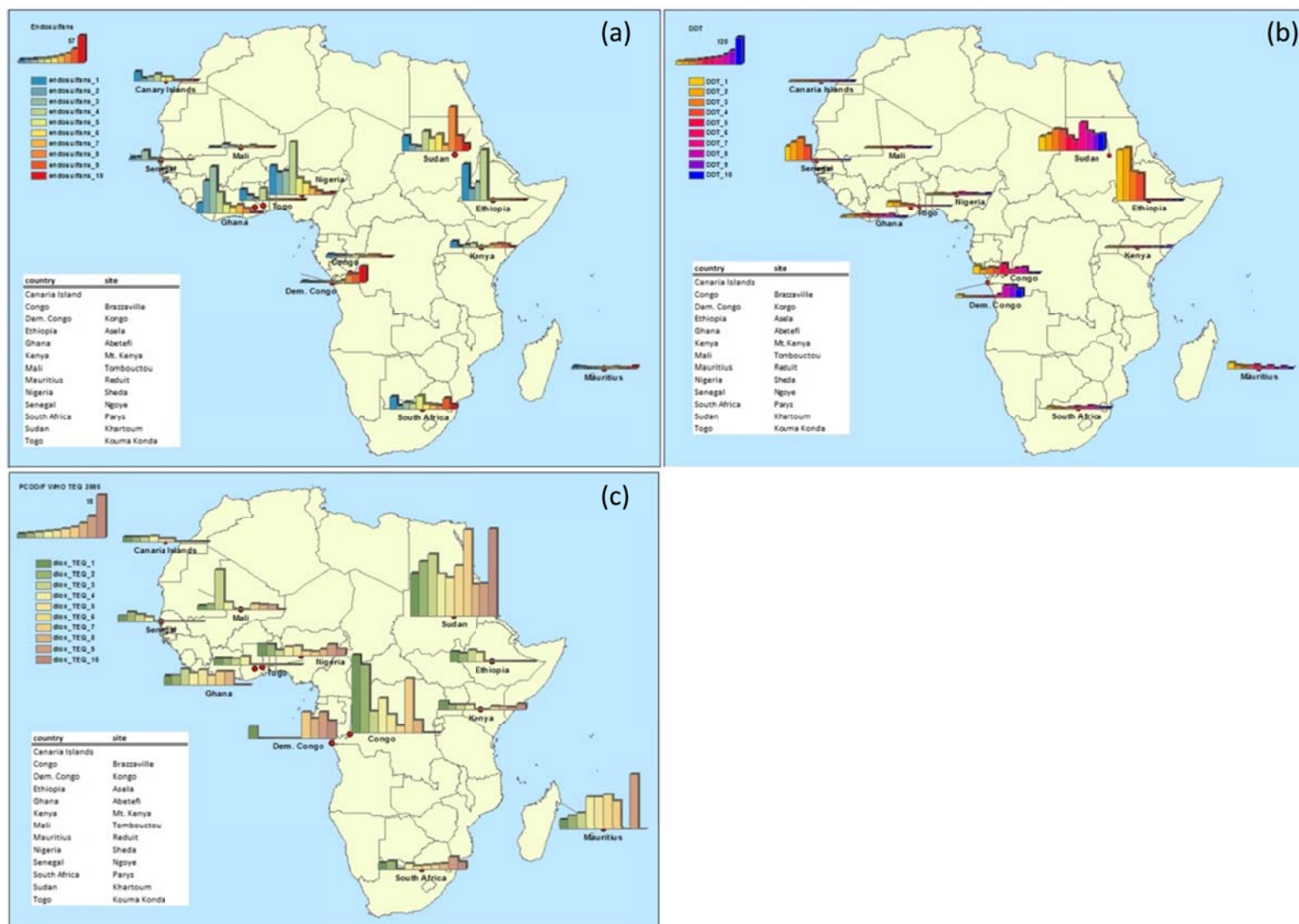


Figure 6.1.2. Spatial variations of selected POPs in Africa from 2010 to 2012: (a) Endosulfan (2 isomers) levels in ambient air (PAS, ng sample⁻¹); (b) DDT levels in ambient air (PAS, ng sample⁻¹); (c) PCDD/PCDF in ambient air (PAS, pgWHO TEQ 2005 sample⁻¹) (Source: Africa Region Report)

Asia and the Pacific

In Asia and the Pacific region, there are 62 countries/states, out of which 48 countries have either ratified, accepted, approved or accessioned to the Stockholm Convention on POPs. In this region, 10 countries have reported air monitoring results based on active air sampling methods and 7 countries reported results from passive air sampling methods. Comprehensive spatial and temporal POP monitoring data are reported by a few countries in this region, e.g. Japan and China. Under the POPs Monitoring Project in East Asian Countries initiated by Japan, sampling was operated in eleven countries from 2009 to 2013. Passive sampling was conducted in Fiji in collaboration with RECETOX since 2006. Some countries are currently developing their own air monitoring programmes, while others still lack the capacity for POPs monitoring. The evaluation of temporal trends and the assessment of long-range transport of POPs on the regional scale is difficult due to lack of data from large parts of the region. Substantial effort will be needed to fill the data and technical gaps in the region. Capacity building is a priority for future effectiveness evaluation.

Regional programmes reported data collected with active air samplers at 1-4 sites between 2009 and 2013 and with passive air samplers at 1-3 sites in 2010 and at 1 site in 2013. National air monitoring programmes in China, Japan and Republic of Korea reported POPs air concentration results from 32 to 55 sites using active air sampling method within the time period of 2006-2012. In addition, Japan measured PCDD/PCDF and dl-PCB at 689-740 sites between 2007 and 2011 with active air samplers.

Where temporal trend results are available, air concentrations of the initial 12 POPs showed statistically significant decreasing tendency in this region. Of note, at Cape Hedo (Okinawa Island), which is background site in Japan, a clear decreasing trend of both total DDTs (sum of six isomers, including *p,p'*- and *o,p'*-DDTs, DDEs, DDDs) and the ratios of DDT (sum of *p,p'*- and *o,p'*-DDT) versus total DDTs during 2009-2013 (Figure 6.1.3.) was observed. This may reflect a possible decrease of new DDT input to the sampling region during this assessment period.

For the newly listed POPs, only baseline results were available in air from some countries. This is due to the lack of air monitoring capacity in many countries in this region. Consequently, data are lacking for evaluating temporal trends and assessing long-range transport of POPs in the region.

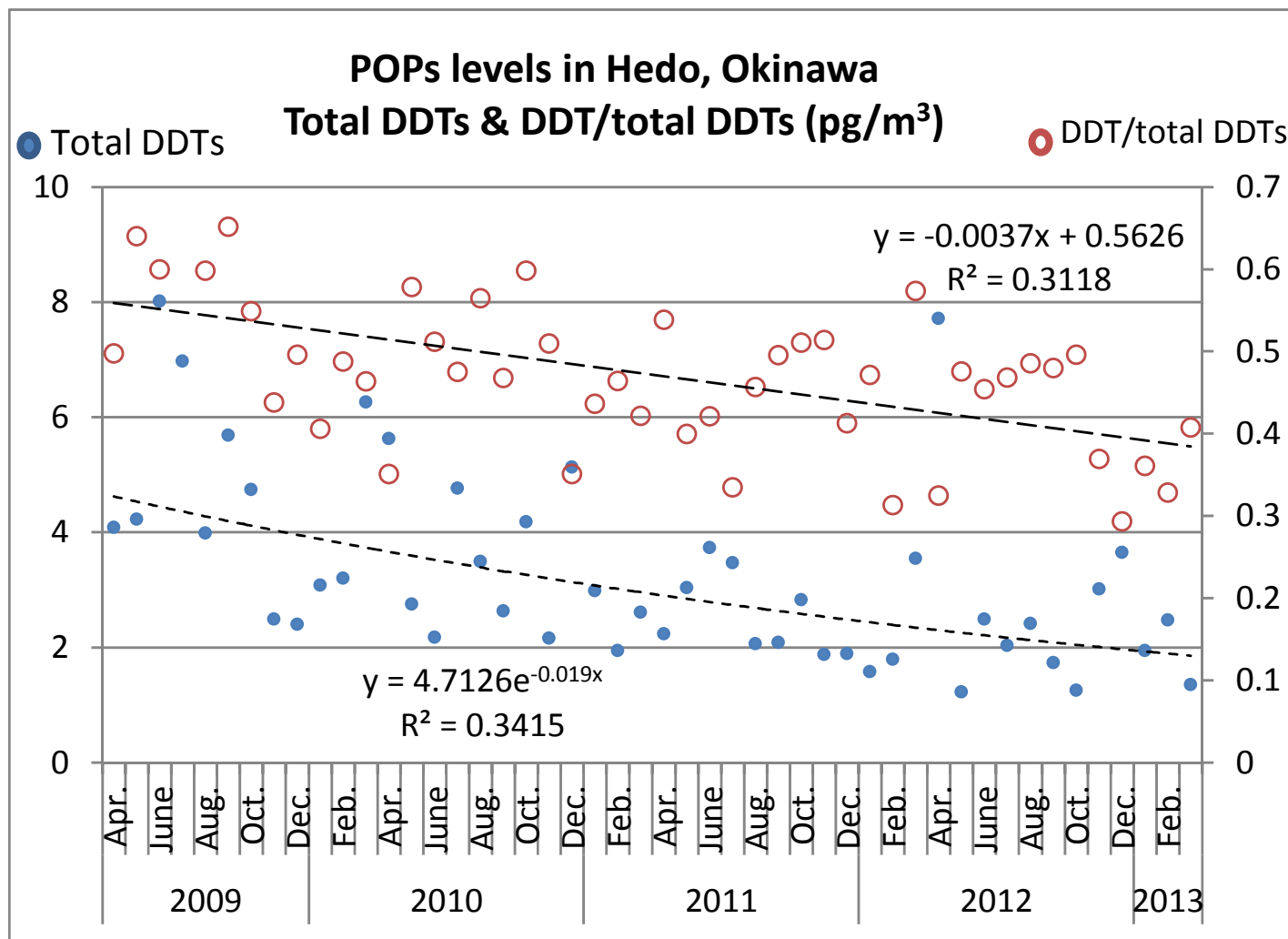


Figure 6.1.3. Changes in monthly total DDT levels in air and the ratios between DDT and total DDTs in Hedo, Okinawa. Total DDTs: sum of six isomers, i.e., *p,p'*- and *o,p'*-DDTs, DDEs and DDDs. DDT: sum of *p,p'*-DDT and *o,p'*-DDT (Source: Asia-Pacific Region Report)

Central and Eastern Europe

The Central and Eastern Europe region covers 28 countries: 23 countries in Central and Eastern Europe and five countries in Central Asia (Kazakhstan, Kyrgyzstan, Tajikistan, Turkmenistan, and Uzbekistan). Strategic partnerships for air monitoring with MONET, GAPS and EMEP significantly contributed to the establishment of monitoring stations in various countries of this region. Overall, four active and 94 passive air sampling stations provided air data collected between 1996 and 2014. Earlier integrated monitoring sites (reporting active sampling results from both air and precipitation) were initiated in the 1980s, with more than 20 years of air concentration data for seven or eight of the listed POPs, representing the Central European background levels. New air monitoring sites were added after 2006 under the MONET networks based on passive air sampling. Results indicate decreasing trends in air concentrations on sufficiently long (minimum five years) passive sampling time series for HCB, PCB, DDT, α -, β -, and γ -HCH and pentachlorobenzene. The long-term active air monitoring station of Košetice, Czech Republic, in the CEE region also confirmed a decreasing trend for HCB, sum 6 PCB, DDT, γ -HCH and pentachlorobenzene in air. Figure 6.1.4 shows available spatial and temporal trends of PCB measured in the CEE region. PCB concentrations in air were measured at 80 sampling sites in 17 countries with variable time spans ranging from 1 to 33 years. Statistically significant decreasing trends (green circles in Figure 6.1.4) were observed at the remote site of Lahemaa in Estonia (2006-2012), sub-urban site in Zagreb Siget, Croatia (2007-2012) and at twelve sites in the Czech Republic (8 remote sites, 1 urban and 3 rural sites). The trends are observed on longer time series (five and 6 years for Croatia and Estonia respectively), and 8-11 years for the Czech Republic. Sites marked in blue circles in Figure 6.1.4 do not exhibit statistically significant trends, largely due to short time series. Grey circles represent sites where monitoring occurred over a short term period (i.e. approximately one year during a pilot study in 2006 or 2007) and was discontinued. Figure 6.1.4b shows decreasing time trend of PCB measured in air at Košetice from 1996 to 2013.

Baseline air concentration data for chlordane, dieldrin, PCDD/PCDF, endosulfan, PBDEs, and PFOS are available. The compounds aldrin, endrin, heptachlor, mirex, and chlordecone in the CEE region are predominantly below level of quantification. No data were identified for toxaphene and hexabromobiphenyl in the region.

Hexabromocyclododecane levels are yet to be determined in samples collected since 2013 and will be reported in the next GMP report.

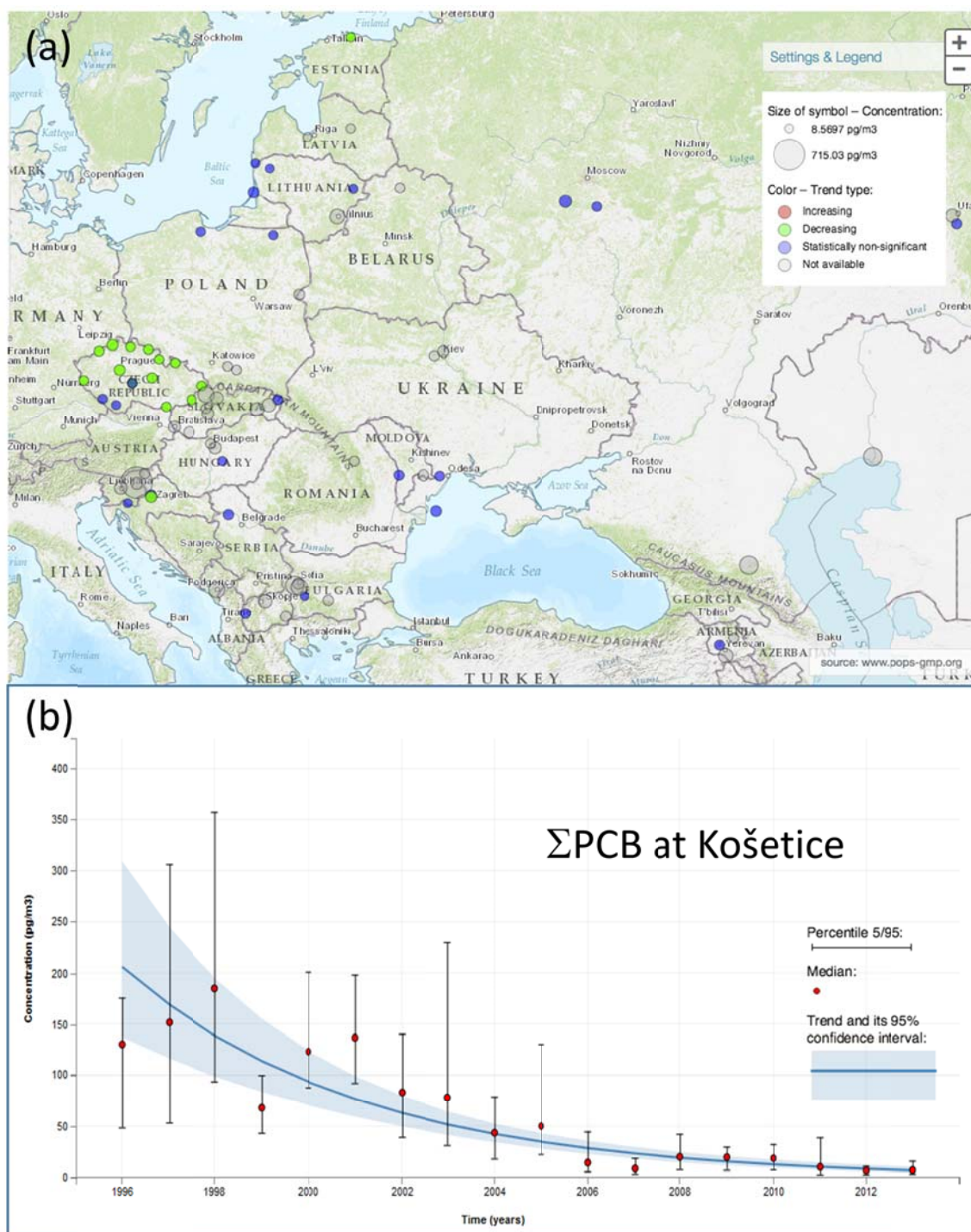


Figure 6.1.4. Trends of PCB measured in air in the CEE region from 1996 to 2014. (a) Spatial distribution of air monitoring sites. Trend directions indicated with colors: decreasing trend in green, statistically non-significant trend in blue, and no trend in grey. The diameter of the circle marker is related to the concentration level (mean) of ΣPCB observed at that site. Map generated with the GMP data warehouse – Data Visualization [http://www.pops-gmp.org/visualization-2014/\(GMP_DWH\)](http://www.pops-gmp.org/visualization-2014/(GMP_DWH)). (b) Decreasing time trend at the Košetice station over 18 years of monitoring (Source: Central and Eastern Europe and Central Asian Region Report).

Latin American and Caribbean States (GRULAC)

The GRULAC region consists of 33 countries in Latin America and the Caribbean. Passive air sampling was started in the GRULAC region through partnership with GAPS in 2004 with 11 stations. GEF financed the implementation of the GMP in eight countries in Latin America and the Caribbean installing passive samplers during four exposure periods of three months from July 2010 to June 2011. Furthermore, SAICM supported capacity-building efforts to Barbados, Bahamas and Haiti to participate in the draft GMP, while Cuba received support on strengthening laboratory capabilities. Additional passive sampling sites were initiated under the LAPAN Project funded by the Research Council of Brazil in recent years, 13 of which generating baseline POPs data in air from 2009 to 2012. There are currently 52 sampling stations as shown in Figure 6.1.5 (left panel) but there was discontinuity in previous sampling sites preventing the development of temporal trends. Spatial gaps also exist, making it difficult to make regionally representative conclusions on measured concentrations, considering the ecological, geographical and sociological complexity of this region. There are no long term active sampling sites in the region. The establishment of at least one active air sampling site in each of the four sub-regions (shaded in different colors in Figure 6.1.5) is recommended to verify passive air sampling results.

Measured air concentrations of selected POPs, namely *p,p'*-DDE, sum of 6 PCB and lindane (γ -HCH), at background sites are shown in Figure 6.1.5. At the remote island of St. Peter and St. Paul Rocks, concentrations in air of DDTs, PCB and lindane were very high in 2009 and 2010 and suspected to be due to long-range transport, although further verification is required. It is noted that the main DDT compound detected in both background and urban sites is *p,p'*-DDE suggesting non-recent use of DDT. The urban site of Porto Velho and rural site of Puerto Maldonado showed high concentrations of DDT due to the incidence of malaria in the area. The site in Havana (Cuba) has highly elevated concentrations of various POPs in air, including Σ drins, Σ DDTs, and in particular Σ PCB7, which is suspected to be due to its location close to an industrial site. Lindane was detected at all sites and was found with the highest levels of targeted POPs. This is related to use of lindane in the region prior to its classification as a POP. Only Uruguay reported PFOS data in air. Decreases of specific POPs at various locations were observed, but with 2 to 3 years of data, time trends cannot yet be established. Continuation of air monitoring at the existing sites is necessary to provide temporal trends for future reporting. Analysis of new POPs is identified as a challenge. Capacity building activities are important for establishing a regional monitoring system with regular interlaboratory assessments to ensure delivery of comparable data.

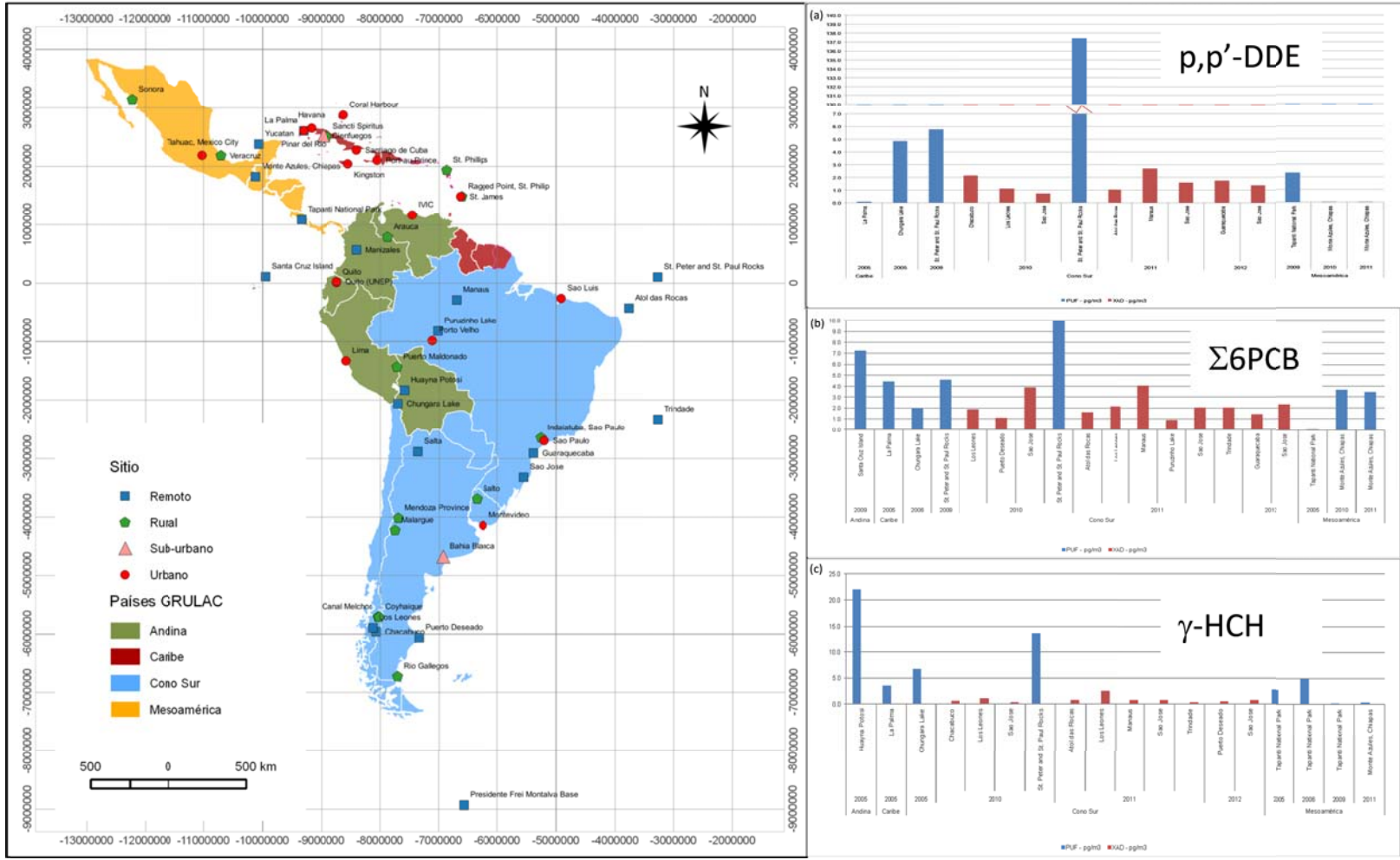


Figure 6.1.5. Distribution and classification of air monitoring sites in the GRULAC region (left panel). Measured air concentrations (pg/m^3) of (a) p,p'-DDE, (b) sum of 6 PCB and (c) γ -HCH at background sites. Different colour bars indicate two different types of passive sampling method used: PUF-disk based passive air sampling indicated by blue bar and XAD-based passive air sampling indicated by red bar (Source: Latin American and Caribbean Group Region Report).

Western Europe and Other Groups (WEOG)

The WEOG region comprises 28 countries in Western Europe, North America and Australasia. Results from the Arctic and Antarctic regions are also included in the WEOG regional report. In this region, 78 active and 88 passive air monitoring stations reported results to the GMP in this round of reporting. Some areas (e.g. Australia, Spain¹⁴) have recently commenced pilot programmes. Most of the longest running air monitoring stations and programmes, which generate considerable information on temporal trends of POPs, operate in this region. In the WEOG region, 20 active air monitoring stations report data series extending up to 20 years (reflected in Figure 6.1.1b for PCB 52). These stations operate in the Arctic under AMAP and Canada's NCP; in Europe under EMEP and the UK TOMPs programme; and in the North American Great Lakes region under IADN/GLB. Data reported at passive air sampling stations operating under the GAPS programme cover a ten-year period at 23 sites (reflected in Figure 6.1.1c for PCB 52). In addition to the important role of these programmes to GMP reporting, they also provided data to the POP Review Committee (POPRC) for assessing candidate POPs and help to identify new chemicals for consideration by POPRC. The data are also invaluable for developing and validating regional and global-scale transport models and investigations of climate effects (see Chapter 7). These long term programmes are also important resources for assisting with the implementation of new monitoring programmes in other regions through training, capacity building, and technology transfer.

In the WEOG region, the AMAP programme contributed heavily to the regional report through the recent AMAP trends assessment (AMAP, 2014). A number of new programmes with both active and passive air sampling stations were implemented in the past several years, which provided baseline information on POPs in air with greater spatial resolution. Most older and previously banned POPs are 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 (Table 6.1.1). Time trends of selected POPs are highlighted below. Time trends for many of the new POPs are not yet established, except PBDEs and PFOS precursors which have some limited trend data. However, baseline data of many new POPs have become available.

The chemicals α - and γ -HCH are well characterized in WEOG air monitoring programmes and demonstrate rapidly declining concentrations in air (Table 6.1.1). An example of γ -HCH time trend measured in air in the Great Lakes is shown in Figure 6.1.6a and a summary pie chart showing mostly declining trends of this chemical in the WEOG region is given in Figure 6.1.6c. The atmospheric decline rates of γ -HCH have accelerated in both the Arctic and the Great Lakes region following North American restriction of the pesticide lindane, which contains almost pure γ -HCH (Venier et al., 2012; Hung et al., 2010).

PCB 52 and PCB 101 at the Arctic station of Stórhöfði in Iceland have shown steadily increasing trends over the past few years of the time series. The time trend of PCB 52 at this location is shown in Figure 6.1.6b and this increase is also apparent in Figure 6.1.1b (shown as red dot). Such instances of increasing trends are attributed to the re-emission of PCB previously deposited and accumulated in water, ice and soil that have started to be released back to air due to a warming Arctic and the associated retreating sea ice and melting glaciers. The Stórhöfði site is an exception in the WEOG region as the summary pie chart of PCB 52 (Figure 6.1.6d) reflects generally declining trends in air across the WEOG region.

¹⁴ Spain's National Plan on POPs (PNA COP) operated since 2008 and is ongoing with passive air sampling at 12 remote (EMEP) stations and 6 urban sites. Data will be reported in the next reporting period

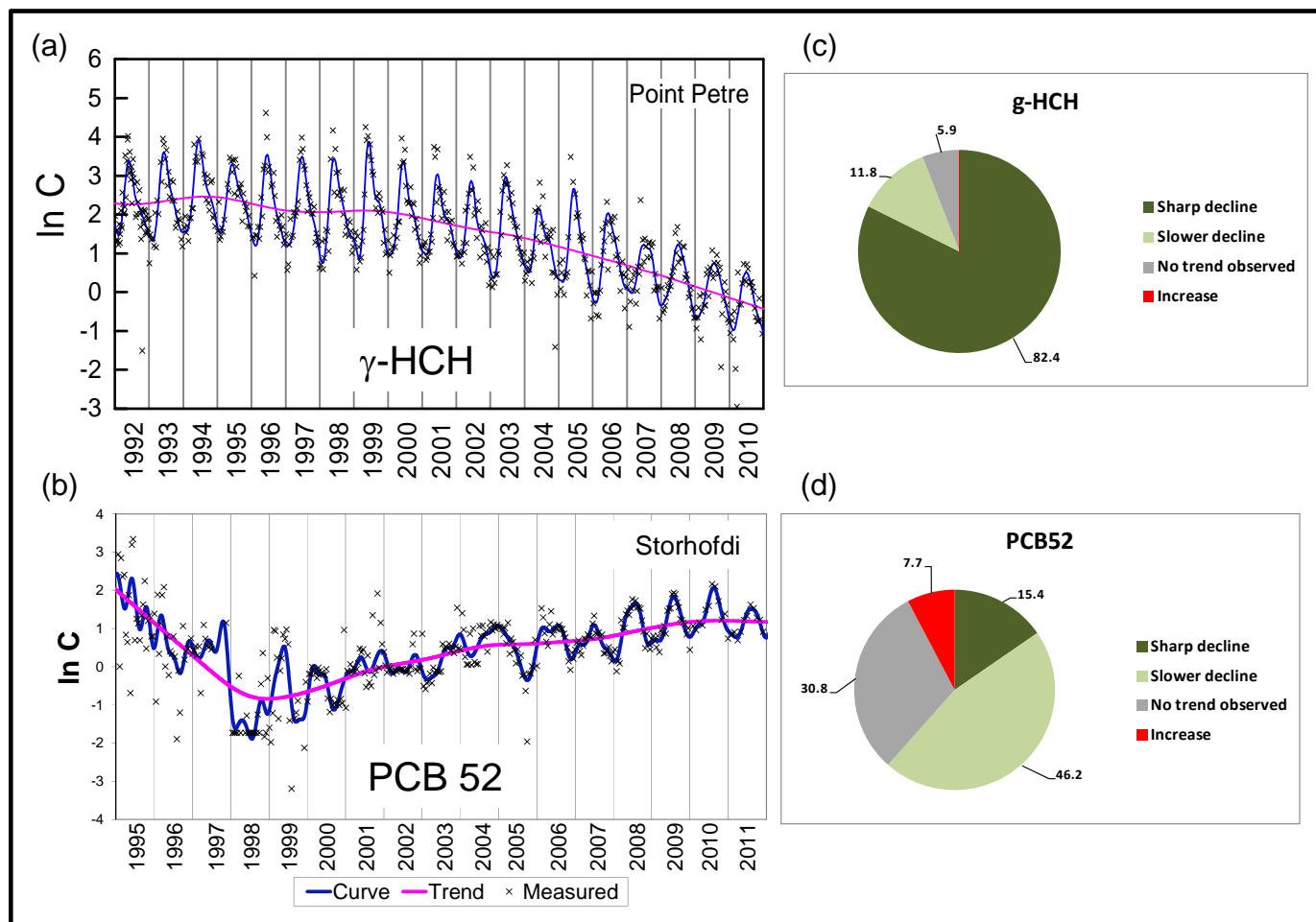


Figure 6.1.6. Time trends of (a) γ -HCH measured in air at the Canadian Great Lake site of Point Petre and (b) PCB 52 at the arctic station of Stórhöfði in Iceland. Also shown are the general summary pie charts of time trends observed in the WEOG region for (c) γ -HCH and (d) PCB 52. Time trends are classified as: “sharp decline” - concentrations half in 0.01 to 5.99 years (>11% per year); “slow decline” - concentrations half in 6.00 to 19.99 years (3.4-11% per year); “no clear trend” - concentrations half in >20 years (<3.4% per year) and/or trends are statistically insignificant; “increasing trend” - concentrations double in 0.01 to 19.99 years (>3.4 % per year). (Source: Western Europe and Others Group Region Report)

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. This observation may be related to the higher historical usage of these compounds in North America as compared to Europe, where declining trends in air are already being observed.

6.2 Human tissues (milk and blood)

Key messages

Since the entry into force of the Stockholm Convention, many countries have implemented harmonized protocols to generate consistent and comparable POPs monitoring data in human matrices.

Quantifiable concentrations are detected for all POPs with the exception of aldrin, chlordecone and endrin, although levels vary by orders of magnitude.

In regions with sufficient data to evaluate changes over time, levels of legacy POPs show a general decline.

For newly listed POPs, information regarding changes over time in their concentrations in human matrices is very limited.

Based on few available long term studies of PFOS and PBDEs, the levels seem to gradually decline.

6.2.1 Human milk

Background

In 2005, at the second meeting of the Conference of the Parties to the Stockholm Convention, it was recognized that human biomonitoring is essential to evaluate whether human exposure to POPs is indeed decreasing over time. Concentrations of POPs in human milk are considered good indicators of the actual body burden. In addition, human milk is considered as one of the best sampling matrices for biomonitoring due to its availability and non-invasive approach when collecting individual samples. Its high lipid content makes the extraction method for POPs easier and the precision of the measurements higher. Over the last decades, human milk has generally been used as a medium to measure contamination in humans, and analytical techniques have been well established for most POPs included in the Stockholm Convention.

Furthermore, the uptake of these chemicals by the infant via human milk is of high toxicological relevance. The risk-benefit assessment of breastfed infants represents one of the most challenging aspects of human toxicology, as possible adverse health effects associated with exposure to POPs concur with significant health benefits of breastfeeding. In this perspective, the results of the human milk survey are not meant to derive a “ranking” of countries with respect to risks for the breastfed infant. The surveys are primarily aimed at identifying worldwide quantitative differences of human milk contamination with these POPs, and provide a baseline for those countries for which such information was previously not available. This will allow in the future evaluating the effectiveness of measures taken to reduce POPs exposure. The quantitative differences observed in these surveys may provide a suitable basis for possible source-directed measures to further reduce levels of specific POPs on a country-by-country basis. Therefore it is useful to interpret the results in a national/regional context, and introduce targeted measures to further decrease human exposure.

The survey

Early WHO surveys performed mainly in Europe and North America in 1987-1989 and 1992-1993 exclusively focused on PCB and PCDD/PCDF. In 2001-2003, a larger global survey was implemented, covering the twelve POPs initially listed in the Stockholm Convention. Following the entry into force of the Stockholm Convention, WHO and UNEP started their collaboration, and two additional global surveys were completed in 2005-2007 and 2008-2012. These significantly enlarged the geographical scope of the study to provide representative results for all regions of the globe. As of 2014, the second phase of the survey is ongoing, with most results to be made available for the development of the third monitoring reports.

In order to promote reliability and comparability of results, samples were collected by the participating countries following a comprehensive protocol and guidelines developed by WHO in cooperation with UNEP. Participating countries were encouraged to adhere as closely as possible to the protocol, which provides guidance on the number and type of samples, selection of donors, collection, storage and pooling of samples, and shipping of samples to the reference laboratory. To further ensure consistency in measurements, all samples are analyzed by the WHO reference laboratory, the State Institute for Chemical and Veterinary Analysis of Food, Freiburg, Germany, using validated methods. Perfluorinated chemicals were likewise analyzed in a single laboratory at the MTM Research Centre, Örebro University, Sweden.

More than 11,000 data points have been generated to date in the frame of the survey covering 23 POPs (see chapters 1 and 2). These are analyzed in detail in the regional monitoring reports. The current global assessment focuses on limited number of POP compounds of major relevance in view of the effectiveness evaluation of the Stockholm Convention.

Results

Concentrations of PCDD/PCDF – reported as TEQ - are found at relatively similar levels worldwide, in both industrialized and less industrialized regions. While it is well-known that combustion and industrial processes are major sources of PCDD and PCDF, equal attention should be given to relevant sources in less-industrialized areas – such as open burning processes or geophagy- and promote measures to reduce releases from such sources.

The results confirm that the islands of the Southern Hemisphere have comparably low levels of PCDD/PCDF. In Africa, the widest variation in contamination of human milk was observed with distinct differences between PCDD/PCDF and PCB. Kenya and Uganda clearly have the lowest levels observed in this study for both groups of compounds. In contrast, West and Central African countries like Côte d'Ivoire, the Democratic Republic of Congo, Ghana, Mali, Nigeria, Sudan and Senegal have much higher levels of PCDD/PCDF in human milk, which can be more than four times higher as those observed in the East African region. These results indicate that exposure to dioxin-like compounds are significant and among the highest observed worldwide (UNEP/POPS/COP.6/INF/33).

The practice of eating clay, or other non-nutritious substances is usually referred to as "pica" or "geophagy". This practice is most common in early childhood, and in pregnant women and is of high relevance in certain sub-regions in Africa. The potential for adverse effects with oral ingestion of clay may thus be high, in particular through significant exposure to heavy metals and toxic organic compounds such as PCDD/PCDF (Reeuwijk et al.2013).

Reeuwijk et al.2013 have analyzed the possible consequences of clay contamination with PCDD/PCDF for the food chain and bioaccumulation in humans. They conclude that the relatively high levels of PCDD/PCDF measured in human milk from some African countries and the similarity of the congener patterns with those from the clays strongly suggest that oral ingestion of clays during pregnancy contributes to these high levels measured in human milk.

In addition to the UNEP/WHO human milk survey, other national and international efforts have contributed valuable data on POPs concentrations in milk and serum.

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.

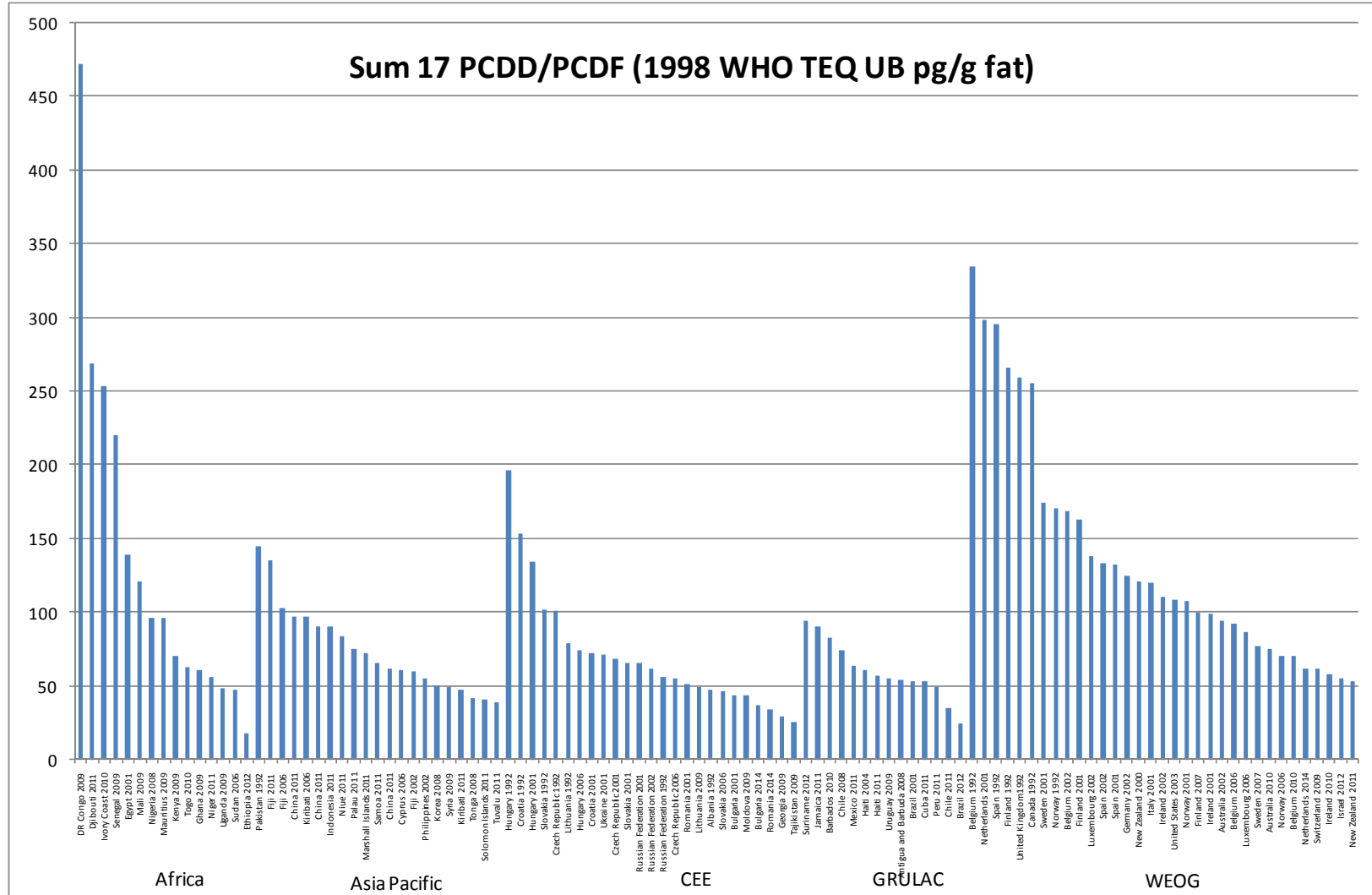


Figure 6.2.1. Concentrations of PCDD/PCDF in human milk (Sum 17 PCDD/PCDF; WHO1998-TEQ UBpg/g fat)

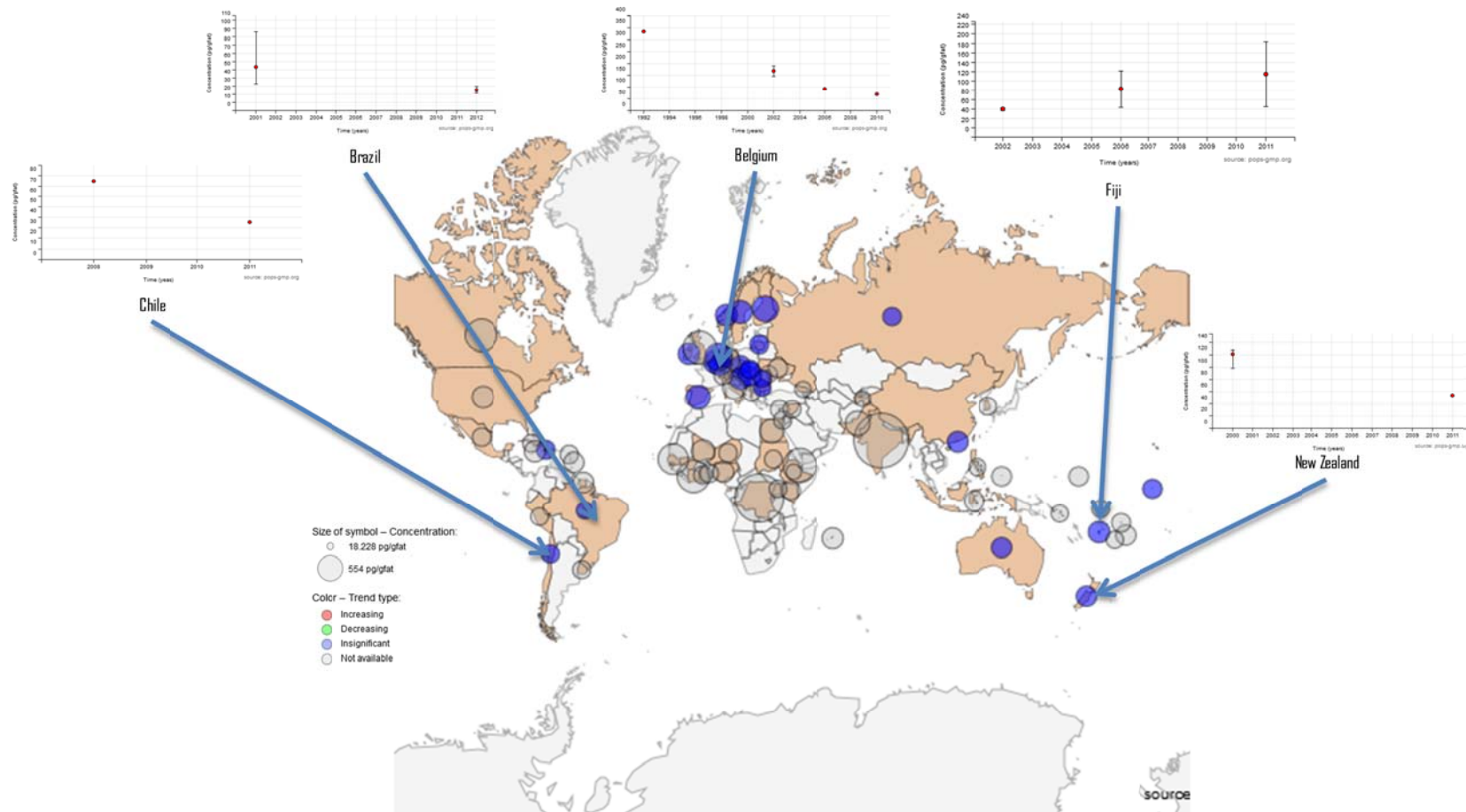


Figure 6.2.2. Trends in concentrations of PCDD/PCDF in human milk (Sum 17 PCDD/PCDF; WHO1998-TEQ UB pg/g fat)

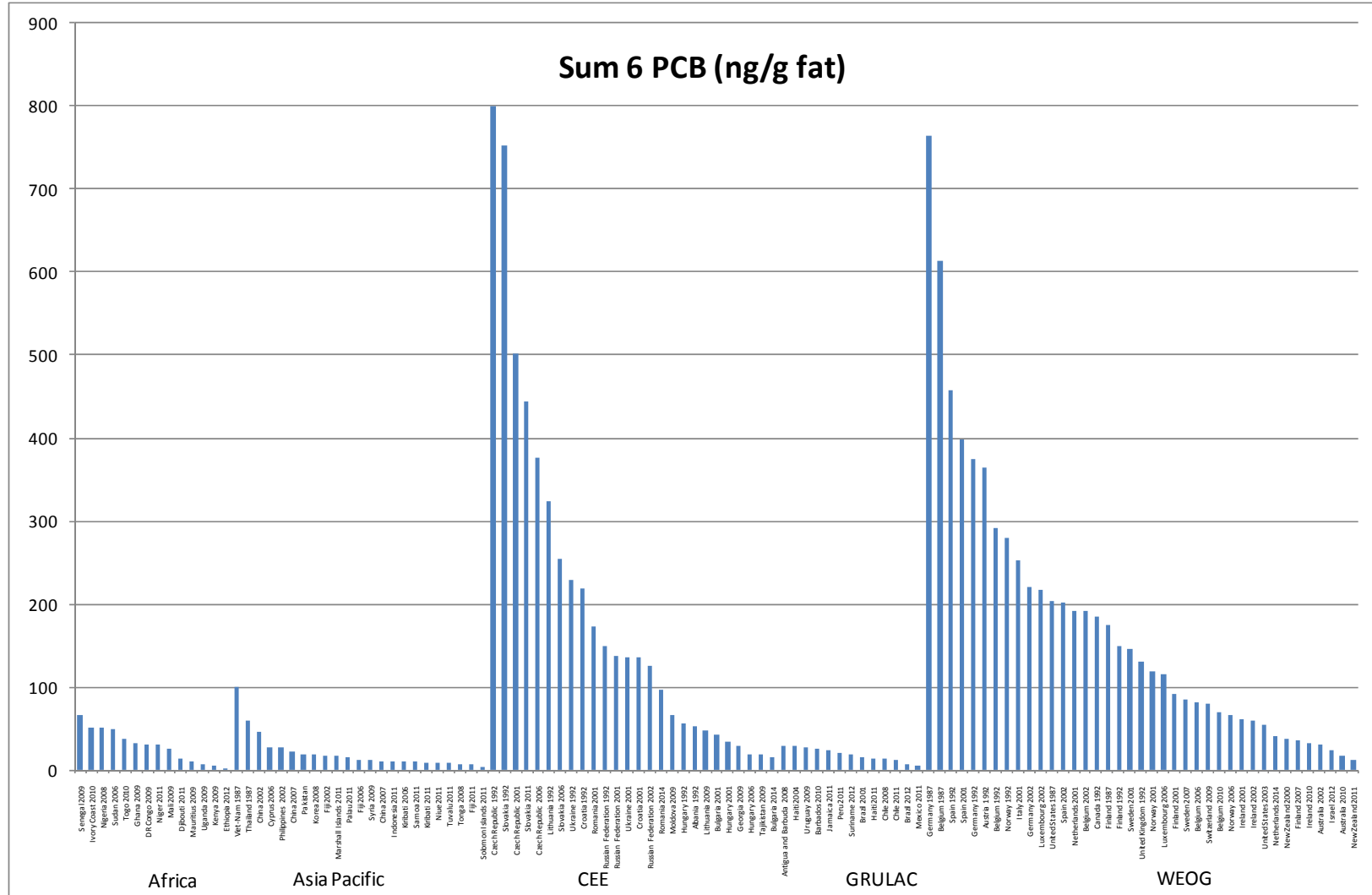


Figure 6.2.3. Concentrations of indicator PCB in human milk (Sum 6 PCB; ng/g fat)

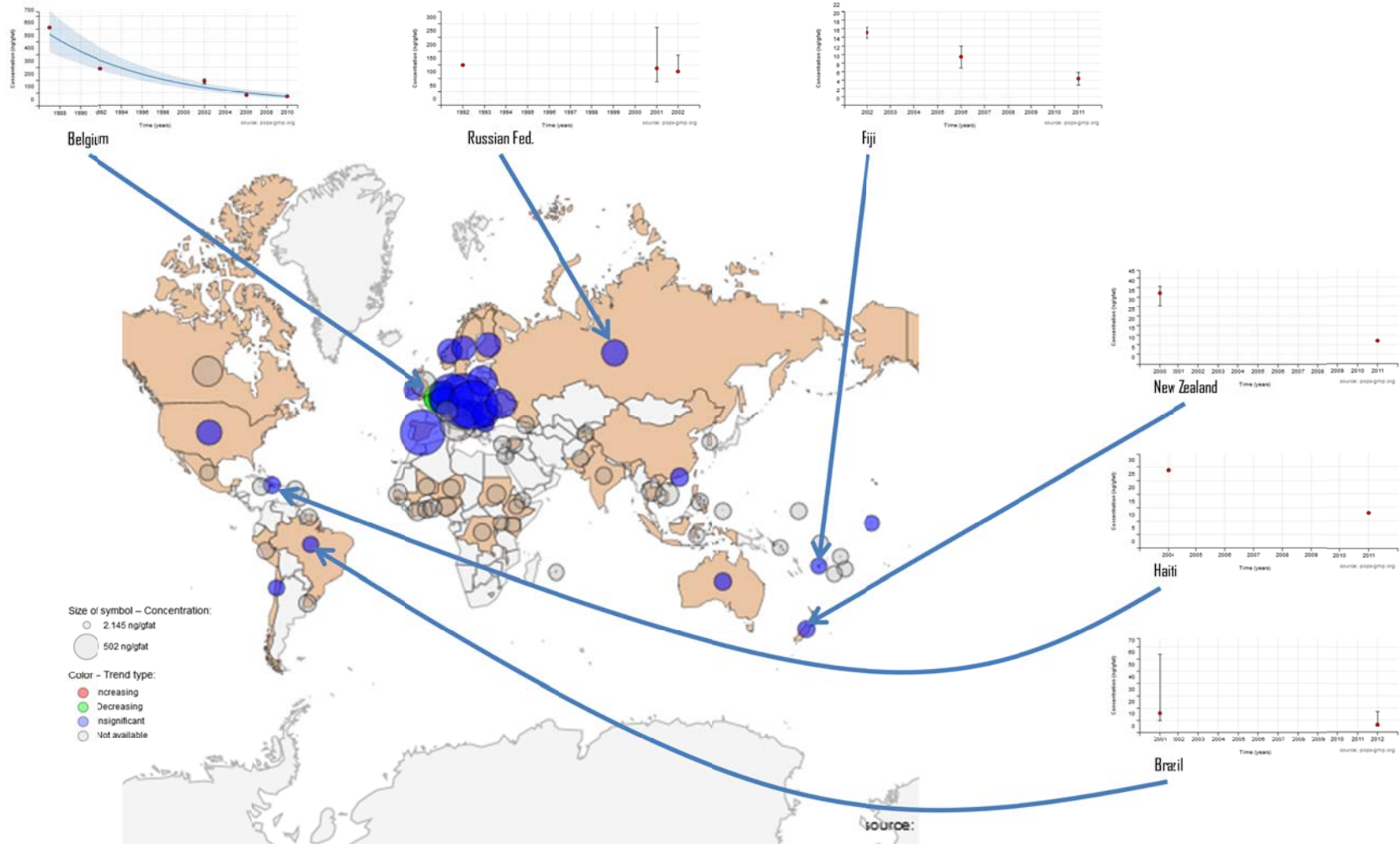


Figure 6.2.4. Trends in concentrations of indicator PCB in human milk (Sum 6 PCB; ng/g fat)

Overall, data from the last decade suggest that the levels of PCDD/PCDF in human milk have fallen steadily from their earlier high levels, indicating the effectiveness of measures implemented to reduce environmental releases. For PCB, the picture is less clear for some countries, but in general, declining levels are observed. The higher levels observed before 2000 in a number of industrialized countries have been successfully mitigated. The measures implemented in these countries to address releases of and contamination with PCDD/PCDF and PCB are thus shown to be successful in achieving their objectives and could be replicated in other parts of the world with similar positive outcomes (UNEP/POPS/COP.6/INF/33).

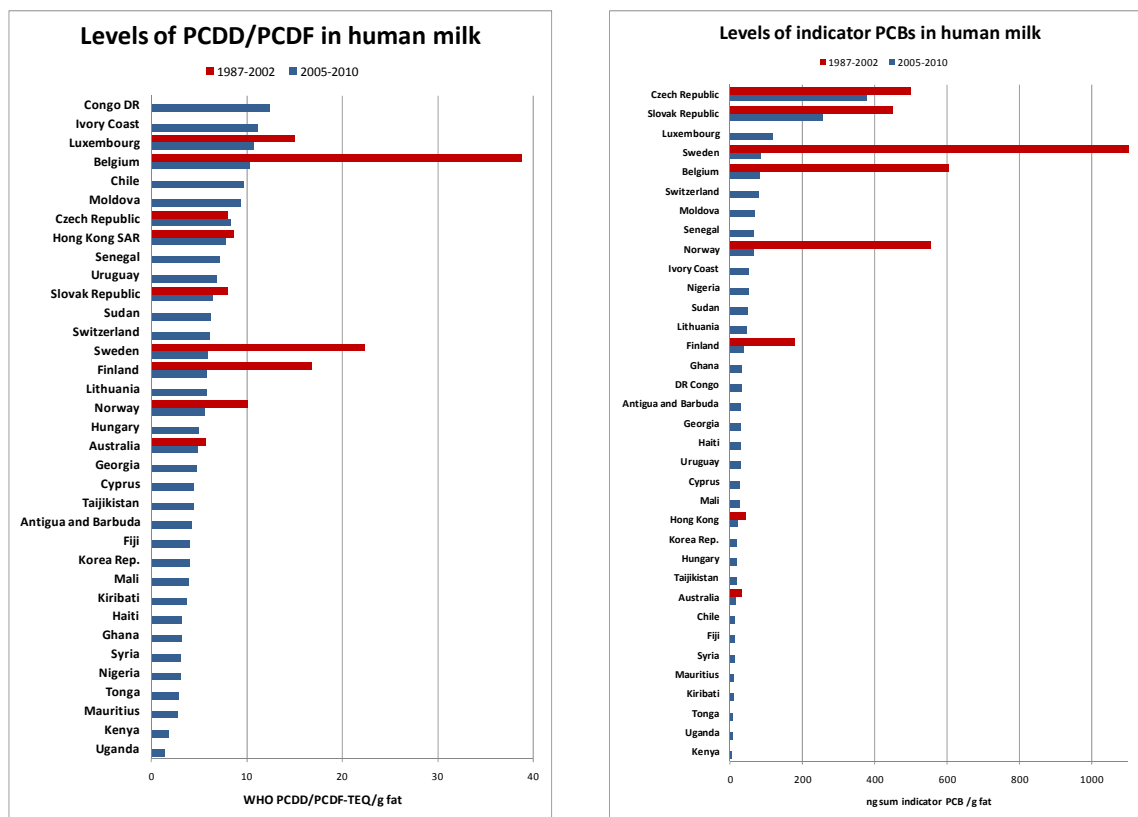


Figure 6.2.5. Levels of PCDD/PCDF (Sum 17 PCDD/PCDF) and indicator PCB (Sum 6 PCB) in human milk: survey results in 2005-2010 and comparison with 1980s levels

As for DDT, the highest levels were found in tropical and sub-tropical countries: Côte d'Ivoire, Ethiopia, Hong Kong SAR, Uganda, Mali, Mauritius, Haiti, Solomon Islands, Sudan and Tajikistan. This distribution reflects its use in relation to the occurrence and prevention of malaria in these regions. It is important to note a significant contribution of the DDE metabolite to the sum DDT, which suggests legacy contamination through past exposure (UNEP/POPS/COP.6/INF/33).

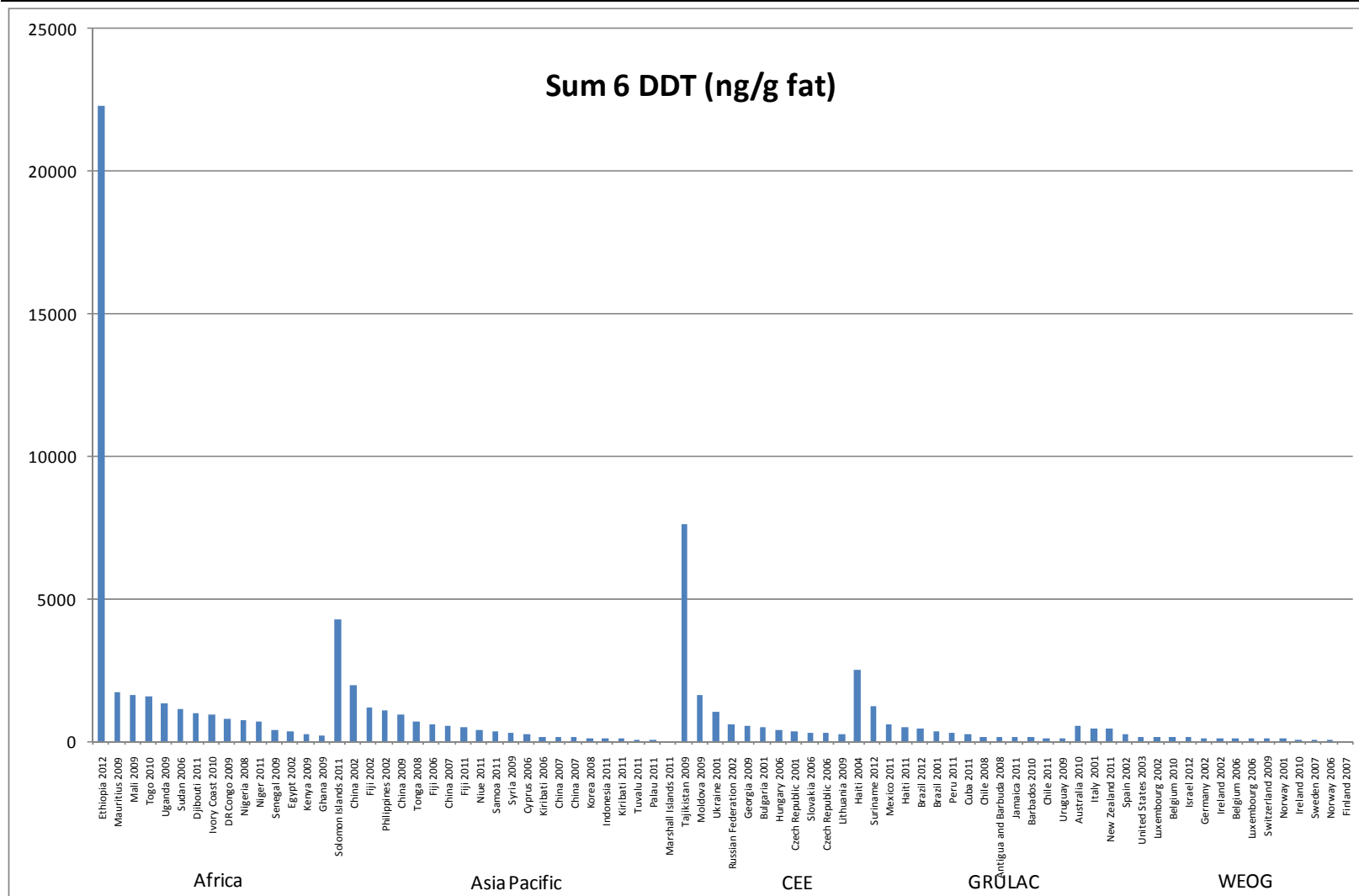


Figure 6.2.6. Concentrations of DDT in human milk (Sum 6 DDT; ng/g fat)

Among the new POPs, quantifiable concentrations of perfluorinated chemicals have been detected in human milk. PFOS was quantified in 67% of the milk samples analyzed, with concentrations ranging from <4 to 65 ng/L. The fact that PFOS could be detected at values above LOQ for the majority of samples shows that contamination and human exposure to PFOS in all regions where results are available is of concern. Other perfluorinated compounds that are currently not listed in the Stockholm Convention have been quantified in limited number of samples, with relatively low levels compared to studies reported from other countries (UNEP/POPS/COP.6/INF/33).

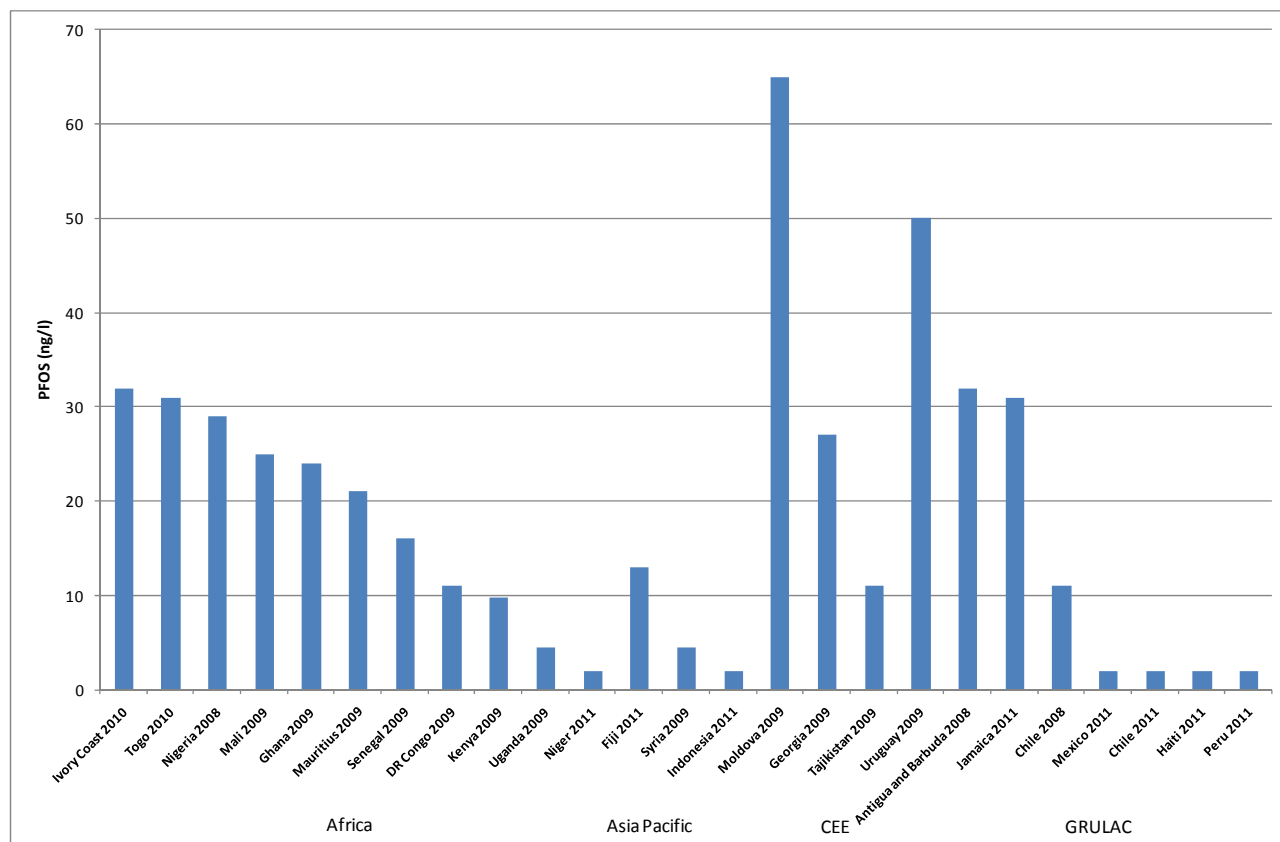


Figure 6.2.7. Concentrations of PFOS in human milk (ng/l)

Although PFOS is measured at low concentrations in human milk and better detected in human blood, there is good correlation between measurement results in these two matrices. A strong association between blood and milk concentrations of PFOS has been reported (Kärman et al., 2007).

The results for PBDEs are shown in Figure 6.2.8 below. High concentrations have been measured in pooled samples from industrialized countries such as USA and Australia, but also in the Pacific Islands (Fiji, Tonga) and in the GRULAC region (Antigua and Barbuda, Haiti, Jamaica, Mexico).

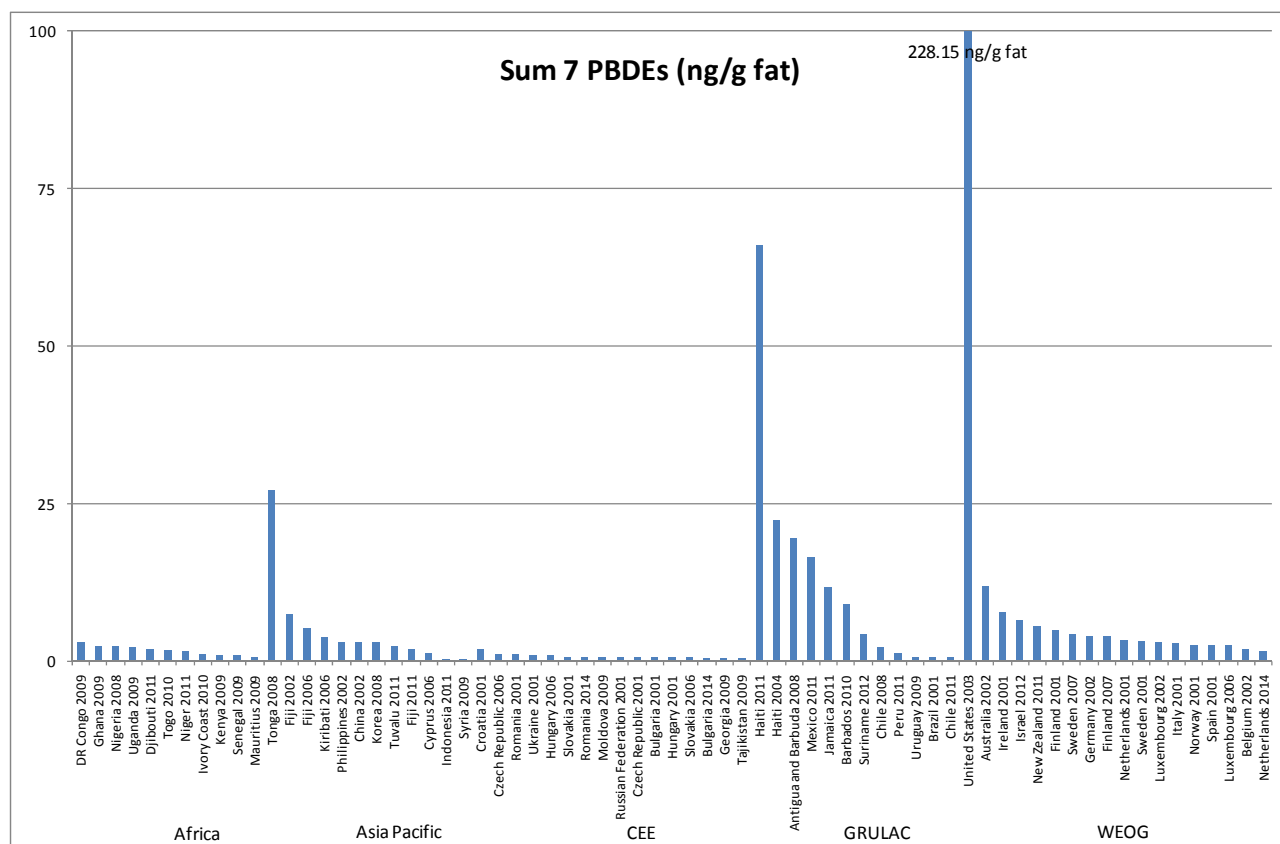


Figure 6.2.8. Concentrations of PBDEs in human milk (Sum 7 PBDEs; ng/g fat)

Endosulfan has only been quantified in two samples. High levels of lindane have been measured in certain African countries, Central and Eastern Europe, and in Asia and the Pacific.

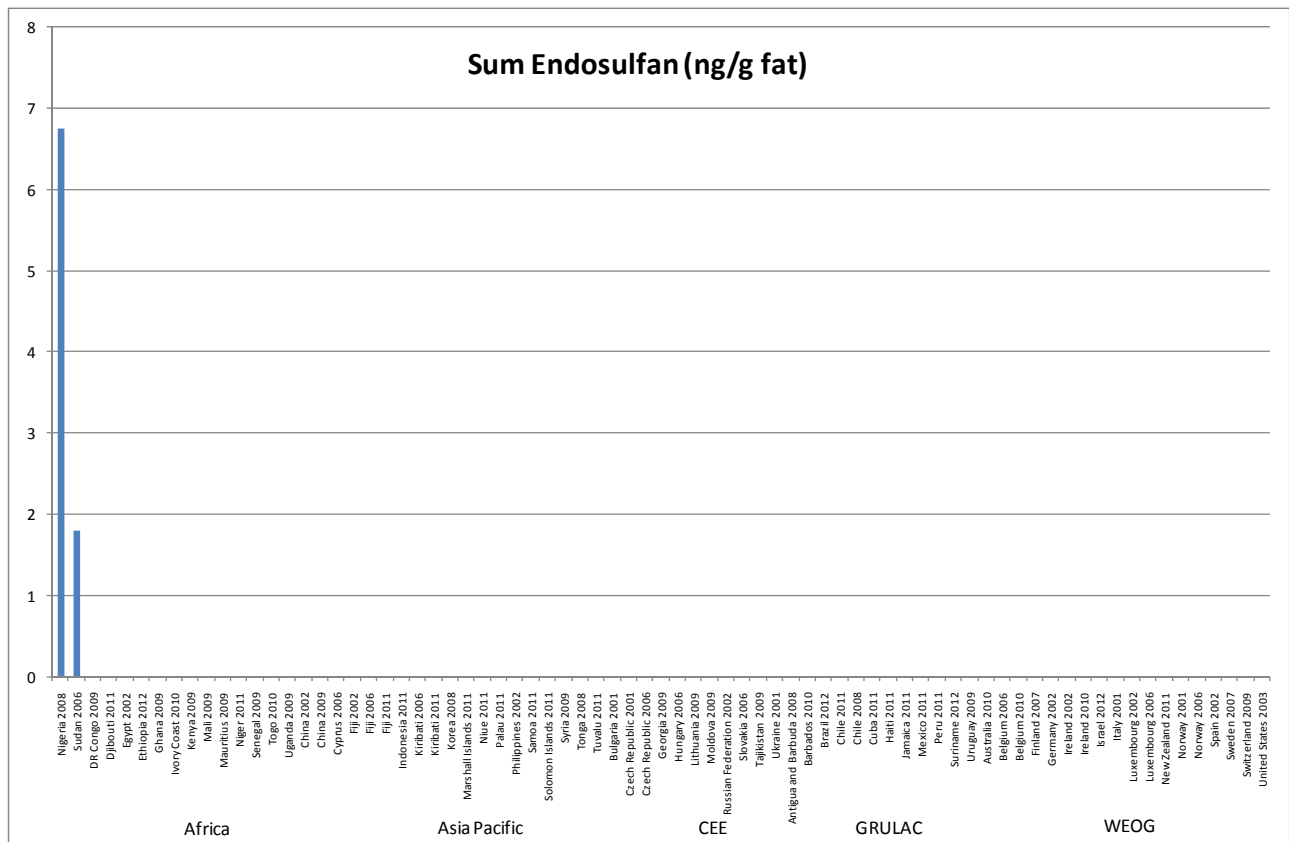
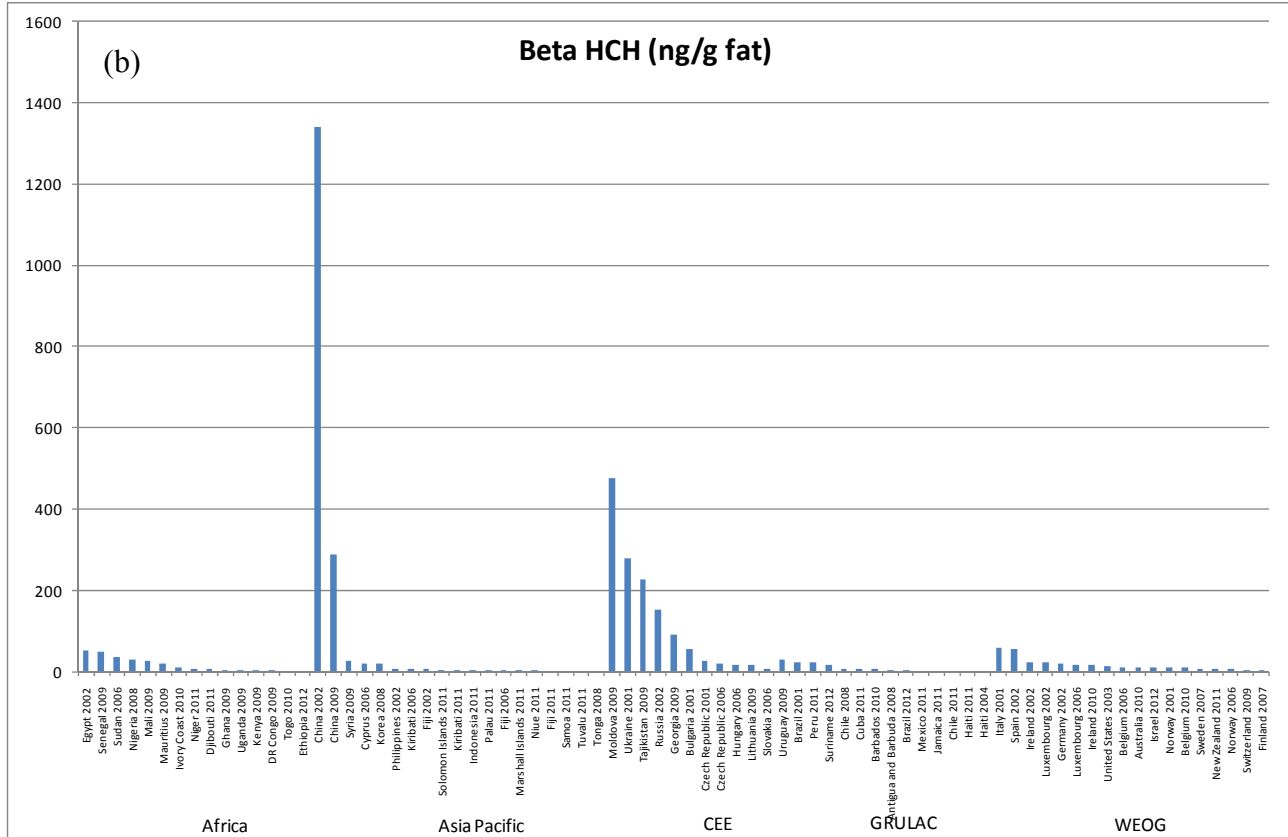
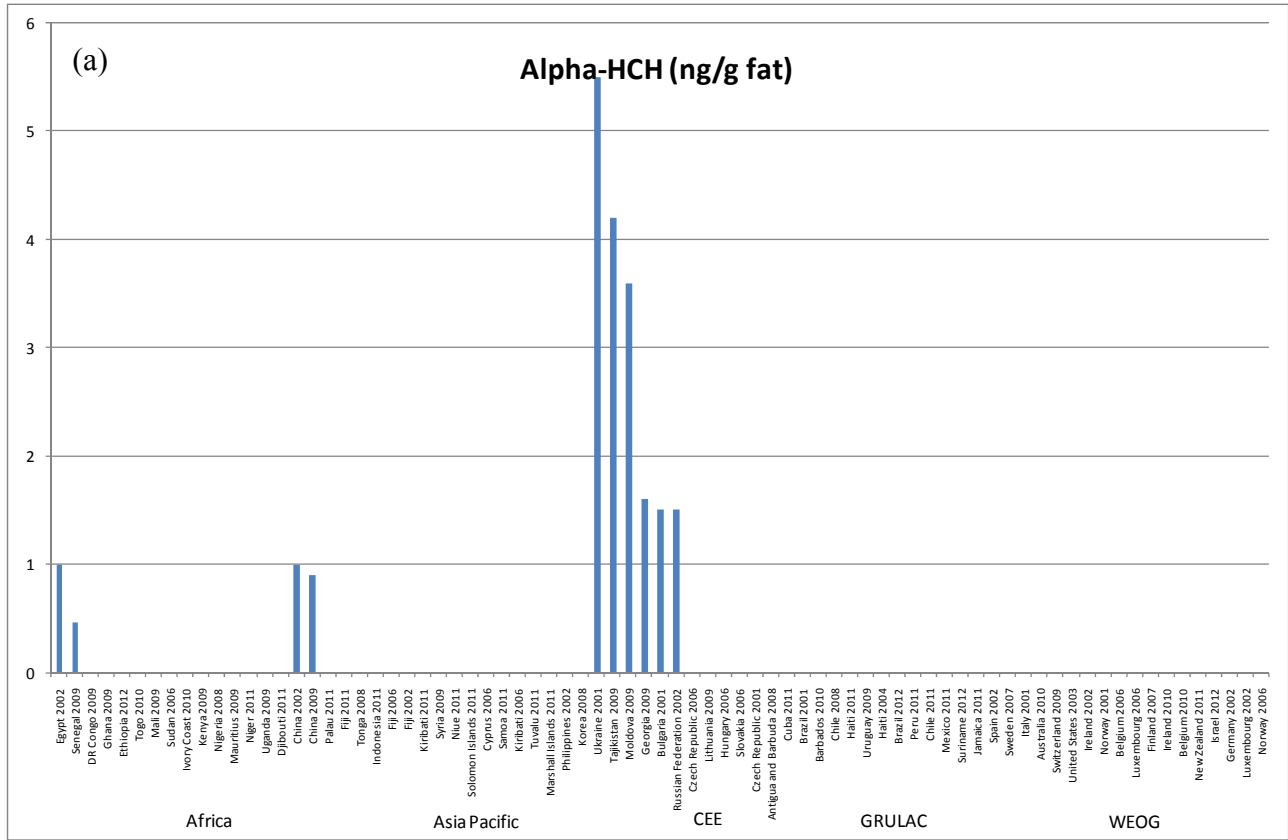


Figure 6.2.9. Concentrations of endosulfan in human milk (ng/g fat)



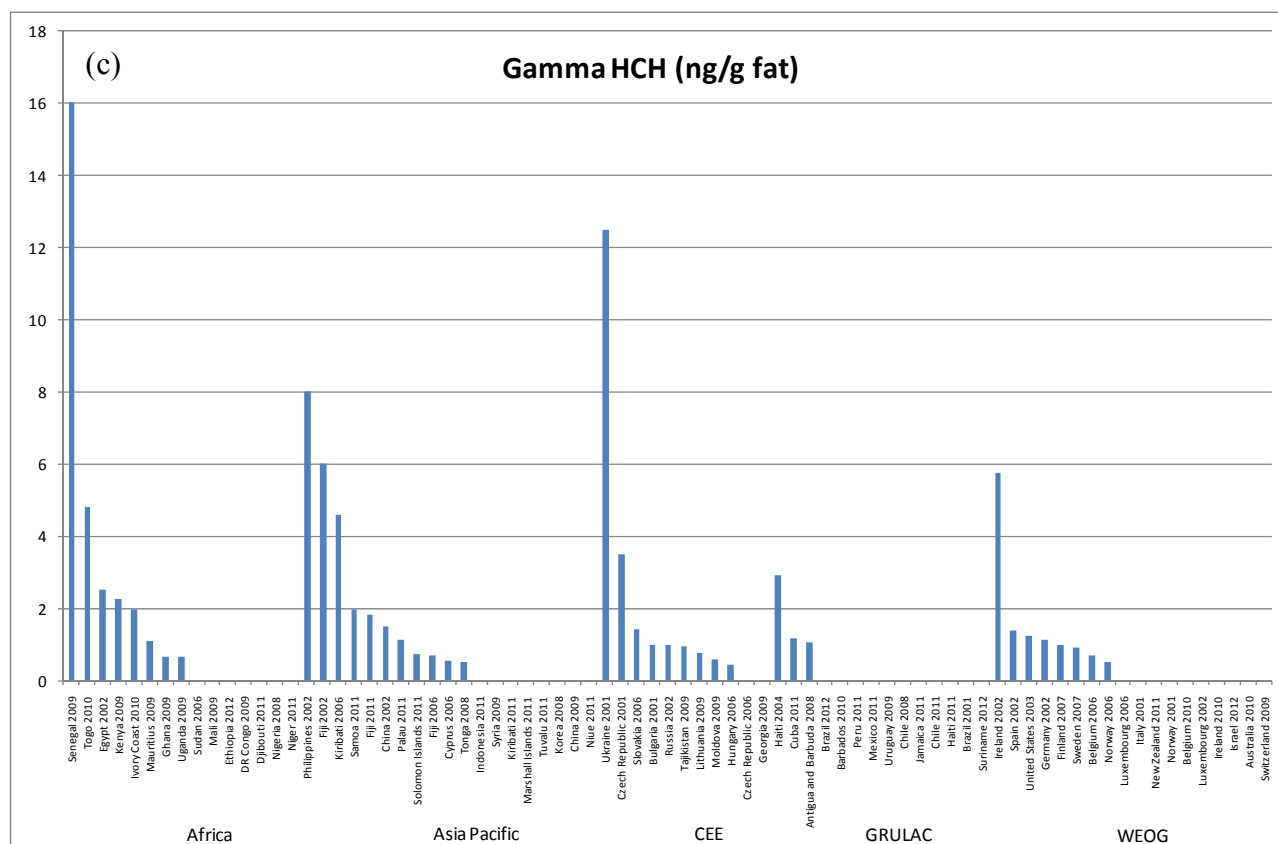


Figure 6.2.10. Concentrations of HCHs in human milk (ng/g fat): (a) – alpha; (b) - beta; (c) - gamma

6.2.2 Human blood

The sampling of blood for contaminants has taken place in WEOG and in Asia-Pacific. 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. These data sets provide an opportunity to assess temporal trends in pregnant women and, in some cases, in adults (both men and women). In the Asia-Pacific region, POPs monitoring programmes on human blood are also available. In Japan, national monitoring programme on human blood is performed and POPs concentrations in human blood in Japan were reported in several research papers.

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. In the WEOG region, 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 such overall findings.

The results of recent biomonitoring studies suggest that the concentrations of certain POPs such as 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)(AMAP 1998; AMAP 2003).

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 6.2.11). 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.

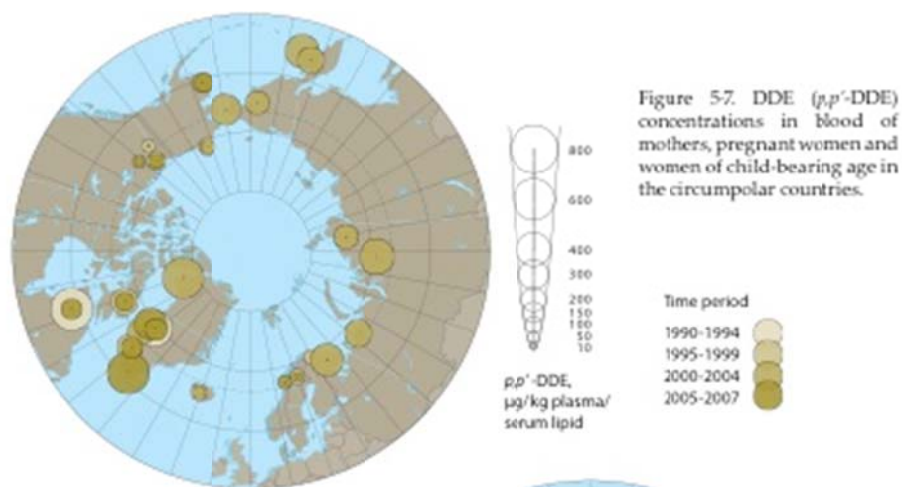


Figure 6.2.11. DDE (*p,p'*-DDE) concentrations in blood of mothers, pregnant women and women of childbearing age in the circumpolar countries (AMAP 2009).

The data sets suggest that concentrations of legacy POPs have decreased in many populations. 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 DDE.

Elevated human concentrations of PBDEs are 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 6.2.12). 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).

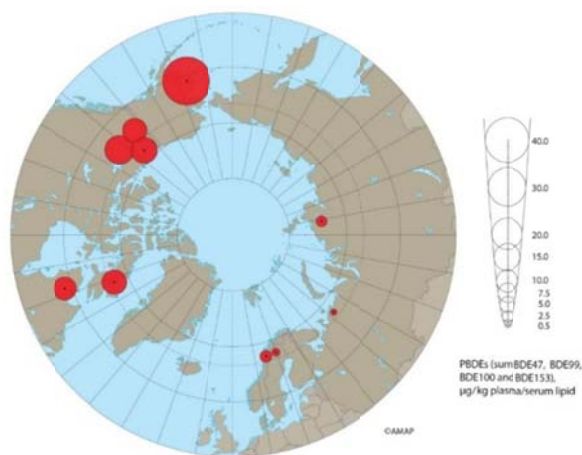


Figure 6.2.12. PBDE (sum of BDE-47, BDE-99, BDE-100 and BDE-153) concentrations in blood of mothers, pregnant women and women of childbearing age in the circumpolar countries (AMAP 2009).

The geographical distribution of human PFOS exposure across the Arctic provides no clear spatial distribution or distinct differences between countries (Figure 6.2.13.). 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.

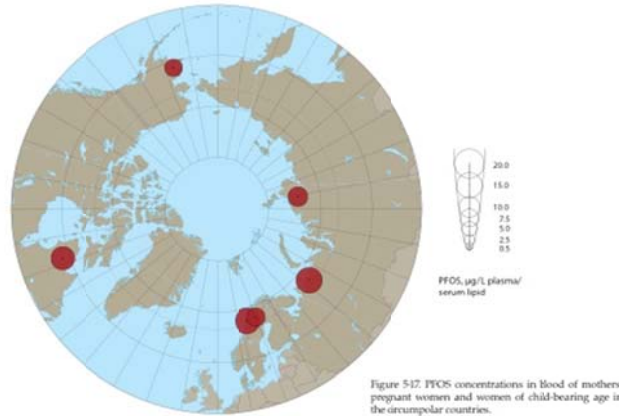


Figure 6.2.13. PFOS concentrations in blood of mothers, pregnant women and women of childbearing age in the circumpolar countries (AMAP 2009).

The levels of POPs 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). 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 6.2.14).

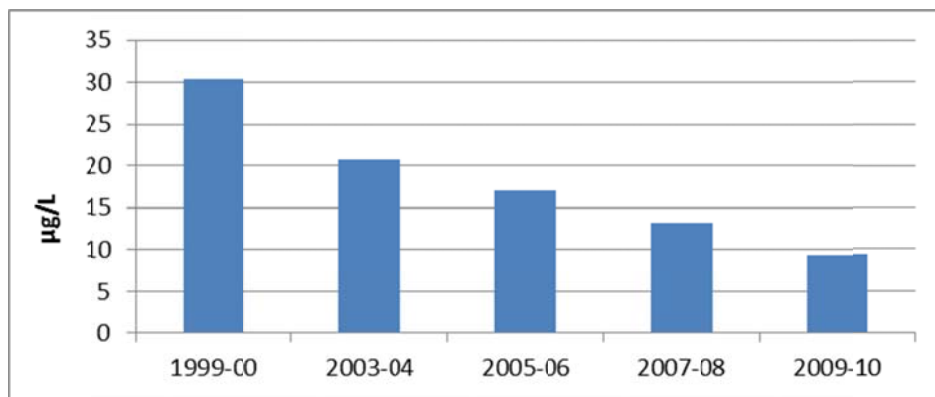


Figure 6.2.14. Levels of PFOS (µg/L) in the NHANES population between 1999 and 2010 (Regional monitoring report of WEOG, 2015).

PFOS has also been analyzed in blood serum samples from Australia 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 analyzed and compared with samples from 2006/2007 previously analyzed. 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.

In Kyoto, Japan, historical serum samples collected from females demonstrated that PFOS concentrations have increased by factor of 3 over the past 25 years (Harada et al., 2004). On the other hand, PFOS concentrations in blood of pregnant woman in Hokkaido, Japan showed that concentrations have decreased from 2003 to 2011 (Kunisue et al., 2006).

6.2.3 Summary

The amount of available information on levels of POPs varies for different compounds and regions. Table 6.2.1 below provides an overview of the changes over time in POPs concentration measured in human matrices for the five UN regions.

Table 6.2.1 Changes over time in POPs concentrations in human matrices for the five UN Regions. Shadings indicates: **green** – generally decreasing trends; **red** – increasing trends; **blue** – no change or cannot establish trend; **white** – no trend data; **★** - warning to indicate that trend assessment is based on limited data.

Chemical	Africa	Asia and the Pacific	Central and Eastern Europe	Latin American & Caribbean States	Western Europe and Other Groups
aldrin	Below LOQ	Below LOD or <LOQ	Below LOQ	Below LOQ	Below LOD
chlordanes	degradation product oxychlordanes detected	No decrease since 1998 in Japan; Oxychlordanes detected with decreasing levels over time in Fiji ★	degradation product oxychlordanes detected	degradation product oxychlordanes detected	degradation product oxychlordanes detected
chlordecone	-	-	-	-	-
DDTs	Baseline data available.	Decrease from 1972 to the first half of 1990s, then leveling off in Japan; Decreasing concentrations over time measured in Fiji ★	No detectable trend.	Declining concentrations in Haiti, no change in Chile ★	Declining trend in human milk (Swedish mothers), or Below LOD
dieldrin	Baseline data available.	Declining trend in Japan; Decreasing concentrations over time measured in Fiji ★	Baseline data available	Declining concentrations measured over time in Haiti, Chile ★	Measured at low levels
endosulfan	alpha-endosulfan detected in one sample ; beta-endosulfan <LOQ; endosulfan sulphate measured in two samples	Baseline data available	Below LOQ	Below LOQ	Below LOD
endrin	Below LOQ	Below LOD or <LOQ	Below LOQ	Below LOQ	Below LOD
HBB	Levels below LOQ but in one country	Baseline data available	Below LOQ	Below LOQ	Concentrations are low and mostly undetected
HBCD	Baseline data available	Increasing concentrations measured over 1974-2006 in Japan	Baseline data available	Baseline data available	Increasing till 2002, then leveling off in 2003-2004 in Sweden
HCB	Baseline data	Decrease from 1980 to the first half of 1990s,	Significant decrease in concentrations from	Decreasing concentrations over	Declining trend from

Chemical	Africa	Asia and the Pacific	Central and Eastern Europe	Latin American & Caribbean States	Western Europe and Other Groups
	available.	then levelling off in Japan; No change in levels in Fiji ★	two consecutive years in the Czech Rep ★	time measured in Brazil, Haiti ★	German ESB data
α-HCH	Below LOQ		Baseline data available	Below LOQ	Below LOD
β-HCH	Baseline data available.	Decrease from 1972 to the first half of 1990s in Japan, then leveling off	Baseline data available	Decreasing concentrations over time measured in Brazil, Chile ★	levels of β-HCH detected, but not in all samples
γ-HCH	Baseline data available	Baseline data available	Baseline data available	Baseline data available	Measured at low levels
heptachlor	Baseline data available	Declining trend in Japan. Below LOD in Pacific islands and China	Below LOD for heptachlor and trans-heptachlorepoxyde; decrease for cis-heptachlor suggested from two data points in the Czech Rep. ★	Baseline data available for trans-heptachlorepoxyde	Metabolite detected
mirex	Below LOQ	Mostly below LOQ, measured at low levels in China	Below LOQ	Below LOQ	Below LOD
PBDEs	Baseline data available.	Baseline data available.	Baseline data available.	Baseline data available.	Increasing concentrations in Nunavik (Canada); Concentrations reported to be leveling off or decreasing in Sweden and Norway; No significant time trend in Australia
PCB	Baseline data available.	Decreasing trend from 1972 to 1990s in Japan, then leveling off; Decreasing concentrations in Fiji ★	Significant decrease in CEE countries that used PCB in paints ★	Declining concentrations measured over time in Haiti and Chile ★	Declining concentrations over time in human milk and blood
PCDD/PCDF	Baseline data available.	Declining trend in Japan till 1998, then leveling off	Decrease observed in several countries in the region	Declining concentrations measured over time in Haiti and Chile ★	Declining concentrations over time in human milk and blood
PFOS	Baseline data available	Two studies from Japan indicate: 1. concentrations have increased over the past 25 years; 2. concentrations in blood have decreased from 2003 to 2011	Baseline data available	Baseline data available	Declining trend in NHANES, declining as of 2000 in German ESB data, declining in Australia
PeCBz	Levels below LOQ but in one country	Baseline data available	Baseline data available	Baseline data available.	Below LOD
toxaphene	Baseline data available	Mostly <LOQ, measured at low levels in China and Pacific Isl.	No significant change in concentrations from two data points in the Czech Rep. ★	Baseline data available	Measured at low levels

International global programmes such as the UNEP/WHO milk survey generate comparable data that are essential to evaluate temporal and spatial trends at the global level. In addition, national programmes evaluating time trends of chemicals in milk and/or blood, 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.

The available human biomonitoring data mainly covers PCB, PCDD/PCDF, DDT/DDE, 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 and endrin. Human monitoring data generated to date confirm that the levels of legacy POPs in human milk and blood, such as PCDD/PCDF, PCB, and DDT/DDE, have been and continue to be on the decline.

Among the newly listed POPs, the levels of PFOS and PBDEs show a slightly different temporal pattern. In the few available long term studies of PFOS from the WEOG region, the levels increased in the 1980s and 1990s, reflecting the industrial production, and have then declined in the areas where time series data were available. Long time series of PBDEs have shown that the levels peaked around the late 1990s and early 2000s. For some PBDEs, the levels seem now to gradually decline.

6.3 Water

Key messages

A large number of studies reports concentrations of PFOS in rivers, lakes/reservoirs, estuaries and coastal waters in the northern hemisphere nations of the WEOG and Asia-Pacific regions.

Monitoring of PFOS in water has been initiated on pilot basis in the Africa and CEE regions. No information is currently available from GRULAC.

Spatial trends of PFOS in ocean waters are relatively well studied with measurements of surface waters in all oceans as well as in some deep basins.

In addition to environmental measurements, river discharges have been estimated and modelled for a small number of rivers.

Temporal trend information for PFOS in water is very limited. Differences in sampling locations and in detection limits preclude any robust assessment of trends.

The objective of this chapter is to summarize the current state of knowledge of PFOS in water. With the addition of PFOS to the Stockholm Convention, the need to have data for water has become important because of the hydrophilic properties of this chemical. Water was not previously included in the GMP. Long-term PFOS monitoring in water is lacking in most of the regions, except WEOG and parts of the Asia and Pacific regions. However, a significant amount of data has been published on POPs in surface waters (Muir and Lohmann 2013) and PFOS in water monitoring activities have been initiated on pilot basis in the CEE and Africa regions. 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).

This review draws, in addition to the relatively scarce data collected and validated by the regional organization groups and published in the second regional monitoring reports, on a previous review of the literature on PFOS in water by Zareitalabad et al. (2013), as well as from the available peer

reviewed literature, and government technical reports. Such complementary information is set out in annex to this report.

Asia and Pacific

In the Asia-Pacific Region, several POPs monitoring programmes for PFOS in water are available. China is monitoring PFOS in the water at 10 sites of two coastal waters and 6 sites of two lakes in mainland in 2013. The concentrations of PFOS were ND – 47ng/L in the water. PFOS concentration in marine water surrounding Hong Kong SAR was monitored by Hong Kong Environmental Protection Department.

Japan is continuously monitoring PFOS in the water throughout the nation (48 to 49 sites) since 2009. The concentration range from 2009 to 2012 was between 0.02 and 230 ng/L. PFOS concentration in marine water surrounding Japan is monitored in another project. Also information on PFOS concentrations in sea water is reported in Yamashita et al.(2005).

United Nations University has been conducting capacity building program “Environmental Monitoring and Governance in the Asian Coastal Hydrosphere” in which PFOS monitoring in East/South Asian countries were conducted. Data from Republic of Korea, Philippines and Thailand were submitted through the focal point of the countries, and are compiled in this report. The PFOS concentrations in rivers and lakes, reservoirs range from 0.12 to 33 ng/L in Republic of Korea, 0.39 to 4.2 ng/L in Philippines, and from ND to 54 ng/L in Thailand, with averages of 4.9, 1.7, and 13ng/L, respectively. PFOS concentrations in coastal seawater in Thailand ranges from ND to 17 ng/L in general, and from ND to 730 ng/L in industrial areas, respectively. In addition, two published papers were submitted through the focal point of Thailand, and the data on environmental water levels are included in this report. In the report, PFOS concentrations in mainstreams and tributaries of Chao Phraya river range from 0.25 to 8.5 ng/L with average 1.7 ng/L. The average concentration of PFOS in waste water was 260 ng/L with maximum 6200 ng/L.

Africa

Limited information is available for PFOS in the Africa Region. Concentrations of PFOS from active water sampling in 2014 were 4.70 ng/L for River Niger in Mali and 4.6 ng/L for Sabaki River estuary in Kenya. Passive water sampling from MONET Africa pilot study provided additional PFOS data for rivers in Congo, Egypt, Kenya, Mauritius, Morocco and Nigeria. The concentration of PFOS in water from the site in Nigeria was 1.39 ng/L while the lowest was measured in Congo and Morocco having concentration of 0.04 ng/L. Medium concentrations were recorded in water from Kenya, Mauritius and Egypt. Variations in levels of PFOS were observed displaying the diversities of socioeconomic and industrial activities and local environmental conditions at the sampling sites in different countries. The concentrations measured cannot be directly compared due to differences in site characteristics. However, the levels of PFOS in water samples were comparable with some levels measured in river water samples from Spain at concentration ranging from <0.24 ng/L – 5.88 ng/L (Erickson et al., 2008). The concentrations of all PFOS salts were below the limit of quantification; PFOSA (2.00 pg/L), NMePFOSE (100.00 pg/L) and NEtPFOSE (50 pg/L).

Central and Eastern Europe

Limited information exists from various sources i.e. surface water, ground water and through various activities (NORMAN - NORMAN Association former NORMAN project of EU FP6 - Network of reference laboratories, research centres and related organizations for monitoring of emerging environmental substances), or Joint Danube Survey (2009), undertaken by the JRC in Ispra, Italy (Joint Research Centre of the European Commission).

PFOS in water bodies of the CEE region is not regularly monitored except the EU countries in the region (it is required by the EU legislation since 2013, where Water Framework Directive amendment included PFOS to the priority substance list as priority hazardous substance).

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

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

GRULAC

Only Uruguay reports data on PFOS in air within the UNE/GEF “Establishing the tools and methods to include nine new POPS in the Global Monitoring Plan”. It also includes PFOS in water, though the results are not yet available.

6.4 Other media

Key Messages

Many good quality data are available for biotic and abiotic media in some regions, which are important for supporting the effectiveness evaluation.

Delays in the establishment of control measures for some POPs resulted in environmental repositories in some environmental media which sustained/sustain levels in other media.

Guidance for sampling and analysis of POPs in other media are available under established monitoring programmes.

Natural archives and sample banks can be used for retrospective analysis to increase spatial coverage and assess changes over time.

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 media beyond 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 biogeochemical and commercial pathways of POPs mixtures in the local environment and the consequent exposure routes to humans and ecosystems.

This chapter reports the main findings describing concentrations of POPs in non-core media reported in the regional reports. The reports from Africa, Asia-Pacific and WEOG contain some information on other media. The reports by CEE and GRULAC include the arguments why the data on other media were not included and these are related to their local and episodic nature as well as the difficulty of comparing results due to lack of common QA/QC.

Africa

Other, non-core media that are frequently analyzed in the region include: soil, sediment, fish and foodstuff. The most commonly analyzed POPs are pesticides and PCB, although PCDD and PCDF have been analyzed recently through the UNEP/GEF project. The data presented in the Regional report were mainly produced under UNEP/GEF project, since in it the samples were collected within the same time period and analyzed centrally using the same methodologies.

Data for other media were obtained from 12 countries that participated in the UNEP/GEF project, and the key matrices included sediments, fish and soil.

The most common pesticides detected in other media were DDTs, HCB, dieldrin, HCHs and the concentrations were generally low in sediments, fish and soil from background sites. The concentration of PCB were also relatively low in sediments ranging from bdl to 1.2 ng/g. Similar trend was observed in fish samples with concentrations ranging from below detection limit to 0.15 ng/g. Fly ash sample analyzed was dominantly contaminated with PCDD/PCDF and dioxin-like PCB. PCDD/PCDF were also detected in some fish samples with concentrations ranging from bdl to 59 ppg fat⁻¹. However, the levels of dioxin-like PCB in fish were higher than PCDD/PCDF.

Data from fish samples were submitted by five out of the six participating countries in the East and Southern Africa sub region.

The concentration of PCDD/PCDF in fish was highly variable across the countries and across the individual PCDD/PCDF and dioxin-like PCB. PCDD/PCDF concentrations in fish varied from below detection limit to as high as 59 pg. g fat⁻¹. The observed trend in the concentration of PCDD/PCDF in fish was similar to that observed in sediments where dioxin-like PCB in the in fish were in orders up to 100 times higher than PCDD/PCDF in fish lipid.

A survey of literature reports showed that research work is being done within the African region on the contamination of water, soil, sediments, and food by pesticides with a focus on organochlorine POP pesticides. The interest in POPs seems to have been enhanced in a certain extent due to sensitization brought up by the Stockholm Convention. In the regional report, the ROG decided to incorporate some monitoring data on non-core media dealing with the contamination of water, soil, sediments and food by POP pesticides in order to show that the African region does have some relevant technical infrastructure and effective expertise that need to be strengthened to enable the region to participate fully in future Effectiveness Evaluations.

The monitoring data on soil, sediments, water, and food presented in the regional report cannot be compared across sites as they were not obtained from harmonized protocols/programmes, and in addition have been recorded for different time periods.

In summary, some data are available for the region which seem to indicate relatively low levels in background sites but higher levels in some soils and other media in potentially locally contaminated sites.

No data are available at this point concerning more recently listed substances such PBDEs or HBCD. It would be helpful in the future to build on the existing competences and infrastructures to acquire regular and comparable data.

Participation of more countries is required to increase the data coverage and achieve regional representation. Future efforts to provide data for other media should include detailed protocols and repeat of similar matrices to allow comparison of temporal trends in POPs levels in other media.

Asia-Pacific

The Regional report includes a vast and very valuable collection of data from Japan with measurements of POPs (Aldrin, Chlordane, DDT, Dieldrin, Endrin, Heptachlor, HCB, Mirex, Toxaphene, Chlordecone, Endosulfan, HBB, HBCD, HCHs, PBDEs, PeCBz, PFOS, PCDD/PCDF, dl-PCB) in fresh water, sea water, ground water, bottom sediment in water, sediment cores, soils and marine and terrestrial biota in hundreds of sites throughout the nation over decades. These data provide a very valuable base to study the development over time for a number of substances in multiple media and locations obtained in a regular and comparable manner. An extended summary of these data is presented in the Annex to the report prepared by the ROG.

The very valuable and complete data collection presented for Japan are representative for one country in the region but it is difficult to know to what extent these results are comparable with the situation in other countries, with very different economic and industrial history and structure.

No data for other countries in the region are reported, reflecting the fact that there are no regular monitoring institutional arrangements or infrastructures at this point in time. A number of scientific publications have reported data for other parts of the region but these are not regular and comparable to assess time trends or differences in the region.

Overall the data from Japan seem to indicate that significant decreases for most early POPs (OC pesticides, PCB, dl PCB, PCDD/PCDF) between 1970 and 2000 and much smaller changes and no significant trends since then while the concentrations of more recently listed POPs (PBDEs, PFOS, HBCD) are either increasing or leveling off in recent years but no significant decreases or decreasing trends can be identified. These results are coherent with the results presented by ROG WEOG.

WEOG

In the WEOG region several well established long term monitoring programmes have produced a wealth of data since the 1980s. These include AMAP, NCP, the Great Lakes programmes, OSPAR, HELCOM and MEDPOL.

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. The AMAP 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 Thematic Data Centre 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. AMAP provided a specific report for the GMP with a complete summary of trend analysis on all the series obtained for biota distinguishing the fraction of them that show significant trends (increasing or decreasing) and the fraction of time series that do not show significant trends.

The results of the AMAP study are described in the WEOG regional report and its Annex 5. The WEOG ROG has compiled some of the main findings published by the long term monitoring programmes that are strategic partners in the GMP effort. These are summarized in the table presented below.

Table 6.4.1. 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) ¹⁵ . Levels in 2009 <30ng/g ww	
chlordan	-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	
DDT	-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
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

¹⁵ Aldrin and endrin once in the environment transform into dieldrin and thus monitoring efforts are focused on this more persistent compound

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>Mytilusgalloprovincialis</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>Mytilusgalloprovincialis</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

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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 PBDE99 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 Walleyerose from 1970s to the early 2000sand 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. ¹⁶	
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

¹⁶ Source: Yang et al. ES&T 2012

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, PCB and PBDEs	PFOS are the predominant PFOA in biota, increasing trends of 7-10% per year since the 1970s in common guillemot (<i>urialga</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
PeCBz	-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, seabirds 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					
ΣPCB	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>

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<p>PCDD/PCDF</p>		<p>Concentrations in Lake DV09 core peaked in the 1970s with a maximum TEQ value of 0.07 ng/g dw detected in 1978.</p> <p>Concentrations in the blubber of ringed seals from Ulukhaktok.</p> <p>8.6–14.6 pg/g did not change between 1981 and 2000.</p>	<p>Although top sediments show lower concentrations compared to deep sediments, trends have not declined in fish over the period 1990-2005.</p>		<p>Significant decreases 1970s to 2000 Significant levels in some matrices and in some areas near population and industry</p>	<p>Declined in waterbirds 1970s – 2009 in all Lakes.</p> <p>Consumption advisories in all lakes.</p>	<p>Levels of concern in 2002 in Adelaide Penguins and South polar skua eggs.</p>
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Summary

Data availability, consistency and comparability

The situation reflected in the regional reports is that there is an abundance of published information on POPs in other media, but for the most part its difficult or impossible to establish quantitative comparisons due to the differences in the media monitored (different species, locations seasons), and lack of common QA/QC procedures. Only a few well established long term international programmes (AMAP and NCP for the Arctic, Great Lakes of North America, OSPAR for the north Atlantic, HELCOM for the Baltic and MEDPOL for the Mediterranean) and a few national programmes (such as in Japan) can at this point in time produce data on spatial and temporal trends. In the future it would be useful to be able to make better use of existing data and to support and consolidate existing infrastructures that can help make monitoring of other media more consistent and integrated with global modeling and assessment efforts.

Main findings

The overall picture that emerges is that OC pesticides and legacy POPs (PCDD/PCDF, PCB) did decrease significantly from peak values in the 1970s to the early 2000s but the measured values since then do not show significant trends and in some cases small increases have been observed. More recently listed POPs (such as PBDEs, HCB, PFAS, endosulfan show increasing trends over the past decade, the increases in some cases (PFAS) seem to slow down or stabilize. Despite the significant decreases of some POPs since the 1980s the ubiquitous presence of mixtures of relatively low levels of a numerous multiplicity of POPs gives reasons for concern.

Natural archives (see for example Blais et al. 2015) and sample banks could play a very significant role to assess long term trends for POPs in non-core media in a rigorous and cost effective manner on a global scale.

It would be helpful to include recommended methods to sample and analyze non-core media (such as sediment, fish, etc) in the GMP guidance document for the work in the future, and monitor such other media in the existing established monitoring programmes.

7 Long range transport on regional and global scales

Key Messages

Emissions, long-range transport and levels of POPs in the global environment are integrated into a coherent picture by models.

Models facilitate assessment of factors that drive changes in POP levels, such as changes in primary and secondary emissions and climate variability.

Improved availability and accessibility of monitoring data through databases like the GMP data warehouse supports modeling.

Modeling of POPs synergistically supports implementation of both the CLRTAP and Stockholm Conventions.

Models inform the identification of substances with POP-like properties and in the preparation of risk profiles.

One of the key limitations on modeling POPs at the global level is a lack of complete and reliable release inventories.

Background

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

Compelling evidence of LRT is available for POPs that are measured in regions of the world that are remote from sources, and results of monitoring programmes are summarized in other chapters of this report. Chemical fate and transport models can be used in combination with monitoring data to better 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 understanding LRT, and thus to the implementation and effectiveness evaluation of the Convention.

Why model the long-range transport of POPs in the environment?

Models help to understand the levels and trends of POPs that are observed at monitoring stations. Mathematical equations in the models describe physical and chemical processes in the environment, and link the concentrations of POPs in air, water, soil and vegetation to emissions. When emissions are scheduled for reduction due to restrictions on the production and use of POPs, models can forecast the expected decline in concentrations in the environment. Furthermore, models can isolate the effect of emission reductions from other factors, such as climate change, that might affect levels and trends of POPs.

It is important that models be evaluated against data. Comparing the models to monitoring data and investigating discrepancies provides a basis to improve our overall understanding of the sources, transport, and ultimate sinks for POPs in the environment. The “integrated approach” of combining emission inventories, models and measurement data is the only way to compose a complete picture of environmental contamination by POPs. The integrated approach reveals inconsistencies in available information, and helps set priorities for further research that will support decision-making (UNECE, 2010). Models are the backbone of the integrated approach, and can be viewed as a repository of knowledge and conceptual understanding about POPs in the environment (Figure 7.1, MacLeod et al. 2010).

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

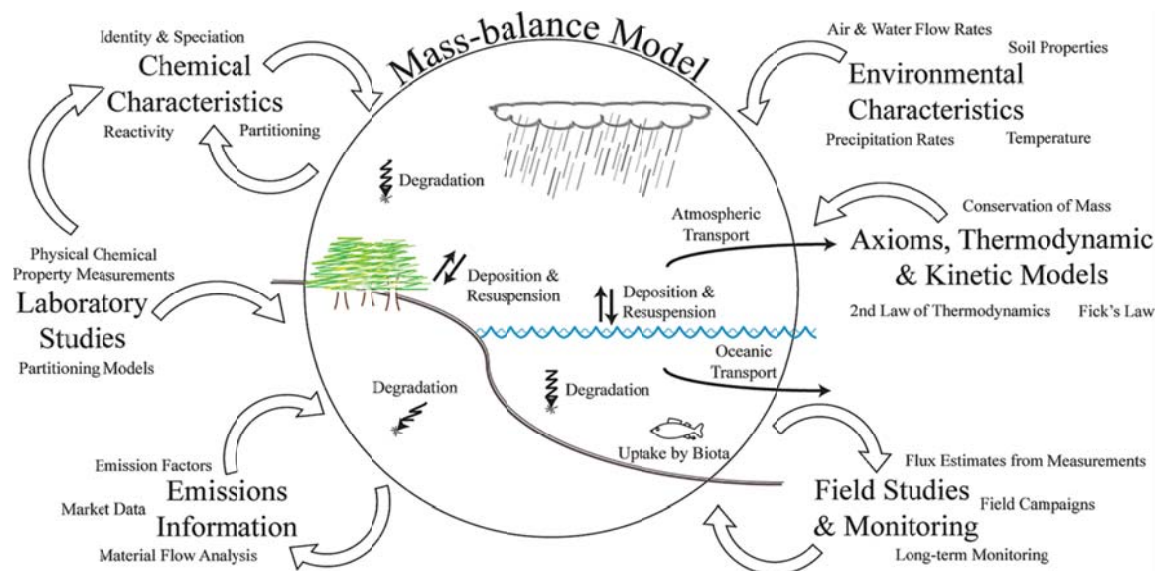


Figure 7.1 Mass-balance chemical fate and transport models are repositories of knowledge about POPs in the environment. The curved arrows illustrate the flow of information about chemical and environmental properties that determine the behavior of POPs in the environment, laboratory and field studies, and a mass balance model that integrates the information. The model assembles different aspects of the system into an integrated picture. (Figure reproduced from MacLeod et al. 2010 with permission).

LRT modeling in support of the Stockholm Convention

One of the limiting factors for assembling global descriptions of POPs in the environment using models is a lack of emission inventories (Breivik, et al. 2006). However there are published emission inventories available for the mixture of technical HCHs (Li 1999, Wöhrnschimmel et al. 2012) and for PCB (Breivik et al. 2007). We used these emission inventories as input data for two global-scale chemical fate and transport models, calculated concentrations of α -HCH and PCB-153 in the global atmosphere over their use histories, and compared the modeled concentrations with measurements included in the GMP data warehouse (GMP DWH, 2015). The models used in this exercise are the “Research” version of the Berkeley-Trent Global contaminant fate model (BETR Global, MacLeod et al. 2011, Wöhrnschimmel et al. 2013), which has been developed in the WEOG region, and the Global EMEP Multi-media Modeling System (GLEMOS, MSC-E, 2015), developed in the CEE region.

The two models provide very similar descriptions of the spatial variability of α -HCH and PCB-153 in the global atmosphere, and broadly agree with monitoring data from the GMP data warehouse (Figure 7.2). For α -HCH highest concentrations in the period between 2004 and 2013 are in India and China, where the phase-out of HCH usage occurred last. For PCB-153 highest concentrations are in central and eastern Europe and the east coast of North America, corresponding to areas of high historical usage of PCB. Concentrations of both α -HCH and PCB-153 are generally higher in the atmosphere of the Northern Hemisphere compared to the Southern Hemisphere.

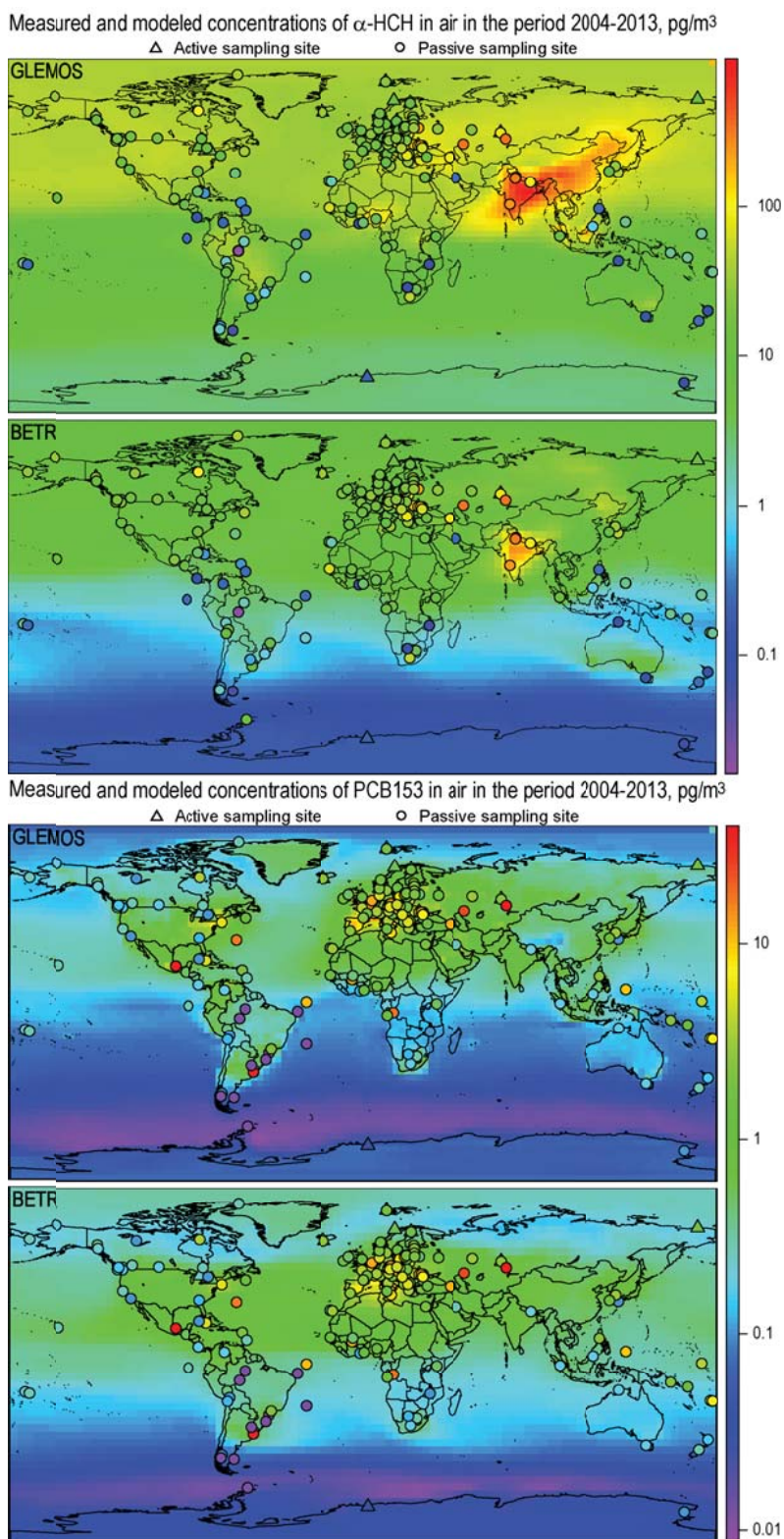


Figure 7.2 Median measured concentrations (triangles for active sampling and circles for passive sampling) of α -HCH and PCB-153 in air in the years 2004-2013 compared to median modeled concentrations (color field) calculated by GLEMOS and BETR Research. Measurement data were collected from the Stockholm Convention GMP data warehouse.

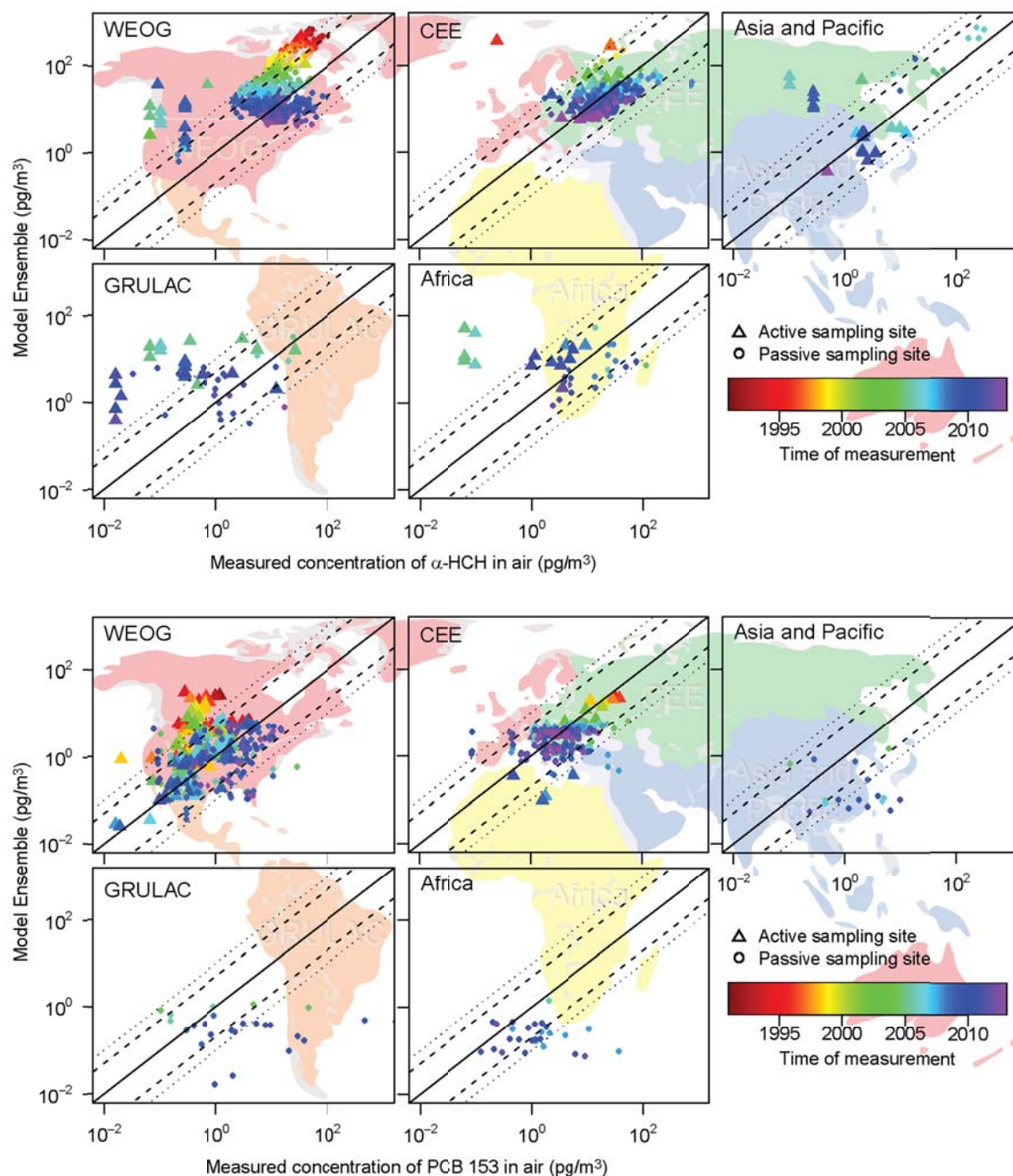


Figure 7.3 Geometric mean of concentrations of α -HCH (top) and PCB-153 (bottom) in the atmosphere (pg/m³) modeled by GLEMOS and BETR Research (model ensemble) plotted against measured concentrations at monitoring sites in the 5 UNEP regions collected from the GMP data warehouse. Individual data points are color coded to indicate the year of the measurement. The solid line in the plots indicates perfect agreement, dashed lines agreement within a factor of 5 and dotted lines agreement within a factor of 10.

The comparison between model results and measured concentrations from the GMP data warehouse in each of the five UNEP regions shows that most monitoring data is available for the WEOG and CEE regions (Figure 7.3). Both the models and the measurement data indicate declining concentrations of α -HCH and PCB-153 in these regions between 1990 and 2013, and a large majority of the monitoring data are within a factor of 5 of the geometric mean concentration calculated for the ensemble of the two models.

Models can provide useful insights into the factors that are controlling levels and trends of POPs that are observed in monitoring data. The BETR Research model calculates secondary emissions of POPs from vegetation, soil and water as a function of relative concentrations in air and the surface media, chemical properties and temperature. In the model scenario for HCHs, primary emissions of both HCH isomers are lower than secondary sources to the atmosphere after the year 2000, and are completely phased out after 2012 (Figure 7.4). After 2012, levels of the two HCH isomers in the atmosphere are primarily controlled by secondary emissions that are a result of cycling of HCHs from vegetation, soil and water back to the atmosphere. The model scenario forecasts that levels of α -HCH in the atmosphere will eventually be higher than levels of β -HCH because the β isomer is expected to be more persistent in the environment (Wöhrnschimmel et al. 2012).

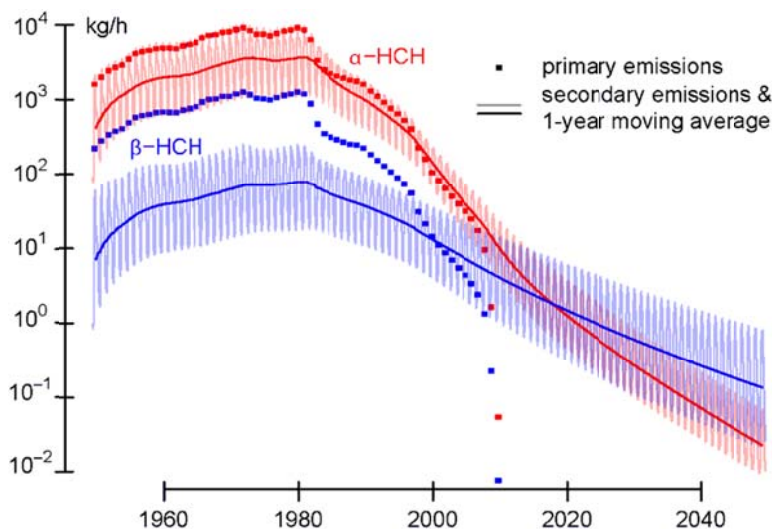


Figure 7.4 Primary emissions of α -HCH and β -HCH to the atmosphere from usage of technical HCH as a pesticide compared to secondary emissions from soil, vegetation, fresh water and oceans calculated in the modeling scenario of Wöhrnschimmel et al. (2012) using the BETR Global model.

Modeling capabilities and research priorities

The case studies for α -HCH and PCB-153 demonstrate that global scale transport models for POPs can describe levels and trends of POPs in the atmosphere with good fidelity to the data in the GMP data warehouse. However these case studies represent the best case situation for existing POPs.

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 among these are 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:

- a. Improve emission inventories;
- b. Improve understanding of mechanisms and rates of degradation of POPs in air, water, soil and sediments;
- c. Enhance modeling capabilities, especially for describing air-surface exchange.

The regional assessment reports provide details of specific LRT assessment activities in each of the UNEP regions and interested readers should refer to these reports for details. At this time modeling of LRT for POPs is mostly taking place in the WEOG and CEE regions, and the Asia Pacific region is also becoming more active.

Models for identifying new POP candidates and preparing risk profiles

Insights gained from measuring and modeling existing POPs 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 distinct 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 dataset. 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). First principles methods based on these calculations should avoid the “streetlight effect” observational bias (Wikipedia, 2014) that is introduced by searching for unrecognized POPs among chemicals in commerce by relying on professional judgment and QSPR models trained with data for relatively well-studied chemicals.

Chemical fate and transport models are now well-established as useful tools for conducting screening-level chemical hazard classification 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).

Modeling the effects of climate change on POPs and other scenarios

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 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 usage of industrial chemicals in an ice-free Arctic, and intensified application of agrochemicals due to higher 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 location.

Other modeling studies at global (Lamon et al. 2009, 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. The effect of climate change on future concentrations of POPs is expected to be small compared to the effect of emission reductions that are possible under regulatory instruments like the Stockholm Convention. 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).

Summary and outlook

The development, application and continued refinement of fate and transport models for POPs is a key scientific contribution to the implementation and effectiveness evaluation of the Stockholm Convention. Models provide unique scientific input for identifying potential new POPs, and in the risk profiling process. For existing POPs, models provide estimates of POP levels in regions where there is currently no monitoring, a framework to describe and explain the levels and trends 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. Models can help determine whether the trends are due to changes in emissions or other factors. 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.

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 complements 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).

Synthesizing emissions scenarios with monitoring data using models provides opportunities to improve the science that supports global management of POPs and the GMP. Monitoring of POPs in the atmosphere is still most extensive in the WEOG and CEE regions, however in recent years spatial coverage has been improved considerably using passive sampling that was motivated by requirements of the GMP. As more monitoring data are added to databases like the GMP data warehouse it will become feasible to apply global model calculations in reverse, and to calculate emissions from the measured concentrations at the global scale. This "inverse modeling" of emissions has already been applied at local scales to derive emission factors for POPs and some POP candidates (MacLeod et al. 2007, Moeckel et al. 2014, Bogdal et al. 2014, Diefenbacher et al. 2015). Similar modeling at the global scale has the potential to contribute to formulating more reliable emission inventories and tracking progress of emission reductions efforts more effectively, as envisioned by Hung et al. (2013).

8 Conclusions and recommendations toward the third GMP phase

Conclusions and recommendations toward the third GMP phase

General considerations

Progress in the second phase of the Global Monitoring Plan (GMP)

1. The second phase of the GMP was conducted in compliance with the amended global monitoring plan for persistent organic pollutants,¹⁷ the amended implementation plan for the global monitoring plan for persistent organic pollutants,¹⁸ and the updated guidance on the global monitoring plan.¹⁹ These documents provided an appropriate framework and sufficient guidance to perform the required activities.

Recommendation: *Third phase of the global monitoring plan should continue to use the amended global monitoring plan, implementation plan and guidance document as its foundation.*

2. Since its entry into force the Stockholm Convention has triggered new POPs research and monitoring activities worldwide, and brought together research findings from around the world. Data availability and coverage has significantly increased at the global scale in the second phase of the GMP as compared with the first phase. In the first GMP report, temporal trends were available from a few regions with long time series monitoring data for some of the initial POPs listed under the Convention. Through sustained monitoring since the first phase of the GMP as of 2004, information on temporal trends is now becoming available globally. Furthermore, long-term monitoring programmes have enlarged the scope of their activities to cover newly listed POPs in addition to legacy POPs, and new programmes have emerged. Activities for sampling of PFOS in water have also been initiated as part of the second phase. In most cases, monitoring data show clear decreasing trends for legacy POPs, suggesting that, when regulations are established and implemented, they can successfully address global environmental contamination problems.

Recommendation: *Ensure sustainability of ongoing monitoring activities in the long term in developed and developing countries to provide the important information required to support the effectiveness evaluation of the Stockholm Convention. Intensify and diversify efforts as required to address remaining gaps in data coverage and to monitor new POPs as they are added to the Convention.*

3. Enhanced comparability within and across monitoring programmes, to evaluate changes in concentrations over time and the regional and global transport of POPs, was an important milestone in the second phase of the GMP. QA/QC practices have been and continue to be essential for ensuring comparability, along with inter-laboratory comparison exercises and intercalibration studies. A major focus of the work in the second phase of the GMP was to develop a GMP data warehouse to enhance data harmonization, accessibility and to support data handling by the regional organization groups and the global coordination group, and aiding in the production of regional and global monitoring reports.

Recommendation: *Efforts towards ensuring comparability and consistency in monitoring data at the global level should continue. The regional and global monitoring reports should be broadly shared and GMP data warehouse should be serviced and supported to support*

¹⁷ UNEP/POPS/COP.6/INF/31/Add.1.

¹⁸ UNEP/POPS/COP.6/INF/31/Add.2.

¹⁹ UNEP/POPS/COP.6/INF/31.

data handling in the frame of the GMP and to provide access to up-to-date POPs monitoring data.

4. The GMP guidance document provides essential information supporting implementation of the Convention in the five UN regions. The guidance is continuously updated to include the most recent technical and scientific information and to address monitoring needs for new chemicals (sampling and analysis), as they are listed in the Convention.

Recommendation: *The latest version of the guidance should always be used as the reference document.*

5. Sample archiving and sample banks have proven to be useful to address data needs for listed POPs to support the GMP and effectiveness evaluation and for screening studies on chemicals under consideration for listing.

Recommendation: *Monitoring programmes should be encouraged to maintain long-term sample archives for retrospective analysis.*

Capacity building

6. Systematic capacity building activities have been carried out in developing countries, including strategic partnerships with well-established monitoring programmes. Despite these efforts, several regions still have limited capacity to monitor POPs. The addition of new POPs to the Convention creates additional demand for training to implement and sustain POPs monitoring activities.

Recommendation: *There is need for further capacity building and training for sample collection and analysis, for data analysis, and for assessment of long-range transport. Regions maintaining or seeking to build capacity should be encouraged and supported to form and /or maintain strategic partnerships with existing monitoring programmes.*

7. ROGs in some regions have experienced challenges in coordination due to limitation in communication and access to information exchange infrastructure.

Recommendation: *There is need to strengthen regional communication and information exchange structures to enhance information sharing among the regional organization groups and to strengthen regional coordination. Parties should maintain updated lists of contact points internally and with the Secretariat.*

8. Limitations in sustained financial resources for existing monitoring programmes and new financial resources for programmes addressing data gaps are a major constraint in ensuring the sustainability of the GMP.

Recommendation: *Global monitoring of POPs, should be sustained in the long term to confirm decreasing concentrations of legacy POPs in the environment and in humans and to identify trends in the concentrations of the newly listed POPs. Continued support to monitoring programmes is required to ensure continuity of the monitoring activities including sampling, analysis and data QA/QC and storage, in order to provide adequate data to assess temporal trends and long-range transport of POPs, for existing and new monitoring activities.*

9. Data quality, consistency and comparability is key to assess temporal trends and evaluate effectiveness of measures that have been undertaken.

Recommendation: *Laboratories in programmes contributing monitoring data to the GMP should participate in international interlaboratory assessments.*

10. There is an abundance of untapped capacity in regions that could be used to enhance future work under the GMP.

Recommendation: *The ROGs and the regional centers should strive to improve intra-regional coordination among experts (including academia) to address GMP data requirements.*

Challenges

11. The growing list of POPs and chemicals proposed for listing adds pressure on monitoring programmes and analytical laboratories.

Recommendation: *Additional funding and resources will be needed to respond to pressures for analysis of new POPs. In addition, monitoring programmes may need to adjust their protocols and resources to better align with new priorities. Some pressure can be relieved by reducing analysis frequency for legacy POPs (e.g. PCB, organochlorine pesticides) where declining trends have been established, optimizing analytical methods, and establishing partnerships among laboratories to address specialized analytical needs. It is not necessary for every laboratory to be an expert for every class of POPs.*

12. In addition, alternatives to the listed POPs are being used without a sufficient evaluation of their potential POPs properties. Increased concentrations of some of these alternatives were monitored in some regions.

Recommendation: *To establish an effective link between the POPRC and the GMP on the issue of alternatives and make best use of the available monitoring data.*

13. Although the burden of individual POPs may be on the decline in some regions, the overall number of man-made chemicals present in environmental samples is increasing. Sensitive in vitro methods to assess some toxicity endpoints of mixtures in the environment are currently available and further developed. They are explored by some programmes to assess environmental impacts and health effects indicators.

Recommendation: *Strategies should be considered for making better connections between POPs monitoring and toxicity tests for the assessment of long term effects of mixtures in the environment.*

Monitoring activities to evaluate changes in POPs levels over time

Ambient Air

14. Significant improvements in global coverage in air monitoring data and new capacity for POPs monitoring have been realized in all regions as a result of the Stockholm Convention. These improvements are largely attributed to adoption of passive sampling techniques, the development of successful partnerships with existing passive monitoring programmes such as the Global Atmospheric Passive Sampling (GAPS), the MONitoring NETwork for POPs (MONET), the Latin American Passive Atmosphere Monitoring Network (LAPAN) and through the implementation of Global Environment Facility (GEF) and Strategic Approach to International Chemicals Management (SAICM) projects.

Recommendation: *Continue passive air sampling and capacity building in a sustainable manner to enhance information on temporal trends and to improve spatial coverage.*

15. Monitoring data for POPs in air are reported for all five UN regions. Some geographic regions (e.g. Europe) have very good spatial coverage while improvements in reporting/coverage is needed in some other regions.

Recommendation: *Spatial coverage of monitoring activities should improve in Central and Northern Africa, Russia, and large parts of Asia. Improved coordination and partnership with established programmes (e.g. the Arctic Monitoring and Assessment Programme - AMAP, the European Monitoring and Evaluation Programme - EMEP, GAPS, MONET, POPs Monitoring Programme in East Asian countries) is recommended as a means towards addressing data needs and to fill technical and data gaps in future GMP reporting.*

16. Long-term monitoring data are available for most legacy POPs from active air sampling programmes that predated the Stockholm Convention (e.g. AMAP, EMEP, the Northern Contaminants Program - NCP, the Integrated Atmospheric Deposition Network - IADN/GLB). Several air monitoring programmes using active samplers have also been newly implemented to address the needs of the GMP (e.g. in China, Australia, East Asia and Africa). The GRULAC region is the only region that has not reported active air sampling results.

Recommendation: *Continue air monitoring using active samplers according to programme QA/QC protocols to ensure data consistency for trend development. The GRULAC region should strive to implement such air monitoring and deliver results from at least one station during the next phase of the GMP.*

17. For legacy POPs, baseline data are available for all regions. Among the newly listed POPs, HCHs are the only group of compounds that has adequately resolved time trends, largely due to their listing in various multilateral agreements predating the Stockholm Convention. Data are becoming available for the other newly listed POPs. However, for some of the newly listed POPs (e.g. HBCD, PFOS and its precursors) data are only available from a few monitoring programmes.

Recommendation: *Air monitoring for newly listed POPs should be continued and expanded to provide representative baselines and trends.*

18. There is a low reporting rate for some legacy POPs such as toxaphene and mirex. This is largely attributed to low abundance in air due to limited past uses (e.g. mirex), declining air concentrations coupled with the low volatility of these compounds and, in some cases, relatively high analytical costs (e.g. toxaphene).

Recommendation: *Regional experts should define monitoring priorities based on available resources and information on concentrations in air and emissions, while considering the GMP guidance document.*

19. In addition to the regional and global monitoring reports, international and global databases such as EBAS (<http://ebas.nilu.no/>) and the GMP data warehouse (<http://www.pops-gmp.org/visualization-2014/>) are important in compiling and making monitoring data accessible to international and national policy makers, to modelers for assessing fate and transport, and to the general public. These databases provide a long-term, publicly-available repository for these data.

Recommendation: *Databases need to be maintained and updated to ensure data quality, consistency and compatibility among databases, data continuity, and ease of access.*

20. Temporal trend data on POPs are available mainly from the long-term active air monitoring programmes. The Stockholm Convention triggered the implementation of passive air monitoring programmes to deliver additional information for assessing temporal trends.

Recommendation: *Continue air monitoring with both active and passive sampling methods to allow further development of long-term temporal trends.*

21. For most legacy POPs, concentrations in air have declined and continue to decline or remain at low levels due to restrictions on POPs that predated the Stockholm Convention. Primary emissions are believed to be the main driver for POPs levels in air, however secondary emissions (of previously deposited POPs) and climate factors can also influence temporal trends for POPs. For some chemicals, e.g. PCB, PBDEs and other new POPs, emissions continue from stockpiles, continued product usage and waste disposal/dismantling/ recycling practices.

Recommendation: *Factors that determine concentrations of POPs in air, including changes in primary and secondary emission sources and climate effects must be considered, e.g. with the help of models, in order to properly interpret observed trends.*

22. For many newer POPs (e.g. HBCD, endosulfan, PBDEs) concentrations in air are beginning to show declining tendencies although in a few instances, increasing and/or unchanging concentrations over time are observed.

Recommendation: *Continue air monitoring of newer POPs to develop trends.*

Human tissues (milk and blood)

23. Monitoring data for POPs in human matrices are reported with good geographical coverage. Since the entry into force of the Stockholm Convention, many countries have implemented harmonized protocols to generate consistent and comparable POPs monitoring data in human matrices, especially a large number of developing countries being included in the global UNEP/WHO human milk survey. Furthermore, valuable baseline and trend information on POPs concentrations in human blood from the Arctic region is contributed by the Arctic Monitoring and Assessment Programme.

Recommendation: *POPs monitoring in human matrices needs to be sustained in the long term in view of generating information on changes in concentrations over time to support effectiveness evaluation, and further efforts will be needed to fill remaining gaps.*

24. The global assessment of POPs concentrations in human matrices is made possible through the long term implementation of the UNEP/WHO milk survey that generate comparable data to evaluate changes over time. In addition, national and international long-term programmes (e.g. AMAP) monitoring chemicals in milk and/or blood are important for assessing time trends. The levels are often not directly comparable across regions or programmes due to different study designs and populations.

Recommendation: *Opportunities should be explored with incipient or planned human monitoring activities in regions to complement existing data sets under the GMP.*

25. Since the 1980s, PCDD/PCDF have been monitored in human milk, and PCB to a lesser extent. As of 2000, the full spectrum of the POPs listed in the Stockholm Convention and their transformation products have been analyzed in the frame of the UNEP/WHO human milk survey. Quantifiable concentrations are detected for all POPs with the exception of aldrin, chlordecone and endrin, although levels vary by orders of magnitude.

Recommendation: *Monitoring should be continued and expanded for newly listed POPs to provide the information needed to assess changes over time.*

26. In regions with sufficient data to evaluate changes over time, levels of legacy POPs including their transformation products, such as PCDD/PCDF, PCB, and DDT/DDE, have generally declined.

For newly listed POPs in the Stockholm Convention, information regarding changes over time in their concentrations in human matrices is very limited. Based on studies available from WEOG and Asia Pacific, the levels of PFOS and PBDEs seem to gradually decline.

Recommendation: *Monitoring should continue at the global level to further develop trends of legacy POPs and to evaluate trends for newly listed POPs.*

27. Although PFOS is measured at low concentrations in human milk and better detected in human blood, there is good correlation between measurement results in these two matrices.

Recommendation: *Results for PFOS in both human milk and human blood can be used for assessing changes over time.*

28. According to the GMP guidance and for the purpose of the effectiveness evaluation, pooled samples are analyzed to generate one data point per country in the frame of the UNEP/WHO human milk survey. The human milk surveys are scheduled to take place every five years. For the initial campaigns that have produced several pools or individual samples per country, the median concentration from all national samples is used.

Recommendation: *This approach should continue to be used for consistency purposes.*

29. Monitoring of human matrices cannot be implemented without the involvement of public health sector and ethical clearance. These arrangements often lead to delays in implementation at the national level.

Recommendation: *Participating countries should facilitate communication between the environment and health sectors for smooth implementation of human monitoring programmes at the national level.*

30. Sample archiving proved to be a useful tool for conducting retrospective analysis of the newly listed POPs.

Recommendation: *Archiving of human samples should be encouraged as a cost effective means to generate a consistent set of baseline data for the POPs newly added to the Convention.*

31. The most important criterion in the implementation of the global UNEP/WHO human milk survey is the selection of donors, who must be first-time mothers. This is the major criterion enabling comparison among data at the global scale and between years.

Recommendation: *To enable comparison among different programmes/studies, the main criterion to be considered is the selection of first-time mothers as donors.*

32. The partnerships with the WHO and AMAP are important for assessing levels and trends in human tissues and to address any human health risk related aspect, among others.

Recommendation: *Continue cooperation with strategic partners on issues relevant to human health risks of POPs.*

Water

33. According to the regional monitoring reports, a large number of studies is available in the WEOG region on PFOS in rivers, lakes, estuaries and ocean waters; in the Asia and the Pacific PFOS has been analysed in water collected from China (including Hong Kong Special Administrative Region and Macao Special Administrative Region), Japan, Republic of Korea, Philippines and Thailand; monitoring of PFOS in water has been initiated on pilot basis in the Africa and CEE regions; no PFOS monitoring data in water are currently available from GRULAC. Despite of compiling complementary information on PFOS concentrations in water from other information sources, analysis of temporal trends is currently not possible due to insufficient data.

Recommendation: *All regions should strive to implement sustainable programmes for monitoring PFOS in water.*

34. The approach for water sampling and PFOS analysis varies among studies and has not yet been harmonized, but a guidance document for PFOS analysis in water for the GMP has been published (2015). Progress has also been made via international projects on PFOS in water conducted in the frame of the MONET project, the UNEP pilot projects in Africa, Asia-Pacific, GRULAC and WEOG funded by the GEF, and the United Nations University project.

Recommendation: *With progress having been made on capacity-building for determination of PFOS in water, laboratories should be encouraged to participate in inter-laboratory studies organized with the help of UNEP or by other organizations (e.g. Quality Assurance of Information for Marine Environmental Monitoring in Europe - QUASIMEME, AMAP)..*

35. Spatial trends of PFOS in ocean waters are relatively well studied with measurements of surface waters in all oceans as well as in some deep basins. The transect from Western Europe (North Western France) to West Africa is the most thoroughly studied with results from four separate cruises available. Open ocean concentrations of PFOS are typically two orders of magnitude lower than for freshwaters and estuaries.

Recommendation: *Collaborative monitoring programmes along key cruise transects sites should be encouraged for monitoring of the oceans. Models for this include the Joint Global Ocean Flux Study (JGOFS; 1987-2003). SCOR (Scientific Committee of Oceanic Research) and JGOFS developed fieldwork for several process studies which included sampling for POPs in the North Atlantic, Equatorial Pacific, Indian Ocean, Southern Ocean and North Pacific.*

36. Most studies of PFOS in surface waters have analyzed unfiltered samples. Several studies have shown that PFOS is entirely in the dissolved phase in ocean waters and mainly (>80% dissolved) in river waters. However, some PFOS precursors have been found in the particulate phase.

Recommendation: *While most studies to date have recommended analysis of unfiltered water samples, except for those with high suspended solids, further study is needed to develop more precise guidance for filtering of water samples with high suspended solids in order to consider PFOS and precursors.*

37. Almost all monitoring and surveillance studies of PFOS in water have focused on total PFOS anions, i.e. combined measurement of the linear and branched isomers. The limited information available suggests that PFOS isomer profiles are enriched in branched

content, especially in river waters. L-PFOS is more hydrophobic than branched isomers, and L-PFOS is thus removed more readily by sinking particles and sediment sorption.

Recommendation: *Future monitoring of water should report both total PFOS isomers and linear PFOS.*

38. In addition to environmental measurements, river discharges have been estimated and modeled for a small number of rivers. The River Rhine outflow and the Aire/Calder River system in northeast England have had relatively detailed studies.

Recommendation: *The design of water monitoring programmes for PFOS should include the capacity to estimate mass flows (kg/time (day, year)). These 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, as well as estimating per capita emissions.*

39. A major gap in knowledge of PFOS in water is the relative importance of neutral PFOS precursors including perfluorooctane-sulfonamide (FOSA), N-methyl perfluoroalkane sulfonamide (MeFOSA), N-ethyl-perfluoroalkane sulfonamide (EtFOSA), N-methyl perfluoroalkanesulfonamidoethanol (MeFOSE) and N-ethyl perfluoroalkanesulfonamidoethanol (EtFOSE), as well as less well-known precursors identified in fire-fighting foams. FOSA is known to be an important PFOS related compound, particularly in ocean water. At present FOSA data is available for most ocean cruises but for only about 1/3 of river water analyses.

Recommendation: *Future monitoring should include investigation of precursor compounds in water in order assess their relative importance to total "PFOS related" substances.*

40. Temporal trend information for PFOS in water is very limited. For rivers it consists of sampling 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.

Recommendation: *River water monitoring offers the best opportunity to assess temporal trends provided that sources e.g. waste water treatment plants, tributaries, accidental spills etc, are well documented. Systematic temporal trend studies at a few key riverine sites within each UN Region should be considered which can build on past measurements. As noted above, ocean monitoring along key cruise transects sites would enable future temporal trend assessment.*

Other media

41. Large collections of good quality data in biotic and abiotic media have been reported that include POP concentrations which are available for areas such as the North American Great Lakes, the Arctic, the Baltic and in Japan. Some data were reported for Africa; whereas the CEE and GRULAC Regional Reports did not include data on other media.

Recommendation: *Data sets on the presence and changes of POP levels over time can be used to identify contaminant pathways and to support effectiveness evaluation.*

42. Data show clear declines for legacy POPs from the 1970s until 2000 and little changes thereafter. This observation may reflect the effectiveness of measures taken earlier. Primary emissions (e.g. from stockpiles/waste/recycling) and secondary emissions (e.g.

reemission from environmental sinks) may sustain levels in biotic and abiotic environments long after the implementation of regulations. More recently listed POPs (such as PBDEs, HBCD, PFOS and endosulfan) show increasing trends over the past decade, the increases in some cases (PFOS) seem to slow down or have stabilized.

Recommendation: *Make best efforts to decrease the timeline for implementing control measures for POPs to avoid building up of unaccountable repositories that may continue emissions long after control.*

43. There is no systematic compilation of guidance for the sampling and analysis of POPs in other media under the GMP.

Recommendation: *Refer to guidance and QA/QC documentations from established monitoring programmes, e.g. AMAP/NCP, the Helsinki Commission (HELCOM), the Commission for the Protection of the Marine Environment of the North-East Atlantic (OSPAR), in order to obtain comparable data.*

44. Natural archives (e.g. sediment and ice cores, tree rings, etc.) and sample banks have shown to be useful for retrospective analysis for the occurrence and changes over time of POPs, in particular for newly listed substances, as well as to increase spatial coverage in regions with limited data.

Recommendation: *Encourage information exchange through collaboration with existing monitoring programmes and sample banks in other media to support GMP data needs.*

Long range transport

45. Models enable the integrated approach (i.e. combining emission, transport models and measurements) to understand concentrations and trends of POPs in the global environment, and can be applied to explore alternative emission reduction scenarios that inform effectiveness evaluation.

Recommendation: *Reporting under the GMP organized by the ROGs should exploit models as tools to synthesize and interpret monitoring data.*

46. The integrated approach has benefited from increased data availability and accessibility from new and existing monitoring programmes and data sharing through international and global databases including the GMP data warehouse.

Recommendation: *Maintain and expand efforts to monitor levels of POPs in all 5 UN regions, and make data available in openly accessible databases.*

47. Models can help to determine if changes over time in monitoring data are attributable to changes in emissions or other factors such as climate variability or remobilization of POPs that were deposited in the past.

Recommendation: *Expand the use of models to interpret monitoring data and identify and quantify the key factors that drive temporal changes in concentrations of POPs.*

48. Combining models with monitoring data has been shown to be useful in the GMP to understand the long-range transport of POPs.

Recommendation: *Modeling tools should be further explored, applied and compared to support interpretation of monitoring data and for risk evaluation under Article 8.*

49. Models have contributed to interpretation of environmental monitoring data and evaluation of regional and global transport of POPs in scientific activities organized by both

the Convention on Long-Range Transboundary Air Pollution (CLRTAP) and the Stockholm Convention.

Recommendation: *Improve the co-ordination of scientific activities undertaken under the CLRTAP and the Stockholm Convention to realize synergies.*

50. One of the key limitations on modeling POPs at the global level is a lack of complete and reliable emission inventories. A study confirmed that modelling of global dispersion of PCDD/PCDF using a global inventory of emissions compiled under the Stockholm Convention using the Toolkit for Identification and Quantification of Releases of Dioxins, Furans and Other Unintentional POPs under Article 5 of the Stockholm Convention on POPs reasonably reproduces observed levels of air concentrations.

Recommendation: *Parties should pay more attention to issues related to QA/QC of POPs release inventories and consistency and comparability of data reported for various reference years. The process for updating release estimates in order to reveal trends over time should be considered in conjunction with the revision (recalculation or correction) of previous release estimates. The Toolkit for Identification and Quantification of Releases of Dioxins, Furans and Other Unintentional POPs under Article 5 of the Stockholm Convention on POPs should be used for this purpose. Alternative approaches to estimate emissions, for example, using inverse modeling that leverages monitoring data and campaign-based field studies to derive emission estimates for POPs, should be explored, and could benefit effectiveness evaluation.*

Annex: Complementary information to chapter 6. 3 on water

This annex is containing complementary information to the relatively scarce data collected and validated by the regional organization groups and published in the second regional monitoring reports. It is based on a previous review of the literature on PFOS in water by Zareitalabad et al. (2013), as well as on the available peer reviewed literature, and government technical reports. It includes data for studies published from about 2004 and utilizing LC-MS/MS with mass labeled standards in almost all cases.

A global survey of PFOS in urban waters was carried out by Kunacheva et al.(2012). A total of 539 river samples were collected from 41 cities in 15 countries between 2004 and 2010. PFOS was detected above the LOQ of ~0.1 ng/L in 81% of samples at a median of PFOS concentration of 1.9 ng/L. Most samples were collected from nearby or downstream of urban industrialized areas (404 samples) during non-storm periods. PFOS median concentrations in river water were in the order of: London(14.4 ng/L) > Singapore (5.5 ng/L)> Taiwan (3.5 ng/L)> Japan (3.2 ng/L)> Nepal (2.6 ng/L)> China (1.7 ng/L)> Malaysia (1.5 ng/L)> Laos (1.3 ng/L) > Sweden (1.2 ng/L)> Sri Lanka (1.1 ng/L)> Turkey(1.0 ng/L) > Thailand (0.8 ng/L). PFOS concentrations in industrialized areas were 7, 21, 31 and 5 times higher than non-industrialized areas in Thailand, Malaysia, China and Japan, respectively. The study did not include non-industrial or background sites in other regions.

The main focus is on PFOS which is 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 (Schultz et al. 2006, Martin et al. 2010). Several studies of PFAS in water have included perfluorooctane-sulfonamide (FOSA) and N-methyl-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, although only PFOS itself is tabulated or presented graphically.

A. 1. Western Europe, Canada, USA, Australia, New Zealand, Antarctica (WEOG)

The majority of the available data for the WEOG region are 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. 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 which includes WEOG and CEE sampling sites (Loos et al. 2008a).

A. 1.1. River waters

About 70 datasets for PFOS in background sites on rivers within WEOG were identified based on 29 peer reviewed papers and reports. 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).

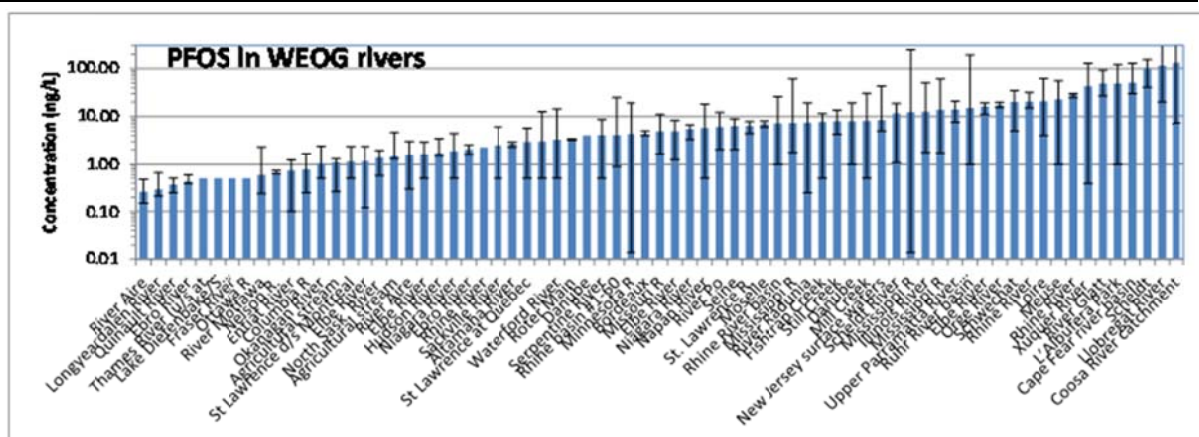


Figure A.1a PFOS in river waters (ng/L) of the WEOG region. Vertical lines represent the range of reported concentrations.

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)(Skutlarek et al. 2006, Loos et al. 2008a, Quinete et al. 2009a, Möller et al. 2010). 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.

A. 1.2. 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. 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) (**Error! Reference source not found.**).

Detailed measurements have made in open waters and coastal areas of the North American Great Lakes(Kim and Kannan 2007, Furdui et al. 2008, Scott et al. 2010, De Silva et al. 2011, Gewurtz et al. 2013). 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); 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 (Furdui et al. 2008, De Silva et al. 2011).

Highest concentrations were 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). 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, Lescord et al. 2015). All of these lakes had PFOS levels well above the median value of 2.0 ng/L i.e. they were essentially outliers among the results for all lakes (**Error! Reference source not found.**).

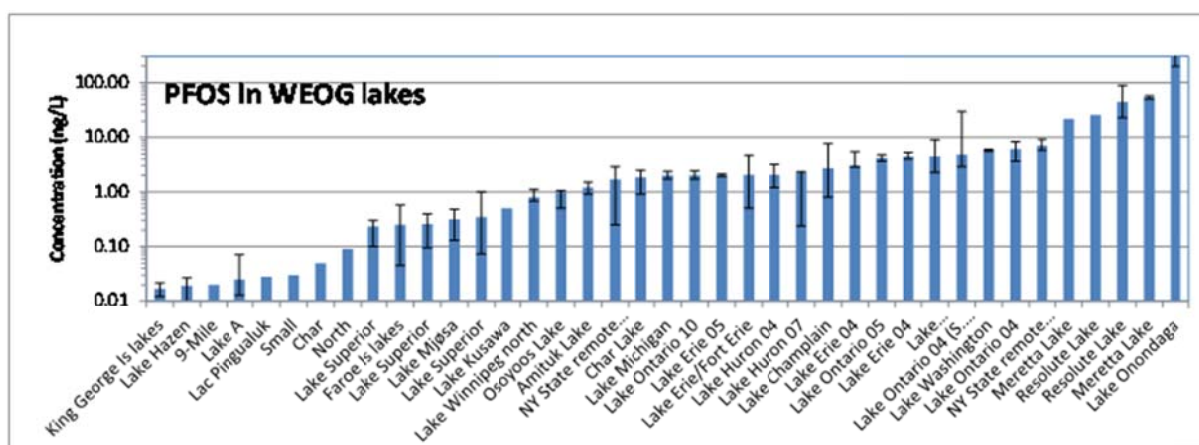


Figure A.1b PFOS in WEOG lakes (ng/L). Vertical lines represent the range of reported concentrations.

A. 1.3. Estuaries and coastal waters

Detailed measurements have been made for PFOS and other PFAS in the Baltic (Kallenborn et al. 2004, Ahrens et al. 2010a, Kirchgeorg et al. 2010) and the eastern North Seas in or near the Elbe estuary (ICES 2005, Theobald et al. 2007, Ahrens et al. 2010a). 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 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 coastal waters within the WEOG region. 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), North Western Spitzbergen, and coastal East Greenland (**Error! Reference source not found.**). 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 (**Error! Reference source not found.**).

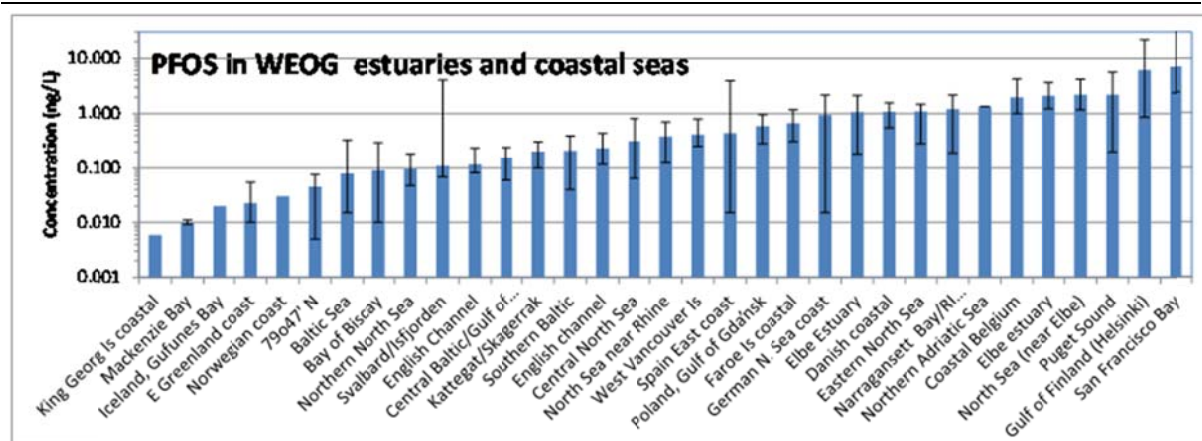


Figure A.1c PFOS in WEOG coastal water and estuaries (ng/L). Vertical lines represent the range of reported concentrations.

A. 2. Asia-Pacific

The Asia-Pacific Region has had numerous independent monitoring studies for PFOS in water and several national monitoring programmes are ongoing. The majority of the available data for the Asia-Pacific region are published in 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.

A. 2.1. Rivers

Approximately 55 datasets for PFOS in rivers waters of Japan, South Korea, China, India and South-East Asia were identified and are presented in Figure A.2, A.3. and A.4. Results for wastewater effluents, groundwater and drinking water supplies were not included. Where possible, results for urban, wastewater influenced sampling sites were omitted, in order to focus on background levels. PFOS concentrations in river waters ranged widely from less than detection limits (typically <0.05 ng/L) to 157 ng/L (median 1.4 ng/L). Median concentrations were higher in South Korea (N=12; 3.3 ng/L) (Figure 6.3.2.) than in China (N=57, 1.6 ng/L) (Figure A.3.) or Japan (N=133, 1.2 ng/L) (Figure A.2.). However this may simply reflect greater numbers of samples from more urban areas in South Korea and limited data from background areas. PFOS data were available for rivers in India, Malaysia, Thailand, Taiwan, Singapore, Sri Lanka and Vietnam (Figure A.4.) However, sample numbers from South East Asia were much smaller than for China or Japan and not fully representative of background concentrations. For example, data from Taiwan (Touchien River and Xiaoli River) were from waters influenced by waste water effluents from the semi-conductor industry (Lin et al. 2010) and surface waters from Singapore were from urban rivers and reservoirs (Fujii et al. 2007, Hu et al. 2011, Nguyen et al. 2011). Lowest concentrations of PFOS in all Asia-Pacific countries were found in Vietnam, in both large rivers in urban areas and in rural areas (Fujii et al. 2007, Kim et al. 2013, Duong et al. 2015). Results from a United Nations University study “Environmental Monitoring and Governance in the Asian Coastal Hydrosphere” (UNU 2014) in which PFOS monitoring was conducted in East / South Asian countries, as well as data from Republic of Korea, Philippines and Thailand that were submitted through the focal point of the countries, were also included. However, as with results from China and Japan, sites known to be influenced by urban and industrial waste water sources were excluded from the graphical presentation and calculation of median values.

A. 2.2. Lakes and Reservoirs

Results for PFOS in lakes and reservoirs were available for China and Japan (Figure A.5) as well as Sri Lanka (Figure A.4; Guruge et al. (2007)). Concentrations were generally lower than river

waters (median in China 0.75 ng/L, N=24; Japan = 1.3 ng/L, N=4). However Tangxun Lake in China had much higher concentrations and was not included in Figure A.4. The lake is influenced by water waters from the fluorochemical industry in Wuhan located nearby (Zhou et al. 2013).

A. 3.3. Coastal waters

Results for PFOS in Asia-Pacific coastal waters were available for China, India, Japan, Singapore, Thailand, and South Korea (Figure A.6). Concentrations were generally 10-fold lower than for river waters except for estuaries and coastal lakes in South Korea which had relatively higher concentrations due to influence of industrial and urban waste waters (Naile et al. 2010, Naile et al. 2013). PFOS concentrations in the South and East China Sea was strongly affected by the ocean currents and were correlated with socio-economic development and population densities of the coastal areas (Kwok et al. 2015). PFOS concentrations in coastal seawater in Thailand range from <0.02 to 17 ng/L in rural areas, and from <0.02 to 730 ng/L in industrial areas.

China is monitoring PFOS in the water at 3–5 coastal waters and lake sampling sites in mainland and 9–13 coastal waters sampling sites in Hong Kong SAR and Macao SAR. The concentrations of PFOS of 2013 were ND– 47ng/L in the water.

Japan is continuously monitoring PFOS in the water throughout the nation (48 to 49 sites) since 2009. The concentration range from 2009 to 2012 was between 0.02 and 230 ng/L. PFOS concentration in marine water surrounding Japan in monitored in another project (Japan Ministry of the Environment 2014). Also information on PFOS concentrations in sea water is reported in Yamashita et al. (2005).

The levels of PFOS in the Yangtze and Pearl Rivers (Soet al., 2007) were of the same order of magnitude with those measured in the Po River, Italy (2e12 ng/L and 2e237 ng/L) (Looset al., 2008), the Ruhr River (5.0 and 48.0 ng/L) in Germany (Skutlarek et al., 2006) and the Cape Fear River basin (28.9 and 12.6 ng/L) in North Carolina, USA (Nakayama et al., 2007).

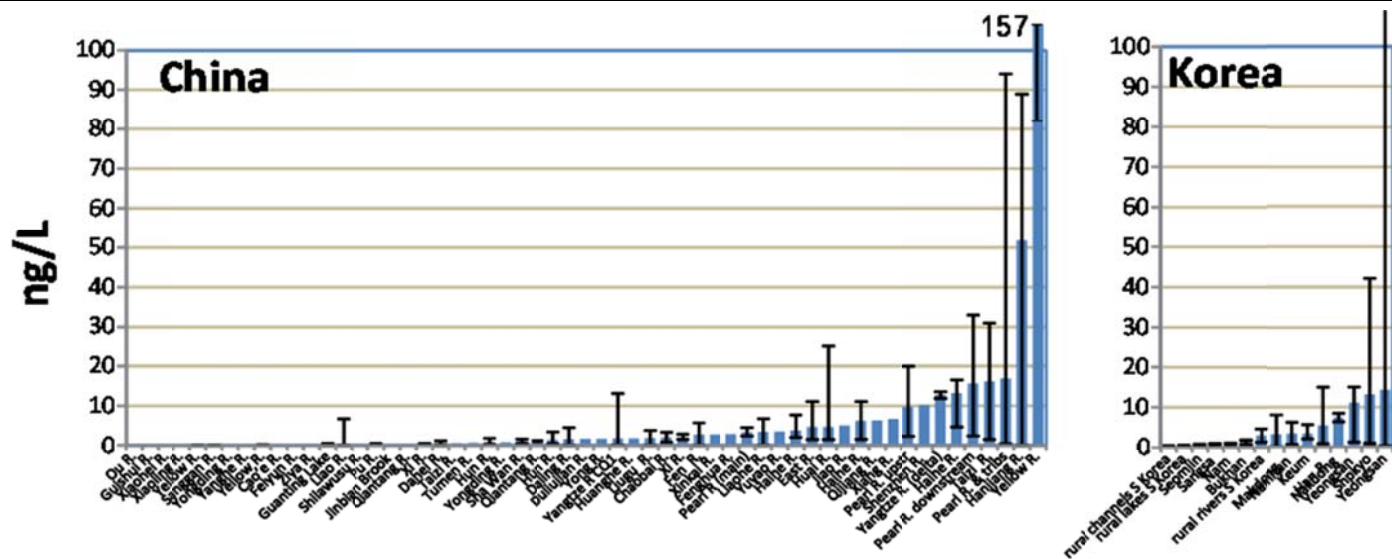


Figure A.2. PFOS (ng/L) in river waters from China and South Korea. Bars show average concentrations and vertical lines are ranges.

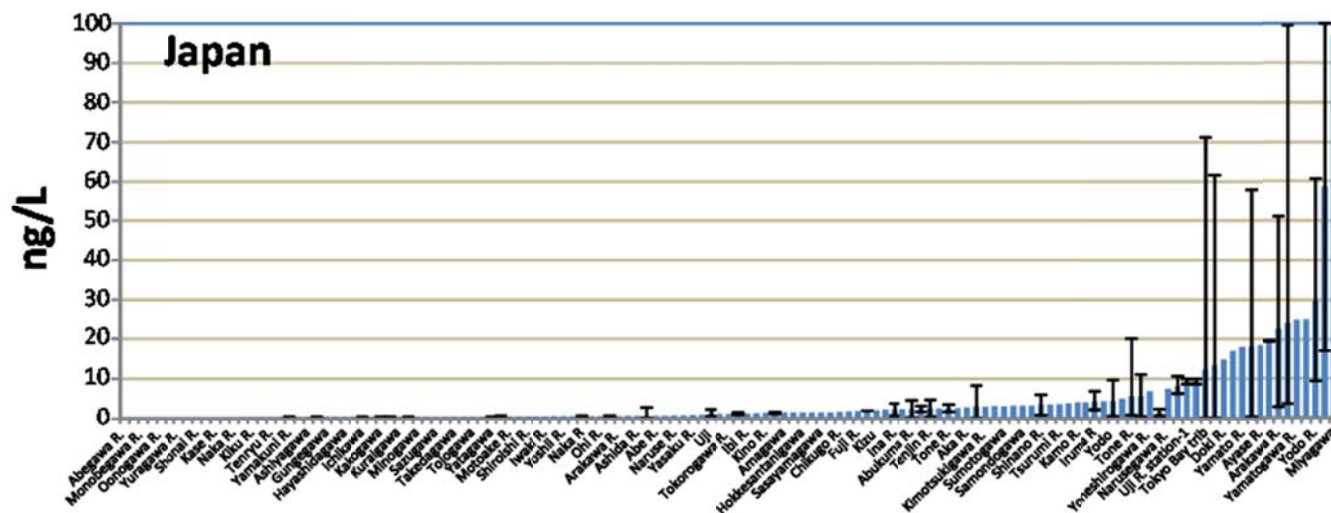


Figure A.3. PFOS (ng/L) in river waters from Japan. Bars show average concentrations and vertical lines are ranges.

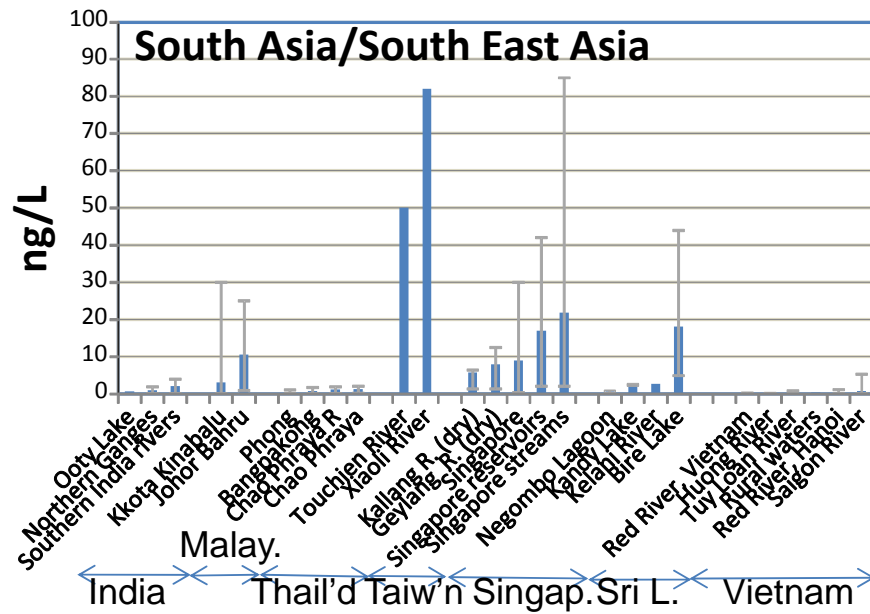


Figure A.4. PFOS (ng/L) in river waters in India and south-east Asian countries. Bars show average concentrations and vertical lines are ranges.

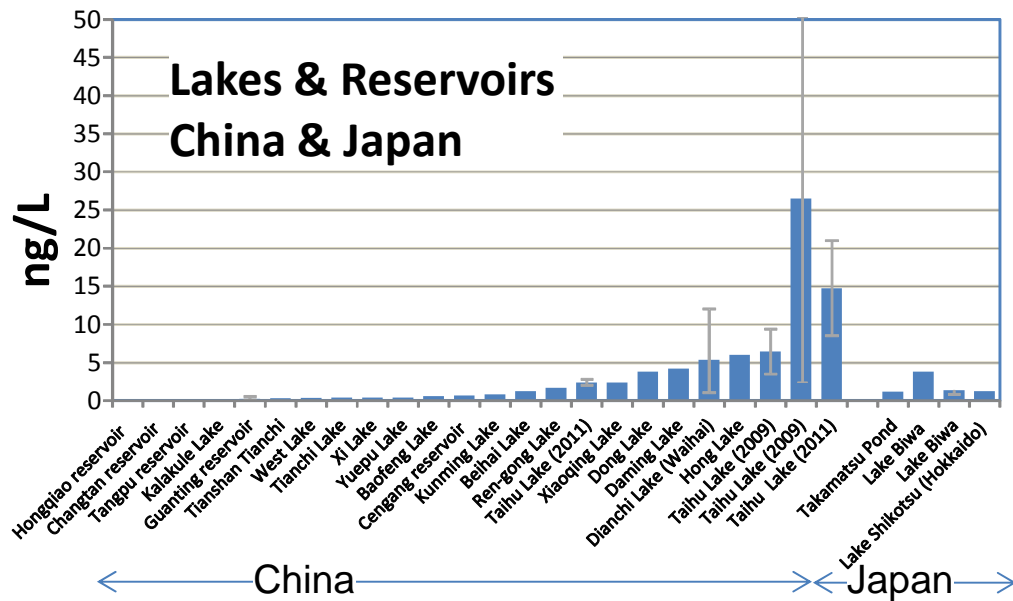


Figure A.5. PFOS (ng/L) in lake waters in China and Japan. Bars show average concentrations and vertical lines are ranges.

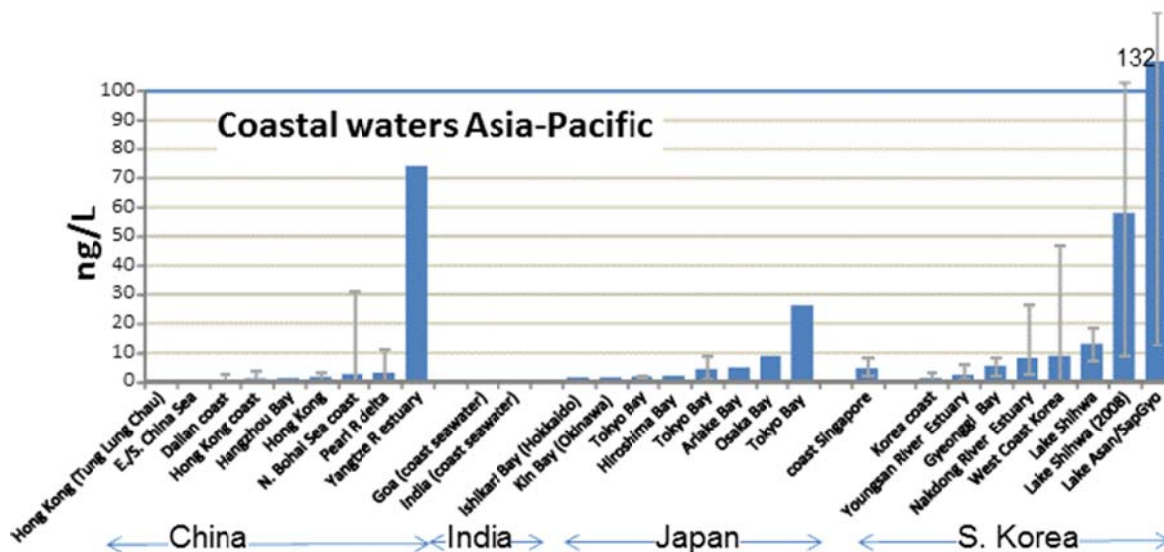


Figure A.6. PFOS (ng/L) in coastal waters of Asia-Pacific countries. Bars show average concentrations and vertical lines are ranges.

A. 3. GRULAC

Only one published study was available for river waters in the GRULAC region. Quinete et al. (2009b) reported PFOS in the Paraiba do Sul River at concentrations ranging from 0.64 to 1.3 ng/L. In the same study, PFOS was detected in coastal waters (Guanabara Bay (0.4-0.9 ng/L) and off the mouth of the Paraiba do Sul River, <0.1-0.17 ng/L).

Two ocean cruises have detected PFOS in waters of the South Atlantic off of Brazil and Argentina (Benskin et al. 2012, González-Gaya et al. 2014). See Section A.6.

A. 4. Central and Eastern European (CEE) and Central Asian Region

Limited information is available in relation to the CEE region. There are no systematic regional nor national monitoring programmes related to PFOS in water, however the PFOS was included among priority substances under the EU Water Framework Directive in 2013 and thus should be monitored by all EU countries since 2013. Monitoring results are summarized in Figure A.6. Results are mainly stemming from research project undertaken by European Union in 23 countries along Danube river including its tributaries (summer 2007). The survey looked into occurrence of 34 polar organic contaminants including PFOS and perfluorooctanoate (PFOA) in major European rivers and their tributaries. The results show that occurrence of both chemicals were observed in 94 and 97% cases/samples respectively. For the CEE region, a relatively high PFOA levels were detected in the Rivers Danube and “elevated” PFOS concentrations in Krka. A higher median concentration for all river samples was found for PFOS (6 ng/L), compared to PFOA (3 ng/L). Data are not included into the GMP data warehouse.

In addition, the same research group looked into occurrence of polar organic contaminants in Danube river (Loos et al. 2010) and found that the PFOS concentration was quite constant in the upstream part of the Danube (about 10 ng/L). Then, at the river mouth in Romania 6 ng/L were reached. In the following tributaries higher PFOS concentration levels were detected: Morava (CZ) (20 ng/L), Jantra (57 ng/L), and Arges (RO) (101 ng/L). In Tisza River, low concentrations of PFOS (3 ng/L) were detected (Figure 6.3.7).

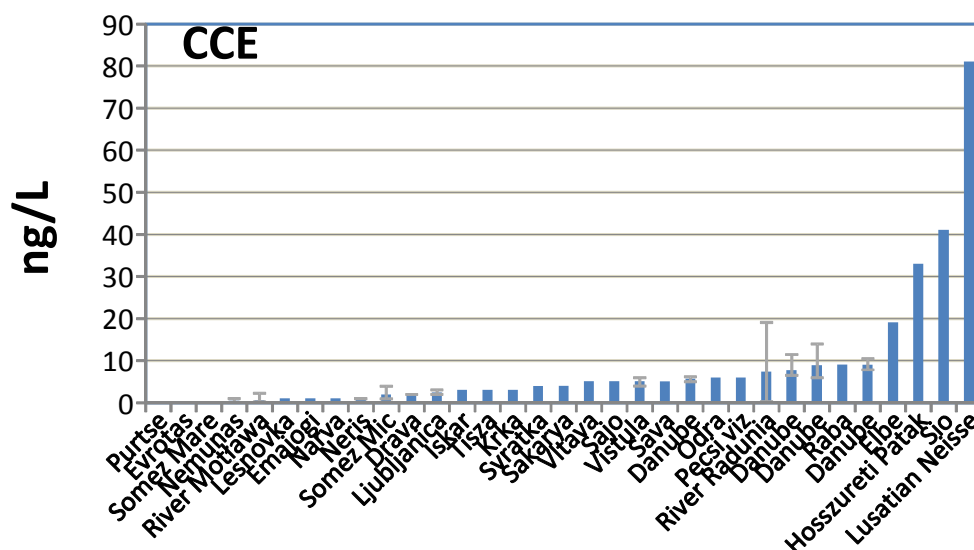


Figure A.7. PFOS concentrations in CEE rivers and their tributaries (Loos et al. 2008a, Rostkowski et al. 2009). Bars show average concentrations and vertical lines are ranges.

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

A. 5. Africa

Orata et al. (2009a, 2009b) determined PFOS in rivers that drain into Winam Gulf of lake Victoria near and within the city Kisumu. Concentrations ranged from <0.4 to 8.5 ng/L and were influenced by urban waste waters. Lower concentrations were found in Lake Victoria near shore waters than in rivers. Mudumbi et al. (2014) determined PFOS in rivers in the in the Western Cape (South Africa) and found relatively high concentrations (<0.03-182 ng/L). In this study PFOS concentrations varied seasonally; they decreased (< detection limits) during the dry season, while increasing during the wet season for all three rivers.

A. 6. Ocean waters

Compared to freshwaters and estuaries, open ocean concentrations of PFOS are very low (median 33 pg/L). Figure A.8 presents average results for various sectors of each ocean. Lowest mean concentrations (<10-20 pg/L) are reported for the Greenland Sea and the Labrador Sea, as well as in the Southern Ocean.

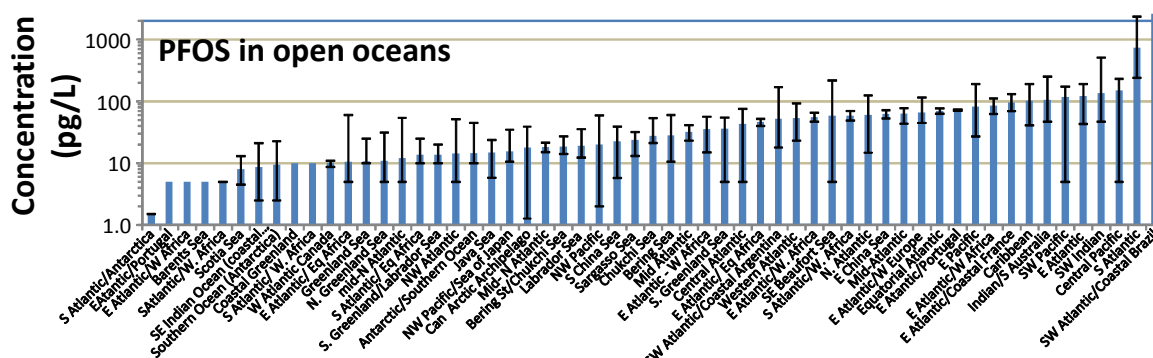


Figure A.8. Average concentrations and range (vertical bars) of PFOS in open ocean waters for various ocean areas. The transect from Western Europe (North Western France) to West Africa is the most thoroughly studied with results from four separate cruises available (Ahrens et al. 2009a, Ahrens et al. 2010c, 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 northeast Atlantic Ocean. 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.

However, a recent study by González-Gaya et al. (2014) reported elevated PFOS in the ocean offshore of Brazil with concentrations ranging up to 6560 pg/L. Maximum concentrations for PFOS observed near Brazil were at sampling points strongly affected by the currents, but not in the sites closest to the continental shelf. Miyazawa et al. (2014) also observed higher concentrations of PFOA and PFOS at open ocean sites east of Japan following the Great Japan earthquake of 2011, which they attributed to transport by the Kuroshio Extension current.

A. 7. Discussion

A.7.1. Temporal trends in water

Unlike air or human and wildlife tissues, there are no robust temporal trend datasets yet available for PFOS in natural waters. However, given the extensive sampling programmes in many countries this will be possible in future global assessments. Boontanon et al. (2013) combined data for the Chao Phraya River, which flows through the urban area of Bangkok to assess temporal trends of PFOS. They noted lower concentrations of PFOS in August 2008 and 2009 compared to previous sampling times (Figure A.9). They noted that this could be due to the influence of higher flows during the rainy season (August) as well as variation in industrial activities (Boontanon et al. 2013). Reductions in use of PFOS could also be a factor explaining the overall decline from. Temporal trends for other rivers have not been reported however it may be possible to further assess trends from published data. For example, in their global survey of PFOS in urban rivers, Kunacheva et al. (2012) included samples from Kyoto, Osaka and Shiga in Japan with 5 or 6 sampling times over the period 2004-2007 but did not assess temporal trends.

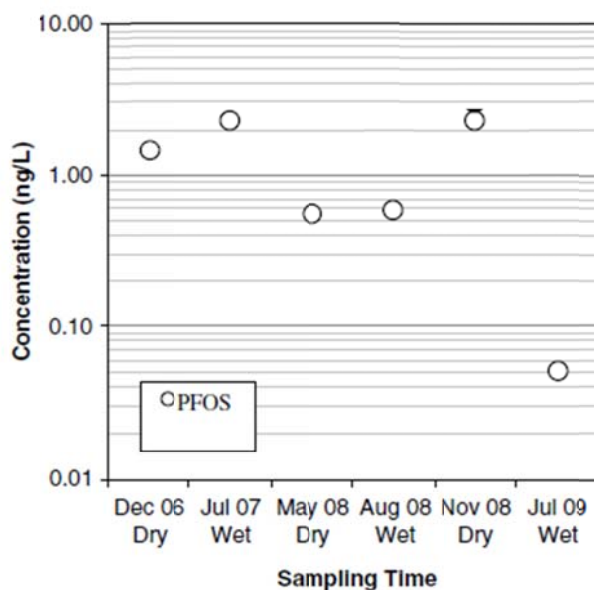


Figure A.9. PFOS concentrations in the Chao

Phraya River 2006-2008 (Boontanon et al. 2013)

Sakurai et al. (2010) conducted a detailed study of the variability of PFOS concentrations in Tokyo Bay over the period 2004 to 2006 (Figure 6.3.10.). They found no apparent trend in the concentration over time after adjustment for volume and salinity. However Ahrens et al. (2010b) reported range of 0.9–2.2 ng L for samples collected from Tokyo Bay in 2008 which was about 2-

fold lower than data reported by Sakurai et al. and 15 times lower than values found in water samples collected in 2002 (Taniyasu et al. 2003).

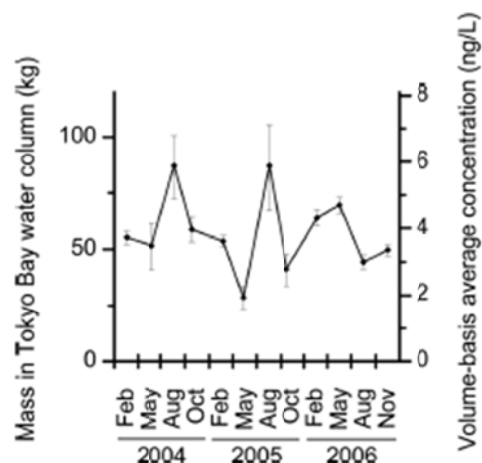


Figure A.10. Time series of masses and volume-based average concentrations of PFOS in the water column of Tokyo Bay. Error bars indicate uncertainty due to assignment of pycnocline depth as well as that due to sampling and analytical variability (Sakurai et al. 2010)

A. 7.2. PFOS precursors

The majority of water measurements have been for total perfluorooctane sulfonic acid (usually analyzed along with other perfluoroalkane sulfonates and PFCAs). However a limited number of studies have reported perfluorooctanesulfonamideethanols (FOSEs) and perfluorooctanesulfonamide (FOSA), the amide derivative of PFOS. The FOSEs and FOSA have been shown to degrade abiotically (Martin et al. 2006, D'Eon and Mabury 2007) 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 A.1.). 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. 2010c). 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.

Table A.1. 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

¹Includes 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 and EtFOSA), and N-methyl and N-ethyl perfluoroalkanesulfonamidoethanols (MeFOSE and EtFOSE) 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 <0.2-17pg/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 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.

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).

A. 7.3. 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 harbors 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).

A. 7.4. 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 (Huset et al. 2008, Loos et al. 2008b, Ahrens et al. 2009b, Scott et al. 2009, Möller et al. 2010, Earnshaw et al. 2014). 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 analyzed 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.

A. 7.5. Particles vs dissolved concentrations

Most studies of PFOS in surface waters have using unfiltered samples. 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, PFASs 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.

A. 7.6. Effect of ice cover

Measurements of PFOS and other PFASs 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 PFASs 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 PFASs 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.

A. 8. Summary

- There is a large number of studies for PFOS in rivers, lakes, estuaries and ocean waters in the WEOG region
- Data on PFOS concentrations in water was gathered for base line in this report. Analysis of temporal trend is future work due to insufficient data at this phase.
- 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 modeled (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
- What is needed for the future are systematic temporal trend studies at a few key sites which can build on past measurements
 - Results for rivers offer perhaps the best opportunity to assess temporal trends provided that sources e.g. 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). SCOR (Scientific Committee of Oceanic Research) and JGOFS developed fieldwork for several Process Studies which included sampling for POPs (North Atlantic, Equatorial Pacific, Indian Ocean, Southern Ocean and North Pacific).
- FOSA is an important PFOS related compound, particularly in ocean water, and should be included in all future analyses. At present FOSA data is available for only about 1/3 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

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Chapter 6.4

Most references below are not cited in the text of this section but provide a concise summary of the information provided by the ROGs. A detailed list of sources for the Table 6.4.1 can be found in the 2015 WEOG regional report.

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