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PART C: PERSISTENT ORGANIC POLLUTANTS

AIR POLLUTION STUDIES No. 19

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Chemical Symbols, Acronyms and Abbreviations

Chemical Abbreviations

BDE 28 – 2,4,4′- tribromodiphenyl ether
BDE 47 – 2,2’,4,4’- tetrabromodiphenyl ether
BDE 99 – 2,2’,4,4’,5-pentabromodiphenyl ether
BDE 209 – 2, 2’,3, 3’,4, 4’,5, 5’,6, 6’-decabromodiphenyl ether
decaBDE – decabromodiphenyl ether
octaBDE – octabromodiphenyl ether
PBDE – polybrominated diphenyl ether
PeBDE – pentabrominated diphenylether
pentaBDE – pentabromodiphenyl ether
BaP – benzo(a)pyrene
BbF – benzo(b)fluoranthrene
BkF – benzo(k)fluoranthrene
C – carbon
CC – cis-chlordane
TC – trans-chlordane
CFC – chlorofluorocarbon
CO – carbon monoxide
CO₂ – carbon dioxide
CH₄ – methane
DDD – dichlorodiphenyldichloroethane
o, p’-DDD – ortho, para’-DDD isomer
p, p’-DDD – para, para’-DDD isomer
DDE – dichlorodiphenyldichloroethylene
o,p’-DDE – ortho, para’-DDE isomer
p,p’-DDE – para, para’-DDE isomer
DDT – dichlorodiphenyltrichloroethane
o,p’-DDT – ortho, para-DDT isomer
p,p’-DDT – para, para’-DDT isomer
FTOH – fluorotelomer alcohols
HBB – hexabromobiphenyl
HBCD – hexabromocyclododecane
HBU – hexachlorobutadiene
HCB – hexachlorobenzene
HCBz – hexachlorobenzene
HCBD – hexachlorobutadiene
HCH – hexachlorocyclohexane
α-HCH – alpha hexachlorocyclohexane (isomer)
β-HCH – beta hexachlorocyclohexane (isomer)
γ-HCH – gamma hexachlorocyclohexane (isomer)
HEPT – heptachlor
HEPX – heptachlor epoxide
HpCDD – heptachlordioxin
Hg – mercury
I_P – Indeno[1,2,3-cd]pyrene
NH₃ – ammonia
NO₂ – nitrogen dioxide
NO₃ – nitrate
NOₓ – nitrogen oxides
O₃ – ozone
OCP – organochlorine pesticide
OH – hydroxyl
PAH – polycyclic aromatic hydrocarbon
PAH16 – 16 PAH compounds listed as priority pollutants by EPA (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz(ah)anthracene, benzo[ghi]perylene, and indeno(1,2,3-cd)pyrene)
PCB – polychlorinated biphenyl
PCDD – polychlorinated dibenzo-p-dioxins
PCDD/F – polychlorinated dibenzodioxins and dibenzofurans
PCDF – polychlorinated dibenzofurans
PCN – polychlorinated naphthalenes
PCP – pentachlorophenol
PeCB – pentachlorobenzene
PFAS – polyfluoroalkyl sulphonates
PFC – polyfluorinated compounds
PFCA – perfluorinated carboxylates
PFOA – perfluorooctanoic acid
PFOS – perfluorooctane sulphonate
PVC – polyvinyl chloride
SCCP – short-chain chlorinated paraffins
SO2 – sulphur dioxide
SOx – sulphur oxides

**Acronyms and Abbreviations**

\( \alpha \) – Alpha isomer
\( \gamma \) – Gamma isomer
\( \rho \) – Density
2D – Two-dimensional
3D – Three-dimensional
AC&C – Atmospheric Chemistry and Climate (International Geosphere-Biosphere Program-World Climate Research Program)
AeroCom – Aerosol Comparisons between Observations and Models (a global aerosol model intercomparison project)
ALT – Alert Station (Canada)
AMAP – Arctic Monitoring and Assessment Programme
AO – Arctic Oscillation
AQUA-GAPS – Global Aquatic Passive Sampling
ASP – Africa Stockpile Program
BAT – Best available techniques
BEP – Best environmental practices
BETR – Berkeley-Trent modeling framework
BGLTS – Binational Great Lakes Toxics Strategy (US/Canada)
\( {}^\circ \)C – degrees Celsius
\( C_A \) – Gaseous concentration in air
\( C_W \) – Dissolved concentration in water
CAA – Clean Air Act
CACAR – Canadian Arctic Contaminant Assessment Report
CAFE – Clean Air for Europe
CalTox – Multimedia mass balance/multiple pathway exposure model
CanMETOP – Canadian Model for Environmental Transport of Organochlorine Pesticides
CC – Clausius-Clapeyron
CCC – Chemical Coordinating Center (EMEP)
CCS – Carbon dioxide capture and storage
CEC – Commission for Environmental Cooperation
CEEC – Central and Eastern European Region
CEPA – Canadian Environmental Protection Act
ChemRange – Multimedia mass balance model
CILSS – Comite Inter Etats de Lutte contre la Secheresse dans la Shel
ClimoChem – Multimedia mass balance model
CLRTAP – Convention on Long Range Transboundary Air Pollution
cm – Centimetres
CMAQ – Community Multiscale Air Quality Model
CMP – Chemicals Management Plan
COP – Conference of the Parties
CORINAIR – Coordination of Information on the Environment – Air (EMEP emission inventory guidebook)
CTD – Characteristic travel distance
CTM – Chemical transport model
DEFRA – Department for Environment Food and Rural Affairs (UK)
DEHM-POP – Danish Eulerian Hemispheric Model- Persistent Organic Pollutants
DG TREN – Directorate-General for Energy and Transport (European Commission)
DGEF – Division of Global Environmental Facility Coordination (UNEP)
DHR – Dynamic harmonic regression
DROPS – Development of Macro and Sectoral Economic Models to Evaluate the Role of Public Health Externalities on Society
EA – East Asia
EB – Executive Body (of CLRTAP)
EC – Environment Canada
EC – European Commission
ECHA – European Chemical Agency
EE – Effectiveness evaluation
EF – Enantiomer Fraction
EMEP – European Monitoring and Evaluation Programme- Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe
ENSO – El Niño Southern Oscillation
EPER – European Pollutant Emission Register
ESP – Electrostatic precipitator
ETP – Energy Technology Perspectives
EU – European Union
EU – Europe
EUSES – European Union System for Evaluation of Substances
EVn-BETR – European Variant of BETR
fA – Fugacity of a chemical in air
fW – Fugacity of a chemical in water
FD – Deposition flux
FN – Net Flux
FV – Volatilization flux
FAO – Food and Agriculture Organization of the United Nations
FF – Fugacity fraction
FGD – Flue gas desulphurization
FR – Fugacity ratio
g – Grams
GAPS – Global Atmospheric Passive Sampling Network
GAW – Global Atmospheric Watch
G-CIEMS – Grid-Catchment Integrated Environmental Modelling System
GFF – Glass fiber filter
GIS – Geographical Information Systems
GJIC – Gap Junctional Intercellular Communication
GLEMOS – Global EMEP Multimedia Modeling Modelling System
GMP – Global Monitoring Plan (of the COP)
GRULAC – Group of Latin American Countries
h – Hour
HiVol – High volume
HLC – Henry’s Law Constant
HELCOM – Helsinki Commission- Baltic Marine Environment Protection Commission
HM – Heavy Metals
HMW – High molecular weight
ΔH_{SA} – Enthalpy of soil-to-air exchange (J mol^{-1})
HTAP – Hemispheric Transport of Air Pollution
HYSEPLIT-SV – Hybrid Single Particle Langarian Integrated Trajectory Model
IADN – Integrated Atmospheric Deposition Network
IARC – International Agency for Research on Cancer
IEA – International Energy Agency
IGCC – Integrated Gasification Combined Cycle
IMPACT-2002 – Multimedia mass balance model
IPCC – Intergovernmental Panel on Climate Change
IPY INCATPA – International Polar Year - Intercontinental Atmospheric Transport of Anthropogenic Pollutants to the Arctic
J – Joule, a unit of energy or work equal to a force of 1 Newton applied over 1 meter
K – Kelvin, unit of temperature (K= °C + 273.15)
K_{AW} – Partitioning constant that quantifies the ratio of concentration for a chemical between two phases, air and water
K_{OA} – Partitioning constant that quantifies the ratio of concentration for a chemical between two phases, octanol and air
K_{OW} – Partitioning constant that quantifies the ratio of concentration for a chemical between two phases, octanol and water
K_{IA} – Temperature dependant equilibrium snow surface/air sorption coefficient
K_{Particle-Air} – Partitioning constant that quantifies the ratio of concentration for a chemical between two phases, particle and air
K_{Snow-Air} – Partitioning constant that quantifies the ratio of concentration for a chemical between two phases, snow and air
kg – Kilograms
km – Kilometres
KNG – Kinngait station (Canada)
kt – Kilotonnes
L – Litres
LD_{50} – Lethal Dose, defined as the dose necessary to kill 50% of the members of a tested population in a controlled study
LFL – Little Fox Lake station (Canada)
LMW – Low molecular weight
LoVol – Low volume
LRTP – Long-range transport potential
LRT – Long-range transport
LRTAP – Long-range Transboundary Air Pollution
m – Metre
M – mole
MAP – Mediterranean Action Plan
MAPPE – Multimedia Assessment of Pollutant Pathways in Europe, mass balance model
MASL – Metres above sea level
REACH – Registration, Evaluation, Authorization and restriction of CHemical Substances (a regulation of the European Commission)
RECETOX – Research Centre for Toxic Compounds, Masaryk University, Czech Republic
SA – South Asia
SAICM – Strategic Approach to International Chemicals Management
SAMP – Soil and Air Monitoring Program
SAR – Special Administrative Regions (of China)
SAT – Surface air temperature
SC – Stockholm Convention
SCR – Selective catalytic reduction
SH – Southern hemisphere
SIP – Sorbent impregnated PUF
SMOC – Sound Management of Chemicals
SOC – Semi-volatile organic compounds
SPMD – Semi-permeable membrane devices
S-R – Source-receptor
SSA – Specific surface area
SVHC – Substances of Very High Concern
t – Tonnes
T – Temperature
T1/2air – Half-life of a compound in air
T1/2soil – Half-life of a compound in soil
T1/2water – Half-life of a compound in water
T1/2env – Half-life of a compound in all media
TD – Transport distance
TEF – Toxicity equivalence factors
TEQ – Toxic equivalent
TF HTAP – Task Force on Hemispheric Transport of Air Pollutants
TFEIP – Task Force on Emission Inventories and Projections
TOMP – Toxic Organic Micro Pollutants program (UK)
TRI – Toxics Release Inventory program (of the EPA)
TSCA – Toxic Substances Control Act
U.S. EPA – United States Environmental Protection Agency
UK DEFRA – United Kingdom Department of Environment, Food, and Rural Affairs
UN – United Nations
UNCED – United Nations Conference on Environment and Development
UNECE – United Nations Economic Commission for Europe
UNEP – United Nations Environment Programme
VKK – Valkarkai Station (Russia)
VOCs – Volatile organic compounds
vPvB – Very persistent and very Bioaccumulative substances
WACAP – Western Airborne Contaminants Assessment Project
WBO – Waliguan Baseline Observatory (China)
WEOG – Western Europe and Others Group
WHO – World Health Organization
WMO – World Meteorological Organization
WNR – Wolong Nature Reserve (Sichuan Province, China)
XAD-2 – Resin used for air sampling
XVPCA – Xarxa de Vigilancia I Previsio de la Contaminacio Atmosferica
y – Year
ZPN – Zeppelin Mountain Station (Norway)
Preface

In December 2004, in recognition of an increasing body of scientific evidence suggesting the potential importance of intercontinental flows of air pollutants, the Convention on Long-range Transboundary Air Pollution (LRTAP Convention) created the Task Force on Hemispheric Transport of Air Pollution (TF HTAP). Under the leadership of the European Union and the United States, the TF HTAP was charged with improving the understanding of the intercontinental transport of air pollutants across the Northern Hemisphere for consideration by the Convention. Parties to the Convention were encouraged to designate experts to participate, and the task force chairs were encouraged to invite relevant experts to participate from countries outside the Convention.

Since its first meeting in June 2005, the TF HTAP has organized a series of projects and collaborative experiments designed to advance the state-of-science related to the intercontinental transport of ozone ($O_3$), particulate matter (PM), mercury (Hg), and persistent organic pollutants (POPs). It has also held a series of 15 meetings or workshops convened in a variety of locations in North America, Europe, and Asia, which have been attended by more than 700 individual experts from more than 38 countries. The TF HTAP leveraged its resources by coordinating its meetings with those of other task forces and centres under the convention as well as international organisations and initiatives such as the World Meteorological Organization, the United Nations Environment Programme’s Chemicals Programme and Regional Centres, the International Geosphere-Biosphere Program-World Climate Research Program’s Atmospheric Chemistry and Climate (AC&C) Initiative, and the Global Atmospheric Pollution Forum.

In 2007, drawing upon some of the preliminary results of the work program, the TF HTAP developed a first assessment of the intercontinental transport of ozone and particulate matter to inform the LRTAP Convention’s review of the 1999 Gothenburg Protocol (UNECE Air Pollution Series No. 16).

The current 2010 assessment consists of 5 volumes. The first three volumes are technical assessments of the state-of-science with respect to intercontinental transport of ozone and particulate matter (Part A), mercury (Part B), and persistent organic pollutants (Part C, this volume). The fourth volume (Part D) is a synthesis of the main findings and recommendations of Parts A, B, and C organized around a series of policy-relevant questions that were identified at the TF HTAP’s first meeting and, with some minor revision along the way, have guided the TF HTAP’s work. The fifth volume of the assessment is the TF HTAP Chairs’ report to the LRTAP Convention, which serves as an Executive Summary.

The objective of HTAP 2010 is not limited to informing the LRTAP Convention but, in a wider context, to provide data and information to national governments and international organizations on issues of long-range and intercontinental transport of air pollution and to serve as a basis for future cooperative research and policy action.

HTAP 2010 was made possible by the commitment and voluntary contributions of a large network of experts in academia, government agencies and international organizations. We would like to express our most sincere gratitude to all the contributing experts and in particular to the Editors and Chapter Lead Authors of the assessment, who undertook a coordinating role and guided the assessment to its finalisation.

We would also like to thank the other task forces and centres under the LRTAP Convention as well as the staff of the Convention secretariat and EC/R Inc., who supported our work and the production of the report.

André Zuber and Terry Keating
Co-chairs of the Task Force on Hemispheric Transport of Air Pollution
Chapter 1
Conceptual Overview

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1.1. Purpose of the HTAP 2010 Assessment on Persistent Organic Pollutants

Persistent organic pollutants (POPs) have the unique properties of persistence and bioaccumulation and the ability to cycle through a variety of environmental media. A PCB that one may ingest in a meal and absorb, for instance, may have previously travelled and resided through several environmental media (e.g. air, soil, water) during its lifetime following loss from an electrical plant on the other side of the world many years ago. The levels of POPs in this meal, particularly in the case of ‘higher trophic level’ foods such as fish or meat, may have been multiplied to dangerously high concentrations (biomagnified) because of the manner in which energy and contaminants flow through and accumulate in food chains.

POPs are multimedia chemicals meaning that they partition to air, water, soil, sediment, snow/ice, aerosols and other environmental compartments according to their key physical-chemical properties. This creates obvious challenges for understanding and predicting their environmental fate and transport. Furthermore, unlike other classes of pollutants that have a natural background and have been cycling on the earth indefinitely, most persistent organic pollutants have only anthropogenic origins, with the first POPs manufactured approximately 80 years ago. It has only been in the last 30-40 years however, that the inherent toxicity, bioaccumulation and persistence of POPs has been realized, leading to their regulation and control, mainly in industrialized regions. About 25 years ago, regional-scale air sampling programs were established to monitor POPs to better understand their transport and trends. And only in the last 10 years or so, our understanding and concern regarding the abundance of POPs in the multi-media environment, and the associated potential to harm human health and the environment, have led to the ratification of two major international treaties on POPs (i.e. Stockholm Convention on POPs and the Convention on Long-range Transport of Air Pollution POPs Protocol).

Our understanding of POPs has greatly improved in recent years. Superior computing power has allowed global scale atmospheric models to run at high resolution. Advances in process research have enhanced model parameterisation. National reporting practices and improved estimation methods have provided better emissions inventories for a greater number of compounds. Perhaps the greatest and most significant advances however, have been in the area of measurements. Long-term monitoring data for POPs have demonstrated interesting temporal patterns and insights to the atmospheric response to regulation and how this differs among compounds. Research investigations have shown the important role of soil and ocean reservoirs and the dynamic-equilibrium between the atmosphere and these compartments that results in contaminant cycling. In some cases (e.g. α-HCH), old reservoirs such as the Arctic Ocean have surprisingly become sources to the atmosphere, maintaining and prolonging atmospheric burdens [Jantunen and Bidleman, 1995; Li et al., 2004]. The adoption and increasing popularity of relatively inexpensive passive air samplers for POPs in recent years has led to an increasing amount and quality of comparable regional- and global-scale data for POPs. This enhancement in spatial resolution is invaluable for assessing regional and global transport of POPs and for improving and validating transport models and emissions inventories.

Coupled with the increase of information on POPs are new methods and strategies of interpretation of data. Models, emissions and measurements are increasingly being combined in complementary ways to assess regional and global transport, interpret temporal trend data, predict future concentrations under various scenarios, and identify areas where key information is missing. In
recent years, driven by international treaties on POPs, expert groups have been assembled to integrate and assess key information [Decision SC-31, section B, UNEP, 2009].

This first POPs assessment report under the Task Force for Hemispheric Transport of Air Pollution (TF HTAP) builds on previous work by this group in assessing source-receptor relationships at the hemispheric scale with a special focus on Europe and the broader UN-EE region. The current assessment demonstrates the need to expand the scope of the Task Force to the global scale and extend the expertise of the research community. This will help to answer the call of the Stockholm Convention (SC) on POPs, which, in its first Global Monitoring Plan report adopted at COP4 in May 2009, (1) identified the need for closer collaboration with the modelling community to address questions on EE of the Convention and (2) recognized that temporal trend data for POPs, particularly for air, cannot be interpreted properly without the aid of transport models and information on meteorological parameters.

In addition to providing the current state of knowledge and understanding on POPs in the context of an integrated approach, one of the key outcomes of the POPs assessment is in identifying key findings and recommendations for further work. For instance, the topic of climate interactions is becoming increasingly relevant as we recognize that gradual changes in climate and climate variability, including extreme events, may greatly impact the fate, transport and exposure to POPs.

Lastly, as the international treaties consider listing additional POPs under their action annexes, new challenges will be presented to experts in the field, as these chemicals do not always behave according to the classic POPs and may impact the environment and human health in different ways. Investigations of ‘new’ POPs will warrant testing and validation of new sampling and analytical methods, new approaches to accounting for emissions, and new parameterization of models for describing their fate and transport.

1.2. International Policy on POPs

Domestic regulations and regional agreements on some POPs were first introduced in the late 1970s (DDT, PCB) at which time monitoring programmes were also established. The earliest international binding agreement on POPs was established in 1998 on a regional basis under the UN/ECE/Convention on Long-range Transboundary Air Pollution (LRTAP)1 of 1979.

1.2.1. The POPs Protocol under the UN ECE LRTAP Convention

The scientific work on POPs carried out under AMAP2 and other international efforts (OECD3, OSPAR4, HELCOM5, MAP6) in the 1980s and 1990s established clearly that long range atmospheric transport was one of the main routes by which POPs were deposited in remote regions, far from sources, such as the Arctic. These findings led the Executive Body of the LRTAP Convention to negotiate and adopt a Protocol on POPs in 1998, including an initial list of 16 substances (see Table 1.2). This protocol, since its entry into force for 29 Parties in 2003, has provided a dynamic international framework to develop knowledge on POPs and make it available to interested users. The technical groups under the LRTAP agreement have established a valuable body of information on the properties of the listed substances, as well as the best available techniques (BAT)/best environmental practices (BEP) to decrease unintentional releases, dispose of waste, and reduce intentional use. The LRTAP Protocol has also provided a framework for monitoring in the atmosphere (under the European Monitoring and Evaluation Programme, EMEP) and modelling

1 http://www.unece.org/env/lrtap/lrtap_h1.htm
2 Arctic Monitoring and Assessment Programme http://www.amap.no/
3 Organisation for Economic Co-operation and Development http://www.oecd.org
4 OSPAR Commission, protecting and conserving the North-East Atlantic and its resources http://www.ospar.org/
5 HELCOM Baltic Marine Environment Protection Commission http://www.helcom.fi/
6 Mediterranean Action Plan MAP under UNEP http://www.unepmap.org/
emissions, transport and fate under EMEP (Meteorological Synthesizing Centre (MSC)-East and the UN ECE, Task Force on Hemispheric Air Pollution (TF-HTAP).

The ultimate objective of the Protocol is to control, reduce or eliminate discharges, emissions and losses of POPs. Substances under the scope of the original Protocol are listed in its Annexes I-III. The original Protocol bans the production and use of some products outright (aldrin, chlordane, chlordecone, dieldrin, endrin, hexabromobiphenyl, mirex and toxaphene). Others are scheduled for elimination at a later stage (DDT, heptachlor, hexachlorobenzene, and PCBs). Finally, the original Protocol severely restricts the use of DDT, HCH (including lindane) and PCBs. The original Protocol includes provisions for dealing with the wastes of products that will be banned. It also obliges Parties to reduce their emissions of dioxins, furans, PAHs and HCB below their levels in 1990 (or an alternative year between 1985 and 1995). For the incineration of municipal, hazardous and medical waste, it lays down specific limit values.

The Protocol on POPs makes provisions for inclusion of additional POPs to Annexes I – III (Article 14 of the Protocol and EB decision 1998/2). At present a number of substances are under consideration for the inclusion of the Protocol (see Section 1.3.2 below).

1.2.2. SC on POPs and the GMP

The United Nations Environment Programme (UNEP)/SC on POPs entered into force in 2004 and has to date 164 parties. When it entered into force, the SC called for international action on 12 POPs grouped into three categories: 1) pesticides: aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, mirex and toxaphene; 2) industrial chemicals: hexachlorobenzene (HCB) and polychlorinated biphenyls (PCBs); and 3) unintentionally produced POPs: dioxins and furans.

Governments are to promote BAT and BEP for replacing existing POPs while preventing the development of new POPs. Provision was also made for a procedure to identify additional POPs and the criteria to be considered in doing so.

Key elements of the treaty include: financial resources to enable developing country Parties and Parties with economies in transition to fulfill their obligations under the Convention; the requirement that developed countries provide new and additional financial resources; measures to eliminate production and use of intentionally produced POPs; measures to eliminate unintentionally produced POPs, where feasible; measures to manage and dispose of POPs wastes in an environmentally sound manner; and substitution involving the use of safer chemicals and processes to prevent release of unintentionally produced POPs. Precaution is exercised throughout the SC, with specific references in the preamble, the objective and the provisions, for identifying new POPs.

The Convention has procedures for listing additional POPs in the action annexes: Annex A contains chemicals to be eliminated; Annex B contains chemicals to be restricted; and Annex C calls for the minimization of unintentional releases of listed chemicals.

The SC includes in Article 16 provisions to evaluate the effectiveness of the measures undertaken, including the gathering of comparable monitoring data on the presence of the listed chemicals and on their regional and global environmental transport. To put this into effect, the COP established the Global Monitoring Plan (GMP, SC3/19). Work was initiated after 2004 and the first EE was completed in 2009 [UNEP, 2009].

At the COP4 meeting in May 2009, several decisions were adopted concerning new substances to be added [including polybrominated diphenyl ethers (PBDEs) and perfluorinated compounds (PFCs)]; synergies with the Basel and Rotterdam Conventions; further implementation of the GMP; and the development of tools and methods to evaluate the effectiveness of the measures undertaken.

The reports of the GMP for EE presented at COP4 [UNEP, 2009] stress the importance of information on LRT in interpreting measured trends and the need to consider the role of meteorology and climate variability. The reports also recommend further cooperation of the SC/GMP with UN/ECE/LRTAP/TF_HTAP.
1.2.3. International Programmes and Assessment

Other POPs-related international efforts can be organized in two groups: (I.) regional agreements dealing with POPs in a wider environmental context that have carried out monitoring in biotic and abiotic environments over several decades (AMAP; HELCOM, OSPAR, MAP) and (ii.) international agreements dealing specifically with toxic chemicals on a global scale: SAICM\(^7\), Basel\(^8\), Rotterdam\(^9\).

Concerning global international agreements dealing specifically with toxic chemicals on a global scale, a coordinated international, regional and national effort on the assessment and management of hazardous chemicals was outlined in the 1992 United Nations Conference on Environment and Development (UNCED). UNCED Agenda 21, Chapter 19 provides a base for the environmentally sound management of toxic chemicals. This was further developed in the Basel, Rotterdam and SCs and in 2006 by adopting the Strategic Approach to International Chemicals Management (SAICM). Active work has been undertaken to cooperate and establish synergies between the Stockholm, Rotterdam and Basel Conventions and this is reflected in the decisions taken at COP4 of the SC in May 2009 (Decision SC4/34).

The compilation of information carried out under the first EE of the SC in 2009 and the Sufficiency and Effectiveness review of the LRTAP protocol in 2005 provide an update of the current situation and reflect disparity in resources available for monitoring and regulatory activities in different regions.

In Africa, regulatory actions are being taken by many countries on hazardous chemicals, including POPs, particularly through the Rotterdam Convention requirements. Most countries have banned DDT in agriculture but some allow its use in vector control, especially for malaria. Pesticide Formulation Laboratories have been/are being established by many African countries. Most African countries are signatories to chemical conventions: Bamako/Basel, Rotterdam, Stockholm, Vienna/Montreal, Kyoto Protocol. Most African countries participate in regional and international programs on chemicals regulation: International Forum on Chemical Safety IFCS, Strategic Approach to International Chemicals Management SAICM, Global Harmonised System GHS, Risk Management of the UN Institute for Training and Research UNITAR; Africa Stockpile Program ASP, Comité Inter Etats de Lutte contre la Sécheresse dans la Shel CILSS, Common Regulations on Pesticide and other similar ones in other Regional Economic Communities RECs. Most African countries have developed or are developing their National Implementation Plans (NIPs) on POPs. The World Health Organisation (WHO) Monitoring Program of POPs in breast milk and human tissues, the RECETOX programs of POPs in environmental media, Global Atmospheric Passive Sampling (GAPS) Network, UNEP/DGEF Capacity building Programs, are on-going. [From p39 in GMP-Africa, 2009]

The Asia Pacific Region report outlined some of the activities producing information on POPs for the first report and identified regions with data gaps: “In the Pacific and East Asian subregions, there are some baseline data on ambient air for the first EE. On the other hand, such data sets are lacking in South and West Asian subregions. In China, eleven background sampling sites were selected and PM10 high volume sampling was carried out to analyze dioxins and other POPs. In Hong Kong SAR of China, monitoring of some POPs (dioxins and total PCBs) in ambient air has been conducted since mid-1997 as part of the regular toxic air pollutants monitoring programme. Fiji has conducted a pilot study on the application of passive samplers for the determination of POPs in ambient air from June 2006 to May 2007 at three sampling sites in Fiji Islands through collaborations with RECETOX. In India, there have been a few historical studies of POPs in air, which, however, are

7 Strategic Approach to International Chemicals Management http://www.saicm.org
9 Rotterdam Convention, Prior Informed Consent http://www.pic.int
Japan has been monitoring POPs in the air by high volume sampler throughout the nation since 1997 for dioxins, and since 2002 for other POPs. In addition, background air monitoring has been conducted every month by using high volume sampler at Hateruma Island since 2004. In Oman, air samples were analyzed for DDT in 2005. The POPs Monitoring Project in East Asian Countries has also monitored POPs (9 pesticides) in the air by high volume sampler in Cambodia, Indonesia, Republic of Korea, Lao PDR, Malaysia, Mongolia, Philippines, Thailand and Vietnam since 2005.” [from p 9 of GMP-Asia-Pacific, 2008]

The Group of Latin American Countries (GRULAC) region report indicated clearly that monitoring activity was sparse and intermittent, and needed local and international support to achieve the EE objectives in the future. From page 19 of the GRULAC GMP report: Over 90 per cent of the countries in Latin America and the Caribbean have signed Multilateral Environmental Agreements MEAs such as the Montreal and the Kyoto protocols and the Basel Convention. MEAs related to biological diversity and desertification had even higher levels of participation. By contrast, participation in MEAs (signatories) such as the Cartagena Protocol and the Rotterdam and Stockholm conventions, was considerably lower, at 76, 45 and 64 per cent, respectively. Ensuring compliance with MEAs continues to be a major challenge, as enforcement depends on national (and sometimes sub-regional) action in which governmental capacities are critical. The Wider Caribbean (the Cartagena Convention) and its protocols are important multilateral regional agreements and action plans for the future.

Several countries of the region also belong to the Antarctic Treaty (Argentina, Brazil, Chile, Peru, Ecuador, and Uruguay) and many of them perform research activities within the Antarctic region, but there are no publications available related to POPs research. The countries of the GRULAC region have been working in many coordinated efforts, addressing regional problems during several years. However, even when these efforts have been very effective in the international forums, they have remained insufficient for building sustainable POPs programs with a proper regional structure.

Concerning the regional environmental agreements in the European Region, two important new developments deserve to be mentioned: the entry into force in 2009 of the EU Marine Strategy Framework Directive (MSFD) and the entry into force in 2007 of the REACH Regulation. These two instruments are innovative and propose an integrated approach to identify and limit sources in REACH and to harmonize large-scale, long-term environmental monitoring in the MSFD.

The EU MSFD framework will enhance cooperation and consistency in monitoring and research among regions (Atlantic, Baltic, Mediterranean, Black Sea) and develop an integrated framework in which the current “environmental status” of regions and subregions is established, including levels of contaminants, and measures and targets identified and implemented to maintain or improve such status.

important commitments relating to the protection of the marine environment from pollution, and to which the Community is not yet a party but in respect of which it has observer status.

The EU Regulation REACH on production and use of chemicals in the European Union entered into force in June 2007. As stated in the Regulation, its purpose is to ensure a high level of protection of human health and the environment. In particular, one of the important objectives of the Regulation is to reduce emissions of substances of very high concern (SVHC) by restriction of use and replacement by less dangerous substances or technologies. REACH implements the precautionary principle and requires the industry to prove that the substances do not adversely affect human health or the environment before they are allowed on the market. This Regulation can be considered as a driving force for international activities on hazardous chemicals.

According to the Regulation, chemical substances shall not be manufactured or placed on the market in the European Community unless they have been registered in the European Chemical Agency (ECHA). Within the registration process certain information on a substance should be submitted by the industry. In particular, this includes the information on physical-chemical properties of a substance, its environmental fate properties, its toxicological and ecotoxicological properties, possible harmful effects on human health and the environment, emission estimates, and monitoring data for substances of very high concern.

The notion of substances of very high concern includes so-called persistent bioaccumulative and toxic substances (PBT) and very persistent and very bioaccumulative substances (vPvB). The criteria for a substance to be considered as PBT or vPvB are similar to those used under CLRTAP and the SC (see Section 1.3.1 below). It should be mentioned that POPs form a subclass of the class of SVHC. The work on selecting substances of very high concern is a permanent activity under REACH, involving the preparation of a dossier evaluating possible risk for human health and the environment arising from exposure to a substance. Such a dossier should include, inter alia, all available information from assessments carried out under other international and national programmes.

As estimated by the ECHA, the number of substances that are to be registered in 2010 is about 9000 including SVHC. At present, active work on registration is carried out for over 2000 substances, providing a very large and growing volume of information on physical-chemical, toxicological and ecotoxicological properties of industrial substances. This information can be used for evaluating new substances (such as hexabromocyclododecane, trifluralin, pentachlorophenol, etc.) under international legislations and for improving the knowledge of properties for the substances that are already under consideration.

Further, for substances manufactured in or imported to the European Community in essential quantities (more than 10 tons per year per manufacturer/importer) REACH requires submission of a Chemical Safety Report. This report is aimed at exposure estimation and characterization of risks posed by a substance to human health and the environment and to elaboration of risk management measures (RMMs) for reducing these risks. The approaches to risk assessment worked out under REACH legislation can also be of use for environmental protection activities at the international level.

Canadian efforts to regulate chemicals over the past two decades have been guided by the Canadian Environmental Protection Act, 1999 (CEPA 1999). CEPA 1999 specified that new substances manufactured or imported into Canada above certain thresholds since 1994 must undergo government-led human health and environmental assessments. Canada’s Domestic Substance List (DSL) forms the basis for distinguishing new substances from the inventory of ‘existing substances’ that were manufactured, imported or used in Canada on a commercial scale in the mid-1980s. As a first step in scientifically assessing all chemical substances known to be in commerce in Canada, CEPA 1999 required that the approximately 23,000 existing substances be examined to determine if they were potentially harmful to human health or the environment and to identify which ones...
warranted further attention. This resulted in a large-scale priority-setting exercise called “Categorization” wherein Government of Canada scientists worked with their partners to identify substances that were inherently toxic, persistent, bioaccumulative and substances to which people might have the greatest potential for exposure. With the completion of Categorization in 2006, Canada became the first country to have systematically examined all substances known to be in commerce domestically.

Building on Canada’s Toxic Substances Management Policy, and guided by revisions to CEPA in 1999, the Chemicals Management Plan (CMP) was launched in 2006 to bring all existing federal programs together into a single strategy. The CMP is a science-based approach, which aims to protect human health and the environment. The CMP identifies timelines for action on chemical substances, setting ambitious objectives to assess and, where required, developing risk management strategies for all Categorised existing substances in Canada by 2020.

In the United States, two key federal laws regulate toxics chemicals. The Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) regulates the production, sale, and use of pesticides; and the Toxic Substances Control Act (TSCA), regulates industrial chemicals. However, before the United States can ratify the SC on POPs, additional regulatory authority must be sought from Congress to ensure that the United States can effectively implement the obligations of the agreement. Since the United States signed the agreement in 2001, both the House and the Senate have put forward implementing legislation in the relevant committees of jurisdiction, but neither chamber has voted on the bills. The Obama administration has expressed strong support for the ratification of the SC and is hopeful that Congress will pass the necessary implementing legislation.11

The Sound Management of Chemicals (SMOC) initiative is a tri-national effort between Mexico, Canada and the United States to reduce the risks of toxic substances to human health and the environment. Developed by the Commission for Environmental Cooperation (CEC) in 1995, SMOC targets specific substances for phase out, stringent controls, or virtual elimination through North American Regional Action Plans (NARAPs). The NARAPs represent a long-term commitment to regional action. They include a commitment to work cooperatively by building upon international environmental agreements, existing policies and laws. They also bring a regional perspective to international initiatives that are in place or being negotiated on persistent toxic substances. To date, NARAPs have been developed for: chlordanes, DDT and its metabolites, PCBs, lindane and Mercury. Recently, instead of a NARAP, the CEC developed the North American Strategy for Catalyzing Cooperation on dioxins, furans and hexachlorobenzene.

Signed in 1997 by Environment Canada (EC) and the United States Environmental Protection Agency (US EPA), the Great Lakes Binational Toxics Strategy (GLBTS) targets 12 Level 1 persistent toxic substances (mercury, polychlorinated biphenyls (PCBs), dioxins and furans, hexachlorobenzene (HCB), benzo(a)pyrene (B(a)P), octachlorostyrene (OCS), alkyl-lead, and five pesticides: chlordane, aldrin/dieldrin, DDT, mirex, and toxaphene), and several Level 2 substances for pollution prevention measures. Under the Strategy, EC and US EPA conduct monitoring of the atmospheric deposition of toxic chemicals to the Great Lakes basin under the Integrated Atmospheric Deposition Network and consider additional substances that may present threats to the Great Lakes ecosystem.

1.3. Properties of POPs

POPs are mainly anthropogenic chemicals that have been manufactured to exploit some characteristic property that makes it advantageous for a particular purpose. For instance, DDT can be made cheaply and is effective against agricultural pests and for combating disease vectors such as mosquitoes. PCBs have thermal properties and stability that make them well-suited as electrical fluids. Unintentionally produced POPs, such as the PCDD/Fs, do not fall into this category of chemicals manufactured for a specific advantage.

11 Correspondence from Karissa Kovner, Stockholm Convention Official Contact Point, Senior Policy Advisor, Office of the Assistant Administrator for Prevention, Pesticides and Toxic Substances, USEPA.
Like any other chemicals, POPs have intrinsic physical chemical properties that determine their environmental fate and transport when released into the environment. Since these properties vary with temperature, climate variability and global warming will affect fate pathways, including partitioning dynamics between media, and influence observed concentrations and trends. The first report of the SC-GMP specified that an improved understanding of these influences is essential in order to correctly interpret monitoring data and associated temporal trends for the purpose of assessing effectiveness of international control measures on POPs. [UNEP, 2009].

1.3.1. Types and sources of POPs

POPs are chemicals that persist in the environment, can resist degradation, bioaccumulate in organisms and biomagnify through the food chain, may be toxic and cause adverse health effects in humans, wildlife and the environment.

The following 4 criteria, as defined by the United Nations, are used to identify a chemical as a POP:

1. Persistence (P) – the ability to resist degradation and stay in different environmental media, including air, soil, water and sediment;
2. Bioaccumulation (B) - the ability to accumulate in living tissues to levels higher than the surrounding environment;
3. Toxicity (T) - the ability to cause adverse effects in humans or the environment;
4. Long-range transport potential (LRTP) – evidence showing that the chemical can transport to regions where they have never been used or produced.

LRTP is a main criterion for evaluating the ability of POPs to be transported at the hemispheric/global scale. In addition, persistence of chemicals in environmental media such as water or soil leads to the potential for these substances to undergo multi-hop transport (see below). Table 1.1 compares the criteria used under CLRTAP and the SC with those used in some national legislation (US TRI reporting guidelines, CEPA and REACH). Substances that meet criteria given in Table 1.1, based on sound scientific evidence, may be considered for inclusion in international control initiatives.

Under national legislations, LRTP is not mentioned directly. However, the criteria used under US TRI reporting and CEPA include the half-life in the atmosphere as a persistence characteristic. This parameter can be considered as an indirect characterization of LRTP of chemicals. Methods of more direct characterization of LRTP, important for consideration of chemicals at the international level, are discussed in Section C1.3.3. Under REACH, the vast amount of information compiled on industrial chemicals will facilitate the evaluation of new substances.

POPs vary widely. Some of the chemicals considered under CLRTAP and the SC are intentionally produced, e.g. organochlorine pesticides (OCs, such as chlordane, DDT and toxaphene), and some are combustion by-products (e.g. PCDD/Fs and PAHs).
Table 1.1. Criteria for identifying chemicals as POPs

<table>
<thead>
<tr>
<th></th>
<th>Long-range transport potential (LRTP)</th>
<th>Persistence</th>
</tr>
</thead>
<tbody>
<tr>
<td>CLRTAP&lt;sup&gt;12&lt;/sup&gt;</td>
<td>Vapour pressure &lt; 1,000 Pa and an atmospheric half-life &gt; 2 days;</td>
<td>Half-life in water &gt; 2 months;</td>
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<td></td>
<td>or Monitoring data showing that the substance is found in remote regions.</td>
<td>or Half-lives in soil or in sediment &gt; 6 months;</td>
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<td></td>
<td></td>
<td>or evidence that the substance is otherwise sufficiently persistent to be of concern within the scope of the POP protocol.</td>
</tr>
<tr>
<td>SC&lt;sup&gt;13&lt;/sup&gt;</td>
<td>Monitoring data showing that long-range environmental transport of the chemical may have occurred via air, water or migratory species;</td>
<td>Half-life in water &gt; 2 months;</td>
</tr>
<tr>
<td></td>
<td>or Environmental fate properties and/or model results that demonstrate that the chemical has a potential for long-range environmental transport through air, water or migratory species;</td>
<td>or Half-lives in soil or in sediment &gt; 6 months;</td>
</tr>
<tr>
<td></td>
<td>or For a chemical that migrates significantly through the air: half-life in air &gt; 2 days.</td>
<td>or Evidence that the chemical is otherwise sufficiently persistent.</td>
</tr>
<tr>
<td>US TRI reporting&lt;sup&gt;14&lt;/sup&gt;</td>
<td>–</td>
<td>Half-life in air &gt; 2 days.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Persistent: half-life in water, soil or sediment &gt; 2 months;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Very persistent: &gt; half-life in water, soil or sediment 6 months.</td>
</tr>
<tr>
<td>CEPA&lt;sup&gt;15&lt;/sup&gt;</td>
<td>–</td>
<td>Half-life in air &gt; 2 days;</td>
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<tr>
<td></td>
<td></td>
<td>Half-life in sediments &gt; 1 year;</td>
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<tr>
<td></td>
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<td>Half-life in soil and water &gt; 6 months.</td>
</tr>
<tr>
<td>REACH&lt;sup&gt;16&lt;/sup&gt;</td>
<td>–</td>
<td>PBT&lt;sup&gt;17&lt;/sup&gt;: half-lives in sea water &gt; 60 days, in fresh water &gt; 40 days, in marine sediments &gt; 180 days, in fresh water of estuaries sediments &gt; 120 days and in soil &gt; 120 days.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>vPvB&lt;sup&gt;18&lt;/sup&gt;: half-life in water &gt; 60 days, and in soil and sediments &gt; 180 days.</td>
</tr>
</tbody>
</table>

<sup>12</sup> Convention on Long-Range Transboundary Air Pollution
<sup>13</sup> Stockholm Convention on Persistent Organic Pollutants
<sup>14</sup> US EPA final rules for Toxic Release Inventory reporting
<sup>15</sup> the Canadian Environmental Protection Act
<sup>16</sup> EU Regulation “Registration, Evaluation, Authorization and Restriction of Chemicals”
<sup>17</sup> Persistent, bioaccumulative and toxic substances
<sup>18</sup> Very persistent and very bioaccumulative substances
Based on multimedia models that use partitioning properties ($K_{ow}$, $K_{aw}$, $K_{oa}$, see Figure 1.1) of individual POPs to evaluate their potential to reach the Arctic and deposit there, Wania [2006] has classified POPs as fliers, multi-hoppers, single hoppers and swimmers (Figure 1.1). Most legacy POPs, e.g. lower molecular weight PCBs, highly chlorinated chlorobenzenes, HCHs, lower molecular weight PCDD/Fs, PAHs and many OCPs, are multi-hoppers. These are ‘multimedia’ chemicals with partitioning properties that allow for efficient exchange between air and terrestrial or aquatic surfaces. Multimedia partitioning enables the long-range transport of these chemicals through the atmosphere by means of repeated cycles of deposition and re-evaporation, driven by temperature changes along the path. Partitioning between different environmental media will be further discussed in Section 2.4.

Less volatile chemicals, e.g. higher molecular weight PCDD/Fs, PAHs and decabrominated diphenyl ether (decaBDE), are “single hoppers”. In the bulk atmosphere, they tend to associate with particles and so their ability to undergo LRT is controlled by the LRTP of the atmospheric particles to which they sorb. They do not volatilize effectively after deposition to the Earth’s surface and therefore must reach the receptor region, e.g. the Arctic, in one single hop without deposition along the path. As discussed below, climate variability can set these single-hoppers free to take a second hop through extreme events like dust storms, forest fires or floods. Their potential to re-enter the atmosphere via soil dust resuspension and sea-spray aerosols needs further investigation.

![Figure 1.1. Major modes of transport of perfectly persistent, hypothetical chemicals defined by their partitioning properties $\log K_{aw}$ and $\log K_{oa}$, calculated with the Globo-POP model assuming 10 years of steady emissions into air. (Partitioning constants quantify the ratio of concentration for a particular chemical between two phases that have come to equilibrium. $K_{ow}$, octanol and water; $K_{aw}$, air and water; $K_{oa}$, octanol and air.) [Reprinted with permission from Figure 1 in Wania, Frank [2006] Potential of degradable organic chemicals for absolute and relative enrichment in the Arctic, Environmental Science & Technology, 40(2): 569-577. Copyright 2006 American Chemical Society].](image-url)

While the atmosphere has been identified as the most rapid and major transport route for most legacy POPs, some new and emerging POPs, e.g. PFOS and perfluorinated carboxylates (PFCA), and some legacy POPs, e.g. $\alpha$- and $\beta$-HCH, are “swimmers” or have become swimmers. In
some cases, chemicals may be both swimmers and multi-hoppers, with air-water exchange and varying degrees of transport in both air and water playing key roles in their LRT. These sorts of chemicals partition significantly into water, and, provided the chemical is persistent in water, the balance of LRT can shift from atmospheric initially to oceanic as the upper ocean accumulates the chemical. It is a matter of time-scale whether transport in air or ocean prevails. The comparison of two isomers of HCH, α- and β-HCH, provides an elegant example. For α-HCH during the period of high use of technical HCH, the dominant pathway for transport to the Arctic was through the atmosphere. Evidence for this is the strong link between concentration in Arctic air and the global usage and emission patterns of this compound from 1979 to the early 1990s, when the usage/emissions of technical HCH were still high [Li et al., 1998; Li and Bidleman, 2003]. The key role of atmospheric transport was further delineated over time using a mass balance model for α-HCH in the Arctic Ocean [Li et al., 2004]. In contrast, the dominant pathway for the delivery of β-HCH to the Arctic is via ocean currents. The aquatic pathway for β-HCH is almost entirely due to its 20-fold lower Henry’s law constant, H, compared to that of α-HCH [Li et al., 2002] (e.g. at 5 °C, H for α- and β-HCH were found to be 0.094 and 0.0054 Pa·m³·mol⁻¹, respectively [Sahsuvar et al., 2003]), which favours wash-out by precipitation and suppresses revolatilisation from the sea-surface. Transport of β-HCH to the Arctic Ocean is therefore mainly through ocean currents. The net effect is a divergence in the pathways and times of arrival for α-HCH and β-HCH, the latter compound manifesting a delay of about 20 years. This has been reflected in differing spatial and temporal trends for these two isomers in Arctic abiotic and biotic media [Li and Macdonald, 2005]. After decades and despite processes which export contaminants into the deep sea, the ocean surface layer may become saturated, leading to the reversal of the direction of air-sea exchange, i.e. the ocean returns the pollutant to the atmosphere. This has been found for α-HCH and DDT for parts of the Arctic and Atlantic Oceans and some other highly contaminated sea regions [Bidleman et al., 1995; Stemmler and Lammel, 2009].

Although “fliers” are generally considered too volatile to deposit even under Arctic temperatures, the presence of volatile PFOS precursors, e.g. fluorotelomer alcohols (FTOHs), in Arctic air may indicate their atmospheric degradation to form PFCA which are detected in Arctic animals, i.e. the potential for indirect atmospheric LRT of PFOS and PFCA via precursors.

POPs and POP-like chemicals can be released directly to the environment during usage (e.g. spraying of pesticides; volatilization of PBDEs and other flame retardants from consumer products) or production (e.g., combustion releasing PAHs and PCDD/Fs; production of PFCA). These pathways comprise the primary emission. When previously-deposited chemicals re-volatilize into the atmosphere from environmental media, like snow, soil, vegetation and water, often as a result of seasonal and diurnal changes in temperature, this is considered a secondary emission. Recently, research has shown that chemicals, e.g. PCBs, can be released indirectly as a result of biomass burning (e.g. forest fires and agricultural fires), and be transported to the remote Arctic [Eckhardt et al., 2007; Hung et al., 2010]. It has also been found that reduced ice-cover may allow chemicals previously deposited into the Arctic Ocean, e.g. α-HCH, to volatilize back into the atmosphere [Jantunen et al., 2008]. It is therefore important to take into consideration the distributions of historical accumulations of POPs in environmental media like soil, vegetation and water, when assessing the effectiveness of controls as reflected in atmospheric temporal trends.

In the case of secondarily formed POPs, long-range atmospheric transport of precursors may add to their occurrence in regions far removed from sources. For instance, the presence and abundance of volatile PFOS and PFCA precursors (e.g. fluorosulfonamides, PFASs and fluorotelomer alcohols, FTOHs, respectively) in Arctic air may be important contributors to inputs to this environment. [Martin et al., 2004; Shoeb et al., 2006]

1.3.2. Legacy POPs and new POPs

Some POPs were regulated locally or regionally more than 30 years ago and thus in these areas, these substances are not in current use or production. The informal term ‘legacy POPs’ has been used to describe substances that have been subject to past regulation for a long time. This
distinguishes them from other substances that are being considered for regulation or substances that have been regulated more recently and are still in use and/or production. POPs included in the initial list of the LRTAP Protocol and the SC were “legacy” POPs for many countries. The inclusion of new substances in the list of regulated POPs poses new challenges.

CLRTAP POPs Protocol (Article 14 and EB Decision 1998/2) and the SC on POPs (Article 8) make provision for inclusion of new POPs into their lists of harmful substances. The list of POPs originally included to these Conventions (legacy POPs) and substances included later or currently under review for addition is given in Table 1.2.

**Table 1.2.** Legacy and new POPs considered under CLRTAP and SC

<table>
<thead>
<tr>
<th>Substance</th>
<th>POP Protocol (CLRTAP)</th>
<th>Stockholm Convention</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Originally included</td>
<td>Recognized as a POP(^{19})</td>
</tr>
<tr>
<td>Aldrin</td>
<td>√</td>
<td></td>
</tr>
<tr>
<td>Chlordane</td>
<td>√</td>
<td></td>
</tr>
<tr>
<td>Dieldrin</td>
<td>√</td>
<td></td>
</tr>
<tr>
<td>Endrin</td>
<td>√</td>
<td></td>
</tr>
<tr>
<td>Heptachlor</td>
<td>√</td>
<td></td>
</tr>
<tr>
<td>Hexachlorobenzene (HCB)</td>
<td>√</td>
<td></td>
</tr>
<tr>
<td>Mirex</td>
<td>√</td>
<td></td>
</tr>
<tr>
<td>Toxaphene</td>
<td>√</td>
<td></td>
</tr>
<tr>
<td>Polychlorinated biphenyls (PCBs)</td>
<td>√</td>
<td></td>
</tr>
<tr>
<td>Dichlorodiphenyltrichloroethane (DDT)</td>
<td>√</td>
<td></td>
</tr>
<tr>
<td>Polychlorinated dibenzodioxins and dibenzofurans (PCDDs/Fs)</td>
<td>√</td>
<td></td>
</tr>
<tr>
<td>Chordecone</td>
<td>√</td>
<td></td>
</tr>
<tr>
<td>Hexachlorocyclohexanes (HCHs)</td>
<td>√</td>
<td></td>
</tr>
<tr>
<td>Hexabromobiphenyl (HBB)</td>
<td>√</td>
<td></td>
</tr>
</tbody>
</table>

\(^{19}\) These substances are recognized as POPs but are not yet included to the Annexes of the POPs Protocol

\(^{20}\) Conference of the Parties
<table>
<thead>
<tr>
<th>Substance</th>
<th>POP Protocol (CLRTAP)</th>
<th>Stockholm Convention</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Originally included</td>
<td>Recognized as a POP(^{19})</td>
</tr>
<tr>
<td>Polycyclic aromatic hydrocarbons (PAHs)</td>
<td>√</td>
<td></td>
</tr>
<tr>
<td>Pentabromodiphenyl ether (PentaBDE)</td>
<td></td>
<td>√</td>
</tr>
<tr>
<td>Octabromodiphenyl ether (OctaBDE)</td>
<td></td>
<td>√</td>
</tr>
<tr>
<td>Pentachlorobenzene (PeCB)</td>
<td></td>
<td>√</td>
</tr>
<tr>
<td>Perfluorooctane sulfonate (PFOS) (Perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride)</td>
<td></td>
<td>√</td>
</tr>
<tr>
<td>Hexachlorobutadiene</td>
<td></td>
<td>√</td>
</tr>
<tr>
<td>Polychlorinated naphthalenes (PCNs)</td>
<td></td>
<td>√</td>
</tr>
<tr>
<td>Short-chain chlorinated paraffins (SCCP)</td>
<td></td>
<td>√</td>
</tr>
<tr>
<td>Endosulfan</td>
<td></td>
<td>√</td>
</tr>
<tr>
<td>Hexabromocyclododecane (HBCD)</td>
<td></td>
<td>√</td>
</tr>
<tr>
<td>Dicofol</td>
<td></td>
<td>√</td>
</tr>
<tr>
<td>Trifluralin</td>
<td></td>
<td>√</td>
</tr>
<tr>
<td>Pentachlorophenol (PCP)</td>
<td></td>
<td>√</td>
</tr>
</tbody>
</table>

\(^{19}\) These substances are recognized as POPs but are not yet included to the Annexes of the POPs Protocol

\(^{20}\) Conference of the Parties

At present, the process of revision of POP candidates under these Conventions is ongoing. Under both Conventions a tiered approach is applied. At the first tier (screening), Parties to the Convention select substances for further consideration and make a proposal according to screening criteria (potential for long-range transport, persistence, bio-accumulation and toxicity). At the second tier (detailed discussion) these proposals are discussed by the corresponding Bodies of the Conventions and the final decision on including the substance to the given Convention is taken. It should be mentioned that at the first stage (screening) a large number of substances are to be evaluated. In particular, lists of hazardous industrial substances in the EU (Annex VI to EC
Regulation 1272/2008 and Annex XIV to EU Regulation REACH) include several thousands of entries.

Although the approach to include new substances is similar under CLRTAP and the SC, the process of including them is different. In particular, some substances (e.g., polycyclic aromatic hydrocarbons and hexachlorobutadiene) are considered under CLRTAP but not under the SC. On the other hand, some substances (such as pentachlorobenzene, PFOS and others) recognized as POPs under the SC are not yet included in the corresponding Annexes to the POP Protocol. Efforts are underway to identify synergies between these two Conventions. The risk assessment process of candidate POPs is an obvious area where overlap and duplication of effort can be reduced.

Evaluation of environmental fate of POP candidates is a challenging task. Core media chosen for monitoring the effectiveness of the SC on POPs include air and human tissues. Some of the new POPs and new chemicals of concern are more polar and/or have higher tendencies to bind to particles compared to the legacy POPs. Therefore, it is necessary to adapt current sampling methods to capture these priority compounds. For instance, current passive and active air monitoring programs that use polyurethane foam plugs (PUFs) as a vapour-phase sampling medium will have to adapt with the inclusion of XAD resins or other high capacity sorbents to capture more polar and/or volatile chemicals such as PFCs. Also, high volume air sampling is required to distinguish particle-bound versus gas-phase pollutants, which is important for understanding the transport of particle-bound PBDEs, other flame retardants, and PFCs. Atmospheric monitoring techniques are discussed in Section 2.2.2.

Some of the new POPs that are polar or ionizing, e.g. PFOS and PFCAs, have higher water solubilities and are susceptible to oceanic transport. However, there are relatively few studies on oceanic transport of either new or legacy POPs, mainly due to complicated logistics of seawater sampling at different depths and the requirement of large water volumes to detect these compounds. Also, transport via ocean currents is slow, taking years, compared to atmospheric transport, taking days to weeks, rendering delayed response in environmental concentrations to emission decline. Studies on oceanic transport are summarized in Section 2.3.

The recent “Arctic Pollution 2009” Report [AMAP, 2009c] pointed out that there are two pathways of transport for PFOS-related chemicals, namely indirect transport via precursors and ocean transport, and that there is currently no model to address the role of these different pathways. The observations of PFOS and some PFCAs in snow cores from ice caps and relatively fast changing Arctic wildlife concentrations are consistent with atmospheric transport.

Efforts to model new POPs would benefit from further research on physical-chemical properties and investigations to quantify and assess emissions and human exposure. This presents challenges as many of the new POPs are used on consumer products, e.g. flame retardants and PFCs, and exposure through the indoor environment becomes an important consideration. Data on production volumes for many new POPs are lacking or unavailable. The impact of local sources in remote communities also needs to be investigated. Consumer products used in homes and offices, disposed in landfills and incinerated in northern communities may contribute to observed Arctic air concentrations, making it difficult to assess the contribution from long-range transport. While human exposure to most legacy POPs is dietary, recent research indicates significant human exposure from indoor air and dust for PBDEs and PFCs [Shoeib et al., 2005; Wilford et al., 2004].

To overcome these difficulties, various methodologies are employed to assist in the evaluation of POP candidates when data is lacking. For example, QSAR methods can be applied for estimating required physical-chemical properties of considered substances. Evaluating important substance properties such as their LRTP and persistence in the environment can be performed on the basis of model simulations of POP fate and transport from conventional emission sources, when information on real emissions is not available.

Models of different types can be used at different stages of the evaluation process. For instance, at the screening stage (when large numbers of substances are under consideration) simple box models (e.g., the OECD Pov and LRTP Screening Tool) may be most feasible because they
require minimal information and computing time. In contrast, for subsequent stages of the evaluation process, spatially and temporally resolved models (such as G-CIEMS, Evn-BETR, MSCE-POP, etc.) can be used in order to obtain information with greater detail. For more highly resolved simulations, the availability of emissions data, physical-chemical properties and degradation rates can be limiting. This data requirement is addressed under REACH, where a vast amount of information is being generated on industrial chemicals. Further discussion on evaluation of new POPs can be found below in Section 1.3.3.

1.3.3. Metrics of Long Range Transport (LRT)

One of the key properties of POPs is that they can travel long distances. A high potential for LRT of a POP implies the possibility for intercontinental transport. Further, the ability to travel long distances is the basis for one of four criteria for recognizing a substance as a POP under CLRTAP and the SC on POPs (Table 1.1).

To evaluate the potential of a substance to undergo long-range transport, numerical evaluation (LRT metrics) is required. Various metrics for quantifying the LRT of substances have been proposed and can be classified as either transport-oriented or target-oriented [Klasmeier et al., 2006]. These metrics are typically calculated with the help of multimedia POP models. The choice of a particular metric strongly depends on model design (see 4.3). Multimedia POP models permit the inclusion of complex fate processes of POPs in the environment (repeating cycles of transport in various media, including deposition and subsequent re-volatilization – the so-called multi-hop transport).

Transport-oriented metrics evaluate LRT either by fraction of emissions transported over a fixed distance from the source location or by the distance travelled by a chemical during its residence time in the atmosphere. At present there exist many metrics of this kind: transport distance, characteristic travel distance, spatial range and others. For example, transport distance can be defined as a distance from the source at which concentrations of the considered pollutant drop below the prescribed threshold level. The half-life of a substance in the atmosphere can also be considered as a metric of its LRT (e.g., in screening criteria used under CLRTAP and the SC). Transport oriented metrics are frequently used in POP multicompartment fate models (OECD Pov and LRTP Screening Tool, SimpleBox, Impact2002, ELPOS, ChemRange, MSCE-POP and others) [Scheringer, 2009].

Target-oriented metrics are calculated on the basis of the relation between emissions of a chemical in a source region and its deposition (or concentration) in a target region. Normally it is supposed that source and target regions are located far from each other. Examples of such metrics include Transport Efficiency (in particular, calculated by a spatially resolved steady-state model BETR North America for Great Lakes region [MacLeod and Mackay, 2004]), and the Arctic Contamination Potential [used by Globo-POP model, Gouin and Wania, 2007]. These metrics depend not only on atmospheric LRT but also on deposition velocities in the chosen target region.

It should be mentioned that the variety of different metrics and the dependence of particular metrics on model design (list of processes taken into account by the model, model resolution, etc) hampers their use for LRT evaluation. To overcome this difficulty the so-called benchmark approach was proposed (discussed, in particular, at the Ottawa Workshop on multimedia models in 2001). According to this approach, one or more well-known substances are chosen as benchmarks against which the calculated LRT metrics for other evaluated substance are compared. Under EMEP, benzo[a]pyrene (B[a]P) is used as a benchmark substance of regional concern and hexachlorobenzene (HCB) is a benchmark substance of global concern.

It is also important to note that all LRT metrics are dependent on source location and meteorological conditions. At the screening level, averaged estimates of LRT by simple mass balance models should be used since such models require small computational resources. However, for obtaining more precise information on LRT of substances, the application of spatially resolved models is preferred. This is discussed further in sections 1.4.3 and 4.3.
1.4. Integrated Approach for Understanding POPs Transport: Observations, Emissions and Models

1.4.1. Observations and Process Studies

Measurements of POPs in the environment became more intensive starting about 30-40 years ago in response to realization and concern over their environmental impacts on humans and wildlife. Measurements of POPs in abiotic media (i.e. air, water, soil, vegetation etc.) provide information needed to assess the environmental fate and transport of POPs. These data allow for exposure assessment, assessing effectiveness of regulation of POPs, and for understanding the fate and transport of POPs. The data are also invaluable for testing/comparing against emissions information and model predictions.

Chapter 2 provides a broad overview of the current state of knowledge based on measurements of POPs in abiotic media. These measurements range in scope and design and can be applied for a variety of purposes as outlined below.

i.) Continuous Monitoring: Long-term monitoring (years+) provides information for assessing temporal trends and changes in trends that may be due external factors such as regulatory efforts on POPs or some other change in the environment (e.g. climate effects).

ii.) Short-term monitoring (snap-shots): These are often short-term research studies (e.g. work of graduate students) and typically range in duration from several weeks to a year or two. These studies are often novel and provide the first data of their kind. These include screening studies (reconnaissance work - i.e. looking for a chemical in a new environment where data do not previously exist) or studies to assess short-term temporal trends (directly), long-term trends (indirectly, e.g. historic samples; sediment or ice cores) and/or spatial trends.

iii.) Process Studies: This category includes laboratory- and/or field-based investigations of intermedia exchange, measurements of physical-chemical properties and techniques/tools for better understanding chemical transport and fate (e.g. tracer techniques). Results from such studies are used to build and parameterize models and to interpret observations.

1.4.2. Emission inventories

Both primary and secondary emissions need to be considered when assessing emission inventories for POPs to air. The relative contribution of secondary emissions is expected to increase in the future for many classes of POPs as primary emissions are reduced in response to successful regulation through international treaties and agreements on POPs.

The assessment of secondary emissions often requires observational data of legacy compounds that have built-up in temporary reservoirs (soil, ocean). These reservoirs are dynamic and may return their burden to the atmosphere. Process studies and empirical models of surface-air exchange help to quantify these sources and provide a more complete emission inventory that can be applied to regional and global transport models.

Chapter C3 summarizes the current state of knowledge regarding POPs emissions. Limitations and gaps in knowledge are revealed as emission inventories are available for only some POPs, for some regions, and for some time periods. For information that is available, uncertainty is a key consideration. Emissions inventories are often based on surrogate data and are estimates of estimates. Optimistically, these estimates may result in information that is accurate within an order of magnitude but it is more often the case that uncertainties span more than an order of magnitude.

1.4.3. Modelling approaches

At present, models are increasingly used to simulate the environmental distribution of POPs [e.g. Gusev et al., 2005a; Hansen et al., 2006; Scheringer et al., 2003]. This helps to address data gaps in the spatial and temporal monitoring information available for POPs. Advantages of using POP models include insight and understanding of the trends and behaviour of POPs in the environment, and the evaluation of source-receptor relationships and projections based on future emission scenarios.
The structure of POP models depends on specific processes governing POP cycling in the environment. Due to their properties, POPs exchange between media (air, water, soil, and biota). Further, high persistence of POPs in mobile environmental compartments allows them to be transported far away from their emission locations. As a consequence, POP models include multiple compartments and are typically designed for large (regional or global) spatial scales.

In construction of POP models, two different approaches can be distinguished. The first, based on multimedia partitioning, is generally used in multimedia box or mass balance models. Models of this type include relatively few interconnected “boxes” and assume homogeneous distribution of concentrations within each box. Such models are characterized by low complexity, require relatively small computational resources, and are suitable for screening a large number of substances. This is important since, at present, there are thousands of potentially dangerous industrial substances that require preliminary evaluation. For example, Annex VI to EC Regulation 1272/2008 contains approximately 2900 entries. A typical example of such a model is OECD Pov and LRTP Screening Tool [http://www.sust-chem.ethz.ch/docs/Tool2_0_Manual.pdf]. This approach has been extended to the development of spatially resolved mass balance models to address the strong temperature dependence of POP inter-media exchange coefficients and degradation rates, environmental conditions and their spatial and temporal variations. Examples include BETR-Global and G-CIEMS [MacLeod et al., 2005; Suzuki et al., 2004].

A more detailed description of spatial and temporal variability of POPs contamination can be achieved using chemical transport models (CTMs). According to Seinfeld and Pandis [2006], models of this type can be classified as either as Eulerian (fixed grid that the contaminant passes through) or Lagrangian (contaminant parcel is followed along its route). Lagrangian models [including trajectory models, Cohen et al., 2002; Eckhardt et al., 2007; van Jaarsveld et al., 1997] describe atmospheric transport by calculating the transformation of a parcel of a chemical over time during its movement in the atmosphere. These models can be run both forward and backward in time. However, such models do not presently cover surface exchange and, hence, do not take into account secondary sources (e.g. re-emission to air from soils, oceans).

Atmospheric transport in Eulerian models is considered as fluxes between grid cells. Models of this type can include dynamic evaluation of the inter-media exchange with allowance for variability of types of underlying surface and meteorological conditions (the so-called multi-compartment chemical transport models – MCTMs). Typical examples of such models are MPI-MCTM [Lammel et al., 2001; Semeena and Lammel, 2003], CAN-POPs [Gong et al., 2003], MSCE-POP [Gusev et al., 2005b], and CanMETOP [Ma et al., 2003]. MCTMs are used to obtain a sufficiently detailed view of POP fate in the environment to evaluate contamination levels and source-receptor relationships as well as examine trends and projections of POP contamination. In particular, the MSCE-POP model is used as an operational tool for the evaluation of POP LRT under the LRTAP Convention. MCTMs are also useful in the negotiation process for inclusion of POP candidates under international legislations as they can provide information on the ability of substances to transport over long distances and their persistence in the environment.

Model intercomparison studies have been conducted to reveal similarities and distinctions in predictions made by different models, as presented in Section 4.4.

1.4.4. Impacts

POPs are known to have impacts on human health and ecosystems [AMAP, 2009b]. Several POPs have been shown to have endocrine disrupting effects interfering with the development of neural, immune and hormonal systems, especially during embryonic stages. Some POPs are known or suspected carcinogens. These effects can result from the long-term cumulative exposures to which people and other organisms in the environment are generally subjected. Additionally, the effects of acute exposures to POPs may result from occupational exposures or accidental releases. These effects are summarized in Chapter 5.
As detailed in Section 5.2, the physical and chemical properties of POPs often result in bioaccumulation in ecosystems. Depending on a substance’s solubility and partitioning behaviour, as captured by the $K_{oa}$ and $K_{ow}$ values, POPs accumulate particularly in species with relatively high body fat content. Given the importance of fat in polar ecosystems, POPs can play an especially important role in the Arctic.

Most human exposure to POPs occurs through the diet. Ingestion of POPs occurs largely through meat and through breast milk. Exposure to POPs both in utero and via breast milk can impact fetal or infant development. Additionally, because game and high-fat animals comprise a large fraction of the traditional Arctic diet, human exposure to POPs in the Arctic is high, even with relatively few local sources of POPs.

A variety of impacts on health and ecosystems have been attributed to POPs, including developmental and reproductive effects, cancers, and thinning of bird eggshells. These impacts are detailed in Chapter 5.

1.4.5. Monitoring-modelling assessment

The assessment of POP environmental pollution generally includes the analysis of contamination patterns (e.g. changes in time or space), information on emission sources (local, regional, and global) and their contributions to the pollution levels, and predictions of future levels of concentrations and deposition. Traditionally applied approaches to the evaluation of pollution are based on monitoring of concentration levels and/or application of models to evaluate chemical dispersion based on available emission inventories. In the case of POPs, environmental monitoring is expensive and there is a need to more closely link and integrate measurement campaigns and modelling efforts in order to achieve optimum benefit from the information that can be made available.

Assessment of environmental contamination by POPs is a challenging task due to the variability of physical and chemical properties and the complexity of fate processes in the environment. Particularly, the distribution of POPs in the environment is governed by a large set of interrelated physical and chemical processes occurring in the atmosphere, soil, seawater, vegetation, etc. Thus monitoring of POPs concentrations in one or several compartments may not provide sufficient information on which to base appropriate political decisions. Additionally, the occurrence and quantities of POPs in various environmental compartments is not only determined by current levels of emission but also by historical loadings that have accumulated in environmental media and the ability of these chemicals to cycle between compartments and be redistributed. Hence the development of emission inventories requires the use of models that account for primary and secondary emissions.

Figure 1.2 is a schematic representation of an integrated monitoring-modelling approach to the assessment of pollution by POPs. At the first stage, adjustment of all three components of the assessment process (monitoring, modelling and emission inventories) is performed on the basis of the analysis of agreement between measurement data and modelling results. This is an iterative process that may require re-evaluation of one or more of the components to achieve agreement. This integrated process will lead to better understanding of POP fate in the environment and to reduction of overall uncertainty in the assessment of POP environmental contamination. At the second stage (final assessment), adjusted models, emission, and monitoring data are used for the assessment of contamination levels, source-receptor relationships, etc.

It should be stressed that modelling results may also be used in a proactive way to improve strategies of monitoring networks depending on their objectives and inform the development of new monitoring networks.
Figure 1.2. General scheme of an integrated approach to POP contamination assessment (feedback loops are shown in green).

All of this relates very well to the objectives of the EE of the SC on POPs and the existing and new monitoring activities that contribute to its Global Monitoring Plan (GMP). The integrated approach presented above will also inform the process that tries to assess how the environment responds (i.e. levels and trends of POPs in core media) to restrictions and bans on the use of POPs. Under EMEP, the integrated approach to the assessment of environmental contamination by POPs is currently being implemented. This topic is dealt with further in Section 4.5.

1.5. Interactions between climate and POPs

Climate variability and climate change operate on every aspect of a POP’s lifetime in the environment. Although the environment offers a lot of complexity in POPs pathways (Figure 1.3), there are large-scale processes at play that allow us to project at least qualitatively how climate change might alter POPs behaviour [AMAP, 2009a]. We also have sufficient knowledge of the chemical properties of many POPs [e.g., Mackay et al., 2006] to model the effects of altered partitioning between phases and thus evaluate how; for example, air-sea exchange of a given chemical would be affected by global warming [e.g., Mckone et al., 1996]. The sophistication and skill of general circulation models have been steadily improving, and ensembles of results from these and validation data sets provide ever increasing confidence in the projections of climate change, globally and regionally [IPCC, 2007]. However, because our concern about POPs is directed mostly toward the risks they present to ecosystems and humans, climate change continues to present a very complex challenge.

To get a sense of how climate change might interact with POPs in the environment requires an understanding of three relatively simple concepts. First, we may consider the globe as a set of reservoirs (air, water, soil, vegetation, snow and ice) connected by a set of exchange or transport pathways among these reservoirs [Figure 1.3, MacDonald et al., 2000]. Fortunately, some of the reservoirs may spell the end of the POP insofar as the biosphere is concerned (e.g., degradation or burial). POPs emissions go directly into air and directly or indirectly into water, which sets them into motion.
Over time, POPs distribute themselves globally, rapidly through the air and more slowly through water. With continued emissions, POPs accumulate in various global reservoirs according to where they were released, the environmental processes along the transport pathways (rainfall, exchange), and the properties of the POPs themselves (volatility, persistence, air-water partitioning, etc.). While some persistent contaminants favour air (CFCs), some favour water (HCHs), and some favour soils and vegetation (PCBs, PBDEs), they all distribute to some degree between environmental reservoirs depending on their partition coefficients. In the case of the major legacy POPs, we have released kilotonne to megatonne quantities \cite{Li and Macdonald, 2005}, much of which now resides in the soil, water and vegetation reservoirs. When we control POPs emissions, these reservoirs, which have been increasing in significance as secondary sources to the atmosphere as they become loaded, become dominant sources, which are easily manipulated by change in environmental parameters like temperature, moisture, and winds. Referring to Figure 1.3, climate change has the capacity to alter the fugacity (escaping tendency) of POPs in the reservoirs (boxes), the intensity and directions of transport pathways in the fluids (arrows), and the stability of the POPs themselves (degradation, burial). Furthermore, if we examine Figure 1.3 carefully, we can see how the reservoir sizes themselves can be changed in manners significant to contaminant storage. For example, the snow and ice reservoir has archived contaminants deposited in the 1950s-60s, when DDT, PCBs and other POPs were in high use. Now, under accelerated melting \cite[e.g.,][]{Barnett et al., 2005}, the world’s glaciers are releasing these stored contaminants into rivers, lakes and coastal waters \cite{Blais et al., 2001; Gieisz et al., 2008; Macdonald et al., 2005}. Another example of reservoir destruction occurs during forest fires, which are projected to increase with climate warming. Forests store contaminants \cite[Wania and McLachlan, 2001]. Forest fires can be of regional significance \cite[e.g.][]{Stohl et al., 2006} and when the organic carbon is destroyed, it releases measurable quantities of the archived POPs \cite[Eckhardt et al., 2007]. Within the cryosphere, the ice reservoir also acts a barrier to transport, locking up deep soil in permafrost, or capping oceans, lakes and rivers. Climate change, which has been dramatically altering the cryosphere \cite[e.g.,][]{Macdonald et al., 2005; Smol and Douglas, 2007; Stroeve et al., 2008}, has also impacted air-water exchange, with consequences to POPs distributions as will be exemplified for HCH below.
Second, climate change, especially rapid climate change, emerges from feedbacks in the environment [Shindell, 2007]. These feedbacks come from three important sources: the hydrological cycle (the distillation and precipitation of water); the cryosphere (the phase shift between solid and liquid water); and the organic carbon system (primary production by plants through to top predators). Water is an especially important medium with respect to POPs exposure in aquatic foodwebs [e.g., Borgå et al., 2002; Fisk et al., 2001]. POPs processes are strongly affected by whether water is solid, liquid or vapour [e.g., Chernyak et al., 1996; Wania and Halsall, 2003]. POPs associate strongly with organic carbon [Gobas and MacLean, 2003; Macdonald et al., 2005]. Large changes in POPs distributions (surprises) are, therefore, likely to emerge in association with these three feedback systems.

Third, the environment contains powerful POPs magnifying processes [Macdonald et al., 2002; Macdonald et al., 2005]. Were this not the case, after emission POPs would gradually mix into air and water away from sources until they were rendered ‘safe’ by dilution. The strong concentrating processes, which are essential for these compounds to present the risks they do to biota including humans, are sensitive to climate change. Concentrating processes can be divided into two distinct categories each of which is differently affected by climate change [Macdonald et al., 2002]. The first category includes all partitioning phenomena that lead to a thermodynamically forced redistribution of chemical (solvent switching), with HCH partitioning strongly into cold water being a particularly good example [Wania and Mackay, 1999]. These sorts of concentrating processes can be adjusted for the effects of temperature (e.g., change in phase, air-water exchange) and therefore climate scenarios and models can be constructed. The second category includes all phenomena that result in the concentration of a POP above its thermodynamic equilibrium [e.g., see Macdonald et al., 2003]. To concentrate above thermodynamic equilibrium requires energy and the best-known example is the aquatic foodweb which has the capacity to biomagnify POPs by transferring fat and fat-soluble chemicals up through trophic systems while metabolizing much of the fat during the process (Figure 1.3-bottom left). These ‘solvent-reducing’ processes are much harder to anticipate and model, but have great potential to be impacted by climate change.

Among many reasons why we should concern ourselves about the interaction of climate with POPs, there are four that stand out: 1) climate change may alter the desire or need to use POPs; 2) trends in POPs established by repetitively sampling any environmental compartment (air, water, biota, soil, vegetation) can be impacted by climate variables and thus these latter need to be considered before such trends can be interpreted in the context of emission controls; 3) exposure of populations and individuals within ecosystems can be altered by changes in any or all of the pathways leading to that population/individual and, 4) climate change can affect the vulnerability of populations to chemical exposure. The remainder of this section will be devoted to a more detailed discussion with examples of these important concepts.

**Climate change and POPs in Physical Systems**

Commencing with POPs emissions, the release of pesticides during application to crops or water directly reflects the intensity, urgency, and geographical distribution of a pest. Protocols on POPs emissions are the result of agreements made under an assumed set of conditions that implicitly incorporate past climate and pest behaviour. When climate changes (i.e., temperature or precipitation increase or decrease), the pest distribution or threat from the pest may also change. There are many examples where insects have become more aggressive or extended their range due to climate change (e.g., pine-bark beetles on the North American west coast and mosquitoes carrying malaria or west-Nile virus). When these changes threaten life or resources, an obvious response by an affected community may be to re-introduce banned pesticides. Immediate hazard usually trumps distant, poorly-quantified risk; thus, the urgent need to develop and make available alternative, effective and affordable approaches to pest control.

When a POP is released, it can be viewed as entering a global chromatographic system that has moving phases (air and water) and stationary phases (soil, vegetation, and ice) (Figure 1.3). Initially, the atmosphere provides a rapid transport route, but as environmental systems become loaded due to POP persistence, the soil and water components gain importance by accumulating an inventory of the chemical which can then transport in the water and/or re-enter the atmosphere by
exchange. The partition coefficients ($K_{oa}$, $K_{ow}$) dictate to a large degree how the contaminant will be distributed among media, and temperature cycles will alter the partitioning and vapour pressures to produce the impetus for multi-hops. As described by Macdonald et al. [2005], chemicals will be more or less prone to re-volatilization depending on how their inter-media distributions are affected by the temperature cycles. Warming generally favours the vapour phase and, thus, atmospheric transport. With global warming, semi-volatile chemicals will be more prone to move again after deposition, to associate less with particles, and to alter their seasonal transport patterns. Likewise, partitioning from air into water is a function of temperature. Chemicals like the HCHs, which partition strongly into water and whose partitioning is a strong function of temperature, will attempt to readjust their partitioning if warming occurs, generally with the chemical being forced back into the atmosphere.

Most POPs have undergone a transient emission, which includes a date of first use, a rapid rise toward maximum emission until an awareness of environmental problems leads to restricting or banning use, followed by a rapid decline in primary emissions. The atmosphere may respond to emissions reasonably quickly provided the residence time of POPs is low in the environment. The rise-peak-decline stages for classical contaminant use have tended to operate over several decades (1930 to 1980), such that the loading of environmental reservoirs never achieves a steady state. For POPs with long residence times, the response of a chemical to banning will depend on how much chemical the major environmental reservoirs (soil, oceans, vegetation) have accumulated during the transient rise period. Exchanges between these reservoirs will then dominate the POP cycle. In the case of PCBs, large Northern Hemisphere soil inventories have continued to supply the global chromatographic system such that lighter congeners re-distil more rapidly [e.g., Gallego et al., 2007], migrating northward [Muir et al., 1996], and atmospheric declines in PCB concentration tend to flatten out after initial rapid declines [Hung et al., 2010]. For HCH and DDT, atmospheric declines mean that the ocean has become oversaturated and is now re-supplying the atmosphere [Bidleman et al., 2007; Stemmler and Lammel, 2009]. In the case of HCH, the interaction between air-water exchange, ice cover in the Arctic Ocean, and timing in the transport of this chemical by atmosphere or ocean decide where and when the HCH will evade back to the atmosphere [Shen et al., 2004]. It is precisely at these points in the POP’s history that climate variability and change can operate so effectively on the transfer and transport cycles.

The atmosphere is a major pathway for LRT of a pollutant and the journey of POPs in the atmosphere is affected by many meteorological variables and conditions. Winds drive transport in the air, temperatures influence half-life, partition, reemission, and dry deposition processes, precipitation determines washout, clouds are potential sorbing and partition media, turbulence disperses and mixes POPs near the surface, and radiation causes photochemical degradation. Changes in meteorological conditions may change transport patterns of POPs. Their temporal variations are linked strongly with temporal trends of POPs from diurnal to decadal scales.

Long-range atmospheric transport patterns of POPs are complex due to rapid and often random changes in meteorology, but follow physical rules in atmospheric circulations and physical-chemical properties of chemicals. LRTP of POPs provides the simplest measure of the characteristic travel distance and ability of a chemical to migrate in the atmosphere away from its sources, driven by mean horizontal wind speeds and subject to physical-chemical properties (see 1.3.3). If LRT and transport pathways are to be assessed in a realistic atmosphere, more meteorological information has to be taken into account. Intercontinental atmospheric transport of POPs in the Northern Hemisphere is, on average, eastward and sporadic in mid-latitudes following dominant westerly winds. The eastward LRT of POPs changes with atmospheric elevations and time. Free atmosphere above the atmospheric boundary-layer (above 1000 m from a underlying surface) is a more efficient pathway where stronger winds can deliver POPs over a longer distance, and lower temperatures can lead to longer life-times of POPs in the air. Stronger westerly winds in the wintertime tend to result in stronger intercontinental atmospheric transport of POPs. However, for some of the POPs with major reservoirs in soils and other surface media, cold winter conditions suppress evaporation, thus reducing LRT. On the other hand, stronger volatilization through surface/air exchange in summer, together with weaker westerly winds may also not favour the LRT of POPs. Abundant monitoring and
modelling has shown that trans-Pacific atmospheric transport of POPs occurs optimally during spring and fall [Bailey et al., 2000; Zhang et al., 2008].

Excepting seasonal changes in the LRT associated with seasonality of winds and temperatures, interannual climate variability has been linked with atmospheric flows across the North Pacific Ocean [Ma and Li, 2006]. Anomalous climate warming in the tropical western Pacific leads to extended atmospheric anomalies, stronger westerly flows, and increased air temperature in Northeast Asia. These, in turn, enhance the re-emission of POPs from contaminated reservoirs in these regions and the frequency of episodic Asian pollution outflow and trans-Pacific transport of POPs.

Meridional LRT of POPs also occurs during favourable atmospheric circulation [e.g., MacLeod et al., 2005], subject to chemical-physical properties of individual chemicals. The arrival of POPs in pristine polar regions provides solid evidence of poleward atmospheric transport of POPs from their sources in lower and mid-latitudes. Several atmospheric transport mechanisms, such as Arctic cold trapping and the grasshopper effect, where seasonal temperature cycles cause the chemical to undergo one or more transport and deposition cycles (hops), have been proposed [Mackay and Wania, 1995]. Seasonality of poleward LRT differs among persistent toxic chemicals. Strong transport of PAHs into the Arctic has been observed in winter, in conjunction with the winter Siberia high pressure system causing the Arctic haze event together with higher emissions in Eurasia during this period. For banned POPs, higher air concentrations observed in the Arctic during spring and fall show more frequent LRT during these seasons when air masses from lower and higher latitudes exchange more often.

The statistics of LRT of POPs on seasonal, annual and longer time scales can be assessed based on the frequency and intensity of episodic LRT events occurring on daily and weekly timescales. Although these episodic events occur randomly, long-term statistics will exhibit a mean state, standard deviation, probabilities of extremes and other statistical properties characteristic of the climate on a variety of temporal and spatial scales beyond that of individual transport events. For example, northward episodic atmospheric transport routes of POPs from the southern United States to Canada have been shown to coincide with west-northwest approaching storm tracks from the United States [Ma et al., 2005]. These storm tracks are climatological wind flows that repeatedly occur with variation in position and strength, but exhibit stable means over a longer time scale. Relationships between interannual variability in POPs air concentration across the Great Lakes and Arctic, and robust climate indices like the North Atlantic Oscillation (NAO) and the El Niño-Southern Oscillation (ENSO), provide further evidence that atmospheric transport of POPs is affected by decadal climatic variability [Becker et al., 2008; Chiovarou and Siewicki, 2008; Ma et al., 2004a; Ma et al., 2004b; Macdonald et al., 2005; MacLeod et al., 2005]. Likewise, deposition from the atmosphere may reflect similar processes [Wang et al., 2010]. Knowledge of these characteristics may also inform atmospheric monitoring strategies. Knowing a major transport route for POPs may enable one to place monitoring sites at either the source or receptor regions along the route, making the field sampling more efficient and cost-effective [Yao et al., 2008].

Association between episodic LRT patterns and mean atmospheric flows provides insight into the influence of climate change on atmospheric transport of POPs. Climate change has the potential to affect all POPs pathways in atmosphere, hydrosphere, cryosphere, soilsphere, and biosphere [Macdonald et al., 2005; Noyes et al., 2009]. Mean air and surface ocean temperature are projected to rise, precipitation patterns are projected to change, and more frequent extreme events (heat waves, storms, floods) are projected to occur under global warming [IPCC, 2007]. These sorts of global change will affect the fate of POPs during transport, both by altered wind and washout patterns and by altered partitioning of chemicals between vapour, particulate and aqueous phases. Although it is difficult to detect climate signals in short and sparse monitoring records characteristic of most POPs data, some field campaigns have found signatures in atmospheric temporal trends that appear to be forced by climate change [Gao et al., 2010].

Figure 1.4 shows de-trended atmospheric concentration of α-HCH averaged over springtime and three monitoring sites on the shores of Lakes Superior, Michigan, and Erie. After removing the linear trend of α-HCH determined from time series, which is driven largely by the half-life of HCH in air, the residual time series of α-HCH exhibits an increasing trend. Given that the increasing trend in
the inter-decadal component of the NAO has been linked to global warming [Hoerling et al., 2001],
the correlation between de-trended α-HCH and inter-decadal variation of the NAO (r = 0.75) suggests
a connection between the air concentration of this chemical and climate warming.

![Figure 1.4](image_url)

**Figure 1.4.** Time series of detrended spring mean α-HCH concentration in the atmosphere,
averaged over the three IADN sites, and mean spring NAO index. Dashed lines indicate fourth-order polynomial fit of detrended spring mean α-HCH and NAO index.

Long time series measurements of POPs in air from the Great Lakes and the Arctic suggest a
high likelihood of a “climate driven residence time” that significantly increases the atmospheric half-
life of POPs. For example, weekly measured atmospheric concentrations of α-HCH from 1993
through 2008 imply an atmospheric half-life of ~8.1 yr. Before 2000, the estimated half life was ~5
yr, and from 2000-2008 it was 19.3 yr. Presently, the best explanation for the change in half life is the
org/column/rapid_ice_melt.html], which has essentially provided an enhanced source of HCH to the
atmosphere from previously deposited HCH, stored in the upper Arctic Ocean waters.

The effect of climate can be seen as an imprint, for example, of the NAO in atmospheric
trends of HCH [Ma et al., 2004a; Ma et al., 2004b; Ma and Li, 2006] produced by either altered wind
patterns or soil temperatures. Over the longer term, change in average and extreme temperatures or
precipitation likewise have roles to play. For the soil and vegetation reservoirs, change in the storage
capacity can be affected by the frequency of biomass fire [e.g., Eckhardt et al., 2007], which itself is a
manifestation of climate change.

Higher frequency of extreme events, a confident projection of climate models [Smith et al.,
2009], may also become an important factor in POPs cycles locally and possibly regionally. Desiccation,
desertification and dust storms may carry pesticide contaminated soils over long distances and into
sensitive waterways [Garrison et al., 2006]. Likewise, hurricanes and extreme rainfall events lead to
inundation and rapid erosion, both of which can set contaminants moving either through contaminated
soils or through poorly stored POPs produced decades ago [e.g., Adams et al., 2007].

**Climate change and POPs in organic systems**

There are many possibilities for change in organic systems that have consequences for POPs
pathways and exposure to biota. This arises because so many of the POPs are fat soluble and partition
strongly into organic-carbon rich substances, or absorb onto carbon-rich particles. The crucial
behaviour of organic carbon in the context of change is that it provides a transient solvent (reservoir)
that can be produced through primary production and destroyed through metabolism. POPs associated
with organic carbon can, therefore, undergo large change in their fugacities [Macdonald et al., 2002],
and they can be concentrated into organisms to levels that elicit toxic responses. The metabolism can occur within soils or within living organisms. The problem we face with these processes is that it is difficult to anticipate changes in processes that elevate POPs fugacities beyond thermodynamic equilibrium. The most notorious example is aquatic foodwebs wherein top predators can exhibit concentration increases of $10^7$ to $10^9$ above that of the ambient water [Muir and Norstrom, 1994]. But there are many other examples as well including metabolism or production of organic carbon in water or soils and the phase switch between ice and water.

Alteration to foodwebs provides what are probably the most significant changes in POPs pathways. Given that POPs increase with trophic level, the number of trophic levels in any foodweb will be of great significance, and any process that affects this will have consequences for top predators. In the Arctic Ocean, we can see opportunities to alter foodwebs from the bottom up by changing upwelling and wind mixing through the removal of ice [e.g., Lavoie et al., 2009], and from the top down, by removing ice as a habitat. Clearly, the demise of polar bears due to the loss of multiyear ice, or the displacement of walrus due to loss of ice in shallow water, or the increase in ringed seals due to greater areas of first-year ice and loss of polar bears, would signal many changes in trophic systematics for the Arctic Ocean [see for example Post et al., 2009]. Perhaps the most difficult change to project, and yet the one most likely to occur, is the invasion of new species [Vermeij and Roopnarine, 2008] that then displace resident species, or the loss of resident species through change in ice climate or ocean acidification [e.g., see Bates et al., 2009]. The potential for altered exposure to POPs inherent in these changes has been discussed [Macdonald et al., 2005], but needs urgently to be placed on a better quantitative basis through modelling.

POPs exposure can also be greatly affected by switching between foodwebs, for example ice and pelagic [McKinney et al., 2009], coastal and interior ocean [Loseto et al., 2008], aquatic and terrestrial [Figure RWM1, Macdonald et al., 2005]. These last two foodwebs have very different contaminant systematics that would lead to different doses to predators [Macdonald et al., 2005; van Oostdam et al., 1999]. Access to food and food security play large roles here; traditional food can become unavailable because the resource is dwindling, because it has migrated elsewhere or because conditions of transport have changed such as to make catching the food difficult. All three circumstances are products of climate change that lead to altered diet. The loss of a food resource, for example the disconnect between polar bears and seals witnessed in Hudson Bay [Stirling and Parkinson, 2006], which itself is a product of change in ice climate, can cause animals to go through extreme starvation cycles. With the mobilization and loss of stored fat, comes exposure to POPs harboured in the fat. These animals receive a POPs dose at a time they can least afford it.

Finally, migratory animals have the capacity to transport and magnify contaminant exposure within their migration routes [Blais et al., 2007; Kruemmel et al., 2003; Michelutti et al., 2009]. The obvious examples include anadromous fish (salmon), whales, and birds. Although the contaminant transport potential inherent in these biovectors is usually a lot smaller than contaminants carried by the atmosphere or ocean, these contaminants are clearly focussed within life cycles and impinge on sensitive areas like nursery ponds or lakes. Climate change affects migrations and populations.

Given our concern about POPs has to do with the risks they present to ecosystems and humans, we need to ask how POPs toxicity emerges in the environment. LRT of POPs will not generally be found to cause outright toxicity. To produce an effect, POPs need to engage in a conspiracy with the environment that involves concentration of the POPs above toxic thresholds (e.g., reproduction, immune function) and multiple stressors (e.g., starvation, disease, temperature) that place the population or individual in a state of vulnerability [Couillard et al., 2008]. These set of circumstances, which are highly affected by climate variability and change, make it difficult to identify confidently where a contaminant has had a telling effect on a population. Perhaps the morbillivirus epidemic that decimated seals along the European coast in the late 1980s provides one clear example [Heide-Jorgensen et al., 1992]. The important conclusion, however, is that when populations face multiple stressors like POPs exposure and manifestations of climate change (temperature rise, invasive species, diseases, extreme events, etc.), room to survive can be created by reducing the components of stress that can be controlled – like POPs emissions [Johannessen and Macdonald, 2009].
1.6. Findings and Recommendations

FINDING: Past research on POPs highlighted their inherent properties that make them a threat to human health and the environment. This has driven international policy and regulation of POPs under frameworks such as the UN-ECE CLRTAP and the Stockholm Convention on POPs. These Conventions have identified the need to better understand the fate and transport of POPs – their source-receptor relationships, temporal and spatial trends, and the response of the global system to the implementation of control measures.

RECOMMENDATION: It is an obligation and a priority to continue to improve our understanding of the fate and transport of POPs through continued efforts in monitoring and process research, modelling, and emissions estimation.

POPs present global-scale risks that require the Task Force to consider broadening its scope and membership to include regions outside of the UN-ECE.

FINDING: ‘New’ POPs continue to be identified through risk assessment activities and listed under international agreements. In many cases, these ‘new’ POPs behave differently compared to their ‘legacy’ counterparts.

RECOMMENDATION: There is a need to conduct process-research and adapt measurement and analytical techniques to target ‘new’ POPs. Transport models will need to be parameterized for these chemicals and new emission inventories developed.

There is also a need to continue screening efforts and investigatory research to identify new chemicals with POP-like characteristics for further consideration. Monitoring programs play a key role in addressing this need by identifying chemicals that are persistent and capable of LRT.

FINDING: To improve understanding of temporal and spatial trends and intercontinental transport of POPs, it is essential to adopt an integrated approach that assimilates information from observations, model outputs and emission estimates. This is an iterative process.

RECOMMENDATION: An integrated approach to POPs assessment requires cooperation and congregation of experts from different backgrounds. The Task Force on the HTAP should continue to move in this direction and promote collaboration between these groups of experts and related programs.

Information on climate effects on POPs is increasingly recognized as a key consideration and should also be integrated into the assessment framework/process.

FINDING: Climate may directly and indirectly affect the fate and transport of POPs. These changes occur in the physical and organic environments. Climate-related changes may also result in altered exposure pathways and increased vulnerability for the biotic environment and related health impacts. Extreme events, which are projected to increase as a manifestation of future climate change, will become more important and present challenges for modelers. The direction and magnitude of these climate-induced changes are difficult to assess and quantify.

RECOMMENDATION: Climate interactions on POPs and the connection between climate and variable meteorology should be considered in the collection and interpretation of data sets to assess spatial and temporal trends for POPs and source-receptor relationships. Further investigations are needed: 1) modelling future global and regional POPs distributions using projected climate change scenarios [e.g., see Lamon et al., 2009], 2) modelling to understand and quantify climate-induced perturbations of POPs between multi-compartment environments, and 3) modelling the impact of increased climate events on POPs environmental fate.
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Chapter 2
Observations and Capabilities

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2.1. Introduction

This chapter summarizes recent observations and measurements of POPs in various environmental media from which a better understanding of POPs transport on a regional, intercontinental or global scale can be derived. As explained in Chapter 1, POPs and POP-like chemicals are a unique group of pollutants that may be transported via the atmosphere or the ocean and has the ability to partition to and from various environmental media, degrade and transform along the transport pathway. Due to this complexity, an understanding of both primary and secondary emissions, as well as POPs degradation and transformation processes, is essential to interpret observed transport episodes, temporal and spatial trends. In this chapter, we have also summarized currently-available measurement techniques that may provide different types of long-range transport information and analytical techniques used to identify the historical signature and potential sources of POPs. While Chapter 3 provides detail information on the modelling aspects of POPs, specific transport and process models have also been derived and used to explain and elucidate various observed concentrations, trends and transport processes. Readers are referred to Appendix B for summaries of these studies where applicable.

2.2. Atmospheric Observations

2.2.1. Atmospheric Monitoring Activities

National and international atmospheric monitoring programs implemented in various countries over the last two decades have provided spatial and temporal trend information on POPs. In addition, various new monitoring programs were established to fill the data gaps identified in the First Global Monitoring Report of the SC-GMP. Activities of these monitoring programs operating in the northern hemisphere are summarized in Table A.2.1 in Appendix A. This table provides an update of similar information given in the First Global Monitoring Report of SC-GMP. Figure 2.1 shows the distribution of sampling stations operated by these programs. Detailed descriptions of these programs are given in Appendix C. The SC-GMP First Global Monitoring Report has pointed out the importance of sustaining long-term monitoring efforts to produce data for the investigation of temporal trends in subsequent effectiveness evaluations.

Other than the organized atmospheric monitoring programs, there exist many independent research initiatives studying long-range transport of POPs and POP-like chemicals. Some examples of these studies are summarized in Table A.2.2 in Appendix A with the relevant references. These studies provide important case- and location-specific information on organic pollutant transport in the assessment of regional and cross-region transport by air. The SC-GMP First Global Monitoring Report has concluded that, “Future evaluations of changes in POPs levels over time should include information on regional and global environmental transport and a coordinated cross-regional approach to analysis and assessment of data to meet that objective should be established” [UNEP, 2009].
2.2.2. Atmospheric Monitoring Techniques

There are two main types of currently-employed atmospheric monitoring techniques: conventional active (pumped) and passive air sampling techniques. While a source of power and constant maintenance is essential for operating the former, the latter are of relatively low cost, low maintenance, easy to operate and do not require a power supply. Data generated with the active techniques are considered quantitative while the passive techniques are mostly semi-quantitative. The active techniques can provide POP concentrations in both gas and particle phases, POP concentrations estimated with the passive techniques are mainly gas phase. On the other hand, the employment of passive air sampling devices (PASDs) allow greater spatial coverage, providing much needed air concentration information where active air sampling is not possible. These two types of techniques provide different types of concentration and long-range transport information which are summarized in Table A.2.3 of Appendix A. The type of technique employed by the various air monitoring programs are given in Table A.2.1 of Appendix A and colour-coded on Figure 2.1.

In terms of interpreting air concentration results generated with different air sampling techniques by different air sampling programs, it was concluded by the SC-GMP that, “programmes had to remain consistent in their methods over time and thus ensure that the data collected within a programme remained comparable and suitable for assessing changes in levels over time…It was noted, however, that it would be extremely difficult to achieve comparability between the various programmes given the many sources of variability, including the use of several laboratories and differing sampling methods or analytical protocols. While comparability across programmes and regions would assist in a global assessment of trends, priority should be placed on internal comparability within a particular programme or region over time”. Data comparability and quality assurance issues will be further discussed in section 2.7.

2.2.3. Long-range Transport Observations

2.2.3.1. LRT assessments using atmospheric observations and modelling tools

Air mass back trajectories are frequently used to determine the source region of POPs. This simple modelling includes the overlay of air mass back trajectories onto satellite images of fire activities to interpret PAH (and other POP) emissions from forest fires [Genualdi et al., 2009a] and the calculation of source region impact factors to determine the relative contributions of different source regions [Primbs et al., 2007; Primbs et al., 2008a; Primbs et al., 2008b]. Integrated source contribution functions, based on backward air mass trajectories, have been recently used to predict the outflow of PAHs from China [Lang et al., 2008] and PAH transport to the Canadian High Arctic [Wang et al., 2010a]. A similar approach uses what are referred to as ‘airshed maps’ that can be generated for a collection of backward or forward air mass trajectories. These are increasingly applied to interpret results for time-integrated passive air samples [Gouin et al., 2007].
More complex atmospheric modelling of POPs includes understanding source regions to the Great Lakes, e.g. [Ma et al., 2005]. Ma and Li [2006] showed a connection between the concentration anomalies of several POPs in the Great Lakes with sea surface temperature anomalies in the tropical Pacific (an indicator of El Nino) through correlation analysis of observations.

A recent development in describing long-range transport is the remoteness index. This metric is based on global transport models simulations and emission scenarios for different chemical classes [Waldow et al., 2010]. It can be displayed graphically as a map and should prove valuable for assessing spatial and temporal trend data and for making informed selection of new air monitoring stations.

2.2.3.2. Arctic Region

As most legacy POPs were never used in the Arctic, their presence in the Arctic environment has been generally regarded as evidence of LRT. Atmospheric LRT events have been identified annually moving polluted air masses within a few days from source regions into the central Arctic region e.g. [Eckhardt et al., 2007]. Since the early 1990s, AMAP has established atmospheric monitoring stations for POPs in the Arctic (Table A.2.1 of Appendix A). Studying the long-term trends and seasonal cycles at different Arctic stations may reveal the influence of local and seasonal factors, such as geomorphology, ambient temperature, elevation, humidity, precipitation, proximity to open or ice covered ocean surface and distance to potential sources, on the air concentrations of POPs at each location. This will give us information on how best to interpret the results of long-term air monitoring programs in assessing the effectiveness of control strategies.

Reductions in global emissions of certain POPs may be reflected in their atmospheric levels in the Arctic. Li and Bidleman [2003] have observed rapid declines in Arctic air concentrations of α-hexachlorocyclohexane (α-HCH) in 1983 and 1990 as a result of usage controls in China and India/former Soviet Union, respectively (Figure 2.2). However, such declines may not be obvious for other chemicals since the transport of POPs to the Arctic is influenced by various local and seasonal factors as mentioned above, as well as the lifetime of the chemicals in different environmental matrices and re-emissions of previously deposited POPs in soil, vegetation and oceans. While some POPs showed more or less consistent declines during the 1990s in Arctic air, this reduction is less apparent in recent years at some sites [Hung et al., 2010]. As an example, Figure 2.3 shows the atmospheric trends of lindane measured at 4 Arctic stations. On the other hand, flame retardant polybrominated diphenyl ethers (PBDEs) were found to be increasing between 2002 and 2005 at Alert (Nunavut, Canada); especially deca-BDE, which is not regulated by either SC or the POP Protocol of CLRTAP, may double in air concentrations in approximately 3.5 years.

Levels and patterns of most POPs in Arctic air are also showing spatial variability, which is typically explained by differences in proximity to suspected key source regions and long-range atmospheric transport potentials. For instance, PCB air concentrations at Zeppelin and Storhofdi in the European Arctic have always been higher than those found at Alert. Also, the air concentrations at Alert were statistically significantly different from the other two stations between 1998 and 2005 [Hung et al., 2010]. The proportion of γ-HCH (i.e. 100*[γ/(γ + α)]) is generally lower at Zeppelin than at Alert, ranging from 13 to 26% at Zeppelin compared to 8 - 26% at Alert [Becker et al., 2008]. These observations indicate that Zeppelin and Storhofdi are more affected by European sources due to proximity while Alert is further away from this source.

The current-use pesticide, endosulfan I, has shown almost constant air concentrations at Alert, Nunavut, Canada, since 1993 with no apparent decline in trend. Su et al. [2008] have shown that endosulfan I had similar concentrations at 5 Arctic stations in November–May, whereas large spatial divergence was found in June–October. This observation indicates the extensive use of this pesticide in summer followed by long-range transport to the Arctic.
Figure 2.2. Rapid decline of arctic air concentrations of α-HCH (red bars) in response to global emission (black line). [Adapted from Figure 2 of Li, Y. F., and T. F. Bidleman (2003), Correlation between global emissions of alpha-hexachlorocyclohexane and its concentrations in the arctic air, *Journal of Environmental Informatics*, 1(1): 52-57.]

Through the comparison of temporal trends, it was observed that atmospheric PCBs and HCB have shown increasing trends at Zeppelin in recent years (2003-2006). A similar increasing trend of HCB was also observed at Alert after 2002. This increase may be the result of a combination of the following two factors: (1) increase in worldwide use of HCB-contaminants pesticides, e.g. chlorothalonil and quintozene (pentachloronitrobenzene), followed by subsequent transport to the Arctic. Chlorothalonil has been identified in arctic air and ocean surface water [Jantunen et al., 2009], and arctic-subarctic lakes in Canada [Muir et al., 2004]. The fungicide has an estimated characteristic travel distance (CTD) of over 2000 km [Matthies et al., 2009]; (2) reduction in sea ice cover on the west coast of Spitsbergen (Svalbard, Norway), which has been ice-free in the past 4 years including winter (2005-2008), where Zeppelin is located, potentially resulted in increased volatilization of previously deposited chemicals from the ocean. Although dramatic decrease in sea ice was also observed in other parts of the Arctic, a permanently ice-free state at 80° N is fairly unique. This signature could be interpreted as a possible influence of regional climate change on POPs distribution in the Arctic environment. On the other hand, recent studies have predicted both net deposition of HCB into [Lohmann et al., 2006; Su et al., 2006] and near-equilibrium or volatilization [Hargrave et al., 1997] from the Arctic Ocean. Gioia et al. [2008a] has suggested greater atmospheric deposition of PCBs along the melting ice margin due to increased air concentrations. However, it was also noted that changes in air and ocean current flow over time can potentially increase or decrease the relative capacity in the two media, subsequently reversing the direction of chemical flux from the air to the ocean and vice versa. Air-water exchange will be further discussed in Section 2.4.4.

Similar increasing trends were seen at Zeppelin for DDTs and penta- and hexa-chlorinated PCBs. However, the re-introductions of DDTs as an insecticide in tropical regions for malaria control purposes and transport from other primary sources (e.g. direct application in agriculture) in low latitudinal source regions may also contribute to the currently increasing levels in the North.
The marked increase of penta- and hexachloro-PCBs, which are semi-volatile with relatively low water solubility ($\log K_{OW} = 6.8$), cannot be solely explained by increased evaporation due to their relatively low volatility. A potential contribution from increased forest fire events from boreal regions and related Arctic haze events may be considered as important additional mechanism. Eckhardt et al. [2007] have attributed high air concentrations of PCBs measured at Zeppelin in July 2004 and spring 2006 to boreal forest fires in Yukon/Alaska and agricultural fires in Eastern Europe, respectively. Several high air concentration episodes of $cis$-chlordane, $p,p'$-DDE and $o,p'$-DDE were also observed at Alert and Zeppelin in 2004 during the forest fire events [Hung et al., 2010]. It is believed that biomass burning can enhance volatilization of previously deposited organic chemicals, such as PCBs, from soil. Trans-Pacific and regional atmospheric transport of biomass burning emissions resulting in elevated PAH, OCP and PCB concentrations observed in the U.S. Pacific Northwest was documented by Genualdi et al. [2009a] and Prims et al. [2008a; 2008b]. These studies will be discussed further in section 2.2.3.4.

Using backtrajectory analysis, Bailey et al. [2000] have found that high concentration episodes of OCPs, e.g. HCH, heptachlor, chlordane and DDT, measured at Tagish on the west side of the Canadian Arctic correspond to trans-Pacific transport from eastern Asia that generally occurred within 5 days. Intercontinental transport will be discussed in details in Section 2.2.3.4.

On a trans-Atlantic Cruise from Sweden to Alaska, Shoeib et al. [2006] measured and reported the first atmospheric concentrations of fluorotelomer alcohols (FTOHs) and perfluoroalkyl sulphonates (PFASs) across the Canadian Arctic Archipelago and North Atlantic region. These findings confirm model results by Wallington et al. [2006] that predict the efficient long-range...
atmospheric transport and widespread distribution of FTOHs and related compounds in the arctic region.

In a special study of atmospheric dioxins and furans at Alert during the winter of 2000/2001, Hung et al. [2002] have shown that the air concentrations of PCDD/Fs peaked at Alert when the airmass originated from Russia and Eurasia 5 days before. In spite of the remoteness of the site, congener profiles in most samples were enriched with PCDFs, corresponding to “source” profiles as suggested by Wagrowski and Hites [2000]. Similar profiles were observed in air and tree bark at other Arctic locations. These profiles were probably the result of: (1) more effective transport of PCDD/Fs to receptors in Nunavut from sources relatively close-by (Canada and the US) than from those further away (Mexico) [Commoner et al., 2000]; (2) a greater chance for less volatile congeners to deposit out of the atmosphere before they reach the Arctic; and (3) the generally low temperature in the Arctic, coupled with low levels of solar radiation during winter, curbs degradation/reaction processes. Therefore, the “source” and “sink” homologue profiles generally applicable to samples collected at temperate sites cannot be applied to those collected in the Arctic. Profiles of PCDD/Fs in southern and northern Baltic Sea sediments were related to source categories (e.g. atmospheric deposition, incineration, chlorophenol use, etc.) through positive matrix factorization [Sundqvist et al., 2010].

Polychlorinated naphthalenes (PCNs) have been measured in arctic air during several campaigns between 1993-2005 and from land and shipboard platforms [reviewed by Bidleman et al., 2010]. Air concentrations in the European Arctic (Svalbard, Bjørnøya, northern Norway and Sweden, and over the Arctic Ocean) were substantially higher than those measured at Alert and Tagish Canada; Barrow, Alaska; Iceland and Dunai, Russia. Concentrations were higher during the cold months in arctic Canada and Russia, but no seasonality was noted in subarctic Canada and Greenland. “Marker” congeners indicative of combustion were evident at some sites. Total toxic equivalents (TEQ) in air due to PCNs + dioxin-like PCBs were dominated by PCNs in arctic Canada and Russia, but not in subarctic Canada. Deposition of PCNs in snow was measured in northern Norway and Svalbard.

2.2.3.3. Alpine regions

The first indications that mountain ranges may act as sinks for POPs were reported in 1998. Deposition of organochlorine compounds in snow from western Canadian mountain ranges increased with altitude [Blais et al., 1998]. Soil and spruce needles sampled along a mountain slope on the Alps showed higher concentrations of almost all studied organic contaminants (OCPs, PCBs, PCDD/Fs, PAHs) at the highest elevation site [Weiss et al., 1998]. Since then, in fact within a relatively short time, much progress has been made in studying and understanding the fate and behaviour of POPs in alpine regions.

Mountains have some features that may enhance deposition and accumulation of POPs in their ecosystems. Temperature usually decreases with altitude (except during temperature inversions) which may result in cold condensation effects [Grimalt et al., 2001, “orographic cold trapping”]. Different from polar regions, the chemicals must travel only short distances to experience large temperature gradients and mountains are often much closer to emission sources. The amount of precipitation may change within a short distance due to the barrier effects of mountains: orographic precipitation frequently occurs on the windward side of mountains. The large-scale updraft of humid air across the mountain ridge results in adiabatic cooling and condensation. Mountains may dramatically alter geographical precipitation patterns towards a manyfold increase of precipitation in the peripheral mountain regions compared to the adjacent lowlands. With increasing altitude, precipitation may change from rain to snow which is supposed to be a more effective scavenger of many relevant organic contaminants which either have an adsorption coefficient at the snow surface $K_{\text{Snow-Air}} \geq 0.1 \text{ m}$ or a particle/air partition coefficient $K_{\text{Particle/Air}} \geq 10^{11}$ at temperatures below $0^\circ \text{ C}$ [Lei and Wania, 2004]. Turnover of organic matter in soil, a relevant POPs sink in terrestrial ecosystems, is influenced by temperature and precipitation and tends to slow down with cooler and/or wetter conditions. Biological activity and growth, affecting breakdown and dilution of contaminants, frequently decrease with the drop in temperature.

Unfortunately, the situation is even more complex. Deposition and accumulation of POPs in mountain areas may vary due to the following influences: distance to primary and secondary emission sources, properties of the chemicals, landscape characteristics and meteorological parameters, uptake,
accumulation, storage and dilution characteristics of the studied ecosystems, matrices or biota [Daly and Wania, 2005; Kirchner et al., 2009]. These parameters vary considerably among mountains in different regions of the world and even within a mountain range or slope (see Table 2.1) – the large number of different combinations of these parameters probably best explains why all the available studies do not give a uniform and general picture of transport and accumulation of POPs in mountains. Multi-media environmental models were developed to better understand the observed mountain cold-trapping effect. These studies are summarized in Appendix B.

**POPs food chain accumulation in mountains**

Studies that found significantly higher POP concentrations in fish of mountain lakes were among the first alerts of POPs in mountains. Donald et al. [1998] showed that fish from alpine and sub-alpine lakes had concentrations of toxaphene that were two orders of magnitude higher than those in fish from nearby lakes at lower altitudes, which indicated that there were processes acting to concentrate these SOCs at high altitudes. An enrichment of SOCs in *Gammarus lacustris* at high altitude lakes in Alberta, Canada, was detected and partly explained by lower growth rates (biodilution effects) as the primary influence on the altitudinal differences [Blais et al., 2003]. Significantly higher POP concentrations in aquatic organisms from higher altitudes and correlations with temperature or altitude were also reported for lakes in the Alps, Pyrenees and High Tatra [Bizzotto et al., 2009; Blais et al., 2006; Gallego et al., 2007; Grimalt et al., 2001; Vives et al., 2004]. Some of these studies raised concern about the toxicological implications of the detected concentrations for aquatic organisms or food chains. WACAP researchers recently found that the POP concentrations in some fish collected from the remote National Parks in the U.S. Rocky Mountains and Sierra Nevada Mountains exceeded USEPA’s contaminant health thresholds for subsistence fishing [Ackerman et al., 2008].

Despite these early indications for enhanced bioaccumulation in alpine aquatic organisms, no study on POP accumulation in terrestrial alpine food chains including predators is available. In addition, other than one study by [Shunthirasingham et al., 2009] on POPs in Swiss cow milk, there is generally a lack of studies on POP accumulation in grazing livestock or dairy produce from the mountains despite its agricultural importance.

**Glaciers as secondary POP sources**

Glaciers represent reservoirs for deposited pollutants, due to cold condensation effects also for POPs. However, the POPs bound in the ice masses may be released into the downstream aquatic ecosystems during times of glacial melt. Results indicate that contaminated ice is the dominant POP source for glacier-fed mountain lakes [Blais et al., 2001b]. The same group of researchers found that at least 10% of the glaciers melt discharging into a sub-alpine lake in Canada originated from precipitation during 1950–70 which was higher contaminated with organochlorines [Blais et al., 2001a]. Backed by this finding the authors warned that climate warming and enhanced glacial melt may increase the release of contaminants to freshwater.

Recently, evidence for this effect has been obtained. POPs and OCPs in a sediment-core of a glacier-fed lake suggest the release of such contaminants from glacial reservoirs due to accelerated glacier dwindling as a consequence of global warming in recent years. Inputs of all organochlorines increased in the 1950s, peaked in the 1960–70s, and decreased again to low levels in the 1980–90s, all in accordance with their emission history. However, since the late 1990s input of all compound classes into the high-alpine lake has increased sharply. Currently, input fluxes of organochlorines are similar to or even higher than those in the 1960s - 1970s. This recent peak led the researchers to hypothesize that there is a relevant recent release of persistent organic chemicals from melting glaciers [Bogdal et al., 2009].

In many regions of the world, mountains represent the reservoirs of drinking water. So, climate change induced glacier melting may also pose a risk for an enhanced release of organic contaminants to drinking water supplies in mountain regions.
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<th>Location/ Program</th>
<th>Brief description of Findings</th>
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<td>The Americas</td>
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<td>Sierra Nevada</td>
<td>In the early 1990’s, organophosphate pesticides in air and wet deposition observed in the Sierra Nevada Mountains were found to be originated from the uses in the Central Valley. Concentrations of current use pesticides in air, dry deposition and surface water samples were highest in the Central Valley during summertime and dropped significantly up to a few hundred meters above the valley. However, levels remained relatively constant between 500 and 2000 m.</td>
<td>[LeNoir et al., 1999; McConnell et al., 1998; Zabik and Seiber, 1993]</td>
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<td>Western U.S. National Parks/ The Western Airborne Contaminants Assessment Project (WACAP)</td>
<td>By measuring POPs in annual snowpack, PASDs, lichens and conifer needles across 20 parks (29 °N to 68 °N) and in elevation from 1 m to 3400 m, it was possible to differentiate POPs from current or historical North American sources and those from long-range sources. Correlations with latitude, temperature, elevation, particulate matter, and two indicators of regional pesticide use revealed that regional current and historical agricultural practices are largely responsible for pesticide distributions in snowpacks in the lower states national parks of Western U.S.; whereas pesticide depositions in the Alaskan parks were attributed to long-range transport. At lower latitudes, the contribution of regional transport to pesticide levels (% RT) was highest in parks with higher regional cropland density and for pesticides with lower vapour pressure and shorter atmospheric half-lives. The presence of historic-use pesticides in snow in the national parks indicates that they still undergo atmospheric transport and deposition to remote ecosystems despite their bans in the U.S. several decades ago.</td>
<td>[Hageman et al., 2006; Landers et al., 2010]</td>
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<td>Western Canadian Mountains</td>
<td>The needle concentrations of more volatile OCPs (P&lt;sub&gt;025&lt;/sub&gt; &gt; 0.1 Pa at 25 °C) increased at higher altitudes whereas the less volatile OCPs were either unrelated or inversely correlated with altitude. Despite being relatively volatile, γ-HCH showed an inverse relationship with elevation; probably related to applications at low altitudes. Back trajectories and congener compositions in needles indicated an impact of transcontinental transport. Shen et al. (2004; 2005) observed significant increases of annual mean air concentrations of α-HCH, γ-HCH, PeCB, HCB and α-endosulfan with altitude in the Canadian Rocky Mountains, whereas Davidson et al. (2004) concluded that summertime SOC air concentrations were not correlated with altitude in the same region. Contrasting gradients between air and soil were observed for PAHs and OCPs at the same elevation transects in the Canadian Rockies, reflecting the complex underlying mechanisms of alpine contamination. Measurements along several altitudinal gradients revealed an influence of nearby roads on the air and soil PAH concentrations. The OCP concentrations in air determined with PASDs were fairly uniform along and between the mountain transects; indicating efficient local and regional atmospheric mixing and a similar atmospheric exposure of mountain ecosystems to those contaminants. However, soil concentrations along the gradients and between the transects varied considerably and often with statistical significance. Such variability was partly explained by the different storage capacity of soils determined by organic carbon content and partly related to atmospheric scavenging, which for many OCPs becomes more efficient when precipitation increases and temperature drops with altitude.</td>
<td>[Choi et al., 2009; Daly et al., 2007c; Davidson et al., 2003; Davidson et al., 2004; Shen et al., 2004; Shen and Wania, 2005]</td>
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Table 2.1. *cont’d* Observations in Alpine Regions (segregated according to regions)

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<th>Location/ Program</th>
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<td>Costa Rica, Central America</td>
<td>Distributions of past and current use pesticides in air and soil at different altitudes and regions of Costa Rica were studied. Soils in some mountain forests displayed much higher concentrations of current use pesticides than soils elsewhere in the country and located closer to the application. While atmospheric endosulfan decreased with source distance, soil concentrations peaked at more remote sites of higher elevation. High pesticide concentrations in high altitude soils were attributed to atmospheric transport from pesticide application sites, efficient deposition by orographic rain and fog, and strong retention in cool soils rich in organic matter and covered by dense vegetation. A mountain region fate model, parameterized for the Costa Rican environment, supported the hypothesis that enhanced precipitation scavenging at high elevations (as a result of lower temperatures and governed by $K_{aw}$) caused pesticides to accumulate in tropical mountain areas.</td>
<td>[Daly et al., 2007b]</td>
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<td>The Andes, South America</td>
<td>An inverse correlation between temperature and SOC content (PCBs, HCB, HCHs, DDTs) of mosses from the Chikan Andes has been found which was independent of the compounds’ origin (e.g. industrial, agricultural or mixed). The sites at higher elevation showed higher contaminations. Concentrations at these very remote sites are among the lowest ever reported. Also, soil samples taken in the Peruvian Andes were characterized by relatively low POP levels (PCBs, DDTs, HCHs, HCB, chlordane). PUF disk passive air samplers deployed seasonally and along an altitudinal gradient in the Bolivian Andes up to 5200 masl showed significant enrichment of HCH and endosulfans at the high elevation sites. This enrichment was attributed to advection from distant source regions which occurred more efficiently at the higher elevation sites.</td>
<td>[Estellano et al., 2008; Grimalt et al., 2004; Tremolada et al., 2008]</td>
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<td>Asia</td>
<td>Less volatile OCPs (DDT and DDD) were inversely related with elevation which may be caused by pesticide applications close to the lower sites. Along a steep altitudinal transect from the highly populated and intensely cultivated Chengdu Plain (China) to the Tibet-Qinghai Plateau, soil concentrations of all studied compounds (HCH, HCB, DDT, PCB) increased significantly and exponentially with altitude. Air concentrations at the same sites did not vary with altitude and were assumed to be highly influenced by atmospheric transport from sources in the Chengdu Plain. From OCP levels in the atmosphere, freshly fallen snow and ice cores taken in the Tibetan Mt. Everest region, Li et al. [2006] and Wang et al. [2007] attributed the Indian subcontinent (monsoons) as the most important source for HCH and DDT detected in that region.</td>
<td>[Chen et al., 2008; Li et al., 2006; Liu et al., 2010; Loewen et al., 2005; Wang et al., 2006]</td>
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<td>Europe</td>
<td>Air measurements showed higher concentrations of current use OCPs (HCHs, endosulfans) during times of applications in the warm season. However, PCB and $p,p’$-DDE without present use showed a similar seasonal trend which was explained by a higher impact of air masses with strong continental inputs in the warm than in the cold periods. Samples whose air masses travelled in the high troposphere (backward air mass trajectories &gt; 6000 m) were observed to carry considerably smaller PCB and $p,p’$-DDE loads. The presence of the SOCs in the atmosphere of these high altitude sites was assumed to originate from long-range atmospheric transport, but from sources located on the European continent.</td>
<td>[Van Drooge et al., 2004]</td>
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<td>Central Pyrenees and High Tatra</td>
<td>Atmospheric SOCs (PCBs, HCHs, HCB, DDTs) above the stable inversion layer (in the free troposphere) showed rather uniform and very low concentrations throughout one year of measurements, independent of the origin of the air masses (high and mid latitudes in the north Atlantic, Western Europe and Western Africa). A close correlation between SOC concentrations and soil total organic carbon (TOC) content was found, with TOC values being higher within the inversion layer’s range. Temperature was correlated with TOC-normalized SOC concentrations.</td>
<td>[Ribeis et al., 2002; Van Drooge et al., 2002]</td>
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Table 2.1. *cont’d* Observations in Alpine Regions (segregated according to regions)

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<td>The Alps/ MONARPOP (Appendix A Table A.2.1 and Appendix C) and other studies</td>
<td>Preferential retention of POPs on the northern (cooler) aspect of the Italian Alps was observed, with approximately doubled the POP soil concentrations on the northern compared to the southern side of one mountain. Seasonal changes of soil concentrations were observed, with lower summertime concentrations. An increase of soil SOC concentrations along an altitudinal gradient was ascribed to the precipitation increase with elevation. Relatively high DDT contents in these samples were related to a nearby source. The amounts of PCBs collected with PUF samplers decreased with altitude while HCB increased with altitude. Also, needle HCB concentrations increased significantly with altitude, in contrast to HCH and PCB levels. Higher ( \alpha/\gamma )-HCH ratios in needles at higher altitudes were taken as an indicator for only weak local influence on HCH concentrations. Similar relations between needle ( \alpha/\gamma )-HCH ratio and source distance were reported for the Austrian Alps [Weiss et al., 2000] and for the Canadian Rocky Mountains [Davidson et al., 2003].</td>
<td>Belis et al., 2007; Belis et al., 2009; Iozza et al., 2009; Jaward et al., 2005a; Kirchner et al., 2009; Knuth et al., 2008; Lammel et al., 2009; Levy et al., 2009; Nizzetto et al., 2006; Offenthaler et al., 2008; Offenthaler et al., 2009a; Offenthaler et al., 2009b; Tremolada et al., 2008; Tremolada et al., 2009</td>
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<td>At the summit of Mt. Zugspitze in the Northern Alps air was sampled during periods of reduced influence from the boundary layer. The study indicated a transport of OCPs, PCBs and PAHs in the free troposphere of Europe. The detected air concentrations were among the lowest ever reported for mid latitudes or tropics. They were clearly lower than those detected at the same site in continuously sampled air under MONARPOP, suggesting the additional influence of boundary layer POP loads on the atmospheric POP exposure of this summit.</td>
<td>Industrial chemicals like chlorinated paraffins were detected at remote sites in similar concentration ranges as unintentionally emitted or &quot;backyard&quot; SOCs like PAHs. Concentrations of almost all studied SOC's were significantly higher in the exposed lateral zones of the Alps than in the shielded central parts. The location of the lateral parts with higher concentrations is compound- and matrix-specific. For some compounds like PCDD/F, sites with higher soil concentrations were located in areas of higher precipitation, while other compounds (e.g. single PBDEs) showed no correlation with precipitation and are likely the result of different emission gradients in the neighbouring regions. Even for the former compounds, an assumption of a causal relationship between pollutant load and precipitation may be only part of an explanation since peripheral regions of the Alps are also those located closer to the more densely populated and more productive areas with higher emissions. Anyhow, the findings clearly indicate a barrier effect of mountain ranges for atmospheric POPs transport and that the bulk pollution originates outside the Alps. A comparison between POPs bound in the forests of the Alps and their emissions in this region further supported this assumption and suggested that the Alps represent a net sink for such compounds.</td>
<td>[42]</td>
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<td>Marked altitudinal increases of the soil concentrations of OCPs (including those with suspected faraway sources like mirex) have been detected (e.g. up to 10-fold for DDT) along the remote, vertical profiles of the northern and central Alps. Such increases were statistically correlated with temperature but not with precipitation. Other compounds like chlorinated paraffins, PCDD/F and PCB, PBDE and PAH did not show a uniform trend along or among these slopes. Local sources and meteorological influence, like inversions, were assumed to be responsible for these findings. An illustrative example of the varying trend along elevation gradients is the Swiss altitude profile that was – due to the lack of alternatives - located above a village. While pesticides in the soil followed the observed trend of increases with altitude, PCDD/F and PCB showed highest concentrations at the lowest site closest to the village suggesting the influence of local emissions on concentrations. After 1 ½ year of air sampling at the three summits (Sonnblick in Austria, Zugspitze in Germany, Weissfluhjoch in Switzerland), MONARPOP's source-direction specific air measurements did not show a prevailing source region (NW-Europe, NE-Europe, S-Europe) for any of the investigated compounds or summits. For the identification of long-term trends air and deposition monitoring is continued into the future. All SOC's (OCPs, PCDD/F, PCB, PBDE, PAH), even compounds that have been banned in Europe for decades (e.g. DDT) or have not even been used in significant amounts in Central Europe (e.g. Mirex), were detected in air and deposition indicating their steady deposition at the remote summits by atmospheric transport. Annual mean air concentrations at the summits were somewhat higher than Arctic values [compiled in UNEP, 2009].</td>
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2.2.3.4. Intercontinental Transport

With regard to intercontinental transport, trans-Pacific atmospheric transport of POPs from Eurasia to Western North America has been clearly identified [Bailey et al., 2000; Genuaidi et al., 2009a; Genuaidi et al., 2009b; Harner et al., 2005; Killin et al., 2004; Primbs et al., 2008a; Primbs et al., 2008b; Zhang et al., 2008b]. Although trans-Pacific transport of POPs likely occurs at a low level throughout the year, strong transport events occur primarily in the winter and spring and are episodic in nature. Elevated concentrations of α-HCH, particulate-phase PAHs, and HCB have been measured in trans-Pacific air masses relative to regional North American air masses at remote sites in Western North America [Bailey et al., 2000; Genuaidi et al., 2009a; Genuaidi et al., 2009b; Harner et al., 2005; Killin et al., 2004; Primbs et al., 2008a; Primbs et al., 2008b]. These same POPs have also been measured in outflow from Asia [Primbs et al., 2007], including other studies that show outflow of PAHs from China [Guo et al., 2006; Lang et al., 2008]. In addition, the emission of PAHs and re-emission of synthetic organic POPs from soils and vegetation during the large scale summer 2003 Siberian fires and the subsequent trans-Pacific transport of these emission to two sites in the Western U.S. have been documented [Genuaidi et al., 2009a].

POPs may also undergo trans-Atlantic atmospheric transport either from North America to Europe/Africa or vice versa; but observed evidence is scarce. The atmospheric concentrations of POPs have been measured in Western Europe [Lee et al., 1999; Lee et al., 2004] and in the Eastern Atlantic [Gioia et al., 2008b; Lohmann et al., 2001; Nizzetto et al., 2008]. Air masses with elevated POP concentrations in these European regions were primarily tracked back to other parts of Europe but some studies have attributed elevated concentrations in Northern Europe to POPs emissions in Canada [Eckhardt et al., 2009]. POP concentrations are high in regions of Africa. Saharan dust storms, easterly trade winds and the African easterly waves have the potential to transport POPs from Africa to the Atlantic Ocean, as well as North and Central America [Del Vento and Dachs, 2007; Garrison et al., 2006; Pozo et al., 2009; Zhang et al., 2008b]. Monitoring data [Garrison et al., 2006] have shown promising correlations between POPs and microorganisms in dust-event samples from the source region in Africa and downwind sites in the Caribbean. Some POPs that were phased out years ago in North America were extracted from dust samples in the downwind sites as well during the African dust storms, suggesting that the Saharan dust is likely a carrier of POPs from Africa to North America. On the other hand, Baker and Hites [1999] have observed higher atmospheric PCDD/F concentrations in Bermuda in the winter when air parcels originated from North America than when air masses originated from the east (i.e., West Europe and North Africa) in the summer. They have attributed this observation to the relative proximity of the station to North America as compared to western Europe and North Africa.

2.3. Oceanic Observations

Although the primary interest for the TF HTAP is by definition the atmospheric transport and fate of POPs, it is acknowledged that the oceans play an important role in controlling the environmental transport, fate and sinks of many POPs at regional and global scales [Gioia et al., 2008b; Iwata et al., 1994; Li et al., 2002]. For example, the oceans are thought to provide a primary means of transport for some of the perfluorinated substances [Yamashita et al., 2008], and as a medium for exchange i.e. hopping [Bruhn et al., 1999; Gouin and Wania, 2007; Semeena and Lammel, 2005; Stemmler and Lammel, 2009], or as a removal process i.e. sink [Lohmann and Jones, 1998; Lohmann et al., 2006; Lohmann et al., 2007]. The presence of POPs in surface oceans can also lead to accumulation in marine biota via bioconcentration and biomagnification. Gouin and Wania [2007] suggested that the oceans play a crucial role in delaying arctic contamination; as chemicals that are transported via the ocean can eventually reach the Arctic, albeit on a slower time scale.

Data collected from a number of cruises across the world’s oceans has shown that POP concentrations in the open ocean are often lower than those observed in coastal areas [Iwata et al., 1993b; Schulz-Bull et al., 1998], although the large oceanic volume means that they may represent an important part of the global POPs inventory. Whilst the atmosphere has been regarded as the most important and rapid route of transport for many POPs to remote regions the oceans may account for a significant delivery of substances to Arctic regions. The importance of air-water exchange is thought
to be a dominant process at the global scale when compared to wet and dry deposition [Jurado et al., 2004a]. However, available measurement data of POP air-water exchange fluxes, particularly in remote oceanic regions, are scarce (2.4.4) owing to the difficulties associated with the sampling procedures for POPs (e.g. large volume, partition to colloids, etc), shipboard and laboratory contamination and the costs associated with the use of ships in the open ocean.

It is believed that the total burden of PCBs present in the mixed layer depth of the world oceans (10s - 100s m) is in the order of hundreds of tons [Jurado et al., 2004b]. This may account for approximately 10% of the estimated global releases of PCBs [Breivik et al., 2002, mid range estimate]. On the order of 100 kilotonnes of DDT has been estimated to be stored below the mixed layer [Stemmler and Lammel, 2009]. For more soluble substances, such as PFOS, a large portion of estimated releases of PFOS and its precursors currently resides in ocean surface waters [Paul et al., 2009].

Deep oceans waters are usually considered as a final sink for POPs, although an evaluation of the importance of their role in their environmental fate is uncertain. Once POPs bound to particulate organic carbon sink through the superficial mixed waters, they accumulate in deep sediments. Marine superficial sediments (and in particular those laying on the continental shelf) could therefore represent an important reservoir and are estimated to contain thousands of tons of POPs globally [Jonsson et al., 2003]. On the other hand, [Stemmler and Lammel, 2009] estimated that export to deep sediments accounts for only 3.8-5.5% of the total DDT loss from the oceans, and that most is returned to the atmosphere.

In earlier scientific studies on the fate of organic pollutants in the Arctic, it was presumed that the degradation of POPs in the Arctic Ocean was dominated by abiotic processes. It was assumed that, due to the low temperatures, biotic degradation was too slow to be of any significance. However, when studying the enantiomeric signal of α-HCH (which indicates the extent of microbiodegradation, see section 2.5.1 for details), it became clear that biotic processes were of utmost importance. Furthermore, it became evident that the microbial communities in the Arctic environments are adapted to the cold environments and are highly involved in biodegradation processes resulting in enantioselective transformation patterns for chiral environmental pollutants. In-depth studies of the enantiomer fraction (EF) of α-HCH at different depths in the Arctic Ocean made it possible to provisionally calculate the degradation rates of the individual enantiomers [Harner et al., 1999; Harner et al., 2000; Kallenborn and Huhnerfuss, 2001]. However, this calculation was based on a hypothetical calculation of the ventilation age of the water mass, i.e., how long ago the water at a specific depth had been in contact with the atmosphere and was loaded with racemic, non-biodegraded α-HCH.

2.3.1. Oceanic Measurements

Table A.2.4 in Appendix A provides some examples of cruise data comprising mostly air samples taken over oceans, although some studies analyzed simultaneous air and water samples in order to study exchange processes (see Section 2.4.4). In general, measured concentrations of POPs are higher in the northern hemisphere than the southern hemisphere, which agrees with historical global production for many substances. However, for PCBs source inventories show that the ratio of emissions between the northern and the southern hemisphere (NH:SH) should be approximately 20:1 but ambient concentrations show a smaller difference. Inaccuracies with the source inventories and/or NH ‘dilution’ to the SH over time may explain these observations. For example, high PCB concentrations have been reported off the west coast of Africa which raises interesting questions about unaccounted for sources/processes [Gioia et al., 2008b]. In many parts of the northern hemisphere where production and use of POPs, such as PCBs, were the highest, atmospheric concentrations were declining near these source regions as a result of regulatory controls. On the other hand, over remote areas of the open ocean, it appears there is little change in air concentrations over the period 1990-2005 [Gioia et al., 2008b; Jaward et al., 2004a; Schreitmüller and Ballschmiter, 1994]. This suggests that there is a gradual global scale re-distribution of POPs and a potential shift from the dominance of primary sources to secondary sources. Yet, Breivik et al. [2007] has indicated that primary PCB sources still dominate: current atmospheric levels of PCBs seems to be mainly
driven by primary atmospheric emissions [Gioia et al., 2006; Hung et al., 2005; Jaward et al., 2004b] and model simulations indicate that atmospheric decline in PCB concentrations is mostly dependent on the rate of decline in PCB primary emissions [Hung et al., 2005]. This is also suggested by racemic chiral PCBs observed in air (implying fresh emission) versus nonracemic (biodegraded) PCBs in soil and water [Asher et al., 2007; Jamshidi et al., 2007] (see section 2.5 for details).

2.3.2. Water Monitoring Techniques

As mentioned in the previous section, POP concentrations in open ocean and coastal waters are generally low (often sub pg L\(^{-1}\)) and thus require a sampling system capable of attaining ultra-low detection limits. This is generally achieved by sampling very large volumes of water, often 400 to 1000 litres. Seawater sampling of POPs is usually performed on board research vessels by using a stainless steel pipe deployed at 8-15 m depth, often located in the keel. Smaller volume samples (up to \(\sim 20\) L) can be collected with deep ocean bottles deployed on a hydrowire or rosette. For the analysis of more soluble perfluorinated compounds, usually only 1-2 L of water is required, collected using a rosette without Teflon parts or as grab samples. The sampled seawater is usually filtered using glass fibre filters to remove particulate material, followed by a solid phase extraction column containing XAD-2, PAD-2 [Xie et al., 2007b] or PUF [Sobek et al., 2004]. Average flow rate are generally between 0.5-1.2 L min\(^{-1}\), which allows collection of samples every 12-24hrs.

In order to estimate fluxes between the atmosphere and the seawater, it is useful to sample at shallower depths, for example 2-5 m, because the atmosphere will interact with the first few meters of the surface layer. Sampling at these depths is usually achieved either when the ship is stationary or by using a “FISH” sampler which is towed at the side of the ship with a depth of 2-3 m. From the FISH seawater is pumped to the wet laboratory of the vessel via a totally enclosed system with suction provided by diaphragm pumps. The INFILTREX water sampler is a self-contained device featuring a water pump, a filter assembly housing, and a Teflon column which can be packed with resins such as XAD-2. A microprocessor records the sampling volume from the preset flow rate and sampling time.

Recently, water measurements have been conducted using different types of passive sampling devices, such as those mentioned in Lohmann and Muir [2010]. Similar to passive air samplers, these passive water samplers do not require a pump, are low-cost and can be deployed with minimal training. They usually consists of a sampling medium coated with a sorbent which can sequester the chemicals of interest, e.g. polyethylene (PE) and triolein, housed in a metal casing deployed in surface water. [Lohmann and Muir, 2010] pointed out the importance of global water monitoring to assess the effectiveness of global control agreements, such as the Stockholm Convention on POPs, since a major concern with POPs is their biomagnification through the aquatic food webs. They have suggested the use of PE-based samplers for global monitoring of apolar compounds, since this type of sampler provides more reproducible results than others, and can co-deploy with other sampling device for more polar compounds, such as perfluorooctanoic acid (PFOA). By spiking these passive samplers with performance reference compounds, it would be possible to estimate which compounds have come into equilibrium between the sampler and the water and others can be corrected by non-equilibrium. They have proposed to start a global aquatic passive sampling (AQUA-GAPS) and develop a network of monitoring stations; preferably co-locating with passive air sampling sites to estimate the direction of air-water exchange fluxes in response to changing atmospheric concentrations.

2.4. Air-Surface Interaction, Degradation and Transformation

2.4.1. Atmospheric Processes

Due to their wide range of vapour pressures, the more volatile POPs (such as HCB and HCHs) exist primarily in the atmospheric gas-phase, while other less volatile POPs exist primarily in the atmospheric particulate or aerosol-phase (most PCDD/Fs). Still other POPs, with intermediate vapour pressures (such as PAHs), are distributed between both the atmospheric gas and aerosol phases. As a result, POPs are subject to both gas-phase and aerosol-phase removal mechanisms in the atmosphere, including wet and dry deposition, gas-exchange, and direct and indirect photolysis.
Precipitation, particularly snow, is an efficient scavenger of POPs from the atmosphere [Halsall, 2004; Lei and Wania, 2004; Wania et al., 1999]. Several air monitoring programs, e.g. EMEP, MONARPOP and IADN (Table A.2.1 in Appendix A), include the measurements of atmospheric depositions:

At 5 main stations in the Great Lakes, IADN estimates the loadings of POPs to the lakes, taking into account wet deposition via precipitation, dry deposition of particles and gas absorption at the water interface. In the 2005 IADN report [Blanchard et al., 2008], it was found that loading estimates of banned organochlorine pesticides continue to decline for all lakes. α-HCH absorption has continued to decline and for some Lakes, volatilization is now more significant. HCB is volatilizing out of Lake Superior. γ-HCH absorption is showing signs of decline likely associated with reduced use of lindane as a seed treatment in Canada. PCB gas absorption continues to decline at all main stations while urban areas are important sources of atmospheric PCBs to the Lakes. PAHs such as phenanthrene and pyrene absorption fluxes are largest for Lake Erie, a slight decrease in absorption is seen between the 1990s and the early 2000s however a small increase is observed for 2005. Particulate-bound PAHs such as benzo[a]pyrene are equally deposited via wet and dry deposition to the Lakes but vary from year to year for most lakes.

At the three active air sampling stations of MONARPOP on the European Alps, active air and bulk deposition are sampled in parallel. This allows a comparison of the detected air concentrations with the total deposition of the compounds and with meteorological parameters like precipitation. A noteworthy finding of the observation period so far is a frequent lack of correlations between air concentrations and deposition of the POPs. A site with higher air concentration may have lower pollutant deposition than the other site, and a season with higher air concentrations may be a season with lower pollutant deposition. Furthermore, correlations of the pollutant deposition with the mean precipitation of the monitoring sites are hardly to be found [Offenthaler et al., 2008; Offenthaler et al., 2009b].

The EMEP programme has included precipitation measurements, using either wet only or bulk deposition samplers, for many years. By 2007, precipitation measurements were carried out at 12 background stations in 8 different countries (Belgium, Czech Republic, Germany, Finland, Iceland, Netherlands, Norway and Sweden). The substances monitored vary between sites, but quite commonly selected PCBs, PAHs and OC pesticides are reported. The measurement data are reported and accessible through the EMEP programme [Aas and Breivik, 2009]. For some of these sites, more detailed investigations have been carried out in the past, e.g. with respect to seasonal variability [Brorström-Lundén et al., 1994; Wania and Haugen, 1999], long-term temporal trends [e.g. Holoubek et al., 2007] as well as for comparison with EMEP modelling results (e.g. [Holoubek et al., 2001]).

Deposition allows a better assessment for the input of POPs into food chains and terrestrial sinks like soil than air concentration. Therefore, future air monitoring activities should be more frequently accompanied by measurements of the POP deposition to allow a better assessment of POP input into the landscape as a consequence of long-range transport.

POPs react with photochemically generated OH radical in the atmosphere and this has been shown to be the most significant environmental transformation reaction for some POPs [Anderson and Hites, 1996]. In addition, the reaction of PAHs with NOx and O3 are significant in that these reactions result in the formation of more toxic nitro and oxy-PAHs [Helmig et al., 1992; Pitts et al., 1985; Sasaki et al., 1997].

2.4.2. Air-Soil Exchange

Soils are a vast reservoir for semivolatile organic compounds (SOCs), such as POPs and POP-like chemicals, that are atmospherically deposited or contaminated through direct application. A global survey of PCBs (sum of 22 congeners) in background soils estimated a burden of 21000 t in the upper 5 cm layer [Meijer et al., 2003b], which is about 1.6 % of the known production volume and about 30 % of the 66000 t estimated to have been cumulatively emitted to the atmosphere [Breivik et al., 2007]. Global models for DDT suggests that 50-95% of the total mass in the environment is contained in soils [Guglielmo et al., 2009; Schenker et al., 2008; Stemmler and Lammel, 2009].
Atmospheric deposition and volatilization, degradation rates, fraction of soil organic matter ($\phi_{\text{OM}}$), temperature, vegetation cover and ecosystem carbon turnover all influence accumulation and fate of SOCs in background soils [Kirchner et al., 2009; Sweetman et al., 2005].

In addition to accumulating SOCs, soils act as a source and exchange medium with the atmosphere through primary emissions (e.g., volatilization of applied pesticides in agriculture and PCBs from highly contaminated sites) and secondary emissions (‘grasshopping’). Both single- and multi-hopping contribute to the transport of DDT and HCH [Semeena and Lammel, 2005]. Multi-hopping is thought to be responsible for the slow buildup of a number of SOCs that are persistent in air and surface media in the Arctic once emissions have ceased [Gouin and Wania, 2007], while for some SOCs, (e.g. HCH), accumulation in the Arctic may be explained by single-hop atmospheric transport alone [Semeena and Lammel, 2005]. Soil-air exchange of POPs is a key consideration when attempting to assess the effectiveness of international controls on POPs on reducing air concentrations. Secondary sources may be particularly important in the context of climate interactions and possible remobilization of POPs from soil reservoirs (see Chapter 1.5). The ability to elucidate soil-air exchange and account for emissions from soils is critically important in the development of transport models and in fingerprinting source-receptor relationships. Modelling-related studies are summarized in Appendix B.

2.4.2.1. Equilibrium soil-air partitioning

Within soil, SOCs are partitioned among solids, and water and air within pore spaces, each compartment having its own fugacity capacity (ability to retain chemicals) [Cousins et al., 1999a; Cousins et al., 1999b; Harner et al., 2001]. The potential for gas exchange with soil is expressed by the fugacity ratio (FR) or fugacity fraction (FF), estimated from soil and air concentrations and the octanol-air partition coefficient ($K_{\text{OA}}$) as described in [Li et al., 2010]. FFs of <0.5, 0.5, and >0.5 (or FRs of <1, 1 and >1) imply net deposition, equilibrium and net volatilization. In practice, uncertainties in the terms are such that FF values within a fairly wide range are not judged to be significantly different from equilibrium. These equilibrium ‘windows’ have been estimated as 0.50 ± 0.20 [Harner et al., 2001; Ruzickova et al., 2008] or 0.50 ± 0.35 [Daly et al., 2007a].

Laboratory and field studies of SOC gas exchange with soils have been ongoing since the 1970s and early work has been reviewed [Bidleman, 1999; Cousins et al., 1999a; Majewski, 1999; van der Berg et al., 1999]. Recent measurements have been conducted in laboratory chambers to determine the soil-air partition coefficient, $K_{\text{OA}}$ [He et al., 2009a; He et al., 2009b; Hipplelein and McLachlan, 1998; Hofman et al., 2008; Meijer et al., 2003d; Wolters et al., 2008; Wong et al., 2009b] and soil-air fluxes [Koblizkova et al., 2009; Wolters et al., 2008] for a variety of SOCs. $K_{\text{OA}}$ for PAHs and PCBs [Cabrérizo et al., 2009] and OCPs [Meijer et al., 2003c] have been determined in field-deployed dynamic flux chambers, operated under conditions where soil-air equilibrium was approached.

Experimental measurements of $K_{\text{OA}}$ for the above chemicals agree with values estimated from $K_{\text{OA}}$ [Li et al., 2010; Meijer et al., 2003c; Meijer et al., 2003d] within factors of 2-3 in some cases, but deviate by an order of magnitude in others. Such discrepancies call into question the use of the single physical-chemical property $K_{\text{OA}}$ to describe soil-air exchange. Partition coefficients between natural organic matter and air varied by an order of magnitude when using humic and fulvic acids from different sources and descriptions of soil-air interactions were improved by using polyparameter linear free energy relationships (pp-LFERs) that account for interactions between the sorbate and the sorbent at the molecular level [Niederer et al., 2007]. Sorption is also a matter of organic matter quality. It takes place on ‘carbonaceous geosorbents’, e.g. black carbon, kerogen, through mechanisms which are not adequately described by a single-parameter relationship [Cornelissen et al., 2005]. The $K_{\text{OA}}$ model may not hold for soils with low organic matter fractions, $\phi_{\text{OM}}$, or for polar chemicals which adsorb strongly to the mineral fraction [Goss et al., 2004]. Sorption is furthermore subject to long-term dynamics (‘aging’). Bioaccessibility/bioavailability and extractability often decrease as chemicals age and become more tightly bound to the soil [Gevao et al., 2003; Semple et al., 2004]. The effect of aging of SOCs in soil on their volatilization (and also on bioavailability) is insufficiently described and understood. One set of experiments showed no effect on $K_{\text{OA}}$ of aging.
PCBs in soil for up to 392 d [Cousins et al., 1998]. On the other hand, increases in $K_{SA}$ ranging from 60-400% were found upon aging brominated flame retardants in urban soil for 90 days [Wong et al., 2009b].

2.4.2.2. Large-scale assessments of soil-air exchange

On a global scale, $K_{SA}$ for PCBs ranges over 10 orders of magnitude due to variations in $\phi_{OM}$, temperature and the range of $K_{OA}$ for low- and high molecular weight (LMW, HMW) congeners and, presumably, yet unidentified soil properties. $K_{SA}$ values are predicted to be highest in regions with cold climates and/or high $\phi_{OM}$ (e.g., northern Scandinavia and Russia, boreal areas of Canada), and lowest in tropical and subtropical areas with warm climates and/or low $\phi_{OM}$ [Li et al., 2010]. A similar trend is predicted for the "maximum reservoir capacity" (MRC) of the top 1 mm of soil [Dalla Valle et al., 2005]. Both studies noted the strong influence of seasonal and latitudinal changes in temperature on $K_{SA}$ or MRC, implying dynamic soil-air exchange driven by climate.

Soil-air exchange of SOCs has been assessed by estimating $FF$s from measured concentrations in soils and ambient air, globally for PCBs [Li et al., 2010] and in specific countries or regions, e.g.: PCBs in Sweden [Backe et al., 2004], PBDEs in Turkey [Cetin and Odabasi, 2007a], PCBs and OCPs in Europe [Ruzickova et al., 2008], PCBs [Li et al., 2010; Zhang et al., 2008c] and OCPs [Tao et al., 2008] in China, and OCPs in the southern U.S.A. [Bidleman and Leone, 2004], Canada [Bidleman et al., 2006; Kurt-Karakus et al., 2006; Meijer et al., 2003b] and Mexico [Wong et al., 2010]. These studies document large variations in $FF$s indicative of net volatilization, deposition or near-equilibrium, depending on extent of soil contamination, air concentration, temperature and $\phi_{OM}$. The situation of PCBs is exemplified in Figure 2.4 [Li et al., 2010], which shows $FF$s in background, rural and urban locations of China, the U.K. and Europe. In general, $FF$s predict net volatilization or near-equilibrium for LMW and net deposition for HMW PCBs, and higher $FF$s in urban-rural locations compared to background sites.

Globally, residues of the relatively volatile and mobile chemical HCB in soil were significantly correlated with absolute latitude, with highest concentrations between 55°-70° N [Meijer et al., 2003b], while PCBs in soil maximized in the 30°-60° N latitude band where the bulk of PCB usage occurred [Li et al., 2010; Meijer et al., 2003b]. Fractionation of PCBs was shown along a latitudinal gradient from the U.K. to northern Norway, where the proportions of LMW PCB homologs in soil [Meijer et al., 2002] and air [Meijer et al., 2003a] increased relative to total PCBs, while the proportions of HMW homologues decreased. Surveys of background soils showed strong positive correlations between SOC concentration and $\phi_{OM}$ for higher volatility SOCs, but weak or no correlations for less volatile ones [Meijer et al., 2002; Meijer et al., 2003b; Sweetman et al., 2005; Tao et al., 2008].

Further evidence of fractionation has been documented through measurements along urban-rural gradients [Harner et al., 2004; Jaward et al., 2004b; Motelay-Massei et al., 2005; Ren et al., 2007; Sun et al., 2007; Zhang et al., 2008c]. Strong soil-air correlations in China were found for LMW PCBs at background and rural sites, and for HMW PCBs at urban sites [Zhang et al., 2008c]. Patterns in $FF$s of PCB homologues were classified as due to ‘primary fractionation’ and ‘secondary fractionation’ effects [Li et al., 2010].

During dispersal from urban centres where primary emissions dominate, deposited PCBs are effectively trapped in the soil and not reemitted. This occurred mainly for HMW homologues, for which $FF$s were below 0.5. $FF$s near or above 0.5 were typically observed for LMW homologues, which are freer to undergo cycles of air-surface exchange (secondary emissions; i.e., grasshopping).
The effect of temperature on observed atmospheric concentrations of SOCs is often expressed by a form of the Clausius-Clapeyron (CC) equation, \( \ln \frac{P}{P_a} = \frac{m}{T} + b \) [Hoff et al., 1998; Wania, 1998], where \( P \) is the partial pressure of the chemical in ambient air and \( T \) (K) is temperature. The slope, \( m = -\Delta H_{sa}/R \), where \( \Delta H_{sa} \) is the enthalpy of soil-to-air exchange (J mol\(^{-1}\)) and \( R \) is the gas constant (8.31 J mol\(^{-1}\) K\(^{-1}\)). Sometimes concentration is used instead of partial pressure, in which case the slope is related to the internal energy, rather than enthalpy, of exchange [Wania, 1998]. This relationship properly holds only for soil-air equilibrium, nonetheless it is often used to gain insight to the gas exchange state of SOCs under ambient conditions. Slopes close to those for liquid-phase vapour pressure are suggestive of local soil-air gas exchange controlling atmospheric concentrations, whereas shallower slopes indicate dominance of advection from source regions [Hoff et al., 1998; Wania, 1998]. However, other factors complicate the interpretation of these slopes. These include changes in air concentrations due to reactions with OH radicals, atmospheric mixing height and atmospheric stability [MacLeod et al., 2007], freezing of the soil [Carlson and Hites, 2005; Hoff et al., 1998; Wania, 1998] and proximity of sources [Venier and Hites, 2010].

2.4.2.3. On-site emissions measurements

OCPs have been measured in air a few meters over agricultural soils at concentrations above background, even when the chemicals have resided in the soil for decades [Bidleman and Leone, 2004; Bidleman et al., 2006; Eitzer et al., 2003; Kurt-Karakus et al., 2006; Leone et al., 2001]. Diurnal cycles of PCBs and PBDEs were measured in air 1.5 m above the forest floor [Gouin et al., 2002]. Concentrations of PCBs and OCPs in ambient air were much higher at European sites with heavy soil contamination than in residential and background areas [Ruzickova et al., 2008].
Advection associated with volatilisation of OCPs from soil under field conditions have been estimated by multiplying measured concentrations gradients in air above the soil by the average wind speed at different heights [Waite et al., 2001] and deploying flux chambers over the soil [Waite et al., 2007]. Micrometeorological techniques have been used to estimate site-specific fluxes, especially for OCPs and current-use pesticide emissions from agricultural soil [e.g., Kurt-Karakus et al., 2006; Leistra and Van den Berg, 2007; and earlier work reviewed by Majewski, 1999; Prueger et al., 2005; Rice et al., 2002]. Fluxes are related to the concentration gradient in air over the soil and the eddy diffusivity of the gaseous chemical in air.

Estimates of the latter are obtained from vertical gradients of heat, momentum or water vapour. Correlations have been established between measured fluxes from individual fields and physicochemical properties [Woodrow and Seiber, 1997]. Relaxed eddy accumulation measurements from aircraft have been used to estimate pesticide fluxes on regional scales [Zhu et al., 1998].

Chiral POPs offer special advantages as tracers of soil-air exchange processes, because they allow volatilization of microbially degraded residues in soil to be distinguished from sources which have not been subject to microbial attack; e.g. primary emissions. This topic is discussed in Section 2.5.1.1.

2.4.3. Air-Vegetation Exchange

Vegetation has a large capacity to sorb a range of SOCs like POPs from air [Dalla Valle et al., 2004]. It can effectively take up SOCs from air due to large leaf surfaces per unit of ground area. High sorption by fresh foliage led to declined air concentrations after the burst of leaf buds [Gouin et al., 2002]. Organic pollutants were found in various types of vegetation around the globe [Bacci et al., 1986; Collins et al., 2006; Kylin and Sjodin, 2003; Simonich and Hites, 1994]. As an indicator, vegetation was employed to study temporal and spatial distribution of atmospheric pollutants, and to trace their potential sources [Kylin and Sjodin, 2003; Simonich and Hites, 1994; Zhu and Hites, 2006].

Airborne organic pollutants are transferred to vegetation mainly through dry gaseous deposition, dry particle-bound deposition, and wet deposition onto leaf surface [Collins et al., 2006; Simonich and Hites, 1995]. Root uptake is generally negligible for hydrophobic chemicals. Vegetation uptake depends on physical-chemical properties of SOCs, species of vegetation, and ambient environmental conditions. Understanding of vegetation uptake has been greatly advanced in the past 2 decades [Collins et al., 2006; McLachlan, 1999; Simonich and Hites, 1995]. McLachlan [1999] proposed a framework to identify different uptake pathways from air to vegetation based on chemicals’ octanol-air partitioning coefficient (K\textsubscript{OA}). The framework suggests that less-volatile SOCs with logK\textsubscript{OA}>11 mainly deposit to vegetation surfaces via particles, whereas dry gaseous deposition is a dominant uptake pathway for SOCs with logK\textsubscript{OA}<11. Uptake capacity of vegetation is smaller for SOCs with higher volatility. During the lifetime of vegetation, partition equilibrium is established between air and vegetation for volatile SOCs with logK\textsubscript{OA}<8.5. However, dry gaseous deposition is kinetically controlled for SOCs with intermediate volatility (e.g., 8.5<logK\textsubscript{OA}<11) because uptake capacity of vegetation is too large to be saturated before leaves fall. High dry gaseous deposition rates to forests were observed for some SOCs in two different locations [Horstmann and McLachlan, 1998; Su et al., 2006].

The chemicals deposited from air to vegetation are further transferred to soil along with fallen leaves. Effective transfer pathway through “air-vegetation-soil” consequently leads to elevated depositions to soil. Concurrent measurements showed higher concentrations of SOCs in forest soil than in nearby non-forest soil [Meijer et al., 2002]. Modelling studies suggested that the effective filtering effect may reduce concentrations of SOCs in air, ocean, and freshwater at the expense of increased concentrations in soil [Su and Wania, 2005; Wania and McLachlan, 2001]. The pollutants eventually enter terrestrial food chains and pose a risk to human health [McLachlan, 1996]. The effective filtering effect and large coverage of vegetation in the globe may reduce long-range transport potential of SOCs from source regions to remote Arctic [Su and Wania, 2005; Wegmann et al., 2004]. The reduction extent is further enhanced by photo-degradations on vegetation surfaces [McCready and Maggard, 1993; Niu et al., 2004].
Degradation loss is usually slower in forest soil than in air; therefore, pollutants take longer time to be removed from the environment [Su and Wania, 2005]. After primary emissions are reduced around the world, chemicals stored in soils are volatilized to air from secondary sources (see details in Section 2.4.2). The volatilization could be accelerated by warmer temperatures. [Genualdi et al., 2009a] found that 34-100 % of pesticides were lost from burned forest soil relative to unburned forest soil. Episodic high concentrations of some organic pollutants in remote locations were attributed to elevated emissions from biomass burning and subsequent atmospheric LRT [Eckhardt et al., 2007; Genualdi et al., 2009a]. Warming climate may also increase release of pollutants from forest soil [Macdonald et al., 2005].

2.4.4. Air-Water Gas Exchange

Oceans, seas and large lakes play a major role in the global cycling of SOCs, either acting as a sink or a source to the environment. Unlike precipitation and particle dry deposition, exchange of gases between water and air occurs continuously in an attempt to attain equilibrium.

For SOCs with a significant proportion in the gaseous phase, air-water gas exchange dominates over other deposition processes in oceans [Jurado et al., 2004a], seas [Breivik and Wania, 2002a; b] and large lakes [Blanchard et al., 2008; Meng et al., 2008]. This becomes increasingly important when the primary sources are adjacent to oceans; e.g., transport from Europe and Africa to the eastern North Atlantic for PCBs [Gioia et al., 2008b] and PAHs [Nizzetto et al., 2008] and PCB transport from urban centres to the Great Lakes [Miller et al., 2001; Wethington and Hornbuckle, 2005; Zhang et al., 1999]. In these situations, atmospheric concentrations are elevated and deposition is thus enhanced. Revolatilisation also takes place and acts as a secondary source to the atmosphere (Section 2.4.4.5). Gas exchange with water, as well as soils (Section 2.4.2) and vegetation (Section 2.4.3) is a controlling factor in determining the CTD, LRTP and overall persistence (POV) of the chemical Gouin, 2007 #4946; Scheringer, 2010 #5141; Wegmann, 2009 #5176).

2.4.4.1. Gas exchange processes

The direction of diffusive exchange of gaseous SOCs across the air-water interface depends primarily on concentrations in air and water and temperature, and rates of transfer are controlled by wind speed. The net flux direction can be assessed by comparing fugacities of the chemical in water and air (\(f_W, f_A\)), estimated from gaseous concentrations in air (\(C_A\)) , dissolved concentrations in water (\(C_W\)), and the temperature-dependent Henry's Law constant (HLC) [Bidleman and McConell, 1995; Jantunen and Bidleman, 2003; Jantunen et al., 2008b]. Water/air fugacity ratios (\(FR, f_W/f_A\)) of <1.0, 1.0 and >1.0 imply net deposition, equilibrium, and volatilization respectively.

The Whitman two film model is the most common one used to estimate the rate of air-water gas exchange. Deposition, volatilization and net fluxes (\(F_D, F_V, F_N\), mol m\(^{-2}\) d\(^{-1}\)) can be calculated from the individual air and water fugacities [Bidleman and McConell, 1995; Jantunen and Bidleman, 2003]. Non-fugacity relationships are also used [e.g., Meng et al., 2008; Qiu et al., 2008; Rowe et al., 2007].

2.4.4.2. Complications and uncertainties in gas exchange calculations

\(C_A\) and \(C_W\) refer to gaseous chemical in air and dissolved chemical in water. These are usually measured as the fractions of the total chemical which pass through an air or water filter and are retained in a solid adsorbent trap. The particle/gas distribution can also be predicted through models based on the compound's liquid-phase vapour pressure or octanol-air partition coefficient, and soot-air partition coefficient for PAHs [Lohmann and Lammel, 2004]. Such models do not capture the complex interactions that occur between compounds of differing polarity and aerosols of varying composition, and pp-LFERs have been proposed as an alternate approach [Arp et al., 2008; Brown and Wania, 2009; Götz et al., 2007]. Compounds sorbed to dissolved/colloidal organic matter in water are not retained by filters, which leads to overestimation of \(C_W\) and artificially inflates the volatilization component. Corrections can be estimated using partition coefficients of the chemical to dissolved/colloidal and particulate organic matter [Rowe et al., 2007; Sobek et al., 2004; Zarnadze and Rodenburg, 2008]. Processes in the water column such as plankton activity, dissolved-particle phase partitioning followed by sequestering to deep water, chemical and biological degradation and the salting-out effect on the HLC in saline waters also influence the rate of gas exchange [Dachs et
al., 2000; Gioia et al., 2008a; Gioia et al., 2008b]. If particle sinking fluxes are faster than air-water exchange fluxes, then the system will not be at equilibrium [Gioia et al., 2008a]. Concentration of POPs tend to be higher in the surface microlayer than in underlying water [Wurl and Obbard, 2004]. Flux estimates from the bulk water may underestimate the actual volatilization flux [Garcia-Flor et al., 2005; Guitart et al., 2010]; this becomes increasingly important with increasing hydrophobicity of the chemical [Wurl and Obbard, 2004].

Uncertainty calculations using propagation of errors are an important consideration when estimating volatilization and deposition fluxes. [Bamford et al., 2002; Bruhn et al., 2003; Gioia et al., 2008b; Jantunen et al., 2008b; Nelson et al., 1998; Xie et al., 2005]. The largest uncertainties lie in the HLCs and the mass transfer coefficients, although in some cases temporal variations in air concentrations are also a limiting factor [Cincinelli et al., 2009]. Short term changes in wind speed lead to uncertainties in mass transfer coefficients. Flux calculations which use a Weibull distribution to describe cumulative frequency distribution of wind speed help to reduce this uncertainty [Zhang et al., 1999].

Accurate HLCs are crucial in assessing gas exchange, and literature values are often in poor agreement [Totten et al., 2003]. Progress has been made to achieve thermodynamic consistency among literature values of physicochemical properties, thereby reducing uncertainty in HLCs and other properties [Schenker et al., 2005; Shen and Wania, 2005; Xiao et al., 2004]. The most common method of measuring HLCs is bubble stripping, in which the chemical is purged from a water column by a stream of nitrogen and its loss is followed over time. The technique is subject to an experimental artefact due to adsorption of the chemical onto the bubble surface. As a result, HLCs determined by bubble stripping may be erroneously high, especially for the more hydrophobic and surface active chemicals [Shunthirasingham et al., 2007].

2.4.4.3. Direct measurements of air-water gas exchange

Although fluxes of POPs have been directly measured in the terrestrial environment (Section 2.4.2.4), few such measurements have been made over water. Fluxes of HCHs and HCB over Lake Superior were estimated from shipboard by coupling measurements of $C_A$ at two heights with Bowen Ratio measurements of heat flux [Perlinger et al., 2005]. Gradient $C_A$ and micrometeorological measurements were used to determine fluxes of PCBs in the Hudson River estuary, and it was noted that mass transfer coefficients from the measurements agreed poorly with those calculated in the two-film model [Sandy et al., 2009].

2.4.4.4. Deposition, revolatilisation and secondary sources

International regulations, including SC and CLRTAP, as well as country-specific initiatives have banned the use and production of several POPs, which has successfully lead to reductions in primary emission sources and declining ambient atmospheric levels, as documented in air monitoring programs. Consequently, secondary emissions from water bodies and soil (Section 2.4.2) are becoming increasingly important as sources to the atmosphere. The oceans play a critical role in determining the lag time for chemicals to reach the Arctic, either by transporting dissolved contaminants slowly to higher latitudes, or by providing a relatively nonsticky temporary storage reservoir which is in constant exchange with the atmosphere. Persistent multimedia chemicals which exchange with the oceans, such as short perfluorinated alcohols (e.g., perfluoropropanol), LMW PCBs and HCB, experience a greater number of “hops” during atmospheric transport over the oceans compared to terrestrial surfaces [Gouin and Wania, 2007]. DDT and HCHs reach the Arctic by both single- and multiple hopping, and the latter results in a larger fraction of transported molecules to be deposited into the oceans [Semeena and Lammel, 2005].

A model of DDT in the global environment from 1950-2002 suggests that the global ocean absorbed DDT until 1977 and since then has been losing DDT, although DDT is still accumulating in large sea areas. Volatilization is the main sink to the atmosphere, with the western North Atlantic being the most significant secondary source. Large parts of the tropical ocean and southern mid-latitude ocean underwent flux reversal from deposition to volatilization in the 1980s (Figure 2.5) [Stemmler and Lammel, 2009].
Many investigations have been done over the last two decades to estimate air-water gas exchange of SOCs. Inferences about net flux directions have been made based on FR. Table A.2.5 in Appendix A gives examples for large lakes and oceans, where it can be seen that SOCs are in all states of gas exchange flux, undergoing net deposition or net volatilization or indistinguishable from air-water equilibrium. For simplicity, the net fluxes are referred to simply as “deposition” “volatilization” and “near equilibrium” in the rest of this chapter. They should not be construed as gross deposition or volatilization fluxes. Although often used, net fluxes do not properly express the magnitude of atmospheric loadings to water bodies, and gross fluxes should also be included in gas exchange reports. Fluxes are constantly readjusting seasonally, daily and even diurnally, in an attempt to reach equilibrium due to changes in temperature and air concentrations, and over the longer term to changes in water concentrations. Gas exchange has also been assessed in estuaries, rivers and small lakes [e.g., Asher et al., 2007; Bamford et al., 2002; Gustafson and Dickhut, 1997; Harman-Fetcho et al., 2000; Lohmann et al., 2000; McConnell et al., 1997; Nelson et al., 1998; Rowe et al., 2007; Sabin et al., 2010; Totten et al., 2001; Wilkinson et al., 2005].

![Figure 2.5. Net deposition of DDT to the world oceans: (a) annual mean in 2002 and (b) year in which the ocean turns net-volatilisational. Grey indicates no net-volatilization until 2002. [Reprinted from Figure 3 in Stemmler, I., and G. Lammel (2009), Cycling of DDT in the global oceans 1950-2002: World ocean returns the pollutant, Geophysical Research Letters, 36(L24602).]]

Studies in the Great Lakes have shown that PCBs and OCPs were generally close to air-water equilibrium or undergoing volatilization [Blanchard et al., 2008; Hornbuckle et al., 1994; James et al., 2001; Jantunen and Bidleman, 2003; Jantunen et al., 2008b; Meng et al., 2008; Ridal et al., 1997; Swackhamer et al., 1999]. Deposition of PCBs was noted in areas of the lakes that were impacted by plumes from urban areas [Miller et al., 2001; Wethington and Hornbuckle, 2005; Zhang et al., 1999]. Gas exchange of polychlorinated naphthalenes (PCNs) was investigated in Lake Ontario, with results showing volatilization of trichloro- and near-equilibrium of tetrachloronaphthalenes [Helm et al., 2003].

PCBs were near equilibrium over most of the South Atlantic, but depositing in the North Atlantic off the west coasts of Africa and Europe [Gioia et al., 2008b] and in the Arctic [Gioia et al., 2008a]. Volatilization of anthracene and phenanthrene, and near equilibrium of fluoranthene and pyrene, were found in remote open-ocean areas of the North and South Atlantic, while deposition occurred in the eastern North Atlantic off Europe and Africa [Nizzetto et al., 2008]. HCB and p,p’-DDE were near equilibrium in the North and South Atlantic [Booij et al., 2007].
The state of gas exchange for HCHs depends strongly on location and time. Concentrations of α-HCH in the arctic atmosphere declined by 10-fold between the 1980s and 1990s due to emission reductions in Asia [Li and Macdonald, 2005]. This decline forced a reversal of exchange in the Bering-Chukchi seas, from deposition in 1988 to near equilibrium or volatilization in 1993 [Jantunen and Bidleman, 1995; Sahsuvar et al., 2003]. A global model of α-HCH fate also predicted reversal of its exchange direction in the Arctic Ocean in the early 1990s [Wania and Mackay, 1999]. The exchange of γ-HCH in the Bering-Chukchi seas shifted from deposition in 1988 to near equilibrium in 1993 [Jantunen and Bidleman, 1995; Sahsuvar et al., 2003], and this situation continues in the Canadian Archipelago [Jantunen et al., 2008a; Su et al., 2006; Weber et al., 2006]. In the eastern Arctic Ocean where water concentrations are lower, near-equilibrium or deposition was found for both HCHs [Harner et al., 1999; Lakaschus et al., 2002; Lohmann et al., 2009]. Deposition of HCHs was indicated in waters of the Southern Ocean and Antarctica [Cincinelli et al., 2009; Dickhut et al., 2005; Jantunen et al., 2004; Lakaschus et al., 2002; Schreitmüller and Ballschmitter, 1995], while HCB was near equilibrium [Cincinelli et al., 2009].

HCHs in the Baltic Sea were near equilibrium, with occasional excursions toward volatilization or deposition, depending on season and advection of air masses [Wiberg et al., 2001], while deposition was noted in the Kattegat Sea [Sundqvist et al., 2004]. A mass budget for HCHs, based on data from European Monitoring and Evaluation Program (EMEP) stations, showed that the bulk of loadings to the Baltic Proper were through gas exchange and precipitation, with river flows accounting for only 12-13%. Riverine input was relatively higher in the Gulf of Finland and Gulf of Riga. Cycles of α-HCH deposition and volatilization were predicted during cold and warm seasons [Breivik and Wania, 2002a; b].

In the South China Sea, α-HCH was near equilibrium, γ-HCH and chlordanes were depositing and p,p’-DDE was volatilizing. Compared to a similar study in the same area fifteen years earlier, the flux direction of α-HCH had changed from deposition to volatilization in response to declining atmospheric concentrations [Zhang et al., 2007]. Volatilization of HCHs and chlordanes, and deposition of o,p’-DDT and endosulfan, were found at Taihu Lake, China [Qiu et al., 2008].

Studies of air-water gas exchange are sparse for in-use chemicals. Currently used pesticides (CUPs) were generally being deposited from the air to the water in the Great Lakes and the Arctic [Blanchard et al., 2008; Jantunen et al., 2008b; Jantunen et al., 2009; Weber et al., 2006]. Volatilization or deposition was reported for the CUPs chlorpyrifos and metolachlor, respectively, in a sub-estuary of Chesapeake Bay [Harman-Fetcho et al., 2000]. Deposition of chlorpyrifos took place during summer in the main stem of Chesapeake Bay, while volatilization was estimated during spring [McConnell et al., 1997].

Most phthalates were being deposited into the North Sea, except di-(2-ethylhexyl) phthalate, which was volatilizing in the North Sea and near equilibrium in the Arctic [Xie et al., 2005; Xie et al., 2007a]. Volatilization was estimated for polycyclic musks [Xie et al., 2007a] in the North Sea and deposition into subarctic and arctic waters. Polycyclic musks were volatilizing from Lake Michigan, where wastewater treatment plants were the main source [Peck and Hornbuckle, 2004]. Atmospheric processes for PBDEs were investigated in Izmir Bay, a coastal site on the Aegean Sea [Cetin and Odabasi, 2007b]. BDE 209 was the most abundant congener in air and water. Volatilization of BDE 28 and gas-phase deposition of other congeners were estimated, but for all PBDEs fluxes by dry particle deposition were generally an order of magnitude higher than those due to gas exchange.

Boulanger et al. [2005] conducted a mass budget of perfluorooctane surfactants for Lake Ontario. Main sources were inflow from Lake Erie and wastewater treatment plants, while outflow via the St. Lawrence River accounted for the major loss. Atmospheric deposition and volatilization were minor. Modelling suggests that after their phase out in 2000-2002, atmospheric levels of volatile precursors to perfluorooctane sulfonate (PFOS) have declined and air-sea exchange has strongly reversed from deposition to volatilization [Armitage et al., 2009].

The Clausius-Clapeyron (CC) equation, discussed in Section 2.4.2.3, gives insight to the gas exchange state of the compounds over water as well as over soil. Subject to the limitations discussed
in that section, slopes close to those of HLCs are suggestive of local air-water gas exchange controlling atmospheric concentrations, whereas shallower slopes indicate dominance of advection from source regions. Gioia et al. [2008b] noted significant CC slopes for PCBs over the South Atlantic, but insignificant slopes over the North Atlantic. CC slopes for PAHs were not significant over either the North or South Atlantic [Nizzetto et al., 2008]. It may be that advection from source regions dominates over revolatilisation in the North Atlantic, and over both oceans for PAHs [Gioia et al., 2008b; Nizzetto et al., 2008]. Significant CC slopes have been found for OCPs and PCBs at coastal stations on the Great Lakes [Venier and Hites, 2010], over the lakes themselves (Table A.2.5 in Appendix A), and in some cases in the Arctic [Jantunen et al., 2008a; Su et al., 2006; Su et al., 2008]. PCBs undergo latitudinal fraction in the ocean water and atmosphere, as they do over land (Section 2.4.2.3), with greater abundance of the LMW congeners/homologs being found in the colder high-latitude regions. Although temperature-driven fractionation affects these distributions, other contributing processes include transport in the water column by settling particles and inhibition of gas exchange by ice cover in the Arctic [Gioia et al., 2008a].

2.4.4.5. Effect of sea ice on gas exchange in arctic regions

The “lid” of ice cover in the Arctic Ocean and its regional seas provides an effective barrier to gas exchange of SOCs [Jantunen and Bidleman, 1996]. Each summer the ice pack recedes, thereby enabling air-water gas exchange to recommence. Doubling the area of open water in the arctic effectively doubles the air-water exchange of SOCs [Macdonald et al., 2005].

*FFs of HCHs in arctic-subarctic waters range from deposition to volatilization, depending on the region (Table A.2.5 in Appendix A). Decline in technical HCH emissions since the early 1980s led to a ten-fold reduction in concentrations of α-HCH in arctic air between 1979-1998 [Li and Macdonald, 2005] and this decline continues to the present [Hung et al., 2010]. As a result, gas exchange of α-HCH in the western Arctic Ocean reversed from deposition to volatilization [Jantunen and Bidleman, 1995; 1996; Sahsuvur et al., 2003; Wania and Mackay, 1999]. The evasion predicted by fugacity calculations has been confirmed by measurements of higher α-HCH concentrations in air over ice-free regional seas [Jantunen and Bidleman, 1995; 1996], and abrupt increases in air accompanying ice breakup in the Archipelago [Jantunen et al., 2008a; Wong et al., 2011], and by employing α-HCH enantiomers to trace release from the ocean (Section 2.4.4.7). Concentrations of HCB in air at Svalbard had been declining since 1994, but then underwent an increase between 2003-2006. One factor may be an increase in ice-free conditions around Svalbard, which would facilitate sea-to-air exchange. Another factor may be use of HCB-contaminated pesticides such as chlorothalonil [Becker et al., 2009].

PCBs are being deposited into the Arctic Ocean, but when the ice melts not only does air-water gas exchange recommence, the melting snow enriched in PCBs also increases the surface water and/or air burden thus affecting the air-water flux [Daly and Wania, 2004; Gioia et al., 2008a].

Climate change in the Arctic will lead to reduced ice cover and generally warmer surfaces. Less ice cover will increase the release of α-HCH and possibly other SOCs from the Arctic Ocean, remodeling them into the atmosphere for redistribution. In the case of chemicals which are predicted to undergo gas-phase deposition to the Arctic Ocean, loss of ice cover will provide more open water for such deposition to occur. Precipitation is expected to increase in the Arctic, which will increase loadings of chemicals to the Arctic Ocean directly through washout over the ocean and indirectly through river runoff. Melting ice can also impact the nutrients in the water column, affecting primary productivity. Biological processes in the water column affect the gas exchange of SOCs through sorption to settling particles. Plankton blooms can deplete dissolved phase PCBs, especially the more hydrophobic ones, and alter gas exchange fluxes [Dachs et al., 2000; Gioia et al., 2008a, Section 2.4.4.3]. With higher temperatures more wintertime polynyas will be present which will lead to an increase in sea fog, which scavenges and deposits SOCs in areas known to be important for biota [Macdonald et al., 2005].
2.4.5. Air-Snow/Ice Exchange

Due to its potential for chemical scavenging and exchange with the lower atmosphere snow notably influences the transport dynamics of POPs in the Northern Hemisphere. A change in the extent of snow cover brought about by a changing climate may affect the global fate of POPs [Macdonald et al., 2003; Stocker et al., 2007].

Falling snow is highly efficient at scavenging both vapour and particle-bound POPs from the atmosphere. Vapour scavenging is a function of the air temperature and the specific surface area (SSA) of the snow and is predicted to be most pronounced for snow possessing high SSA (e.g. 1 m$^2$/g) and at cold temperatures (<-10°C), resulting in scavenging ratios for semi-volatile chemicals being generally higher than rain (by over an order of magnitude) [Lei and Wania, 2004]. The seasonal snowpack therefore serves as a repository for chemicals transported to higher altitudes/latitudes with observed concentrations reported for a number of different POPs in both mountain and arctic snow [e.g., Blais et al., 1998; Herbert et al., 2006].

The snowpack is a highly dynamic compartment with regards to chemical exchange with the lower atmosphere, with substantial re-emission of POPs observed during snow ageing and compaction following fresh snowfall [Herbert et al., 2005]. Furthermore, fresh snowfall and diffusive vapour exchange are processes which will add/remove chemical to the standing snowpack.

To predict vapour exchange between the snowpack and air the knowledge of a chemical’s snow-air partition coefficient ($K_{\text{Snow-Air}}$) and mass transfer coefficient (in snow) are required along with the physical properties of the snowpack (e.g. depth, density and SSA). The availability of a chemical for atmosphere-snow exchange is determined by the chemical’s partitioning between snow grain surfaces and interstitial air. The associated $K_{\text{Snow-Air}}$ value is proportional to the product of snow density ($\rho$), specific snow surface area (SSA), and the temperature dependent equilibrium snow surface/air sorption coefficient $K_{IA} = C_I / C_A$, whereas $C_I$ and $C_A$ are the chemical concentrations in each of the two phases. Snow packs in sub-arctic and arctic regions are likely most influential to the fate of POPs in the Northern Hemisphere, because of their large areal coverage and duration. The chemical fraction available for atmosphere-snow exchange is expected to be larger in sub-arctic snow packs because $K_{IA}$, SSA, and $\rho$ are usually smaller there than in arctic snow [Domine et al., 2007; Taillandier et al., 2006]. Wind pumping significantly increases the extent of chemical mass transfer within snow [Albert et al., 2002; Albert and Shultz, 2002], which is in most cases the limiting factor for atmosphere-snow exchange. Wind induced advective transport in snow increases with higher wind speed above the snow pack, larger snow permeability, and more pronounced snow surface roughness characteristics. Whereas permeability is usually one order of magnitude larger in sub-arctic snow [Domine et al., 2008], wind speed is generally higher above arctic snow packs. A case study related to atmosphere-snow exchange of the semi-volatile pesticide PCB 28 revealed that chemical mass transfer coefficients in snow packs that exhibit relatively strong surface roughness, are two to three orders of magnitudes larger under the influence of moderately strong winds than under still wind conditions [Meyer and Wania, 2010].

The inclusion of a seasonal, single-layer snowpack in POP fate models has demonstrated the importance of the snowpack in affecting the environmental behaviour of POPs [e.g., Daly and Wania, 2004; Hansen et al., 2006; Hansen et al., 2008]. Fluxes of previously deposited chemicals out of the snowpack, particularly during late winter as the snowpack density increases and snow surface area decreases, influence chemical concentrations in air, but this is dependent on the physical-chemical properties of the chemical in question [Daly and Wania, 2004; Hansen et al., 2006]. As the mean winter maximum areal extent of snow cover in the northern hemisphere is 47 million km$^2$ [Armstrong and Brodzik, 2001] then the snowpack will influence levels of POPs in the atmospheric boundary layer, particularly in sub-arctic and arctic regions. The inclusion of an arctic snowpack in a northern hemispheric atmospheric chemistry-transport model (Danish Eulerian Hemispheric Model) was found to improve the fit between modelled and observed concentrations of $\alpha$-HCH in air for a number of air monitoring stations, particularly for the winter and spring seasons [Hansen et al., 2008]. This model provides the capability to assess the role of the seasonal snowpack on the concentrations of POPs in...
the background atmosphere and hence the role of snow in affecting chemical fate on a hemispheric scale.

Currently, knowledge is lacking on the influence of a layered or stratified snowpack on chemical exchange with the atmosphere and the role of particles in influencing chemical re-partitioning within the snowpack during periods of melt. Furthermore, sunlit surface snow layers may provide a significant degradative sink for some POPs through photooxidative processes [Matykiewiczova et al., 2007; Weber et al., 2009], although this loss process is not currently included in chemical fate models.

2.5. Chemical Tracers

2.5.1. Chiral chemicals as tracers of sources and air surface exchange

A chiral chemical contains an asymmetric centre and thus can occur in two non-superimposable mirror-image stereoisomers (isomers that differ only in the three-dimensional orientations of their atoms in space). These stereoisomers are called enantiomers (or atropisomers, for rotational stereoisomers such as PCBs). Chiral chemicals are usually produced as racemates (equimolar mixture of a pair of enantiomers). Once released into the environment, microorganisms will preferentially metabolize one of the two stereoisomers (stereoselective metabolism) leading to accumulation of nonracemic residues in soil and water. For enantiomers 1 and 2 of a specific chiral compound, data are often expressed as enantiomer fraction, \( EF = E_1/(E_1+E_2) \), where \( E_1 \) and \( E_2 \) may refer to the order of chromatographic peak elutions, \( R \) and \( S \) absolute configurations, or (+) and (−) optical signs.

Chiral tracers provide a means of distinguishing emissions of microbially processed and unprocessed residues. The latter may include currently used chemicals or older residues which have been protected from microbial attack [Bidleman and Falconer, 1999; Eitzer et al., 2003; Garrison, 2006; Hühnerfussa and Shah, 2009].

2.5.1.1. Chiral tracers of soil-air exchange

Field-scale studies have shown that when nonracemic OCP residues volatilize from agricultural soil, the \( EFs \) in overlying air are also nonracemic [Bidleman, 1999; Bidleman and Falconer, 1999; Bidleman and Leone, 2004; Bidleman et al., 2006; Eitzer et al., 2003; Leone et al., 2001; Meijer et al., 2003c].

Chlordane was formerly used in the U.S. and Canada for both agriculture and structural termite control. Chlordanes are enantioselectively degraded in agricultural soils, but are racemic in residential air [Leone et al., 2000] and soil near house foundations [Eitzer et al., 2001]. Residues of chlordane in ambient air tend to be closer to racemic in some cities due to evaporation of racemic termicide than in rural locations [Gouin and Wania, 2007; Shen and Wania, 2005], although this was not always the case [Venier and Hites, 2007]. Residues of \( o,p' \)-DDT in soil [Wong et al., 2010] and ambient air [Wong et al., 2009a] were closer to racemic in southern Mexico, where DDT had been more recently used, than in the northern part of the country, and \( o,p' \)-DDD was nonracemic in air at sites in the southern U.S.A. [Venier and Hites, 2007].

Degradation of PCB atropisomers in soil is often stereoselective [Jamshidi et al., 2007; Koblizkova et al., 2008; Lehmier et al., 2010; Robson and Harrad, 2004; Wong et al., 2009c], and chiral tracers have been exploited for source apportionment of PCBs in urban air. Chiral PCBs 95, 136 and 149 were nonracemic in soils, but racemic or nearly so in indoor air and ambient air of U.K. cities. This suggested that the dominant source of PCBs to ambient air in those cities was primary emissions from ventilation of indoor air, not secondary emissions from soils as previously thought [Jamshidi et al., 2007; Robson and Harrad, 2004].

Enantioselective analysis is useful for distinguishing primary from secondary emissions of chiral chemicals [Bidleman and Falconer, 1999; Hühnerfussa and Shah, 2009] and may be helpful in tracing ‘grasshopping’ over large spatial scales. Chlordanes were nonracemic in ambient air sampled in 1998-2001 from two arctic locations and a rural site in southern Sweden, but racemic in atmospheric deposition collected in background locations during the early 1970s. Residues of trans-
chlordane in laminated sediments from a lake in the Canadian Arctic were close to racemic in the 1940s and 1950s, and became increasingly less racemic from the 1960s to 1990s [Bidleman and Leone, 2004]. Similar trends were found for chlordanes in lake and river sediments in the U.S.A. [Ulrich et al., 2009]. These findings suggest that primary emissions of racemic chlordanes dominated in earlier decades, with secondary emissions of nonracemic chlordanes from soils playing a larger role in recent years [Bidleman and Leone, 2004]. Chlordanes arriving via trans-Pacific transport at mountainous sites in the western U.S. were racemic in most cases, with occasional events of nonracemic chlordane transport. Racemic chlordanes were also found in air samples collected at low elevation in Okinawa, Japan. The racemic chlordane signatures and trans-/cis-chlordane ratios similar to the composition of technical chlordane suggest that Asian air masses are influenced by relatively fresh sources of chlordane and/or that limited biotransformation of chlordane has occurred [Genualdi et al., 2009b].

EFs of chiral chemicals in background soils vary greatly due to differences in microbial populations and other soil properties [Koblizkova et al., 2008; Kurt-Karakus et al., 2005; Kurt-Karakus et al., 2007; Shen et al., 2009]. Simulated climate warming experiments and studies in forested vs. deforested soils showed switching in the enantiomer degradation preference of chiral pesticides [Lewis et al., 1998]. Monitoring stereoisomer proportions of chiral chemicals in air may reveal the integrated influence of long-term microbial diagenesis in soil.

2.5.1.2. Chiral tracers of air-water gas exchange

Similar to soil-air exchange processes, chiral compounds allow additional information to be derived on compound origin and air-water gas exchange. Apportionment of an airborne chiral chemical between two sources categories can be done knowing the enantiomer fraction of the chemical in source A (EF_A), source B (EF_B) and in the air sample, resulting from mixing of these sources (EF_M) [Harner et al., 2000]; i.e. percentage from source A = \(\frac{(EF_M - EF_B)}{(EF_A - EF_B)} \times 100\%\).

When the chemical in background air (source B) is close to racemic, EF_B ~0.5. This situation might occur if source B is from current use of a racemic chemical or from air transport of an aged residue that has not been subjected to microbial degradation.

The enantiomers of \(\alpha\)-HCH have been the most used as gas exchange tracers to provide evidence of water-to-air exchange. Enantioselective degradation by microbial processes in oceans and lakes produces nonracemic \(\alpha\)-HCH. Volatilization releases non-racemic \(\alpha\)-HCH into the air boundary layer, where it mixes with the racemic \(\alpha\)-HCH in background air.

Genualdi et al. [2009a] sampled air in the western U.S.A. at mountain sites above and below the marine boundary layer. Nonracemic \(\alpha\)-HCH was found in regional air masses at the low elevation site, possibly due to volatilization from the Pacific Ocean and regional soils. The \(\alpha\)-HCH was closer to racemic during transport events from Asia; EFs in air at Okinawa and in Chinese and South Korean soils were racemic. EFs were consistently racemic at the high elevation site. Nonracemic \(\alpha\)-HCH was generally found in air sampled from shipboard on a transect from the North Pacific to the Beaufort Sea [Ding et al., 2007]. Lohmann et al. [2009] found nonracemic \(\alpha\)-HCH in air and surface water of the northern North Atlantic and eastern Arctic Ocean. EFs of \(\alpha\)-HCH in air and surface water declined in parallel along a transect in the South Atlantic Ocean between 35 to 70 °S [Jantunen et al., 2004].

Shen et al. [2004] deployed passive air samplers from Central America to the Canadian Arctic and reported concentrations and EFs of several OCPs. EFs of \(\alpha\)-HCH were close to racemic at inland sites. Greatest deviations from racemic occurred on the shore of Lake Superior (see above), in the Canadian Archipelago and along the eastern and western seabords of Canada. Nonracemic EFs in air at coastal sites in eastern Canada were associated with volatilization of nonracemic \(\alpha\)-HCH from arctic seawater transported southward by the Labrador Current.

Significant correlations between nonracemic EFs in air and water were found on transects of open water, or where ice had receded, in the Arctic Ocean and regional seas. The \(\alpha\)-HCH in air was close to racemic when traversing ice-covered regions and not correlated to EFs in water [Jantunen
and Bidleman, 1996; Jantunen et al., 2008a; Wong et al., 2011]. The \( \alpha \)-HCH in air of the central and western Canadian Archipelago was racemic during periods of ice cover and became abruptly nonracemic at the onset of ice breakup. Reduction of EFs in air was accompanied by a rise in \( \alpha \)-HCH concentrations (Figure 2.6) [Jantunen et al., 2008a; Wong et al., 2011]. Source apportionment analysis as given above estimated the increase in the central Archipelago at 32\%, compared to 43\% from concentration measurements [Jantunen et al., 2008a].

**Figure 2.6.** Increase in \( \alpha \)-HCH concentrations in air in the Canadian Archipelago at Resolute Bay during and following ice breakup (red diamonds). The rise in air concentrations was accompanied by a decrease in EFs in air from the near-racemic value of 0.496 ± 0.003 to 0.482 ± 0.010, in response to volatilization of nonracemic \( \alpha \)-HCH from seawater. Blue bars are average EFs for the before and after ice breakup periods. [Adapted with permission from Figure 1 in Jantunen, L. M., et al. (2008), HCHs in the Canadian Archipelago. 2. Air-water gas exchange of alpha- and gamma-HCHs, Environmental Science & Technology, 42(2): 465-470. Copyright 2008 American Chemical Society.]

EFs of \( \alpha \)-HCH in air over the Baltic and Kattegat seas were related to more or less local volatilization relative to advection of air masses. The percent contribution to the atmosphere from volatilization ranged from 0-60\% [Sandqvist et al., 2004; Wiberg et al., 2001]. The \( \alpha \)-HCH in air and precipitation on the North Sea coast was nonracemic during late summer – early fall when volatilization from seawater would be expected, but closer to racemic in the colder months [Bethan et al., 2001]. A survey of \( \alpha \)-HCH in air across Europe showed that proximity to water had a large effect on enantiomer signatures. EFs were <0.5 in Baltic air and >0.5 in Mediterranean air. EFs <0.5 were found in air over the North Atlantic at latitudes above 40\º, while no trend in EFs was seen for samples off the African coast and in the South Atlantic. Inland air samples showed a large range in EF values, with racemic signatures for samples with the highest \( \alpha \)-HCH concentrations and an increasing spread in EFs for lower concentrations [Covaci et al., 2010].

Volatilization of \( \alpha \)-HCH from Lake Superior was traced by association of higher air concentrations with EFs farther from racemic. Source apportionment suggested that 40-60\% of \( \alpha \)-HCH in air over the lake in spring came from local volatilization compared to >90\% in late summer [Jantunen et al., 2008b]. Similarly, higher atmospheric levels of \( \alpha \)-HCH with greater deviation from racemic were found on the shore of Lake Superior compared to inland North American sites [Shen et al., 2004]. Ridal et al. [1997] observed a seasonal variation in the EFs of \( \alpha \)-HCH in air over Lake Ontario.
EFs were racemic in spring and fall when deposition occurred, whereas EFs were nonracemic air during summer when α-HCH was volatilizing.

Less use has been made of other chiral OCPs to trace air-water exchange, although they have been employed to follow soil-air exchange (Section 2.5.1.1). Jantunen et al. [2008a] investigated nonracemic chlordanes in the Great Lakes, but EFs in air were not clearly related to those in water. Chlordanes in background air of the region range from nonracemic to racemic and EFs are more related to former usage in agriculture and as termicides in urban areas (Section 2.4.2.6).

Asher et al. [2007] used chiral PCBs to determine the relative contributions of recent vs. historical PCB contamination in the New York/New Jersey Harbor estuary. Atmospheric PCBs 91, 95, 136 and 149 were racemic at all sites and sampling dates. In contrast, PCB 95 was significantly nonracemic in water, suspended matter, plankton and sediments. The authors concluded that PCBs in air were not from local volatilization, but probably from primary sources in nearby urban centres. The nonracemic EFs in the other phases implied dynamic exchange among them, decoupled from the air. EFs in water and suspended matter were correlated with discharge from the upper Hudson River. Source apportionment suggested that 86% or more of PCB 95 in phytoplankton was derived from contaminated sediment rather than air.

2.5.2. Isomer and parent/metabolite tracers of sources and pathways

Ratios of isomers in multicomponent OCPs (e.g., technical HCH, DDT and chlordane) and breakdown products such as DDE can be useful indicators of sources and exchange pathways. Whereas physicochemical properties are identical for enantiomers, they usually differ for isomers and parent/metabolite compounds. For example, the order of liquid-phase vapour pressures for DDT compounds is: p,p'-DDE > o,p'-DDT > p,p'-DDT, and for chlordane compounds: trans-chlordane (TC) > cis-chlordane (CC) > trans-nonachlor (TN) [Hinckley et al., 1990; Shen and Wania, 2005]. Henry's law constants for the HCHs decrease: α-HCH > γ-HCH > β-HCH[Xiao et al., 2004]. Such differences result in fractionation during air-surface exchange which must be considered when using compound ratios for source apportionment.

2.5.2.1. HCHs

The most widely quoted composition of technical HCH is [Iwata et al., 1993b]: 60-70% α-HCH, 5-12% β-HCH, 10-15% γ-HCH and other isomers. [Breivik et al., 1999] report a wider range for these three isomers: 55-80% α-HCH, 5-14% β-HCH, 8-15% γ-HCH. From the Iwata composition, ratios of α-HCH/γ-HCH in the range of 4-7 would be expected to result from air transport of the unfractionated mixture, and this range is often used to discriminate technical HCH vs. lindane (pure γ-HCH). Higher ratios in air might result from preferential volatilization of α-HCH [Xiao et al., 2004] and its longer atmospheric lifetime from slower OH radical reaction [Brubaker and Hites, 1998], and to selective removal of γ-HCH by rainfall scavenging and air-to-water exchange [Iwata et al., 1993a; Su et al., 2006]. Lower ratios imply emissions of lindane superimposed on a technical HCH background.

Historically, highest usage of technical HCH occurred in Asian countries [Li and Macdonald, 2005], but this changed with the switch to lindane in China (1983) and the former Soviet Union (1990) [Li and Macdonald, 2005] and in India (1997) [Primbis et al., 2008b; Zhang et al., 2008a]. Recently measured α-HCH/γ-HCH ratios in Asian air were 1-2.9 in China and Korea [Primbis et al., 2008b and references cited therein], 0.3-3.8 on the Tibetan Plateau [Li et al., 1996; Li et al., 2008; Wang et al., 2010a], 4.5 (mean) in the Wolong Nature Reserve (WRN) of the Sichuan Province, China [Liu et al., 2010], 0.48 at Waliguan Baseline Observatory (WBO), a high altitude Global Atmospheric Watch (GAW) site [Cheng et al., 2007] and 0.11-4 at multiple stations across India [Zhang et al., 2008a]. Ratios of α-HCH/γ-HCH across Europe were generally ≤ 1 [Jaward et al., 2004b].

A wide range of α-HCH/γ-HCH ratios has been reported in North America. Long-range transport and/or volatilization from coastal ocean raised α-HCH/γ-HCH ratios along the east and west coasts of Canada (3.6-14) and in the Canadian Arctic (4.1-9.5), while lower ratios in the interior along
the Canada – U.S. border (0.2-2.6), the southeastern U.S. (0.6-1.3) and Mexico-Central America (0.2-0.5) signified regional lindane usage [Shen et al., 2004]. Ratios in the Canadian Rocky Mountains ranged from 2.3 to 6.8 and generally increased with altitude between 570-2900 m [Daly et al., 2007a; Shen et al., 2005]. At IADN stations, ratios of average α-HCH/γ-HCH concentrations were highest for Lake Superior (3.6-5.0) and lower for the other lakes (1.7-2.8) [Sun et al., 2006]. The higher proportion of α-HCH for Lake Superior resulted from its volatilization from the lake [Jantunen et al., 2008b; Shen et al., 2004].

Relationships between HCH isomers and transpacific transport were identified at Mount Bachelor Observatory (MBO) in Oregon, U.S.A. [Primbs et al., 2008b]. During periods of increased air mass time over the Pacific Ocean and Siberia over the Pacific Ocean and Siberia, the α-HCH/γ-HCH ratio (5.6) was similar to that in upper tropospheric air (5.2). During periods of relatively fast (<10 days) transpacific and/or regional transport at MBO, the ratio was lower (2.9) and was reflective of current impacts from agricultural regions in both the U.S. and in Asia. Events of air transport from mainland Asia to Okinawa showed ratios of α-HCH/γ-HCH averaging 2.5, higher when air was from Japan/Korea/Russia and lower during events from China or open ocean [Primbs et al., 2007].

HCHs in air were reported between 2000-2003 at six arctic stations in Canada: Alert (ALT), Kinngait (KNG) and Little Fox Lake (LFL), the U.S. at Point Barrow (PTB) Alaska, Russia at Valkarkai (VKK) and the Norwegian Arctic at Zeppelin Mountain (ZPN) [Su et al., 2006]. Median ratios of α-HCH/γ-HCH were about the same or higher than the range for technical HCH at KNG, LFL, VKK and PTB (7-13) and lower at ALT and ZPN (3-4), which may be more influenced by lindane transport. Ratios of α-HCH/γ-HCH varied from 0.2-8.3, with a mean of 2.8, on an expedition in the northern North Atlantic and Arctic Ocean [Lohmann et al., 2009].

Ratios of α-HCH/γ-HCH in air are typically lower in the Southern Hemisphere, e.g. 0.2-1.1 in the Ross Sea [Cincinelli et al., 2009] and <0.1-1 on or near the Antarctic Peninsula [Dickhut et al., 2005; Kallenborn et al., 1998]. Low ratios from 0.06-1.2 were found in the Bolivian Andes [Estellano et al., 2008] and 0.12-1 in the Chilean Andes [Pozo et al., 2004].

2.5.2.2. DDTs

The “typical” composition of technical DDT according to the World Health Organization [WHO, 1989] is 77% p,p’-DDT, 15% o,p’-DDT, 4% p,p’-DDE and 0.3% p,p’-DDD. However, DDT has been manufactured in many countries and the composition of these mixtures is generally not known. Spencer and Cliath [1972] reported 74.6% p,p’-DDT, 21.1% o,p’-DDT, 0.8% p,p’-DDE and 0.07% o,p’-DDE in U.S. produced technical DDT. When emission from soil is the main source of DDTs in air, proportions of p,p’-DDT, o,p’-DDT and metabolite p,p’-DDE in air can be predicted from the residue composition in soils and relative volatilities of the chemicals. Higher volatility causes preferential emission of o,p’-DDT and p,p’-DDE over p,p’-DDT from soils [Kurt-Karakus et al., 2006; 2008]. This information has been applied to interpret soil-air fractionation of DDT compounds in Mexico [Wong et al., 2010] and in Chinese cities [Liu et al., 2009].

DDT is metabolized to DDE, DDD and other breakdown products. Ratios of p,p’-DDT/p,p’-DDE are often used as indicators of “fresh” (>1) vs. “aged” (<1) sources of DDT [Pozo et al., 2009], but these limits are not well defined. Kurt-Karakus et al. [2006; 2008] predicted the ratio of p,p’-DDT/p,p’-DDE in air over soil by multiplying p,p’-DDT/p,p’-DDE in soil by the ratio of liquid-phase vapour pressures, which is 0.147 at 20°C [Hinckley et al., 1990]. A survey of DDT residues in global agricultural and background soils found ratios of p,p’-DDT/p,p’-DDE ranging from approximately 0.6-4 [Kurt-Karakus et al., 2008], which when multiplying by 0.147 suggests 0.09-0.6 as an expected range of p,p’-DDT/p,p’-DDE from soil emissions.

At IADN stations on the Great Lakes, ratios of average concentrations of gas-phase p,p’-DDT/p,p’-DDE ranged from 0.25-1.4 [Sun et al., 2006]. The highest ratio was for Lake Superior, which has only ~3% agricultural activity in its watershed, while lower ratios (0.25-0.60) were found at sites on the other lakes which have a greater amount of agriculture in their watersheds. Ratios across the Canada-U.S. border and the southeastern U.S. generally ranged from ~0.1-0.9, with a few high exceptions [Shen and Wania, 2005]. Thus, emissions of old residues from soil is suggested as a
contributing factor. Greater variation was found in the Canadian Rocky Mountains where \( p,p' \)-DDT/\( \text{o,p}' \)-DDE ranged from 0.16-6.7, but unlike HCHs there appeared to be no relationship to altitude [Daly et al., 2007a]. Ratios of \( p,p' \)-DDT/\( \text{o,p}' \)-DDE in the air of Mexico ranged from 0.01-4.9 and showed a gradient from higher values in the south to lower ones in the north [Wong et al., 2009a], and a similar trend was found for soils [Wong et al., 2010]. DDT use in Mexico for malaria control was officially stopped in 2000.

Average \( p,p' \)-DDT/\( \text{o,p}' \)-DDE ratios in the air of 37 Chinese cities varied seasonally from 1.1-2.2. Taking fractionation into account, these imply ratios of 7.7-14.9 in urban soil, which would indicate a fresh source [Liu et al., 2009]. The average ratio at WBO-GAW was 0.29, which is suggestive of aged DDT, but may also be indicative of selective removal of \( p,p' \)-DDT by atmospheric deposition and degradation [Cheng et al., 2007]. Ratios of \( p,p' \)-DDT/\( \text{o,p}' \)-DDE ranging from 0.4-5.1 were reported for the Tibetan Plateau and WNR [Liu et al., 2010; Wang et al., 2010a]. Ratios of \( p,p' \)-DDT/\( \text{o,p}' \)-DDE at Lhasa, Tibet ranged from 0.1-2.4 and displayed daily and diurnal cycles with transport direction [Li et al., 2008]. The average ratio at the high-altitude WBO-GAW site was 0.29 [Cheng et al., 2007]. Zhang et al. [2008a] reported parent/metabolite ratios \( [p,p' \text{-DDT}/(p,p' \text{-DDE} + p,p' \text{-DDD})] \) ranging from 0.014-1 at multiple stations across India.

An additional source of \( \text{o,p}' \)-DDT (as well as \( \text{o,p}' \)-DDE) is contamination of the acaricide dicofol with DDT residues. The \( p,p' \)-DDT/\( \text{o,p}' \)-DDT ratio in Chinese dicofol was reported as 0.14 [Qiu et al., 2004; Qiu et al., 2005] and 0.2 in Turkey [Turgut et al., 2009]. "Dicofol-type" DDT contamination in air, as indicated by low ratios of \( p,p' \)-DDT/\( \text{o,p}' \)-DDT, was reported at some sites in China, particularly in the Pearl River Delta [Jaward et al., 2005b; Qiu et al., 2004; Yang et al., 2008]. However, the situation was re-examined by [Liu et al., 2009] who deduced that low \( p,p' \)-DDT/\( \text{o,p}' \)-DDT ratios in air of the Taihu Lake region may have been mainly due to the higher volatility of \( \text{o,p}' \)-DDT. Spencer and Cliath [1972] measured ratios were higher (0.8-0.9) at VKK and LFL. Median ratios of chlordane (CC) in a TC/CC ratio of 1.0-1.2 [Jantunen et al., 2008; Liu et al., 2010; Wang et al., 2010b] and at WBO-GAW (0.15) [Cheng et al., 2007]. Events of \( p,p' \)-DDT when \( p,p' \)-DDT was below detection were observed at Okinawa for air parcels passing over southeast China [Primbs et al., 2007]. Ratios of \( p,p' \)-DDT/\( \text{o,p}' \)-DDT averaging 0.13, 0.17 and 0.5 were reported for rural, urban and wetland sites in India, unusual since there is no reported use of dicofol in India [Zhang et al., 2008a].

Examination of DDT signatures at six arctic air monitoring stations (see above) was carried out by Su et al. [2008]. Concentrations of total DDT were considerably higher at VKK than at the other sites. Median ratios of \( p,p' \)-DDT/\( \text{o,p}' \)-DDE ranged from 0.2-0.5 at ALT, KNG, PTB and ZPN, suggesting transport of “aged” DDT. Ratios were higher (0.8-0.9) at VKK and LFL. Median ratios of \( p,p' \)-DDT/\( \text{o,p}' \)-DDT at LFL and VKK (1-1.5) were close to that expected for vapour-phase technical DDT (1.2), and lower ratios were measured at ALT, ZPN and KNG (0.3-0.8).

2.5.2.3. Chlordanes

Technical chlordane produced in the U.S.A. contained trans-chlordane (TC) and cis-chlordane (CC) in a TC/CC ratio of 1.0-1.2 [Jantunen et al., 2000; Mattina et al., 1999]. The slightly high vapour pressure of TC [Hinckley et al., 1990] raises the expected TC/CC ratio in equilibrium with technical chlordane to 1.4-1.7 in the temperature range 0-25°C. Technical heptachlor is reported to contain 20-22% TC [WHO, 2006], thus applications of heptachlor may act to increase TC/CC in the environment. Ratios of TC/CC in U.S. cities and Toronto, Canada where chlordane was applied as a termiticide ranged from 1.1-1.9 [Gouin et al., 2007; Offenberg et al., 2004]. TC/CC ratios characteristic of “aged” chlordane are generally lower and more variable in rural and background air, e.g. 0.72-0.95 in the Great Lakes region [Gouin et al., 2007; Sun et al., 2006] and often show a seasonal cycle of lower ratios in summer than winter [Gouin et al., 2007]. TC/CC ratios across North America ranged from 0.1-1.6 and were strongly correlated with TC + CC concentrations. Higher ratios and concentrations were found near urban centres [Shen et al., 2005].
Median TC/CC ratios were 0.3-0.7 at arctic air monitoring stations, and \textit{trans}-nonachlor (TN) was elevated over its proportion in the vapour phase of technical chlordane. Although these signatures generally indicate “aged” chlordane, stations PTB and VKK showed the highest ratios. Moreover, events of TC/CC ~1.5 were occasionally observed at PTB and were associated with elevated heptachlor concentrations. Thus, PTB may be under the influence of recent chlordane emissions. Trends of high TC/CC in winter-spring (mean 0.55) and low in summer-fall (mean 0.30) were observed at ALT, KNG, LFL and ZPN, although this trend was not followed at PTB. While TC was depleted during summer, oxidation products oxychlordane (OXY) and heptachlor epoxide (HEPX) were elevated [Su et al., 2008]. The annual mean TC/CC ratio declined from 0.72 to 0.45 between 1984-1998 [Bidleman et al., 2002]. It was speculated that TC is less stable photochemically than CC, resulting in its depletion during summer [Bidleman et al., 2002 and references therein]. Summertime TC/CC ratios in air over the northern North Atlantic and Arctic Ocean ranged from 0.04-0.88 and averaged 0.24 [Lohmann et al., 2009].

Ratios of TC/CC along a north-to-south transect in Chile were 0.92-1.15, except in the city of Concepción, where a very high ratio of 3.9 was found. This sample also contained a relatively high concentration of heptachlor, so perhaps TC contamination of technical heptachlor accounted for the high TC/CC ratio [Pozo et al., 2004].

China also manufactured chlordane and analysis of one product gave a TC/CC ratio of 0.76 [Li et al., 2007]. A survey of 37 cities in China showed seasonal variation in TC/CC with higher mean values in summer (0.59) and fall (0.61) than in winter (0.25) and spring (0.38). This is the opposite cycle to that found in North America and the Arctic, where lower ratios occur in summer (see above). TC/CC ratios at urban, rural and wetland sites in India ranged from 1-5 [Zhang et al., 2008a]. At MBO in Oregon, mean TC/CC ratios during transpacific transport events were significantly higher for air from the marine boundary layer (1.39) than in the free troposphere (0.87) [Primbs et al., 2008a]. Air outflowing from mainland Asia and samples at Okinawa showed TC/CC averaging 1.2 [Primbs et al., 2007]. TC/CC at sites near Lhasa, Tibet spanned a wide range from 1.13 to 3.49 [Li et al., 2008] and averaged 0.89 at WBO-GAW [Cheng et al., 2007].

From the discussions above, interpretation of compound ratios is a complex matter. Uncertainties arise from shifting patterns of product usage and variation in technical mixture compositions. Differences in physicochemical properties lead to fractionation of isomers and metabolites when undergoing air-surface exchange and further alteration in ratios may result from differences in atmospheric reactions. Interpretation of compound ratios is best carried out in concert with other tracers such as enantiomers (for chiral compounds), combustion products [Genualdi et al., 2009a; Primbs et al., 2008a] and isotopes [Cheng et al., 2007] and diagnostic characteristics of air pathways (trajectories, air boundary layer height, etc.).

2.6. Effects of Climate Variations on LRT and Trends

Observations provide field evidence of relationships between climate events and environment fate of POPs. Continuous monitoring in air has been conducted for approximately 15 year (Table A.2.1 in Appendix A). Available time series of POPs measurement from atmospheric monitoring programs (Table A.2.1) can address the interannual (1-10 years) time scale. The suspected most significant regional-scale climate variation patterns influencing atmospheric levels of POPs on this time scale in the Northern Hemisphere are the North Atlantic Oscillation (NAO) and the El Niño-Southern Oscillation (ENSO). Recent studies have reported that seasonally-averaged POPs air concentrations exhibit the strongest response to the NAO and ENSO during winter and spring, due primarily to more prominent atmospheric circulation patterns occurring in these seasons [Ma et al., 2004a]. Summer air concentrations of POPs (e.g., \textit{\alpha}-HCH and light PCBs) measured over the North American Great Lakes suggest a lag response to preceding winter and spring monthly sea surface temperature anomalies in the tropical Pacific [Ma and Li, 2006]. These are related to ENSO events. The analysis on the connection between POPs and atmospheric circulation in North America indicated that a warmer-than-normal spring in POPs source regions enhances volatilization of POPs from contaminated terrestrial surfaces. Stronger zonal flow patterns associated with the positive NAO and El Nino events were found to be conducive to the transport of POPs from sources to measurement.
sites [Ma et al., 2004b]. On the other hand, during the La Nina events (anti-ENSO), stronger meridional winds favour stronger transport of air pollutants to the Arctic [Zhang et al., 2009].

As POPs total environmental residence times are expected to be mostly in the range 1-10 years, [e.g., Fenner et al., 2005; Lammel et al., 2007], climate variability on the interannual time scale may interfere with POPs atmospheric cycle (residence time in air typically days-weeks), e.g. by influencing air-surface exchange / mobilization of reservoirs surface waters and sediments. Special attention has been paid to more volatile POPs, e.g., HCH, HCB, and low-molecular weight PCBs [Ma et al., 2004b], because these substances' atmospheric levels are affected by air temperature.

Given that the increase in average annual temperatures in the Arctic is approximately double that in global average temperatures, POPs monitoring programs in the Arctic provide valuable data to fingerprint the impact of climate warming on environmental fate of POPs. Figure 2.7 shows the weekly time series of normalized γ-HCH air concentration anomalies and detrended γ-HCH from 1993 – 2008 at Zeppelin, Svalbard (78° 55' N, 11° 56' E).

The linear trends of weekly moving averaged mean air temperature and sea ice concentration anomalies, normalized by their respective standard deviation, averaged over the Arctic, are also plotted in the figure. In contrast to the measured declining trend, detrended α-HCH underwent an increasing trend, corresponding to increasing Arctic mean air temperature and decreasing sea ice concentration.

This suggests likelihood of the influence of Arctic warming and ice melt on POPs' atmospheric cycling. As seen, the interdecadal warming and ice retreat trend in the Arctic seems to be already reflected in the residual (detrended) time series of γ-HCH.

![Figure 2.7. Anomalies of weekly γ-HCH air concentration, normalized by its standard deviation, detrended normalized γ-HCH anomalies, linear trend of mean surface air temperature (SAT) and ice concentration over the Arctic.](image)

Other than the NAO, the Arctic Oscillation (AO) is today considered as another important circulation pattern that affects climate change and atmospheric transport of air pollutants to the Arctic. In particular, the AO describes wind speed/direction and precipitation rates at a Pan-Arctic scale [Becker et al., 2008]. The correlation of negative and positive phases of the AO to HCH concentrations was investigated in a recently published study [Becker et al., 2008]. The Dynamic Harmonic Regression (DHR) model fit was applied on the respective datasets available for both stations Alert and Zeppelin [Becker et al., 2008]. A correlation to AO fluctuations was found in the α-HCH time-series at Zeppelin, but not at Alert (Figure 2.8).
Influence of AO on the atmospheric distribution of $\alpha$-HCH in Zeppelin air data. The DHR model fit is represented by the $R^2$ and uncertainty is to within 95% confidence limits. Dashed lines represent the expected differences between summer and winter concentrations assuming a constant decline, according to Becker et al. [Reprinted from Figure 2B from Becker, S., et al. (2008), Long-term trends in atmospheric concentrations of alpha- and gamma-HCH in the Arctic provide insight into the effects of legislation and climatic fluctuations on contaminant levels, Atmospheric Environment, 42(35): 8225-8233, with permission from Elsevier.]

The differences in intra-annual pattern distributions indicate that much larger concentration variations between the summer and winter months are occurring during the years when AO is in the negative phase (after year 2000). During positive AO years (before year 2000) the concentration difference between summer and winter is much less pronounced. The dashed lines in Figure 2.8 show the predicted variation in summer maxima and winter minima assuming a constant decline in $\alpha$-HCH air concentrations throughout the time series [Becker et al., 2008].

Although the method of Becker et al. [2008] is very intriguing, there are further aspects to be considered. On one side, the AO/NAO index was relatively stable and positive for several years until 1995, but much more variable and on an average neutral since 1995, while the $\alpha$-HCH annual variability signature has emerged in the latter period of AO variability. Another aspect to be considered is the fact that the NAO/AO has a distinct but delayed impact on sea ice cover and dynamics in the Arctic Ocean. It is hypothesized, [e.g., Stroeve et al., 2008], that the period of persisting high positive NAO/AO in the early 1990s triggered a massive export of multi-year ice out of the Arctic Basin through the Fram Strait and thus influenced the recent dramatic summer sea ice extent in the region decisively. The change in the sea ice regime may have promoted the re-emission of HCH from intermediate storages (the ocean) to become the most important source of HCH nowadays (as discussed in Section 2.2.3.2), which shows a more pronounced annual variation in accordance with sea ice extent.

Sediments and ice cores, covering longer time scales ($>>$ 10 years) provide proxy data sets for POPs in atmospheric deposition. Again, the separation between usage patterns and climate variability has hardly been addressed. Several recent analyses from POPs time series in the ice cores collected from Alps and Mt. Everest glaciers have reported evidence that global warming may affect long-term POPs trends [Bogdal et al., 2009; Wang et al., 2010b].
2.7. Assessing the Effectiveness of Control Measures – Observational Data and Quality Assurance

Article 16 of the Stockholm Convention on POPs calls for monitoring data and information on long-range transport to contribute to the assessment of the effectiveness of the Convention. The effectiveness of the Convention will be assessed from three sources of information – i.) a global monitoring report; ii.) national reports and iii.) non-compliance information. For the first global monitoring report of the Convention, core media of air and human tissues were selected. Air was chosen because of its uniformity across all regions and because it is the major conduit for the long-range transport of POPs. The United Nations Environment Programme (UNEP) has prepared a Guidance Document for the global monitoring plan. This ‘living document’ provides information for analysis, sampling and interpretation of monitoring data for trends and in the context of long-range transport and confounding factors such as climate effects. The first global monitoring report adopted at COP4 in Geneva (May 2009) presents the baseline situation for POPs in air and human tissues against which future reports will be compared. The COP decided that reports shall be prepared on a schedule of every 6 years. The COP also adopted several recommendations of the first GMP that relate to measurement campaigns for POPs and how this data is applied. These recommendations were considered further during an HTAP-sponsored workshop in St. Petersburg, Russia (April 2009) dealing with the future of global air monitoring. Key topics/messages are highlighted below.

There is currently a less formal and less structured effectiveness and sufficiency review process under the CLRTAP POPs Protocol. For the first review, conducted three years after the Protocol entered into force, Parties at a session of the Executive Body as described under Article 10 of the Protocol (http://www.unece.org/env/lrtap/pops_h1.htm) reviewed the Protocol, taking into consideration technical and economic documents prepared for this purpose by subsidiary bodies and task forces. For issues related to compliance, the Implementation Committee shall report to the Parties as described under Article 11 of the Protocol.

**Data Comparability Issues.** It was recognized that within-program comparability is crucial for producing reliable temporal trends for EE. This can be assured by adopting and maintaining proper QA/QC measures of sampling and analysis, using reference materials and through intercalibration exercises. Strategies for improving comparability between programs should also be adopted with the intention to produce a common database/dataset that can be used by end-users of data e.g. modelers. It was recognized that sources of uncertainty between different programs include a much broader scope of issues such as sampler type, frequency of sampling, sample handling and analysis, data handling, reporting and interpretation. It is unrealistic to call for a harmonization of all of these steps as this might disrupt the integrity of the valuable time series that have already been produced. A less invasive approach to assess and improve comparability between programs could be to overlap at least one monitoring station between two or more programs.

**New POPs.** The addition of new POPs to the SC on POPs and CLRTAP POPs protocol will add to air monitoring obligations and challenges of existing programs. The group agreed that it is useful to include new POPs and relevant precursors as target analytes investigated under existing monitoring programs for air so that baselines in air can be established. It was recognized that in some instances air may not be the optimum medium (e.g. ionic compounds).

**LRT, climate variability and meteorological variability.** The group recognized that to better understand monitoring data it was essential to incorporate information of transport, and influences associated with variability in climate and meteorology. Understanding data is more important than just reporting levels and trends, especially for the purpose of assessing effectiveness of regulatory efforts on POPs.

It is important to develop tools (e.g. back trajectory techniques, multimedia and transport models and investigations of meteorological and climate variability) to better interpret monitoring data. Meteorological analyses are also recommended for providing information that may assist in the selection of new sites under new monitoring programs.
Existing and new air programs. To help ensure long-term sustainability and comparability of results, it is recommended that new programs grow from strategic partnerships with existing programs, and benefit from their experiences. Training visits for the purpose of capacity building/technology transfer are encouraged and should be supported.

Data availability. Improved access to data would be useful for several purposes e.g. model development. Existing and new programs are strongly encouraged to incorporate data management in their programs, i.e. employ sustainable databases. Consideration should be given to the most suitable format and interface for end users of the data e.g. modelers. There are many benefits to including data management tools (e.g. graphing, mapping, and statistical analysis) as part of the data storage applications.

2.7.1. International QA/QC Efforts on POPs

As discussed above, comparable data are essential for data interpretations (e.g. assessing temporal and spatial trends) and model evaluation. POP measurements in various locations are mostly conducted with different sampling techniques and by different analytical laboratories. For a specific laboratory, analytical methods evolve over time, and analytical capability and experience may also vary with time. Although strict quality assurance and quality control are implemented by each laboratory, measurement discrepancies are inevitable.

A number of inter-laboratory studies were previously carried out to assess variability in different air sampling techniques [Blanchard et al., 2006; Wu et al., 2009], and in analyzing organic chemicals for standard solutions and air samples by different laboratories [Audette et al., 2009; Bidleman et al., 2004; Harner and Kucklick, 2003; Mano and Schaug, 2003]. Apparent inter-laboratory variability was observed in various extents for different analytes. A recent inter-laboratory study was conducted under the International Polar Year project of Intercontinental Atmospheric Transport of Anthropogenic Pollutants to the Arctic [Su and Hung, 2010]. Twenty-one participating laboratories from seven countries compared analytical results for four classes of chemicals: polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), and organochlorine pesticides (OCPs). A tiered approach was set up to trace factors contributing to the inter-laboratory variability through the analysis of: (i) a high-concentration standard solution for each chemical class; (ii) a low-concentration standard solution for each chemical class; (iii) a blind sample composing of a mixed standard solution of the four chemical classes; (iv) an extract of an ambient air sample; and (v) a standard reference material of urban dust (SRM 1649a). Inter-laboratory variability, measured by relative standard deviation (%), was in the range of 10-27% in analyzing standards. However, much larger inter-laboratory variability (27-141%) was found in analyzing POPs in air samples. These results are generally in line with previous inter-laboratory comparison studies. The air samples were cleaned up with various methods by different laboratories, whereas the standards were injected directly for analysis. It was concluded that the major cause for inter-laboratory variability in analyzing air samples is likely related to the sample cleanup process. In general, up to a factor of 2 difference in analyzing air samples can be expected between different laboratories.

2.8. Findings and Recommendations

1. FINDING: Atmospheric monitoring programs provide adequate spatial coverage of atmospheric concentration information of most POPs and other SOCs. Only few air monitoring programs include measurements of these compounds in precipitation from which deposition can be estimated.

RECOMMENDATION: Existing atmospheric and precipitation monitoring programs for POPs need to be continued to provide temporally- and spatially-resolved concentrations and deposition information. To understand how transport and concentrations of these pollutants change with time, the sampling and analytical methods of these programs should remain consistent over time, ensuring that results generated remain comparable.

2. FINDINGS: Long-term air monitoring programs provide temporal trends with a time span of approximately 15 years.
a) In some cases, declining time trends of some substances, e.g. technical HCH, responded to international controls. However, some POPs showed slow or no significant decline in air in response to control, e.g. \( p,p' \)-DDT at the arctic stations of Alert and Pallas.

b) Correlations between these time trends with climate change parameters, e.g. surface air temperatures and sea ice extent etc., and with low-frequency climate variation patterns, e.g. the AO and NAO, have been observed.

RECOMMENDATIONS:

(a) Existing air monitoring efforts should be continued to generate long-term trends to assess the effectiveness of international control initiatives. It is noteworthy that a non-declining atmospheric trend at remote locations may not necessarily indicate ineffectiveness of control. The time required for the target chemical to reach a specific receptor region is influenced by the relative locations of the source and the receptor, the chemical’s transport pathways and its physical chemical properties. Proper interpretation of temporal trends requires an understanding of these influencing factors which can be estimated using appropriate transport models.

(b) Climate change and variations occur on a decadal-scale. To understand how climate change and variations affect the transport and behaviour of POPs in the environment, measurements in environmental media, including air, must be continued to provide temporal trends spanning over similar time-scales as climate change observations, i.e. over decades.

3. FINDING: Spatial resolution for air measurements have increased considerably due to the adoption of passive air sampling methods.

RECOMMENDATION: Passive air sampling programs should be sustained to ensure the ability to develop temporal trends and can be expanded to cover regions where measurements are currently not available. Further development of passive air sampling techniques to include measurements of more polar new chemicals is important for understanding their transport patterns and evaluating the need to control these substances.

4. FINDING: Oceanic measurements were mainly collected via one-time cruise-based studies. There are evidences showing more polar chemicals can be transported over long distances via ocean currents. For multi-hoppers and swimmers, ocean water is also an important partitioning medium, a sink or a source.

RECOMMENDATION: There is a need for continuous measurements of POPs in ocean water to gain a better understanding of the transport behaviour of swimmers and multi-hoppers.

5. FINDINGS: Similar to cold regions at high latitudes, mountains represent convergence zones for POPs due to orographic cold trapping. There is broad evidence for an enrichment of organic contaminants at remote high altitude sites and in peripheral mountain zones exposed to the (often densely populated) lowland. Pollutant loads can be attributed to sources in the adjacent lowlands, but also to transcontinental and transmontane pollutant transport or local emitters. Mountains comprise sensitive ecosystems and are often close to pollutant source areas. In many regions mountains play a vital role in the drinking water and food supply.

RECOMMENDATIONS: The monitoring activities and studies on POPs in various mountain ranges should be continued to improve the understanding of the role of mountains in the global transport and distribution of POPs and their accumulation in mountain ecosystems. There is a strong need for concerted research including different disciplines (e.g. chemistry, biology, meteorology, toxicology and modelling) and environmental matrices.

6. FINDING: POPs are enriched in aquatic organisms at high altitude sites. The (eco-) toxicological impacts of the observed loads are not known. Studies on the POP accumulation in terrestrial and agricultural food chains in mountain regions are lacking.

RECOMMENDATIONS: These gaps of knowledge should be closed by bioaccumulation and effects studies in mountain ecosystems.
7. FINDING: Climate change and accelerated melting of glaciers enhance the release of POPs that were deposited and accumulated in glaciers during earlier times of higher emissions.

RECOMMENDATIONS: The release of POPs from glaciers in alpine and polar regions should be measured and coupled with modelling approaches to forecast its impact on the downstream ecosystems, and drinking water supplies.

8. FINDING: First modelling studies allow a much better understanding of how POPs are specifically enriched in mountains. The results suggest that cold condensation (change of the chemicals from the gas phase to particles, raindrops, snowflakes) along temperature gradients together with the more efficient atmospheric washout are relevant for higher POP deposition in mountain regions.

RECOMMENDATIONS: The promising modelling approaches should be continued, further field studies are needed to validate the models. Modelling should be extended to predict input, accumulation and release of POPs in different matrices in mountain regions. The final goal of such modelling studies should be the prediction of the mountains’ role in global transport and distribution of organic contaminants.

9. FINDING: Air pollution is transported across the Atlantic either from North America to Europe/ Africa or vice versa (see Part A). However, almost no evidence with regard to POPs being part of this intercontinental transport exits. High POP concentrations were found in regions of Africa and Eastern Atlantic which may act as a source to the Americas.

RECOMMENDATION: Surveillance of possible trans-Atlantic transport of POPs is needed as being essential for the assessment of source regions and implications for regulation.

10. FINDING: Other than air, there are limited measurements and few organised monitoring of POPs concentrations in media other than air, e.g. precipitation, dry deposition, ocean, snow, soil and vegetation. Air-surface interaction studies are limited to few groups of compounds, e.g. PCBs, HCHs and some OCPs.

RECOMMENDATION: Integrated monitoring of various media within the same vicinity is essential for understanding partitioning processes that influence transport and estimating flux for model validation and parameterization. Due to the extensive spatial distribution of the atmospheric monitoring sites, it is recommended that existing air monitoring programs measure POPs in other media at the same location, e.g. soil, water, snow and precipitation, to assess air-surface interactions. It is also important to develop an inventory of POPs in sinks, such as soil and ocean water, in order to assess secondary emissions and subsequent transport, especially for legacy POPs that are showing a shift from primary to secondary sources.

11. FINDING: The knowledge of POP abundances and chemodynamics in morphologically heterogeneous compartments (e.g. soil and snow) is very limited. 'Aging' of chemicals in soil, sintering in snow and determining environmental parameters are hardly understood. The same applied for biodegradation in soil and ocean, for many POPs the most significant sink process.

RECOMMENDATIONS:

(a) There is a need to better characterise heterogeneous media, e.g. the ability of different organic matter and mineral matter types in soil and underlying water to retain POPs and other SOCs.

(b) Extend descriptions of soil-air partitioning that go beyond the $K_{OA}$ approach, taking into account the quality of organic matter, various types of chemical interactions of the chemical substance with organic matter, carbonaceous geosorbents and mineral matter, and its dynamics (which includes 'aging' of the substance in the soil).

12. FINDING: Soils are a major reservoir for POPs and source of primary and secondary emissions to the atmosphere.
RECOMMENDATIONS:
(a) Expand large-scale monitoring of POPs in air and soil to validate long-range transport and surface exchange models for the study of the environmental behaviour of legacy chemicals and those of emerging concern.
(b) Improve field-scale pesticide emissions inventories for POPs by modelling situations in which flux measurements have been made.
(c) Improve large-scale emission/residue inventories for POPs by comparing temporally and spatially modelled results with measurements in monitoring programs.
(d) Improve modelling capability by combining the multimedia fugacity and dynamic (meteorologically driven) approaches to describe the temporal variations in chemical concentrations, inter-compartmental transfers, and transport dynamics on global and regional scales.

13. FINDING: Air-water gas exchange is a major loading process of POPs to oceans, seas and large lakes.

RECOMMENDATIONS:
(a) Improve measurements and modelling of physical-chemical properties, especially for Henry’s Law constants (HLCs). Work to eliminate or minimize experimental artefacts in their determination, expand the data base for HLCs as functions of temperature and salinity and measurements of HLCs for emerging chemicals of concern.
(b) Develop techniques to provide better speciation of the "truly dissolved" and "truly gaseous fractions of SOCs so more accurate gas exchange estimates can be made. Revisit the surface microlayer as an accumulation and exchange reservoir for POPs.
(c) Improve estimates of mass transfer coefficients to reduce the uncertainty in gas flux estimates. Extend models to include water surfaces with broken ice for applications in polar regions.
(d) Apply micrometeorologically based experimental techniques to determine gas exchange fluxes for comparison to model estimates.

14. FINDING: Chiral analysis is useful for distinguishing primary versus secondary emission, historical versus fresh usage and local versus distant sources.

RECOMMENDATION: Continue using chiral chemicals as indicators of different types of sources, climate effects on diagenesis in soil and tracers of long-range transport of POPs.

15. FINDING: There are few reference materials available for interlaboratory validation of chiral analytical methods.

RECOMMENDATION: Expand the availability of reference materials for chiral chemicals; e.g., soils, sediment and biota.

16. FINDING: Ratios of isomers and parent/metabolite compounds are useful indicators of sources and chemical aging.

RECOMMENDATIONS:
(a) Characterize technical products of POPs pesticides (e.g., HCH, chlordane, heptachlor, DDT, dicofol, toxaphene) as starting points for understanding emission sources.
(b) Improve estimates of soil-air and water-air fractionation to understand how these processes alter compound ratios from source to sink.
(c) Use compound ratios in combination with other tracers (e.g., enantiomers, isotopes and combustion markers) to distinguish sources.

17. FINDING: Uncertainties in physical chemical properties (e.g. Henry’s Law constants (HLCs), vapour pressures and octanol-air partition coefficients) of some POPs and SOCs, and the lack of
such measurements for new and emerging chemicals, render the understanding of air-surface exchange processes and the role that they play in long-range transport difficult.

RECOMMENDATION: In order to understand the impact of climate change on the intermedia exchange and long-range transport of chemicals, there is a need to improve estimates of temperature- and salinity-dependent physical chemical properties and minimize experimental artefacts in their determination, especially for new and emerging chemicals which such information is lacking.

18. FINDING: Due to its physical properties and dynamics snow greatly interferes with the fate of POPs in the atmosphere. Processes related to scavenging from the atmosphere and atmosphere-snow exchange of POPs are currently not adequately described in contaminant fate models, mainly due to the lack of measured field data and laboratory investigations.

RECOMMENDATION: In order to gain a quantitative understanding of these processes, complementary field, laboratory and modelling studies are needed. Specifically, the influences of physical snow properties such as snow layering and surface roughness, as well as of photooxidation within the upper snow layers need to be investigated. Further, methods should be developed to characterize the potential for scavenging and atmosphere-snow exchange in dependence on climatic and meteorological conditions in order to facilitate integration of those processes into large-scale models.

19. FINDING: There is evidence that climate change phenomena, e.g. elevated temperatures and sea-ice reduction, and extreme climate events, such as forest fires, flooding and glacial melting, will remobilize POPs previously deposited in sinks, e.g. forest soils and vegetations, ocean and lake sediments and glacier.

RECOMMENDATION: There is a need to estimate the amount of POPs that would be re-released by foreseeable climate change conditions by developing residue inventories through measurements in potential sinks, e.g. soils, forests, oceans, sediments and glaciers.

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Chapter 3

Emission Inventories and Projections for Assessing Hemispheric or Intercontinental Transport of Persistent Organic Pollutants

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3.1. Introduction

To reduce the adverse effects of persistent organic pollutants (POPs) and to monitor the effectiveness of existing international agreements concerning POPs, especially the United Nations Economic Commission for Europe (UNECE) and United Nations Environment Programme (UNEP) protocols, the compilation of emission inventories is required. This chapter addresses emission inventories for POPs which are covered by existing protocols, as well as candidate substances which are being considered under the revision of the international protocols (See Section 1.3.2 Old POPs and new POPs). The following substances will be taken into account in this chapter:

- Dioxins and furans (PCDD/F), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), hexachlorobenzene (HCB), pesticides (e.g., HCH, Dicofol and Endosulfan), perfluorooctansulfonate (PFOS), polybrominated diphenylethers (PBDEs), hexachlorobutadiene (HCBD), pentachlorobenzene (PeCB), polychlorinated naphthalenes (PCN), and pentachlorophenols (PCPs).

For all considered substances, emission inventories exist with different qualities, from preliminary estimates to more complete inventories. These inventories are based on different methodologies (measurements, modelling, mass balance approaches, etc.), cover different regions (Europe, North America, Asia, China, etc.) and represent different spatial scales (regional, global) with different spatial resolutions. An overview is given of the current state of the knowledge through a description of the main sources for the specific pollutants, the recent emission levels, and the historical emission levels, including time series and gridded data bases, if available. Furthermore, recommendations to improve POP emission inventories, as well as major obstacles to achieve these improvements, is given.

A further focus of this chapter will be an overview of future trends of specific POPs (e.g., PCB and PCDD/F) until 2050, with special emphasis on the different approaches for compilation of future scenarios for specific substances. The following key questions concerning compilation of projections will be considered here:

- Do we have sufficient data on emissions and the trends in driving forces needed for making reasonable future projections?
- How might emission quantities and spatial distributions change over the next 20 to 50 years?
- How will different source categories change?

3.2. Emission inventories

Knowledge about sources and emissions of POPs into the environment are essential for policy makers to make a plan to reduce the burden of POPs in the environment and also for the scientific communities to understand, quantify, and predict the source-receptor relationships.

There are many different kinds of emission inventories, as reviewed by Breivik et al. [2002a; 2002b; 2007]. To meet the objectives of the Task Force on Hemispheric Transport of Air Pollution (TF HTAP) under the Convention on Long Range Transboundary Air Pollution (CLRTAP), our research on emission inventories for POPs focuses on development of global gridded emission inventories and those gridded emission inventories on regional scales that can contribute directly to
those on a global scale, which can be used by the global transport models to simulate hemispheric/global transport of POPs.

We divide POPs into two categories, agricultural and industrial, due to the very different methodologies to create the emission inventories of these two different kinds of POP substances. The agricultural POPs include all pesticide POPs, such as Aldrin, Dieldrin, Endrin, Chlordane, Heptachlor, Toxaphene, HCHs (technical HCH and lindane), DDT, Endosulfan, and Dicofol, and the industrial POPs include PCBs, PCDDs/Fs, Chordecone, HBB, PAHs, PentaBDE, OctaBDE, (PeCB, PFOS, PFOA, HCB, PCNs, Short chained chlorinated paraffins (SCCP), HBCD, Trifluralin, and PCP. Some POPs, such as HCB and Mirex, belong to both categories. Pesticide POPs are used on crops by three basic application modes, spray or dust application, soil incorporation, and seed treatment, each having an inherent timing in the crop growing season [Li et al., 2000]. After application, major portions of pesticides release directly into the soil, and will emit to the air for many years to come. Thus the soil residue inventories are crucial to produce the emissions of pesticide POPs.

The industrial POPs may be primarily attributed to their production and use, or through some industrial processes. In both cases, the emitted POPs will deposit into environmental reservoirs, such as soil and water bodies, and re-emit to air through sea-air and soil-air exchange, forming the secondary emissions. As time goes on, the secondary emissions will become stronger and stronger, and supersede eventually the primary emissions.

Although the emission inventories should include both primary and secondary emissions, all emission inventories introduced in this Chapter consider primary emissions only. The secondary emissions are mainly covered by environmental fate modelling and in principal are not an issue of emission inventories. On the other hand, the POP reservoirs from former industrial activities re-emit permanently, generating the environmental background concentration. Therefore it is necessary also to compile emission inventories in the future that consider both primary and secondary sources.

Emission factors are crucial for quantifying the emissions of POPs. Emission factors for pesticide POPs represent the emission potential of pesticides in a geographic area and are not emission estimates on their own. The emission factors of pesticides are a very complicated function of a large number of variables, such as the physical and chemical properties and application modes of the pesticides, the local meteorological conditions when they are applied, the soil type, and the temperature. Based on one-year overall emission factors for some pesticides estimated by Scholtz et al. [1997; 1998], annual emission factors were developed for sparing and tilling events for some selected pesticides and were used to estimate the emissions for both currently-used pesticides and the pesticides released into soil due to their use in previous years [Jia et al., 2009a; Jia et al., 2009b; Li et al., 2000; Li, 2001; Li et al., 2001a; Li et al., 2001b; Li et al., 2003].

The compilation of emission factors for industrial POPs in different sectors (industrial processes) is more challenging. The UNECE derived (preliminary) emission factors for the basic process or activities responsible for emissions of the eight candidate POPs, Hexabromobiphenyl, HCB, PBDE, PeCB, PCN, PCP, Endosulfan, dicrof, and SCCP. The procedure of emission factor development by substance is described in more detail by Denier van der Gon et al. [2005; 2007] and Van het Bolscher et al. [2005]. The only candidate POP for which some official reported data are available is PCP.

3.2.1. Global inventories and databases

The efforts to develop global gridded emission inventories can be traced back to the end of the 1990s and the beginning of the 2000s, when global gridded technical HCH usage inventories were published in Li [1999a; b], global gridded α-HCH emission inventories in Li et al. [2000] and global gridded β-HCH emission inventories in Li et al. [2003].

In 2002, Breivik et al. [2002b] presented a global historical emission estimate for selected PCB congeners. And in 2009, Zhang and Tao [2009] compiled global emission inventories for PAHs. A toolkit for compiling national inventories for dioxines and furans on a global scale has been published by UNEP [1999]. A global HCB emission inventory has been compiled by Bailey [2001]. And, a global PFOS emission inventory has been compiled by Paul et al. [2009].
Global $\alpha$- and $\beta$-HCH emission inventory

Technical HCH is the most widely used pesticide in the world. According to Li [Li, 1999b], global technical HCH usage from 1948 to 1997 was estimated to be around 10 million tonnes (t), far more than the tonnage of any other pesticide used in history. Based on global technical HCH country usage data between 1948 and 1997 [Li, 1999b], a gridded usage data of this insecticide on a 1°×1° longitude/latitude grid system has been produced by using the gridded cropland as the surrogate data [Li, 1999a]. The gridded global annual emissions for $\alpha$–HCH for 1980 are given in Figure 3.1. The total global usage of $\alpha$–HCH is estimated to be around 312 kilotonnes (kt) in 1980 and 52.5 kt in 1990. Total global $\alpha$–HCH emissions in 1980 are estimated at 217 kt, among which 95.5% is contributed by the 1980 current year usage and 4.5% by the residues due to usage in the previous 10 years. Total global $\alpha$–HCH emissions in 1990 are estimated at 37 kt, among which 92.9% is contributed by the 1990 current year usage and 7.1% by the residues due to usage in the previous 10 years.

The gridded global annual emissions for $\beta$-HCH for 1980 are given in Figure 3.2. Total global $\beta$-HCH emissions to the atmosphere in 1980 were 9.8 kt, of which 82.8% was contributed by the current use of $\beta$-HCH in 1980 and 17.2% by the residues due to use of technical HCH since 1966. Total global $\beta$-HCH emissions in 1990 were 2.4 kt, of which 78% was contributed by the current use of $\beta$-HCH in 1990 and 22% by the residues due to use of technical HCH since 1976.

Figure 3.1. Gridded global annual emissions for $\alpha$–HCH in 1980. [Reprinted from Figure 5c in Li, Y. F., et al. (2000), Global gridded emission inventory of $\alpha$-hexachlorocyclohexane, Journal of Geophysical Research, 105(D5): 6621-6632.]
For α-HCH, the dominant pathway for transport to the Arctic is through the atmosphere. Evidence for this is the strong link between concentration in Arctic air and the global usage and emission patterns of this compound from 1979 to the early 1990s, when the usage/emissions of technical HCH were still high (see Figures 3.3 and 3.4) [Li et al., 1998; Li and Bidleman, 2003]. The key role of atmospheric transport was further demonstrated in a mass balance model for α-HCH in the Arctic [Li et al., 2004].
Global γ-HCH soil residue inventory

The global γ-HCH soil residue inventory for 2005 is illustrated in Figure 3.5 [Zhang et al., 2008a]. As shown in Figure 3.5, the major sources of γ-HCH across the world in 2005 were in India, China, central Europe, and the Canadian Prairie provinces. The total soil residues of γ-HCH in 2005 were estimated to be 13600 t in the world and 1900 t in China, 3000 t in India, 1200 t in the Former Soviet Union (FSU), 3700 t in Europe and 2200 t in North America (NA). The total amount of γ-HCH in soils of the five regions is 88% of global total residues. It was found that Lindane was still being used in India in 2005 [Abhilasha and Singh, 2008].

Global inventories and databases for PAHs

It was estimated that the total global emission of 16 polycyclic aromatic hydrocarbons (PAH16) was 520 kt in 2004, including naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene,
anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene, indeno(1,2,3-cd)pyrene, and benzo(g,h,i)perylene), listed as the US Environmental Protection Agency’s priority pollutants [Keith and Telliard, 1979]. The major sources of PAHs were straw and firewood burning, wildfire, and consumer product usage, which contributed 31.3%, 25.4%, 17.0%, and 6.9%, respectively [Zhang and Tao, 2009]. Other sources included motor vehicles, domestic coal combustion, coke production, petroleum refineries, waste incineration, aluminum electrolysis, and so on. The emission quantities and relative contributions to the atmospheric emission of PAH16 of various combustion sources are listed in Table 3.1.

Table 3.1. Contributions of various emission activities to the global emission of PAH16 in 2004 (in sum 520 kt) [Zhang and Tao, 2009].

<table>
<thead>
<tr>
<th>Source</th>
<th>Emission(Gg)</th>
<th>Share (%)</th>
</tr>
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<tbody>
<tr>
<td>Firewood</td>
<td>132</td>
<td>31.3</td>
</tr>
<tr>
<td>Straw</td>
<td>163</td>
<td>25.4</td>
</tr>
<tr>
<td>Wildfire</td>
<td>88.4</td>
<td>17.0</td>
</tr>
<tr>
<td>Consumer product usage</td>
<td>35.9</td>
<td>6.9</td>
</tr>
<tr>
<td>Motor vehicle</td>
<td>25.0</td>
<td>4.8</td>
</tr>
<tr>
<td>Domestic coal</td>
<td>19.2</td>
<td>3.7</td>
</tr>
<tr>
<td>Coke production</td>
<td>18.7</td>
<td>3.6</td>
</tr>
<tr>
<td>Petroleum refinery</td>
<td>12.5</td>
<td>2.4</td>
</tr>
<tr>
<td>Waste incineration</td>
<td>9.9</td>
<td>1.9</td>
</tr>
<tr>
<td>Aluminium electrolysis</td>
<td>7.3</td>
<td>1.4</td>
</tr>
<tr>
<td>Other</td>
<td>7.8</td>
<td>1.5</td>
</tr>
</tbody>
</table>

The source distributions of different countries are different depending on their socio-economic and physical conditions, particularly energy structure, status of development, and vegetation coverage. In China, straw and firewood burning in rural families contributed two thirds of the total emissions, while small-scale coke accounted for over 20% of the total emissions. It is expected that the small-scale coke ovens will be phased out in a few years, leading to a significant decrease in the total emission in China. The percentage of biomass burning to the total PAH emission was over 90% in India, where firewood, straw, and animal dung were the main fuels in rural areas. In developed countries like the United States, consumer product use and motor vehicle emission were the major PAH emission sources, followed by waste incineration, biofuel combustion, and petroleum refining (8.7%). In the countries which have relatively high vegetation cover, forest fires and savannah fires could be major emission sources. For example, savannah fires contributed 70% of total emission of PAHs in Sudan and wood fire accounted for 71% of the total PAH emission in Brazil. Zhang and Tao [2009] presented the emissions of 16 PAHs in individual countries in 2004. Of all the countries listed, China and India ranked first and the second by contributing 11 kt/year and 9 kt/year, which account 2.1 and 1.7% of the world total, respectively.

Figure 3.6 presents the geographic distribution of PAH emission density in 2004 [Zhang and Tao, 2009]. The results are presented as the mean emission density of each country. Higher resolution data are available for China [Zhang et al., 2008b]. Similarly, time series of PAH emissions from 1950 to 2005 was only available for China [Zhang et al., 2008b].

Figure 3.6. Geographic distribution of PAH16 total emission in the world in 2004. [Reprinted from Figure 5 from Zhang, Y. X., and S. Tao (2009), Global atmospheric emission inventory of polycyclic aromatic hydrocarbons (PAHs) for 2004, Atmospheric Environment, 43(4), 812-819, with permission from Elsevier.]
Global PCB emission inventory

A global PCB emission inventory has been developed by Breivik et al. [Breivik and Wania, 2002a; b; Breivik et al., 2007]. The overall goal of this inventory has been to present quantitative estimates of the historical, current and future emissions of selected PCBs for use and evaluation in global and regional fate models [Eckhardt et al., 2009; MacLeod et al., 2005; Wania and Daly, 2002; Wania and Su, 2004], mass balance studies [Axelman and Gustafsson, 2002; Jonsson et al., 2003; Mandalakis et al., 2005; Meijer et al., 2003b], and for the interpretation of environmental levels and trends of these contaminants [Breivik et al., 2010; Hafner and Hites, 2003; Hung et al., 2005; Mandalakis and Stephanou, 2002; Meijer et al., 2003a].

Figure 3.7 shows the estimated cumulative global emissions for \( \Sigma \text{PCB}_{22} \) congeners from the start of their production (1930) until 2005, expressed as percentage of their global cumulative production. This scenario suggests that most PCBs were used for closed applications, such as large capacitors and transformers, and that the largest pool of PCBs in remaining use by 2005 would be attributed to this category. The larger historical emissions, however, are associated with emissions from various open usages, such as carbonless copy paper and plasticizers. This particular emission scenario also suggests that the emissions associated with uncontrolled burning of waste containing PCBs, such as open burning and fires, may have represented substantial inputs of these compounds into the atmosphere, in particular for the higher chlorinated PCBs.

Figure 3.8 shows the estimated annual temporal trend in estimated global emissions for \( \Sigma \text{PCB}_{22} \). According to this scenario, atmospheric emissions peaked in 1970 with more than 3000 tons of \( \Sigma \text{PCB}_{22} \) being emitted that year on a global scale. Still, by 2009 about 250 tons of \( \Sigma \text{PCB}_{22} \) were emitted into the atmosphere, which in brief is a combined effect of the persistence of these compounds and the long lifetime of various products and applications containing PCBs. However, as remaining uses of PCBs over time are phased-out, disposed or destroyed, emissions are expected to continue to decline into the future.
The extensive historical uses of products containing PCBs are intimately linked to various human activities (building and construction, electrical equipment, paint, paper, plastics etc). As could be expected, distinct urban-rural gradients in atmospheric levels are therefore typically observed on a local [e.g. Harner et al., 2004] and regional scale [Jaward et al., 2004] with elevated levels recorded in densely populated regions. For this reason, national emission data are spatially distributed on a 1° x 1° latitude/longitude basis, using population data as surrogate (data from Yi-Fan Li, Environment Canada). Figure 3.9 shows the resulting spatial distribution of global ΣPCB₂₂ emissions, illustrated for the reference year 2004. Data for all scenarios, congeners and years are available at http://tarantula.nilu.no/projects/globalpcb/.
The overall goal of the studies by [Breivik and Wania, 2002a; b; Breivik et al., 2007] has been to estimate the “big picture” of the global historical and future atmospheric emissions of selected PCBs. The inventory was not developed with the primary goal of supporting decision makers with information suitable for the development of rational control strategies on a national scale. If this was the case, another approach would have been desirable. It is also noted that these estimates are affected by substantial uncertainties, many of which are detailed and discussed in the original references. In simple terms, the uncertainties in production rates for selected PCBs are less than the uncertainties in consumption patterns, which again are far less than the uncertainties in projected emissions. Thus, any further studies aiming to take advantage of some of this information should preferably use information on production/consumption, rather than emissions, due to the significant uncertainties introduced in the latter exercise. Yet, it is encouraging to note that consecutive global model predictions of congener patterns in remote areas, such as the Arctic, seem to mirror observations [Hung et al., 2005; Wania and Su, 2004], indicating the actual emission fingerprint of key PCB congeners are captured in these estimates. Future studies taking advantage of the global PCB emission inventory data are likely to provide further indications on the strengths and limitations of these estimates.

Global DDT emission inventory

From the 1940s to the 1970s, DDT was extensively used as a pesticide globally (see e.g., UNEP Chemicals, http://www.chem.unep.ch/ddt/DDTHistory.html). But, since the Stockholm convention entered into force, it’s use declined dramatically.

A global emissions inventory of DDT was prepared for the European Union (EU) funded project ArcRisk (Arctic Health Risks: Impacts on health in the Arctic and Europe owing to climate-induced changes in contaminant cycling). Only very limited information was available from national authorities on DDT emissions, except for some information on DDT usage and its restrictions in use, as reported to UNEP (http://www.chem.unep.ch/ddt/ProfileCriteria.html). In the cases of insufficient data, DDT usage was estimated from country-specific information on insecticide usage (information on insecticide usage was available from FAOStat at http://faostat.fao.org/site/424/DesktopDefault.aspx?PageID=424#ancor and from Eurostat).

That is, national partitioning factors (DDT usage/insecticide usage) were used for estimating an average regional partitioning factor consequently used for estimating national data on DDT usage. (The partitioning factor was 0.3 for Africa, 0.0005 for South America, 0.77 for Asia, whilst 0 for North America, Oceania, and Europe). Emissions were estimated by using an emission factor for DDT usage of 0.05 g/g. Emission projections for 2010 were estimated by linking the DDT emissions data with trend analysis on national available arable land. It should be noted that large uncertainties are linked to the emission estimates as well as to the projection estimate.

The global DDT emissions inventory shown in Table 3.2 indicates that about 980 tonnes were emitted in total in the year 2000. As much as 77 percent of the global emissions originated from Asia (mainly India and China). It is expected, however, that emissions from Asia will decline substantially, to a level of 44 percent (of a total of about 430 tonnes) in 2010, leaving Africa as the main emitting region (as a source of 56 percent of the global DDT emissions, mainly because of the reduction in usage in China). It is expected that DDT in some countries will be used for vector-borne disease control in the future.

3.2.2. Regional and national inventories and data bases

POP emission inventories for Europe

The development of global emission inventories depends on the emission inventories on regional and national scales. Many gridded regional and national emission inventories have been presented. For the agricultural POPs, Berdowski et al. [1997] presented emission inventories for some pesticide POPs for Europe. Gridded usage inventories were compiled for technical HCH, lindane, and DDT in China [Li, 1999a; b; Li et al., 1999] and for the former Soviet Union [Li et al., 2006; Li et al., 2004], for lindane in Canada [Li et al., 2004] and for toxaphene in the United States [Li, 2001; Li et al., 2001a].
An early study of the historical environmental releases of PCBs in North America was presented by Nisbet & Sarofim [1972]. Later, Berdowski et al. [1997] reported an estimate of the atmospheric emissions of PCBs in Europe for the reference year 1990.

Table 3.2. Global data about DDT consumption and emissions for the years 2000 and 2010 distinguished by different world regions.

<table>
<thead>
<tr>
<th>Region</th>
<th>DDT consumption¹</th>
<th>DDT emissions¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2000</td>
<td>2010</td>
</tr>
<tr>
<td>WORLD</td>
<td>19677,35</td>
<td>4822,34</td>
</tr>
<tr>
<td>TOTAL RUSSIA</td>
<td>0,00</td>
<td>0,00</td>
</tr>
<tr>
<td>TOTAL AFRICA</td>
<td>4458,76</td>
<td>4815,17</td>
</tr>
<tr>
<td>TOTAL NORTH AMERICA</td>
<td>0,00</td>
<td>0,00</td>
</tr>
<tr>
<td>TOTAL SOUTH AMERICA</td>
<td>7,52</td>
<td>7,17</td>
</tr>
<tr>
<td>TOTAL ASIA</td>
<td>15211,07</td>
<td>760,55</td>
</tr>
<tr>
<td>TOTAL OCEANIA</td>
<td>0,00</td>
<td>0,00</td>
</tr>
<tr>
<td>TOTAL EUROPE</td>
<td>0,00</td>
<td>0,00</td>
</tr>
</tbody>
</table>

¹UNEP reported + Norwegian Institute for Air Research (NILU) estimate

For Europe, Denier van der Gon et al. [2005; 2007] compiled emission inventories for (HCB, hexachlorocyclohexane (HCH), PCBs, and PCDD/F based on officially reported data from the countries. Additionally, Denier van der Gon et al. [2005; 2007] compiled country-specific emission data sets for the eight candidate POPs [UNECE, 1998] for the Aarhus protocol: dicofol, endosulfan, hexachlorobutadiene (HBU), pentabromodiphenyl ether (PBDE), PeCB, PCP, PCN and short- chained chlorinated paraffins. Breivik et al. [2006] have discussed existing emission inventories of PCDD/F, PCB and PAHs for Europe. Pacyna et al. [2003] have built European emission inventories for DDT, HCB, PAH (B[a]P) for the years 1970 to 1995 based on the EU POPCYCLING-Baltic (http://www.nilu.no/projects/baltic/) project. Quaß et al. [2000; 2004] compiled a PCDD/F emission inventory for western Europe (EU15 + Norway and Switzerland). Pulles et al. [2006] compiled PCDD/F emission inventories for eastern and central European countries (Bulgaria, Cyprus, Czech Republic, Estonia, Hungary, Latvia, Lithuania, Malta, Poland, Romania, Slovak Republic, Slovenia and Turkey) for the year 2000. These inventories have been compiled in close cooperation with national experts. Gusev et al. [2007] evaluated the data availability of emission inventories for PAHs (benzo[a]pyrene (B[a]P), benzo[b]fluoranthene (B[b]F), benzo[k]fluoranthene (B[k]F) and indeno[1,2,3-cd]pyrene (I_P)), dioxins and furans, hexachlorobenzene, polychlorinated biphenyls, hexachlorocyclohexane in the EMEP data base (http://webdab.emep.int) for the years 1990 to 2005. Vestreng et al. [2006] reviewed the POP emissions data sets officially reported by the countries and conducted a comparison with expert emission inventories. BIPRO [2009] gives an overview on PAH, PCB and PCDD/F emissions in the EU27 countries based on the data sets officially reported by the countries for the year 2006, expert estimates from the EMEP MSC-East Center, the EU-EPER (http://www.eper.cc.europa.eu/eper/default.asp) data set and the “E-PRTR (http://prtr.ec.europa.eu/) pilot inventory on releases from diffuse sources.

Prevedous et al. [2004] published a European consumption and atmospheric emissions inventory for pentabrominated diphenylethers (PeBDEs) for the period from 1970 to 2000. The main uses for PeBDEs are to flame retard consumer products as well as in packaging and solid elastomers.

**Gridded PCDD/F emission inventories for North America**

For North America, a scientific dioxin emission inventory was compiled for the United States, Canada and Mexico for the year 1996. It is described in detail in Commoner et al. [2000], Cohen et al. [2002] and Commoner et al. [2003].

**Gridded toxaphene emission/residue inventories in the United States**

Emission factors of toxaphene for spraying and tilling events have been applied for the United States on a 1°x1° latitude and longitude grid system. By using the gridded usage [Li, 2001]
and emission factors, inventories of gridded toxaphene emissions and residues in agricultural soil in the United States with 1/6° x 1/4° latitude and longitude resolution have been created [Li et al., 2001b]. Toxaphene inventories in the United States in 2000 on a 1/6°x1/4° latitude and longitude grid system are shown for emissions in Figure 3.10 and residues in Figure 3.11. Total toxaphene emissions were around 190 kt between 1947 and 1999. At the beginning of 2000, almost 20 years after banning the use of toxaphene, there were still around 29 kt of toxaphene left in the agricultural soil, of which 360 t were emitted to the air in 2000. Around 90% of total emissions are from the southeastern part of the United States.

**Figure 3.10.** Toxaphene emissions in the United States in 2000 on a 1/6°x1/4° latitude and longitude grid system. Around 90% of total emissions are from the southeastern part of the United States. Total emissions were 360 t in 2000. [Reprinted from Figure 4 in Li, Y. F., et al. (2001), Toxaphene in the United States: (2) Emissions and Residues, Journal of Geophysical Research, 106(D16): 17929-17938.]

**Figure 3.11.** Toxaphene soil residues in the United States in 2000 on a 1/6°x1/4° latitude and longitude grid system. Total toxaphene soil residues in 2000 were 30 kt. [Reprinted from Figure 5 in Li, Y. F., et al. (2001), Toxaphene in the United States: (2) Emissions and Residues, Journal of Geophysical Research, 106(D16): 17929-17938.]
Emissions of POPs and eight candidate POPs from UNECE-Europe in 2000, 2010 and 2020

An emission inventory for POPs for the year 2000 is based on submissions of emission data from the Parties to the Convention on Long-range Transboundary Air Pollution (LRTAP). The inventory covers the UNECE territory except Canada and the United States. For, sources or compounds lacking in official submissions, default emission estimates have been prepared and applied to complete the inventory. An indicative comparison of the year 2000 emissions with the 1990 emission levels from a previous study has been presented in Denier van der Gon et al. [Denier van der Gon et al., 2005; 2007], as well as emission projections for 2010, 2015, 2020 based on activity scenarios developed in the framework of the EU CAFE programme. The key source analysis of the projected emissions, assuming full implementation of the UNECE Protocols, allows identification of remaining source strengths, which subsequently are briefly discussed in terms of their potential for (further) reduction. A number of chemicals are currently being investigated for inclusion on the UNECE POPs protocol list of priority compounds, but for these substances emission estimation methodologies are scarce or non-existent. For eight of these substances (dicofol, endosulfan, HBU, PBDE, Pentachlorobenzene (PeCB), PCP, PCN and SCCPs) an emission estimation methodology is proposed and a preliminary emission inventory for the year 2000 is presented in Denier van der Gon et al. [2005].

Substances covered

The emission inventory in Denier van der Gon et al. [2005; 2007] covers two groups of substances:

i) the POPs adopted by the UNECE POP Protocol, excluding the substances thought to be no longer emitted in Europe (Table 3.3, left column) and,

ii) eight POP candidates (Table 3.3, right column) in the UNECE Emission Inventory Guidebook [EMEP/EEA, 2009]; selected air pollutants are listed as well as a rather extensive collection of their sources.

However, not all substances are currently adequately covered so additional efforts have been made to develop emission estimation methods. This applies especially to the candidate POPs. The emission inventory followed the guidelines given in the POP Protocol [UNECE, 1998]. This implies that, for the group of polycyclic aromatic hydrocarbons (PAHs), four indicator compounds were inventoried: benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, and indeno(1,2,3-cd)pyrene. For PCDD/F, the emissions of different congeners are given in toxicity equivalents (comparison to 2,3,7,8-TCDD using the system proposed by the NATO Committee on the Challenges of Modern Society (NATO-CCMS) in 1988); no individual species emissions are given.

Table 3.3. Substances addressed in Denier van der Gon, H. A. C., et al. (2005), Study to the effectiveness of the UNECE persistent organic pollutants protocol and costs of possible additional measures Phase I: estimation of emission reduction resulting from the implementation of the POP protocol. TNO Report B&O-A R 2005/194, Netherlands Organization for Applied Scientific Research, Delft, Netherlands.

<table>
<thead>
<tr>
<th>Persistent Organic Pollutants (POPs)</th>
<th>Candidate POPs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexachlorobenzene (HCB)</td>
<td>Dicofol</td>
</tr>
<tr>
<td>Hexachlorocyclohexane (HCH), including lindane</td>
<td>Endosulfan</td>
</tr>
<tr>
<td>Polychlorinated biphenyls (PCBs)</td>
<td>Hexachlorobutadiene (HBU) (HCBD)</td>
</tr>
<tr>
<td>Dioxins and Furans (PCDD/F)</td>
<td>Pentabromodiphenyl ether (PentaBDE, PBDE)</td>
</tr>
<tr>
<td>Polycyclic aromatic hydrocarbons (PAHs)</td>
<td>Pentachlorobenzene (PeCB)</td>
</tr>
<tr>
<td></td>
<td>Pentachlorophenol (PCP)</td>
</tr>
<tr>
<td></td>
<td>Polychlorinated naphthalenes (PCN)</td>
</tr>
<tr>
<td></td>
<td>Short chained chlorinated paraffin’s (SCCPs)</td>
</tr>
</tbody>
</table>

* Polychlorinated dibeno-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF)
  Four indicator compounds shall be used: benzo(a)pyrene, benzo(b)fluoranthene, benzo(k) fluoranthene, and indeno(1,2,3-cd)pyrene, as specified in Annex III of the POP Protocol [UNECE, 1998].

b) Four indicator compounds shall be used: benzo(a)pyrene, benzo(b)fluoranthene, benzo(k) fluoranthene, and indeno(1,2,3-cd)pyrene, as specified in Annex III of the POP Protocol [UNECE, 1998].
The POPs emission inventory is based on submissions of emission data from the Parties to the Convention on LRTAP as available at http://webdab.emep.int/. At the time of execution many country reportings were incomplete [Shatalov et al., 2003], but a complete inventory is required to assess the effectiveness of the protocol as well as the reductions and costs of possible additional measures. Therefore, a default or “TNO reference” database was made to fill gaps for species and/or sources where country submissions lacked data. In the majority of the member countries the relevant experts have been contacted and the feedback by the country experts regarding (corrected) official emission data has been incorporated. A list of country experts contacted and the methodologies followed to obtain the official emissions database and the reference database are described in detail by Denier van der Gon et al. [2005]. To create a final dataset, the official emission values are merged with the reference emission inventory to get complete coverage of all countries and all sectors in the UNECE-Europe region. However, a prerequisite of using official data was that the submitted emission data were split at, at least, the first level of the reporting format (e.g. SNAP or NFR). This is crucial for a first order quality control because otherwise it is impossible to have a general judgement if the reporting was complete, e.g., all emitting sectors included. The officially submitted sectoral data were compared with the sectoral emissions in the reference database. If the official submission did not include emissions for all sectors covered in the reference database, the missing sectors from the reference database were added to the official emission submission, thus resulting in a partly official, partly default emission estimate for the particular country.

Available (sectoral) official emission data are only discarded and replaced by TNO reference data in cases when: (i) the difference between official and expert estimates was large (factor ~3) and could not be understood, (ii) the source in question contributed significantly to the total emissions of the particular substance (> 10%) and, (iii) the choice for official emission data would alter the regional emission pattern and outcome of the key source analysis.

**Source categories, Activity data and Emission factors for year 2000**

The extensive collection of source types in the Atmospheric Emission Inventory Guidebook [EMEP/EEA, 2009] and the POP Protocol Technical Annexes is the basis of the source selection for the inventory. The most important sources for activity data are the International Energy Agency, the ‘Industrial Commodity Production Statistics Dataset 1950-2001’ [UN SD, 2003], Steel statistical yearbook 2003 [IISI, 2004], and the United States Bureau of the Census [2004]. For a pragmatic implementation of the inventory and presentation of the results, the individual sources distinguished in the inventory are aggregated on a higher level of source category (see Table 3.4) but the activity data are collected on a much lower level.

**Table 3.4.** Source categories defined in the POP inventory. [Reprinted from Table 3 of Denier van der Gon, H. A. C., et al. (2007). Emissions of persistent organic pollutants and eight candidate POPs from UNECE-Europe in 2000, 2010, and 2020 and the reduction resulting from the implementation of the UNECE POP protocol, Atmospheric Environment, 41: 9245-9261, with permission from Elsevier.]

<table>
<thead>
<tr>
<th>Sector Code</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHP</td>
<td>Public heat and power; excludes refineries</td>
</tr>
<tr>
<td>RCO</td>
<td>Residential, commercial and other combustion; includes combustion in agriculture</td>
</tr>
<tr>
<td>IND</td>
<td>Industry; includes both combustion and process emission, and refineries and fossil fuel production</td>
</tr>
<tr>
<td>SPU</td>
<td>Solvent and product use; new and existing stocks; Includes wood preservation</td>
</tr>
<tr>
<td>ROT</td>
<td>Road transport</td>
</tr>
<tr>
<td>NRT</td>
<td>Non-Road transport</td>
</tr>
<tr>
<td>WAS</td>
<td>Waste disposal</td>
</tr>
<tr>
<td>AGR</td>
<td>Agriculture; excludes combustion emission in agriculture</td>
</tr>
<tr>
<td>TOTAL</td>
<td>Total of all sectors</td>
</tr>
</tbody>
</table>
The emission factors are obtained from the latest European Monitoring and Evaluation Programme (EMEP) CORINAIR guidebook [EMEP/EEA, 2009] and the European Emission Inventory for HM and POP for 1990 [Berdowski et al., 1997]. If no emission factors are available, other general guidebooks are scanned e.g., PARCOM ATMOS emission factor manual [van der Most and Veldt, 1992]. The emission factors as published in the EMEP CORINAIR guidebook are assumed to be valid for 1990 and 2000. The year 2000 European emission inventory for POPs and candidate POPs by country is presented in Denier van der Gon et al. [Denier van der Gon et al., 2007].

Spatial distribution of emission data

The emission data and projections are spatially distributed over the EMEP 50 x 50 km^2 grid to facilitate the modelling of POP distribution over Europe. The emission data are treated as either point sources or area sources. Emissions of POP are distributed at the level of source sector totals by substance and country. Each source sector has its own set of geographic proxy data. Proxy data include the location of large point sources, location of traffic highways, rural and urban population maps and distribution of agricultural activities. Compared to the 1990 inventory by Berdowski et al. [1997], the geographic proxy data have been updated to the year 2000. The procedure followed is described in detail in Visschedijk and Denier van der Gon [2006]. Point source information has been applied for the distribution of emissions from the energy transformation sector (including refineries), industrial combustion (only larger plants ~ > 50 MWth), the iron and steel industry, the non-ferrous metal industry, the cement industry (for central and eastern Europe), petrochemical industry and municipal waste incineration (for western Europe). Examples of the gridded emissions are presented for HCB (Figure 3.12), PCB (Figure 3.13) and a PAH indicator compound, Benzo[a]pyrene (Figure 3.14). For detailed gridded maps of all POPs and candidate POPs for the year 2000 we refer to Denier van der Gon et al. [2005].

Figure 3.12. Distribution of HCB emissions over the 50 x 50 km2 EMEP grid for UNECE-Europe in 2000. [Reprinted from Figure A5.1.1 in Denier van der Gon, H.A.C., et al. (2005), Study to the effectiveness of the UNECE persistent organic pollutants protocol and costs of possible additional measures Phase I: estimation of emission reduction resulting from the implementation of the POP protocol, TNO Report B&O-A R 2005/194, Netherlands Organization for Applied Scientific Research, Delft, Netherlands.]
Figure 3.13. Distribution of PCB emissions over the 50 x 50 km2 EMEP grid for UNECE-Europe in 2000. [Reprinted from Figure A5.1.4 in Denier van der Gon, H.A.C., et al. (2005), Study to the effectiveness of the UNECE persistent organic pollutants protocol and costs of possible additional measures Phase I: estimation of emission reduction resulting from the implementation of the POP protocol, TNO Report B&O-A R 2005/194, Netherlands Organization for Applied Scientific Research, Delft, Netherlands.]

Figure 3.14. Distribution of Benzo[a]pyrene emissions over the 50 x 50 km2 EMEP grid for UNECE-Europe in 2000. [Reprinted from Figure A5.1.5 in Denier van der Gon, H.A.C., et al. (2005), Study to the effectiveness of the UNECE persistent organic pollutants protocol and costs of possible additional measures Phase I: estimation of emission reduction resulting from the implementation of the POP protocol, TNO Report B&O-A R 2005/194, Netherlands Organization for Applied Scientific Research, Delft, Netherlands.]
The gridded data also allow visualization of policy impacts by making “subtraction” maps. For example, Denier van der Gon et al. [2007] presented the change in PCDD/F emission as projected for the year 2010 assuming current legislation, autonomous measures and current ratification of the POP Protocol compared to the year 2000 inventory (Figure 3.15).

**Figure 3.15.** The difference between projected PCDD/F emissions from UNECE-Europe in the year 2010 with current legislation and the emission inventory for the year 2000 (negative values indicate an emission reduction) (kg Teq/gridcell). [Reprinted from Figure 2 from Denier van der Gon, H. A. C., et al. (2007), Emissions of persistent organic pollutants and eight candidate POPS from UNECE-Europe in 2000, 2010, and 2020 and the reduction resulting from the implementation of the UNECE POP protocol, *Atmospheric Environment*, 41: 9245-9261, with permission from Elsevier.]

3.2.3. Inventories and data bases of new POPs

As described in the previous section, the new POPs considered in Denier van der Gon et al. [2007] are dicofol, endosulfan (pesticide POPs), PFOS, PBDEs, HCB, PeCB, PCN, and PCPs (industrial POPs). Gridded usage [Jia et al., 2009a] and emission/residue [Jia et al., 2009b] inventories were published for endosulfan in China.

**Gridded endosulfan emission/residue inventories in China**

Endosulfan is one of the organochlorine pesticides (OCPs) and also a candidate to be included in a group of new POPs [Jia et al., 2009b]. The first national endosulfan usage inventories in China with 1/4° longitude by 1/6° latitude resolution has been reported by Jia et al. [2009b], based on which, the gridded historical emissions and soil residues of endosulfan in China were developed [Jia et al., 2009a].

Figure 3.16 shows historical gridded emissions of α- and β-endosulfan in China in 2004 with 1/4° longitude by 1/6° latitude resolution; and their residues in agricultural soil in the same year is given in Figure 3.17. Total emissions were around 10,800 t, with α-endosulfan at 7,400 t and β-endosulfan at 3,400 t from 1994 to 2004. The highest residues were 140 t for α-endosulfan and 390 t for β-endosulfan, and the lowest residues were 0.7 t for α-endosulfan and 170 t for β-endosulfan in 2004 in Chinese agricultural soil where endosulfan was applied. Total emissions of α- and β-endosulfan in 2004 were 900 and 410 t, respectively.
Figure 3.16. Distribution of (a) α-endosulfan and (b) β-endosulfan emissions (t/cell) in China in 2004 with 1/4°×1/6° longitude and latitude resolution. [Reprinted from Figure 3 of Jia, H., et al. (2009b), Endosulfan in China 2. Emissions and residues, Environmental Science and Pollution Research, 16: 302-311, with kind permission of Springer Science and Business Media B.V.]

Figure 3.17. Distribution of α- + β-endosulfan in Chinese agricultural soil (t/cell) in 2004 with 1/4°×1/6° longitude and latitude resolution. [Adapted from Figures 4 and 5 of Jia, H., et al. (2009b), Endosulfan in China 2. Emissions and residues, Environmental Science and Pollution Research, 16: 302-311, with kind permission of Springer Science and Business Media B.V.]

Global gridded BDE-47 emission inventories

A preliminary version of global gridded PeBDE emissions in 2005 on a 1° latitude by 1° longitude resolution was developed and is shown in Figure 3.18. Total PeBDE emissions in this year were 820 t.
3.3. Uncertainties and verification of emission inventories

In principal there exist two main possibilities for assessment uncertainties of emission inventories on different spatial scales.

The first option is the qualitative or quantitative assessment of the intrinsic uncertainties of the considered emission inventory itself. These uncertainties are mainly related to the assumed emission factors and activities. For example, the Intergovernmental Panel on Climate Change (IPCC) developed quality criteria which have to be fulfilled by an emission inventory concerning:

- Transparency,
- Consistency,
- Comparability,
- Completeness, and
- Accuracy.

The second option for assessment of uncertainties of emission is validation experiments. In this option, validation experiments compare modelled concentrations with measured concentrations of specific substances. In the following sections, examples for both approaches will be described for some specific POPs.

3.3.1. Assessment of uncertainties/Consistency of POP inventories

The uncertainties of emission inventories for all POPs are at the moment, in principal, not quantifiable. For most substance inventories, no information exists about completeness of the covered sources on global scale as well as on regional scale. The activities of the known sources are relatively certain for the energy-related POP substances. For other POPs (e.g., PCB, pesticides, and especially the “new” POPs), the activities are affected with mainly unknown but high uncertainties.

The uncertainties of the emission factors for all POPs, especially on a global scale are very high. That means the uncertainties of this relevant input parameter are partly unknown or estimated in a magnitude of several times of the estimated mean value.

For instance in the UNEP [1999] toolkit for PCDD/F, the combustion conditions of residential combustions activities in development countries are, in principal, unknown or at least affected with high uncertainties.
For other POPs, like pesticides, the emission factors take into account application conditions that are sometimes unknown. The leakage rates from intentionally produced chemicals, like PCBs, are also mostly unclear.

Furthermore, this chapter shows a mix of scientific research based on global scale and officially reported inventories on regional scale. The scientific value for modelling requirements of official emission data is limited, as there is insufficient information on spatial, temporal and compound coverage. On the other hand, scientific-based, research driven, emission inventories, which are based on aggregated activity data sets, are limited concerning the identification of future control strategies for policy-makers. That means the further improvement of official emission data sets, by taking into account research-based knowledge, would be the best way for improvement. Especially on a global scale, this will be a big challenge.

The empirical data base of current emission inventories is weak. Further research on identification of emission sources and quantification of activities and better understanding and differentiation of emission factors under different conditions of application will be needed in the future.

Pulles et al. [2006] uses an improved emission inventory model to assess the uncertainties in emissions of dioxin and furans associated with both knowledge on the exact technologies and processes used, and with the uncertainties of both activity data and emission factors. The annual total emissions for the year 2000 in 13 countries in central and eastern Europe can be estimated with 90% confidence within a range that is about a factor of 2–3 lower to a factor of 3–5 higher than a point value obtained from a more classical approach. It is also shown that the contribution of small residential sources and larger industrial installations and processes are of the same order of magnitude in these countries. It is argued that, despite these uncertainties, policy options can be evaluated and policy decisions on abatement of dioxin and furan emissions can be made. Dioxins and furans belong to the POPs, an important group of air pollutants that can have long-term effects on ecosystems and human health. Emission estimates for these pollutants all suffer from high uncertainties. This study shows that policy conclusions can still be derived despite these high uncertainties.

3.3.2. Improvement of inventories by observations and modelling data sets

The overall uncertainty in emission inventories is mainly associated with uncertainty in emission factors, which often varies around 4 orders of magnitude. If the main factors affecting emission factors can be identified and quantified, the overall uncertainty is expected to be reduced substantially.

Emission (residue) inventories can be evaluated and improved by monitoring data with large spatial and temporal scales. Chapter B2, section 2.2.1, listed some global, regional and local monitoring programs that may be used for this purpose. On a global scale, the Global Atmospheric Passive Sampling (GAPS) Program collects air samples four times a year at around 60 background sites in Asia, Africa, Europe, and North America. The IPY INCATPA program collects air samples using active air samplers once a week at background sites in the Arctic and along the rims of Pacific Ocean. On a continental/regional scale, EMEP monitoring program for Europe is also very useful for this purpose. A special designed Chinese POPs Soil and Air Monitoring Program (SAMP), concurrently collects both soil samples and air samples by using passive air samplers at around 100 sites across China (Phase I) and soil samples and air samples by using active sir samplers at more than 10 urban centres and 3 background sites across China (Phase II). This program will make important contributions to the development of emission/residue inventories of POPs in China. The data collected by the Integrated Atmospheric Deposition Network (IADN, http://www.msc-smc.ec.gc.ca/iadn/), having been in operation since the 1990s, is a good dataset for evaluation of the emission inventories of POPs temporally. Other data sets include those collected in the northern Contaminants program (Canada), the European Monitoring and Evaluation (EMEP) program (See Table 2.1 in Chapter 2 of Part A. Major ongoing air monitoring programs).

To compare the emission (residue) inventories with the monitoring data, we need to produce the air and/or soil concentration data by using different models with the emission/residue inventories as input data, and then compare the modelled soil and air concentrations with the observation data at
the same sites. In this subsection, several case studies are presented to show how the monitoring results were used to evaluate the emission/residue inventory data.

Case studies:

(1) Global \(\gamma\)-HCH emission inventories

In order to evaluate the global gridded \(\gamma\)-HCH residue inventories in surface soil presented in the previous subsection (3.3.1), the modelled air concentrations of \(\gamma\)-HCH at 1.5 m height above ground level was (Figure 3.19) obtained by the Canadian model for environmental transport of organochlorine pesticides (CanMETOP). Using the residue inventories as input data, the modelled results were compared with measurements by different groups in both spatial and temporal trends.

![Figure 3.19](image)

Figure 3.19. Modelled average daily air concentrations (pg m\(^{-3}\)) of \(\gamma\)-HCH in 2005 at 1.5 m height above ground level. [Adapted with permission from Figure S4a in Zhang, L., et al. (2008a), Modeling Evidence of Episodic Intercontinental Long-Range Transport of Lindane, *Environmental Science & Technology*, 42(23): 8791–8797. Copyright 2008 American Chemical Society.]

Spatial trends

The modelled air concentrations of \(\gamma\)-HCH have been compared with the measured data by GAPS [Pozo et al., 2009], a program designed to create a network for studying the spatial and temporal trends of POPs [Pozo et al., 2009]. Measurements for different periods in 2005 in the major source regions from the GAPS results were selected to compare with the arithmetical means of corresponding modelled daily concentrations. The results showed that the model captured well the spatial variability of \(\gamma\)-HCH at a correlation \(R^2 = 0.65\) (\(P < 0.0001\)) with the GAPS results (see Figure 3.20).
Figure 3.20. Modelled air concentrations and measured results from Global Atmospheric Passive Sampling (GAPS) [Pozo et al., 2009]. Comparison between the measured air concentrations under GAPS Program in 2005 and their corresponding model concentrations (pg m⁻³).

Temporal trends

A comparison between modelled data and the measured atmospheric level of γ-HCH at the 5 Master monitoring sites under IADN (http://www.msc-smc.ec.gc.ca/idadn/) in 2005 are also shown in Figure 3.21. All correlations are significant, with correlation coefficients R from 0.49 to 0.62 for the Person analysis, and from 0.62 to 0.77 for the Spearmen analysis.
**Figure 3.21.** (a) Comparison between the modelled and measured $\gamma$-HCH air concentrations at Great Lakes with 12-d interval in 2005. (EGH: Eagle Harbor, 47°27’47”N, 88°08’59”W at Lake Superior, SBD: Sleeping Bear Dune, 44°45’40”N, 86°03’31”W at Lake Michigan, BNT: Burnt Island, 45° 48’ 30”N, 82°57’00”W at Lake Huron, STP: Sturgeon Point, 42°41’35”N, 79°03’18”W at Lake Erie, PPT: Point Petre, 43° 50’ 34”N, 77° 9’13”W at Lake Ontario). (b). The location of the 5 Master Stations under IADN (http://www.msc-smc.ec.gc.ca/iadn/stations/station_master_e.html).

**Downsview, Canada.** The sampled dataset was collected at Downsview (43°14’0”N, 79°37’E), a suburb of Toronto in Canada by Environment Canada [Zhang et al., 2008a]. There are two sampling periods, one is from June 23 to 29 and the other is from September 22 to 30 to track episodic atmospheric transport events of POPs [Ma et al., 2005]. The modelled and measured $\gamma$-HCH air concentrations were shown in Figure 3.22. Although the model did not catch the high air concentration (586 pg m$^{-3}$) in the episodic event, the modelled and measured data show a strong and significant correlation with $R^2 = 0.44$, and $p < 0.001$ for all 16 daily samples collected during the two periods.
Figure 3.22. Modelled and measured daily γ-HCH air concentrations at Downsview (43°40’N, 79°37’W), Toronto in 2005 on the sampling days. An unusually high air concentration measured on June 28 at 586 pg m⁻³ is not presented. [Adapted with permission from Figure S2 in Zhang, L., et al. (2008a), Modeling Evidence of Episodic Intercontinental Long-Range Transport of Lindane, Environmental Science & Technology, 42(23): 8791–8797. Copyright 2008 American Chemical Society.]

(2) Chinese endosulfan emission/residue inventories

Based on the emission and residue inventories [Jia et al., 2009b, and section 3.2.3], concentrations of α- and β-endosulfan in Chinese air and agricultural surface soil were also calculated for each grid cell. We have estimated annual averaged air concentrations and the annual minimum and maximum soil concentrations across China in 2004, and the data were compared with monitoring data from Chinese POPs Soil and Atmospheric Monitoring Program (SAMP), Phase I. Regression analysis was calculated between monitored and the lowest modelled results in all soil samples in China. While the correlation was not significant for α-endosulfan ($R = 0.2$, $P = 0.07$), the correlation was very strong and statistically significant for β-endosulfan, with $R = 0.77$ ($P < 0.0001$). This could be explained by the fact that β-endosulfan has much longer (~135 days) half-life than α-endosulfan (~35 days), leading to more stable soil concentrations and a stronger correlation between modelled and monitoring concentrations for β-endosulfan (Figure 3.23). Regression analysis was also calculated between the monitored and the lowest modelled results in all air samples in China. Different from the soil case, stronger and more significant correlation was found for α-endosulfan ($R = 0.66$, $P = 0.0001$) than that for β-endosulfan ($R = 0.35$, $P < 0.005$) (Figure 3.24).
Figure 3.23. Comparing the modelled endosulfan soil concentration in 2005 to monitoring data in 2004 for (a) $\alpha$-endosulfan, (b) $\beta$- endosulfan.
Figure 3.24. Comparing the modelled endosulfan air concentration in 2005 to measured data in 2004 for (a) α-endosulfan, (b) β- endosulfan.

(3) Global BDE–99 emission inventories

Using the global gridded PeBDE emissions in 2005 shown in Figure 3.18 as input data, the CanMETOP was used to simulate the transport of BDE-99. A preliminary version of global gridded BDE -99 emissions in 2005 on a 1º latitude by 1º longitude resolution was developed as shown in Figure 3.25.
Spatial trends

The comparison between modelled and monitored air concentrations of BDE-99 at the GAPS station is shown in Figure 3.26, indicating the modelling results match the monitoring data with a significant correlation \( R = 0.28, P < 0.04 \). Mean concentrations of BDE-99 for the 53 GAPS sites are 1.1 for modelled data, and 1.2 for monitoring data.

Temporal Trends

The comparison between modelling and monitoring air concentrations of BDE-99 at Point Petre, Canada, is shown in Figure 3.27, indicating the modelling results are slightly higher than the monitoring data, but with a significant correlation \( R = 0.59, p < 0.01 \).
3.4. Emission Projections

For compiling future projections of specific POPs, the following key questions should be taken into account:

- Do we have sufficient data on emissions and the trends in driving forces needed for making reasonable future projections? How can this data be improved?
- How might emission quantities and spatial distributions change over the next 20-50 years? How will different source categories change?
- How should future emission scenarios be constructed?

3.4.1. Methodologies

For compiling emission projections, there is a need to distinguish between different approaches:

- The emission factor approach for combustion related POPs (PCDD/F, PAHs)
- The mass balance approach for intentional produced chemicals like PCB. This approach based is mainly life cycle driven for e.g. PCBs
- The specific for pesticides projections under specific consideration of effects like illegal use or stockpile use

3.4.2 Future emission scenarios for specific pollutants

In Figure 3.8 is shown an example of the mass balance based approach conducted for PCB emissions until 2100 by Breivik [2007].

Tables 3.5 and 3.6 describe two examples for applying the mainly policy and technique driven emission factor approach. This is an example which has been applied for a regional European data base. This example considers policy driven projections for the pollutants HCB, HCH, PCB, PCDD/F and four PAH indicator compounds.
Table 3.5. Relative contribution (%) of source sectors to remaining POP emissions upon full implementation of the POP Protocol by all UNECE-Europe countries. [Reprinted from Table 10 of Denier van der Gon, H. A. C., et al. (2007), Emissions of persistent organic pollutants and eight candidate POPs from UNECE-Europe in 2000, 2010, and 2020 and the reduction resulting from the implementation of the UNECE POP protocol, *Atmospheric Environment*, 41: 9245-9261, with permission from Elsevier.]

<table>
<thead>
<tr>
<th>Source sector</th>
<th>HCB</th>
<th>HCH</th>
<th>PCB</th>
<th>PCDD/F</th>
<th>PAH indicator compound</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>BaP</td>
</tr>
<tr>
<td>Public power and heat</td>
<td>0.5</td>
<td>0.0</td>
<td>55.7</td>
<td>13.4</td>
<td>0.2</td>
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<tr>
<td>Residential combustion</td>
<td>3.5</td>
<td>0.0</td>
<td>3.9</td>
<td>40.3</td>
<td>81.8</td>
</tr>
<tr>
<td>Industrial combustion and processes</td>
<td>82.4</td>
<td>0.0</td>
<td>33.9</td>
<td>28.0</td>
<td>15.7</td>
</tr>
<tr>
<td>Solvent and product use</td>
<td>0.0</td>
<td>81.5</td>
<td>0.0</td>
<td>0.9</td>
<td>0.1</td>
</tr>
<tr>
<td>Road transport</td>
<td>2.2</td>
<td>1.6</td>
<td>1.7</td>
<td>1.8</td>
<td>2.2</td>
</tr>
<tr>
<td>Non-road transport</td>
<td>1.3</td>
<td>0.2</td>
<td>0.9</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Waste incineration</td>
<td>10.2</td>
<td>4.7</td>
<td>14.7</td>
<td>0.3</td>
<td>0.2</td>
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<td>Agriculture</td>
<td>0.0</td>
<td>18.5</td>
<td>0.0</td>
<td>0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>Total</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
</tr>
</tbody>
</table>

Table 3.6. POP emissions by country group in 2000, projected POP emissions for 2020 following a baseline, current legislation policy scenario (BL_CLE) and assuming full implementation of the POP Protocol in 2020 (BL_CLE_FIPPOP). [Reprinted from Table 11 of Denier van der Gon, H. A. C., et al. (2007), Emissions of persistent organic pollutants and eight candidate POPs from UNECE-Europe in 2000, 2010, and 2020 and the reduction resulting from the implementation of the UNECE POP protocol, *Atmospheric Environment*, 41: 9245-9261, with permission from Elsevier.]

<table>
<thead>
<tr>
<th>Country group</th>
<th>Year</th>
<th>Scenario</th>
<th>HC B</th>
<th>HC H</th>
<th>PCB</th>
<th>PCDD/F</th>
<th>BaP</th>
<th>BbF</th>
<th>BkF</th>
<th>Indeno</th>
</tr>
</thead>
<tbody>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>kg</td>
<td>Teq/yr</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>POP_Protocol ratifieda)</td>
<td>2000</td>
<td></td>
<td>7.8</td>
<td>41</td>
<td>53.9</td>
<td>3.53</td>
<td>254</td>
<td>315</td>
<td>124</td>
<td>187</td>
</tr>
<tr>
<td>POP_Protocol ratifiedb)</td>
<td>2020</td>
<td>BL_CLE</td>
<td>1.2</td>
<td>41</td>
<td>2.0</td>
<td>1.42</td>
<td>177</td>
<td>217</td>
<td>75</td>
<td>120</td>
</tr>
<tr>
<td>POP_Protocol ratifiedc)</td>
<td>2020</td>
<td>BL_CLE_FIP</td>
<td>1.2</td>
<td>41</td>
<td>2.0</td>
<td>1.42</td>
<td>177</td>
<td>217</td>
<td>75</td>
<td>120</td>
</tr>
<tr>
<td>EU25 a/o 2nd S protocol b)</td>
<td>2000</td>
<td>BL_CLE</td>
<td>9.7</td>
<td>20</td>
<td>18.4</td>
<td>2.56</td>
<td>158</td>
<td>181</td>
<td>62</td>
<td>134</td>
</tr>
<tr>
<td>EU25 a/o 2nd S protocol b)</td>
<td>2020</td>
<td>BL_CLE</td>
<td>6.5</td>
<td>20</td>
<td>2.1</td>
<td>1.00</td>
<td>72</td>
<td>89</td>
<td>31</td>
<td>59</td>
</tr>
<tr>
<td>EU25 a/o 2nd S protocol b)</td>
<td>2020</td>
<td>BL_CLE_FIP</td>
<td>0.3</td>
<td>20</td>
<td>2.1</td>
<td>0.96</td>
<td>67</td>
<td>83</td>
<td>28</td>
<td>55</td>
</tr>
<tr>
<td>Otherc)</td>
<td>2000</td>
<td>BL_CLE</td>
<td>0.7</td>
<td>13</td>
<td>61.0</td>
<td>5.66</td>
<td>496</td>
<td>545</td>
<td>273</td>
<td>379</td>
</tr>
<tr>
<td>Otherc)</td>
<td>2020</td>
<td>BL_CLE</td>
<td>0.7</td>
<td>13</td>
<td>4.0</td>
<td>5.90</td>
<td>569</td>
<td>625</td>
<td>342</td>
<td>398</td>
</tr>
<tr>
<td>Otherc)</td>
<td>2020</td>
<td>BL_CLE_FIP</td>
<td>0.0</td>
<td>13</td>
<td>3.4</td>
<td>1.41</td>
<td>353</td>
<td>378</td>
<td>119</td>
<td>285</td>
</tr>
<tr>
<td>Total UNECE</td>
<td>2000</td>
<td></td>
<td>18.25</td>
<td>133.3</td>
<td>11.74</td>
<td>907</td>
<td>104</td>
<td>459</td>
<td>700</td>
<td></td>
</tr>
<tr>
<td>Total UNECE</td>
<td>2020</td>
<td>BL_CLE</td>
<td>8.4</td>
<td>16.8</td>
<td>8.46</td>
<td>851</td>
<td>980</td>
<td>444</td>
<td>622</td>
<td></td>
</tr>
<tr>
<td>Total UNECE</td>
<td>2020</td>
<td>BL_CLE_FIP</td>
<td>1.5</td>
<td>7.4</td>
<td>3.79</td>
<td>597</td>
<td>678</td>
<td>222</td>
<td>460</td>
<td></td>
</tr>
</tbody>
</table>

a) Countries that have ratified the POP Protocol (20 countries)
b) Countries that have not ratified the POP Protocol but part of EU25 and/or ratified 2nd S Protocol (11 countries)
c) No POP Protocol ratification and/or no 2nd S protocol ratification and/or no EU-25 member state (13 countries)
**Future projections to 2050 for PCB and PCDD/F for the European scale**

The results of the EU project DROPS and projections of coal combustion for electricity generation to year 2050 were used projection of POPs emissions to air for future years (see Tables 3.7 and 3.8).

DROPS was considering HM and POPs emissions for 40 European countries with the base year 2000 and scenarios for 2010 and 2020. The baseline scenario to year 2020 is the DROPS BAU+Climate scenario (Business as Usual with Climate Policies scenario), assuming (1) that there will be an economic progress in European countries at a rate dependent on the future development of industrial technologies and emission control technologies and (2) that all agreed (in 2006) EU directives, conventions and protocols on the emissions reduction of the considered pollutants, together with the Kyoto Protocol, will be fully implemented. Detailed assumptions of scenarios for waste incineration (for dioxins) and use of electrical equipment (for PCB) are presented in Panasiuk [Panasiuk et al., 2006].

For fuel combustion, DROPS projects a significant decrease of electricity production in conventional plants to 2020, close to DG TREN [DG TREN, 2003] projections for coal-fired thermal open cycle plants. In this period, an increase of gas combustion in combined cycle gas turbines (GTCC) and use of clean coal technologies (integrated gasification combined cycle, IGCC) is expected in electricity generation.

Emission projections for conventional plants to year 2020, based on changes of activities and emission factors, are contained in Strzelecka-Jastrząb et al [Strzelecka-Jastrząb et al., 2007]. Until 2010, coal-fired combustion plants will be equipped with fabric filters or electrostatic precipitators operated in combination with flue gas desulphurization (FGD) techniques. After 2010, in conventional pulverized boilers, all emission control technologies considered as best available technology (BAT) will be commonly used. Additionally, techniques designed for metal removal (activated carbon, sulphur-impregnated adsorbents and selenium impregnated filters) will be implemented.

For the next period 2020-2030, changes of activities for electricity generation by thermal open cycle from DG TREN [DG TREN, 2003] were used. Until 2030, new multi-pollutant emission technology options [simultaneously controlling emissions of sulphur dioxide, nitrogen oxides and mercury (e.g. electrocatalytic oxidation following the ESP or SCR-wet FGD combination; EPA 2005)] will be employed. The number of fluidised bed plants (atmospheric - AFBC, pressurized – PFBC) will increase. Most power plants (with pulverized and fluidised beds) will be operated with supercritical or advanced supercritical (ASC) parameters.

Finally for the period to 2050, projection of electricity production from Energy Technology Perspectives (ETP) 2006 [IEA, 2006] was used. In the ACT (The Accelerated Technology) scenario, 40% reduction of world electricity generation in conventional plants is expected between 2003 and 2050. This scenario is convergent to DG TREN’s [DG TREN, 2003] baseline scenario (37% reduction of electricity production by thermal open cycle in EU-27 in years 2005-2030). The share of CO₂ capture and storage (CCS) technologies (post-combustion capture, oxy-coal combustion as well as pre-combustion capture in IGCC plants) will increase. In the baseline ETP 2006 scenario, a significant (3-times) increase of production in conventional power plants to 2050 and zero level of CCS technologies is projected; therefore this scenario was rejected. Until 2050, steam cycle coal-fired power plants will operate with supercritical and ultra-supercritical (USC) parameters.

For sources other than the energy sector, DROPS projections of activities and emission factors (for iron & steel, cement production and mercury cells in chlor-alkali production) or projections of emissions (remaining sectors) to year 2020 were used. For the next periods, trends from the IPCC [2007] A1 scenario for cement and steel production in Organisation for Economic Co-operation and Development countries and reduction of emission factors from conventional power plants were used. Separate reductions of emission factors were used for dioxin emissions from waste incineration and PCB emissions from use of electrical equipment.

<table>
<thead>
<tr>
<th>Stressor</th>
<th>Sector</th>
<th>Total Emissions for EU-27 [TEQ/year]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2000</td>
</tr>
<tr>
<td>Dioxins</td>
<td>Fuel combustion</td>
<td>160</td>
</tr>
<tr>
<td></td>
<td>Industrial, residential &amp; commercial boilers</td>
<td>1111</td>
</tr>
<tr>
<td></td>
<td>Iron &amp; steel production</td>
<td>788</td>
</tr>
<tr>
<td></td>
<td>Cement production</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>Non-ferrous metal production</td>
<td>138</td>
</tr>
<tr>
<td></td>
<td>Waste incineration</td>
<td>471</td>
</tr>
<tr>
<td></td>
<td>Transport</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>Other sources</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>2812</td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>Stressor</th>
<th>Sector</th>
<th>Total Emissions for EU-27 [kg/year]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2000</td>
</tr>
<tr>
<td>PCB</td>
<td>Fuel combustion</td>
<td>1819</td>
</tr>
<tr>
<td></td>
<td>Industrial, residential &amp; commercial boilers</td>
<td>1071</td>
</tr>
<tr>
<td></td>
<td>Iron &amp; steel production</td>
<td>1131</td>
</tr>
<tr>
<td></td>
<td>Non-ferrous metal production</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>Waste incineration</td>
<td>194</td>
</tr>
<tr>
<td></td>
<td>Electrical equipment</td>
<td>20300</td>
</tr>
<tr>
<td></td>
<td>Other sources</td>
<td>153</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>24676</td>
</tr>
</tbody>
</table>
3.5. Summary and Recommendations

FINDINGS

- Development of emission inventories on a global scale is a challenging work. Information on activity patterns of emission sources of POPs worldwide is lacking. The data collected for inventory work vary in quality, and show large spatial and temporal gaps. Not every country keeps records or has a reporting mechanism, while in others information is proprietary. In this case, some methodologies (the use of surrogates) are needed to make an estimation and to fill the gaps.

- Significant advances have been made with respect to the development of such emission inventories for some POPs in the last decades. These inventories include those for DDT, HCB, HCHs, PAHs, PCBs, PCDD/Fs, and PFOS on a global scale. For some POPs there exists, in addition, emission inventories on a regional scale, especially for Europe, North America and China. All these inventories have been widely used by modellers and decision makers.

- Besides the emission inventories, there exist soil residue inventories for HCH isomers on a global scale and toxaphene in the United States.

- Emission inventories of all POPs are affected with high uncertainties concerning the applied emission factors. An improvement of emission factors as well as better understanding of the activity patterns is highly recommended. A higher distinction between different kinds of processes and their application conditions in different countries is needed.

- Information on emissions from sources of POPs and their allocations on global and regional scales is lacking. The data collected for inventory work vary in quality, and show large spatial and temporal gaps. Not every country keeps records or has a reporting mechanism, while in others information is proprietary. In particular, there is an urgent and general need for further measurements and characterisation of the emissions of several POPs at the sources of release.

- Many POP substances have direct emissions, not only to air, but also to other environmental media.

- For many so-called new POPs, which are covered already by international protocols, knowledge is very scarce.

- Development and improvement of gridded emission and soil residue inventories for POPs, with both certain temporal and spatial resolutions on a global scale, is crucial for assessing hemispheric or intercontinental transport of these POPs.

- In addition, various users (e.g. modellers, decision makers etc.) need emission data for POPs in order to answer different questions.

- For assessment of the success of the international regulations concerning POPs, i.e., the Stockholm Convention (UNEP, 2001), emission inventories as well as future baseline projections on global scale, are urgently needed.

- In order to understand hemisphere/global transport of POPs, an approach to integrate the major three elements, observations, emissions and models, is important. Among these three elements, however, emission inventory research is the weakest one, receiving the least attention.

- International collaborations in emission inventory research have been much less than those in monitoring and modelling researches.

- Emission inventories should include secondary emissions, however, most, if not all, emission inventories introduced in this Chapter are for primary emissions only. The
emitted POPs will deposit into environmental reservoirs, such as soil and water bodies, and re-emit to air through sea-air and soil-air exchange, forming the secondary emissions. As time goes on, the secondary emissions will become stronger and stronger, and supersede eventually the primary emissions.

- The methodological and empirical basis of emission estimates remains the weakest element in terms of POP control. For example, despite decades of interest and measurement of PCBs around the globe, uncertainty remains about contemporary source inputs and information is lacking to explain the continued elevated levels of PCBs in many terrestrial and aquatic foodchains.

RECOMMENDATIONS

- Although some global emission inventories for some POPs are available now, more emission inventories are urgently needed for POPs to meet the objective of HTAP.

- An ultimate goal should be to present emission data and future baseline projections at least for all substances covered by the Stockholm Convention in a format suitable for decision makers, who aim to develop cost-effective control measures.

- Any future projection of POPs emissions, without considering the secondary emissions, will not be complete, or misleading in some cases. Thus, we strongly suggest that the emission inventories produced in the future take into account the historical development of substance specific releases to the environment. Based on the description of former emissions, models are able to model additional secondary emissions.

- Scientists concerned with risk assessment most often request the cumulative toxicity of the emissions, described by the concept of toxicity equivalence factors (TEF) to allow risk assessment of exposure to complex mixtures of different chemicals, for example, dioxins and furans. Environmental modellers, on the contrary, are increasingly requesting information on the emissions of individual POP constituents (isomers, congeners), due to different fates in the environment. For POPs that are emitted into the environment as spatially and temporally variable mixtures, it is considered a great challenge to provide reliable emission estimates of individual isomers and congeners. This is clearly limiting the possibilities for modellers to evaluate the regional and global source-receptor relationships to very few POP compounds.

- Especially information on temporal trends in emission data from the past to the future are needed by decision makers and scientists that work on verification of implementation of environmental strategies. In such cases, it also becomes imperative that emission data are frequently updated to resemble the current situation in pollution levels. In particular, this should be the case for those toxics for which various measures are strongly influencing the overall emissions, such as PCDD/Fs and selected pesticides.

- Further development of global emission data sets is also dependent on the outcome of future research on the generation of POPs during various anthropogenic and natural processes. This research should focus on the improvement of methodological approaches leading to the establishment of more accurate methods of POP emission estimates.

- A strong recommendation of the authors of this chapter is to make further efforts on the reporting requirements of POP emission inventories and data parameters on a global scale.

- For industrial chemicals, such as the PCBs and the PBDEs, it would be desirable to conduct further experiments that aim to quantify emissions from key usage categories, since reliable empirical data are generally lacking. Specifically, there seems to be a need for further studies that aim to improve the understanding between atmospheric
emissions of PCBs and temperature. Temperature dependency will be a key question in the future, taking into account climate change.

- The relative importance of PCB emissions due to unintentional formation needs further investigation and clarification with respect to the regional and global mass balance for individual PCB congeners. In addition to the general need for improved emission characterisation, additional environmental concentration measurements in air, soil, and water on a global scale, from which trends can be derived, are needed to allow comparison with modelling and serve as a check on emission totals.

- Development of emission inventories for POPs needs international collaboration. This HTAP effort has given an opportunity for scientists from different countries to work together, and their cooperation has been strengthened.

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Chapter 4
Global and Regional Modelling of POPs

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Contributing Authors: Victor Shatalov, Paul Bartlett, Anne Hollander, Sunling Gong, Gerhard Lammel

4.1. Introduction

This chapter describes modelling approaches for quantification of environmental exposure to persistent organic pollutants (POPs), reviews applications of models in conjunction with emissions information and monitoring data, and presents results of model comparison exercises aimed at quantifying intercontinental source-receptor relationships.

One of the defining characteristics of the POPs that are identified in the Aarhus Protocol of the UNECE Convention on Long-range Transboundary Air Pollution (CLRTAP) is that they have properties that permit dynamic exchange between air, water, soils and vegetation. Thus, POPs may undergo several cycles of deposition and revolatilisation/resuspension between the atmosphere and the surface of the earth during their residence time in the environment. As a result, the environmental fate and long-range transport characteristics of POPs are determined not only by processes in the atmosphere, but also by physical and chemical processes that take place in other environmental media (Figure 4.1). This property of POPs has strongly influenced the development of fate and transport models that describe their environmental behaviour at regional and global scales [Wania and Mackay, 1999].

![Figure 4.1. Fate transport processes that determine the long-range transport potential of POPs. Processes that take place in the atmosphere, land, and oceans all play a role in determining the environmental fate and transport of POPs.](image)

To a large extent, the behaviour of POPs in the environment is determined by their physico-chemical properties [Fenner et al., 2005]. Properties of particular importance are equilibrium partition coefficients between air, water and octanol (\(K_{AW}\), \(K_{OW}\) and \(K_{OA}\)), and the degradability of the substance in different environmental media. The media (air, water or soil) that receives emissions of the substance to the environment also exerts an influence on its environmental fate. Finally, the location and time that emissions occur, in combination with the characteristics of the environment, such as temperature, flow patterns of wind and water and availability of degrading reactants (e.g. photo-oxidants) and organic carbon to act as a sorbent all combine to influence the behaviour of POPs in the environment.

All of the POP models described in this Chapter are designed to integrate information about physico-chemical properties, emissions and the environment into a mathematical description of the system.
of chemical and the environment (Figure 4.2). In order to build confidence that the models are useful descriptions of the system of chemical and environment, it is important to evaluate them against empirical observations. However the models can also be used as tools to evaluate the quality and completeness of emission inventories, and to, e.g., identify knowledge gaps in the physico-chemical property data for substances or to evaluate processes. Thus, models are a key component of the integrated approach to understanding the environmental dynamics of POPs, because they allow information about emissions and chemical properties to be rationalized with levels observed in the environment in monitoring studies.

![Figure 4.2](image.png)

Figure 4.2. Chemical fate and transport models integrate independent information about the chemical, emissions, and the environment in a way that it can be evaluated against monitoring data. [Adapted from Figure 3 of Scheringer, M. (2009), Long-range transport of organic chemicals in the environment, *Environmental Toxicology and Chemistry*, 28(4), 677-690, with kind permission of John Wiley and Sons.]

Currently, there are two schools of models that describe the fate and transport of POPs at different spatial scales, different levels of detail, and with different levels of fidelity to the real environment [Scheringer, 2009]. One school of models has developed from the multimedia compartment modelling approach [Mackay, 2001, CRC], and therefore these models have an inherent focus on describing reversible exchange of POPs between the atmosphere and the surface. Generally, models from this school use static descriptions of the environment, and place a focus on understanding how physico-chemical properties of organic chemicals determine their environmental behaviour. However, some models that represent this school have been developed into geographically explicit, spatially and temporally resolved multimedia compartment models.

The second school of models is based on atmospheric chemistry transport models (CTMs) and general circulation models that have been modified and extended to include reservoirs representing surface media and, in some cases the sub-surface, such as the deep sea. Most models from this school are highly spatially and temporally resolved, and describe spatially and temporally variable aspects of the environment with more fidelity than multimedia compartment models. Some of these models incorporate online description of aerosol dynamics and atmospheric reactants chemistry to evaluate POP fate in the atmosphere in more detail. Both types of models have been applied and interpreted in conjunction with emission estimates, physico-chemical property information and field observations to improve our understanding of the long-range transport behaviour of POPs in the environment [Scheringer, 2009].

The objective of this chapter is to evaluate the appropriateness of POP fate and transport models as a scientific basis for decision-making under the UNECE CLRTAP. This is accomplished by first presenting a review of models that represent the two schools of model development and of studies that have been carried out comparing different models of POP fate and transport. Modelling studies that have examined the regional and global transport of POPs, and studies that have estimated
source-receptor relationships at regional, continental and global scales are also reviewed. Studies that examine the level of agreement between models and observations, which is a function not only of the performance of the model, but also of knowledge about physico-chemical properties and emissions as well as environmental processes and their parameterisation are reviewed.

The Task Force on Hemispheric Transport of Air Pollution has designed a set of source-receptor (SR) model experiments to evaluate the agreement between models in their description of large-scale source-receptor relationships. Preliminary results for the "SR1" model experiments for three POPs models (BETR-Global, MSCE-POP, and SimpleBox) and four substances (α-HCH, PCB-28, PCB-153, and PCB-180), are presented here, and recommendations for further improvements and future needs and made. Finally a summary of the current status of modelling capabilities for POPs and recommendations for future development and TF HTAP activities are presented.

4.2. Modelling approaches for the evaluation of POP transport

4.2.1. Theory and Background of models of POP transport in the atmosphere

The transport of any chemical substance in the atmosphere between two locations, A and B, is determined by the residence time of the substance in the atmosphere and the time required for an air parcel containing the substance to travel from A to B. In addition, POPs can reversibly exchange between the atmosphere and the surface between A and B, and this must be accounted for in chemical transport models.

A number of competing influences determine the residence time of POPs in the atmosphere. Depending on the properties and reactivity of the substance, either degradation by reaction with species such as hydroxyl radicals, or deposition to the surface may be the dominant removal process from the atmosphere. Most fate and transport models for POPs describe deposition using pseudo-first order kinetics in which the rate of removal of substance from the atmosphere \( (F, \text{mol/h}) \) is the product of the amount of substance present \( M \) (mol), and a first order rate constant, \( k \) (h\(^{-1}\)). Degradation is described using either pseudo-first order or second order kinetics (see below). Many POPs are semi-volatile (saturation vapour pressure at 298K is in the range \( 10^{-6} - 10^{-2} \) Pa), such that they distribute between the gas phase and aerosols in the atmosphere. This is critical in determining the rates of degradation and removal by wet or dry deposition. Gas-particle partitioning is usually modelled using empirical equations that relate the fraction of POP in the gas phase to its vapour pressure or octanol-air partition coefficient. A dynamic aerosol sub-model is only rarely included, instead aerosols are typically prescribed.

![Figure 4.3](image)

**Figure 4.3.** Processes that are considered in modelling POPs in the environment. The distribution of the POP between the gas phase, aerosols, and precipitation in the atmosphere is usually modelled using distribution coefficients. All other processes are generally modelled using kinetic descriptions. Only one generic surface compartment is shown here, but models usually include many surface compartments.
Many POPs are degraded in the atmosphere principally by hydroxyl radicals (OH) in the gas phase, and often only this degradation process is explicitly modelled in the atmosphere. The fraction of chemical that is sorbed to aerosols is often assumed to be shielded from degrading reactions, although for some substances degradation on particles may also be considered. The rate constant describing degradation in the gas phase is sometimes specified implying constant photo-oxidant concentrations (pseudo-first order kinetics). In spatially and temporally explicit models it is specified as a second order rate constant of the reaction with prescribed distributions of OH radical concentrations. For many POPs no experimental kinetic data are available and QSAR-based estimates of the rate of reaction with OH are used instead.

In multi-media modelling wet and dry gaseous and particulate deposition processes that transfer POPs from the atmosphere to the terrestrial surface or oceans are usually represented as first order rate constants, exploiting a range of empirical and mechanistic relationships. Models for many of these deposition processes have been developed and evaluated using data gathered in field studies, as described in Section 2.4.

Because of the potential for multiple “hops” between the atmosphere and the surface, the atmospheric transport of POPs is more complex than atmospheric transport of conventional air pollutants (Part A). Transport models for POPs must account for re-emission of deposited chemical, and the chemical and physical processes that occur in surface media that permanently remove the substance from the environment. At the global scale, the most important surface media to consider are surface seawater and the vegetation and top soils on land. As in the atmosphere, processes occurring in surface media are generally modelled using first order rate constants estimated from empirical information and mechanistic models. Re-emission of POPs to the atmosphere from surface media is usually modelled as a diffusive process, and is called volatilization. This process is the reverse of dry gaseous deposition. Some models also include physical re-emission processes, i.e., suspension of soils on land and formation of marine aerosols at sea, as processes that mobilize pollutants from the surface to the atmosphere.

POPs can be finally removed from circulation in the environment by two types of processes in surface compartments; degradation and physical sequestration. These processes are generally modelled using first order rate constants estimated from empirical information and mechanistic models. These may be modified to reflect spatial and temporal variability in temperature using estimates of the activation energy of the degrading reactions. In the oceans, physical sequestration of POPs occurs when they are transported to the deep oceans by settling with particles or by mixing out of the surface layer. Likewise, physical sequestration in soils can occur when POPs are irreversibly sorbed to soil solids or are physically mixed in soils to sufficient depth that they are unlikely to return to the surface or leech into ground water.

4.2.2. Overview of existing models and approaches

Available POP models are designed to cover a wide range of applications which include evaluation of compartmental partitioning, estimation of indicators for screening of substances (i.e., long-range transport potential, LRTP, and overall persistence, Pov), and assessment of POP long-range transport, spatial and temporal trends and source-receptor relationships with different level of details. Table 4.1 provides a summary of existing modelling approaches and models for POPs. The table is organized to separate different schools of models, i.e., those based on a multimedia mass balance approach, those based on atmosphere/ocean transport models. The table also includes a number of atmospheric transport models that were applied to study POP LRT, however these do not take into account the influence of secondary emissions sources and accumulation in environmental compartments other than the atmosphere.
Table 4.1. Summary of modelling approaches for POPs with examples and references.

<table>
<thead>
<tr>
<th>Purpose</th>
<th>Multimedia mass balance models</th>
<th>Multicompartment Chemistry Transport models</th>
<th>Atmospheric transport models</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substance screening, hazard ranking</td>
<td>Compartment-based models describing a single region or &quot;unit world.&quot;</td>
<td>Eulerian or semi-Lagrangian chemistry transport models, General circulation models.</td>
<td>Lagrangian and trajectory models, Eulerian CTM.</td>
</tr>
<tr>
<td>Evaluation of LRT and S-R, characterisation of environmental exposure.</td>
<td>Compartment-based models describing connected sets of regions or &quot;unit worlds.&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Local, regional, global, 0</td>
<td>Regional, global, 1-3</td>
<td>Regional, global, 3</td>
<td>Regional, 3</td>
</tr>
<tr>
<td>Air, soil, and water, some also sediment and vegetation.</td>
<td>Air, soil and water, some also sediment, vegetation, snow and ice</td>
<td>Air, soil, water, some also vegetation, sediment, snow, ice</td>
<td>Air</td>
</tr>
<tr>
<td>None, or generic using representative wind speeds and water flow rates.</td>
<td>Climatological in air, ocean</td>
<td>Meteorological reanalysis or model-generated statistics, Oceanographic reanalysis</td>
<td>Meteorological reanalysis</td>
</tr>
<tr>
<td>[Bennett et al., 1998; Mackay and Paterson, 1991; Van de Meent, 1993; Wegmann et al., 2009]</td>
<td>[Mackay, 2001; MacLeod et al., 2005b; Prevedouros et al., 2004b; Scheringer et al., 2000; Strand and Hov, 1996; Sweetman et al., 2002; Wantia and Mackay, 1995]</td>
<td>[Gong et al., 2007; Guglielmo et al., 2009; Hansen et al., 2004; Koziol and Pudykiewicz, 2001; Malanichev et al., 2004; Pekar et al., 1999; Semeena and Lammel, 2003]</td>
<td>[Cohen et al., 2002; Eckhardt et al., 2009; van Jaarsveld et al., 1997]</td>
</tr>
</tbody>
</table>
The sections below provide a brief review of applications of models from each of the different schools to assess POPs fate and transport in the environment.

Multimedia mass balance models

Multimedia mass balance models describe the environment as a set of homogeneous boxes or compartments, each representing a specific medium, for example, air, water, soil or biota. Concentrations of chemical in each environmental compartment are calculated by solving a mass balance equation that relates emissions to the fluxes due to degradation, irreversible sequestration and inter-compartment transfer [Mackay, 2001]. The first examples of multimedia mass balance models were developed in the late 1970s and early 1980s [Mackay, 1979; Mackay and Paterson, 1981; Mackay et al., 1985], and were formulated using fugacity as a criterion of equilibrium of chemical partitioning between air, water, soil and sediments [Mackay and Paterson, 1991]. Over the past decades, the development and use of these models to describe the environmental fate of chemicals has strongly increased, and many multimedia mass balance models exist, based both on fugacity and concentration units [Cowan et al., 1995].

Some multimedia mass balance models were developed for screening evaluation of the environmental fate of toxic substances. These models are intended to be applicable to a wide range of substances and in cases where data availability may be low. Therefore the emphasis is on comparative assessment of substances with different properties or emission characteristics [Mackay, 2001]. Mackay [1996] has outlined a process for evaluating the fate and transport characteristics of chemical substances using model calculations with increasing detail and fidelity to the real situation, designated as Level I to Level IV. Screening-level, single region models usually use Level III mass balance calculations, which assume the system of chemical and the environment is at steady-state with a constant emission rate. In applications designed to assess environmental exposure to specific substances, Level IV calculations are used in which emission rates and environmental properties can vary in time.

Multimedia mass balance models have been extensively applied in support of chemical management and regulation. In the European Union, the EUSES model [Vermeire et al., 1997; Vermeire et al., 2005] is currently being used as a risk policy instrument, and in the USA, CalTOX [Mckone, 1993] and the total risk integrated methodology [U.S. EPA, 2002] are applied for this purpose. Multimedia mass balance models are also recommended by the OECD for ‘benchmarking’ new and existing chemicals [OECD, 2004]. In the benchmarking exercise, model-derived indicators of environmental fate properties of new substances are compared against substances with better characterized behaviour. Indicators used in the OECD benchmarking tool are overall persistence (Pov) and LRTP [Fenner et al., 2005; Klasmeier et al., 2006; Scheringer, 2009; Wania, 2003]. Beside their use in chemicals management, multimedia mass balance models are also used in scientific applications. They can help in understanding the behaviour of substances in the environment, as well as in identifying data gaps (e.g. accuracy of important physico-chemical substance properties or environmental processes and their parameterisation) concerning chemical fate [Newman et al., 2003].

The SimpleBox model is one of the most well-known examples of a multimedia mass balance model. SimpleBox is Level III and Level IV ‘Mackay type’ multimedia fate model that describes the environment as ten environmental compartments at four “nested” spatial scales; local, regional, continental and global scales [Brandes et al., 1996; Den Hollander et al., 2004]. The regional and continental scales distinguish an air compartment (atmospheric mixing layer), a sea water compartment with a sediment compartment, a fresh water compartment with a sediment compartment, and three types of soil compartments (natural, agricultural, other soil) with corresponding vegetation compartments. SimpleBox is a generic model, in which the default environmental settings are set to constant values selected to represent typical, long-term averages [Brandes et al., 1996]. The SimpleBox model structure is currently adapted in the EUSES model [Vermeire et al., 1997; Vermeire et al., 2005], which is applied for regulatory purposes within the European Union.
Spatially resolved multimedia mass balance models

Many multimedia models treat the environment as a set of well-mixed compartments with characteristics that are assumed to be constant in time, and the same in all places, laterally as well as vertically. These models thus have zero spatial or temporal dimensions. However, spatially resolved multimedia fate models have also been developed since the 1990s, often using information from geographical information systems (GIS). In 1996, Wania and Mackay tentatively screened the possibilities for introducing GIS in multimedia fate models [Wania and Mackay, 1996]. More advanced models followed [MacLeod et al., 2001; Wania and Mackay, 1996; Woodfine et al., 2001]. Examples include IMPACT-2002 [Pennington et al., 2005], and G-CIEMS [Suzuki et al., 2004] and MAPPE [Pistocchi, 2008]. Another specific sub-group of multimedia compartment models describe the fate of pollutants in river systems [Coulibaly et al., 2004; Suzuki et al., 2004], of which some focus on in-stream water quality [i.e. GREAT-ER Feijtel et al., 1997].

A family of spatially explicit multimedia mass balance models have been developed based on the Berkeley-Trent (BETR) modelling framework [MacLeod et al., 2001]. These include BETR North America, the European Variant of BETR (EVn-BETR) [Prevedouros et al., 2004a], BETR-World [Toose et al., 2004] and BETR-Global [MacLeod et al., 2005b]. The BETR modelling framework allows spatially explicit models to be built-up by connecting “unit world” regional models, where each region is a seven-compartment mass balance model that includes two air compartments, soil, vegetation, ocean water, fresh water and sediment. Information on the model construction can be found in [MacLeod et al., 2001] and [Woodfine et al., 2001]. All models based on the BETR framework can be applied as steady state (Level III) or dynamic (Level IV) models.

Two notable spatially explicit multicompartment models are the ClimoChem [Scheringer et al., 2000] and ChemRange models [Held, 2001; Scheringer et al., 2001], which treat the global environment in a highly abstract way, yet which have been used to reveal controlling influences on long-range transport of organic chemicals. ChemRange models chemical transport in a closed loop of multimedia regions with a circumference that is equal to the circumference of the Earth. ClimoChem describes the global environment as a set of latitudinal zones, and neglects longitudinal spatial variability. It thus has one spatial dimension. Compartments included are soil, oceanic surface water, troposphere air, vegetation and vegetation soil.

Multicompartement chemistry transport models

More detailed description of the influence of spatial and temporal variation of environmental conditions on POP contamination can be obtained by general circulation models that include atmospheric tracer transport and chemistry modules, and extended to global multicompartment chemistry transport models (MCTM) by inclusion of surface compartments and parameterisations for surface exchange. These models capture the stochastic and deterministic features of fluid transport in air and water, e.g. the large-scale weather patterns and their seasonality. Depending on the description of the substance transport they can be Lagrangian or Eulerian. The dynamics can be driven by observations of wind and sea surface temperature or by prescribed, but realistic climate variability. Transport in various altitudes and episodic transports are resolution dependent and can, at least to a large extent, be captured. Sub-grid scale parameterisations capture additional features, e.g. cloudiness. The diversity and temporal dynamics of the environmental media are represented and geo-referenced. Chemical transformation of POPs and intercompartmental mass exchange are described similar to multimedia mass balance models. Some of these models can include online description of aerosol dynamics and chemical transformation of reactive species in the atmosphere. In the context of various types of applications, the atmospheric and oceanic dynamics and tracer transport of such models have been validated [Cess et al., 1990; Shindell et al., 2008; Textor et al., 2006]. At the same time, the spatial resolution and temporal scale of such simulations may be computationally limited, and input data having adequate detail is often sparse.

A number of multicompartment chemistry transport models have been developed for the evaluation of POP long-range transport, source-receptor relationships, and fate and distribution at high spatial and temporal resolution. In particular, the MSCE-POP model was designed for the evaluation of POP long-range transport on hemispheric and regional scales under the Cooperative
Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe (EMEP) [Gusev et al., 2005b, EMEP Report 5/2005]. It is a nested three-dimensional (3D) Eulerian multimedia POP transport model considering the distribution of POPs within the atmosphere, soil, seawater (including ice), and vegetation (including forest litter fall). The model includes description of 3D transport in atmosphere and ocean water, vertical transport in upper soil layer, phase partitioning and degradation in media, intermedia exchange, and sedimentation in seawater. It provides estimates of pollution levels and intercontinental transport of POPs along with the transboundary fluxes between the European countries distinguishing also primary and secondary sources of POPs. This modelling approach is being currently extended to the global scale in the framework of the global multicompartment multipollutant modelling system GLEMOS of EMEP/MSC-E.

The MPI-MCTM [Guglielmo et al., 2009; Lammel et al., 2001; Semeena et al., 2006] is based on a three-dimensional coupled atmosphere-ocean general circulation model with embedded two-dimensional top soil and vegetation surfaces. Chemicals cycle in atmosphere (gas, water and particulate phase), ocean (dissolved, colloidal, particulate phase), sea-ice, and soil and vegetation surfaces. A nutrient-phytoplankton-zooplankton-detritus ecosystem model is included in the ocean sub-model and a fully dynamic aerosol model is included in the atmosphere. Hence, the model captures gravitational settling of particles in air and ocean. Spatial resolutions used correspond to 100-250 km in the horizontal.

The GEM/POPs model [Gong et al., 2007] is based on a three-dimensional chemistry transport model coupled to a 3D soil model and 2D ocean model with prescribed ocean currents. Chemicals cycle in atmosphere (gas, water and particulate phase), ocean (water) and soil. An aerosol model is included in the atmosphere. Spatial resolution used corresponds to ≈200 km in the horizontal. Simulation results of three PCBs (28, 153, and 180) for the year 2000 indicate that the model captured the main features of global atmospheric PCBs when compared with observations from EMEP, IADN and Alert stations. The annual averaged concentrations and the fractionation of the three PCBs as a function of latitudes agreed reasonably well with observations.

The DEHM-POP model is the POP version of the Danish Eulerian Hemispheric Model. It is a further development of a 3D dynamic atmospheric chemistry transport model covering the Northern Hemisphere, originally developed to study atmospheric transport of conventional air pollutants and other atmospheric constituents (e.g., SOX, heavy metals, and CO2). Four different surface compartments (soil, ocean water, vegetation, and snow) are introduced in DEHM-POP with each compartment including the most dominant dynamic processes determining the exchange between air and the surface type to account for the consecutive cycles of deposition and reemission of POPs.

The global transport of organochlorine pesticides was studied using the 3D model MEDIA [Koziol and Pudykiewicz, 2001]. The model includes the description of atmospheric transport along with the exchange with different types of underlying surfaces such as seawater, soil, snow, and ice.

Atmospheric transport models

Along with MCTMs the long-range transport of POPs was also studied using atmospheric transport models, in particular, Lagrangian dispersion and trajectory models [Cohen et al., 2002; Eckhardt et al., 2009; van Jaarsveld et al., 1997]. These models can be run both forward and backward in time [Stohl et al., 2003], and have been used successfully to study the past distribution and fate of emissions of low-volatility POPs from known primary sources [Cohen et al., 2002] or the source distribution of contamination of remote areas on an event basis [Eckhardt et al., 2007]. So far, secondary sources (due to surface-air mass exchange) have not been included in these models.

The Lagrangian model HYSPLIT-SV has been implemented to preserve source receptor relations, which enables the ranking of source contributions to specified receptors of interest for exposure routes. Air transport coefficient maps independent of emissions are created to show the efficiency of transport from source regions to specified receptors. This method can be used to develop alternative emission scenarios, or, through inverse modelling, to estimate emissions for new chemicals
for which emissions are unknown [Cohen et al., 2002; Commoner et al., 2000]. HYPLIT-SV has been further developed with a Eulerian component to enable global applications.

Atmospheric transport of PAHs, PCBs, and PCDD/Fs was recently studied using Community Multiscale Air Quality (CMAQ) modelling system [Matthias et al., 2009; Meng et al., 2007; Zhang et al., 2009]. Particularly, CMAQ model was adapted to simulate atmospheric transport and deposition of POPs taking into account degradation and gas-particle partitioning processes, however air-surface exchange was neglected.

4.3. Model applications to study POP long-range transport on global and regional scales

Models have been applied to address the problems associated with POPs in a variety of ways, for example, to identify harmful chemicals, to describe current levels of pollution and their temporal trends, to estimate source-receptor relationships, and to project future changes of pollution. Models provide insight into the atmospheric transport of POPs since they represent a quantitative description of processes that limit transport potential that can be scrutinized and compared to other types of information. As a scientific tool, the models can be applied in either evaluative or simulative studies.

In an evaluative application, models are applied to examine how the long-range transport of POP substances depends on different factors, such as physico-chemical properties of the substance, weather conditions, model representations of the environment, release location, etc. In such studies, it is the behaviour of the model that is examined under a range of different assumptions.

In a simulative application, models are used in conjunction with emission estimates and monitoring data to evaluate our understanding of the sources, environmental fate and transport, and ultimate sinks of POPs. In simulative studies, the goal is to apply the model to simulate the real system, compare and contrast the simulation to empirical observations, and thus identify gaps in our knowledge or understanding. Up to now most simulative studies have examined non-polar substances such as PCBs and organochlorine pesticides. There are also some recent studies of brominated flame retardants and fluorinated acids. However, only a small sub-set of POPs and potential POPs have been extensively studied in this way, and studies of amphiphilic substances are particularly lacking.

Currently POP models are extensively applied at different stages of national and international policy activities related to POPs beginning from evaluation of new POPs for their inclusion into regulation legislations up to the detailed assessment of their fate in the environment for evaluation of compliance.

The goal of the TF HTAP is to quantify continental-scale source-to-receptor relationships. By its nature, this is a simulative problem. However, evaluative applications of models provide the basis for extrapolating simulative results from well-studied POPs to substances for which less information is available. Global scale model applications are reviewed in Section 4.3.1 and regional scale applications in Section 4.3.2. In the POPs field, applications of models to identify substances with combinations of properties that lead to high potential for long-range transport has been an area of intense research interest and studies are reviewed in Section 4.3.3.

4.3.1. Applications of POP transport models at global scale

The global-scale mass budget of PCBs has been simulated in several modelling studies. The PCBs are an attractive case study for simulative applications of models because physico-chemical properties [Schenker et al., 2008] and emissions [Breivik et al., 2007] have been relatively well characterized.

Global transport and budgets of three PCBs were investigated with a 3D dynamic model for semi-volatile POPs - GEM/POPs [Huang et al., 2007]. Figure 4.4 shows the intercontinental transport budget information of PCB-28 for several regions to investigate the mass transfers due to anthropogenic emissions and air-surface exchange processes, and the removal processes. Dominant pathways were identified for PCB transport in the atmosphere, with a transport flux peaking below 8 km for gaseous and 14 km for particulate PCB-28, and peaking below 4 km for gaseous and 6 km for particulate PCB-180. The intercontinental transport of PCBs in the Northern Hemisphere (NH) is dominated in the zonal direction by route changes regulated seasonally by the variation of the
westerly jet [Huang et al., 2007]. PCBs from the mid-latitudes flowed northwards into the Arctic via three, two and four entrance sectors in spring/winter, summer and autumn, respectively. Transport from Europe and North America via the North Atlantic Ocean contributed the most PCB mass to the Arctic. PCBs from the three major source regions are found to be partly transported across the equator in three different flow-paths, along with the easterly jet, the Asian monsoon winds, and subtropical high and trade winds. PCBs from the southern hemisphere are expected to be partly exported into the Northern Hemisphere.

**Figure 4.4.** (a) Intercontinental transport of PCB-28. The transport masses at four sides of each region are marked with a pair of numbers (particulate/gaseous PCBs in kg yr⁻¹), an arrow and a bar chart. A positive or negative number indicates the same or opposite transport direction as the arrows. The bar charts beside each arrow show the PCB transport masses of PCB particles (black bars) and gas (gray bars) through the region boundary in winter, spring, summer and fall. (b) (Inner figure) PCB-28 regional budget (kg yr⁻¹). [Reprinted from Figure 3 in Huang, P., et al. (2007), GEM/POPs: A global 3-D dynamic model for semi-volatile persistent organic pollutants 2. Global transports and budgets of PCBs, Atmospheric Chemistry and Physics, 7: 4015-4025.]

The BETR Global model was applied to simulate global-scale emissions, fate and transport, and sink processes for PCB 28 and PCB 153 over their entire use history [Lamon et al., 2009]. The model results using the ‘default’ and ‘maximum’ emission scenarios proposed in [Breivik et al., 2007] were compared against measured PCB concentrations in air at 16 long-term monitoring sites in North America and Europe that have been maintained since the early 1990s. Model results agreed best with the measurement data using the ‘maximum’ emission scenario. The measurements and model agreed within a factor of 3.16 for 64% of the data, and within a factor of 10 for 96%. This study builds upon the work [MacLeod et al., 2005b], where earlier versions of the BETR Global model and emission estimates [Breivik et al., 2002] were applied to seven PCB congeners and comparisons were made between model results and monitoring data collected in North America and Europe.

The BETR Global model has also been applied to assess the contribution of emissions in different parts of the world to deposition of POPs from the atmosphere to the Laurentian Great Lakes [MacLeod et al., 2005a, Report #LBNL-56801]. In this evaluative study, the model was applied to calculate “transfer efficiencies”, defined as the fraction of emissions to the atmosphere that are deposited to the Great Lakes, for a selected POPs. These transfer efficiencies can then be multiplied.
by estimated emissions to derive the relative contribution of emissions in different parts of the world to atmospheric loadings to the Great Lakes. The results of the study indicate that in the year 2000, more than 50% of the PCB loadings from the atmosphere to the Great Lakes are attributable to sources outside of the Great Lakes Basin. These include other sources in North America, and sources in Europe and Asia. Atmospheric loadings of α-HCH to the Great Lakes were mostly attributable to emissions in Asia, consistent with very low usage in North America and efficient transport over the global scale.

Four PCB congeners (28, 118, 153 and 180) were modelled in the Northern Hemisphere using the MSCE-POP model, and compared to concentrations measured in air in 1996 [Malanichev et al., 2004]. Using Breivik’s ‘maximum’ emission scenario [Breivik et al., 2002], the model agreed well with the measurement data, within a factor of 4 in nearly all cases, indicating that the spatial distribution of PCBs in air was well described. The model was further applied to evaluate the relative contributions of PCB sources in different regions of the world to deposition in the Arctic in 1996. The major source regions to the Arctic for all four congeners were North-western Europe, Russia and the Americas.

This study was continued later with the evaluation of significance of intercontinental transport of selected PCB congeners between several regions of Northern Hemisphere, namely, Europe, Russia, Southeast Asia, Americas, Northern Africa and Central Asia [Gusev et al., 2007]. The estimates of contributions of major emission sources of PCB-28, PCB-118, and PCB-153 to deposition over selected receptors regions were obtained based on updated PCB emission inventories [Breivik et al., 2007]. It was found that more volatile PCB congeners have a higher contribution to intercontinental transport compared to heavier congeners, which is shown in Figure 4.6 for the example of the distribution of deposition originated from emission sources in Southeast Asia to selected receptors in 2005.

Figure 4.5. Spatial distribution of PCB-153 concentrations in surface air (a), originated from the emission sources in the Northern Hemisphere (pg/m³), and contributions (in %) of emission sources in Europe (b) and North America (c) for 2005.
Estimates of long-range transport to remote regions like the Arctic showed relative importance of the source regions of the Northern Hemisphere. Particularly, it was observed that the most significant contribution to the deposition of PCB-28 and PCB-118 over the Arctic belonged to emissions from Europe and Russia (about 30-40% each) followed by sources in the Americas (about 15%). A different pattern was obtained for PCB-153, for which the most essential contribution was made by European emissions (about 60%) which might be connected with its physico-chemical properties (relatively higher fraction in the particulate phase) and the difference in the spatial distribution of its emissions.

Next to the PCBs, the group of POPs most studied using global chemical fate models are the isomers of hexachlorocyclohexane. \( \alpha \)-Hexachlorocyclohexane (\( \alpha \)-HCH) was the most prevalent isomer in technical mixtures of HCHs used as pesticides, and it has been the subject of several simulative studies at the global scale. As early as 1995, a global scale mass budget and transport to polar regions of \( \alpha \)-HCH was modelled using the GloboPOP model [Wania and Mackay, 1995]. Koziol and Pudykiewicz [2001] applied a multicompartment chemistry and transport model to simulate concentrations of both \( \alpha \)- and \( \gamma \)-HCH. The model results were shown to be within a factor of two of measurements made at Arctic monitoring sites. Toose et al. [2004] applied a global-scale model with 24 regions based on the BETR framework to simulate the global sources, transport pathways and sinks of \( \alpha \)-HCH, with a particular focus on pathways to the Arctic. Model results were compared against monitoring data in air and ocean water, and agreed within a factor of 10 in most cases. They determined that Europe and Asia have a particularly high potential to contribute to \( \alpha \)-HCH contamination of the Arctic. Most recently, the DEHM-POP model was applied to interpret short-term variability of \( \alpha \)-HCH at monitoring sites in the Northern Hemisphere [Hansen et al., 2008]. Simulated \( \alpha \)-HCH air concentrations were compared with measurements from 21 monitoring stations. Significant correlations were found between simulated and measured short-term atmospheric concentrations of \( \alpha \)-HCH.

The \( \beta \)-isomer of hexachlorocyclohexane has an air-water partition coefficient (\( K_{AW} \)) that is a factor of 20 lower than the \( \alpha \)-isomer. Based on a review of monitoring data and results of a multimedia model, Li et al. [2002] hypothesized that \( \beta \)-HCH is deposited from the atmosphere to oceans before reaching the Arctic, while \( \alpha \)-HCH is carried directly to the Arctic, then deposited to the Arctic Ocean. This apparent contrast highlights the potential for a slower migration of \( \beta \)-HCH and other ocean-born contaminants to the Arctic in ocean currents. Model calculations using the
GloboPOP model demonstrated that contaminants travelling primarily with ocean currents show increasing concentrations in the Arctic even decades after emission restrictions are put in place because of the relatively long timescales for ocean transport [Gouin and Wania, 2007].

Ocean transport is expected to be most important for persistent substances that are highly water soluble and have low vapour pressure and Henry’s Law constant. Perfluorinated acids are a relatively new class of persistent pollutants that have these characteristics. The global transport of perfluorinated acids in oceans has been modelled in simulative studies using GloboPOP [Armitage et al., 2006; Wania, 2007], ClimoChem [Schenker et al., 2008] and BETR Global [Armitage et al., 2009; Armitage et al., 2006] and MPI-MCTM [Stemmler and Lammel, 2010]. Together, these studies demonstrate that oceanic transport of persistent and hydrophilic substances can result in substantial transfer to remote ecosystems such as the Arctic Ocean.

Finally, a few studies have applied global scale models to simulate the fate and transport of dichlorodiphenyltrichloroethane (DDT). Schenker et al. [2008] used a modified version of ClimoChem to simulate the global mass balance of DDT and two transformation products, DDD and DDE. They compared their modelled concentrations of DDT, DDD and DDE to measurement data gathered from a review of 54 different sources, and found good agreement between the model and measurements in terms of temporal trends of concentrations, north-south variability and distribution between air, water and soils. Modelled concentrations were often within the range of measurement data, but discrepancies of up to a factor 100 were found in some cases. In follow-up work, Schenker et al. [2009] used Bayesian updating to optimize the parameterisation of ClimoChem for the DDT case and to attempt to reduce uncertainties in forecasts of future trends in concentrations.

In addition to the simulative applications of global-scale models described above, evaluative model experiments can also provide valuable insights into pathways for long-range transport of POPs. The enhancement of long-range atmospheric transport of long-lived semi-volatiles by the potential to undergo several cycles (grasshopper effect [Wania and Mackay, 1993]) has been studied using combinations of substance properties with and without re-volatilisation potential. It was found that the LRTP is higher, because of re-volatilisation, but it is not necessarily needed for substance accumulation in high latitudes: HCH (but not DDT) would accumulate in the Arctic even without re-volatilisation from land and sea surfaces [Semeena and Lammel, 2005]. It is the combined action of large-scale dynamics and deposition patterns which shapes the distribution evolving over time. Similarly, deposition processes that are specific to mountainous areas are key for the understanding of pollutant accumulation in high altitudes [Wania and Westgate, 2008].

When primary emissions of POPs are decreased, secondary sources (re-emissions from ground surfaces including water bodies) may become predominant. Thus, the source distribution of long-lived substances to the atmosphere may totally change over time. For DDT it has been suggested based on a modelling study, that simulated the combined atmospheric and oceanic transport [Stemmler and Lammel, 2009], that some continental and sea regions downwind of the areas of main historic usage, e.g. in the North Atlantic Ocean, had turned into the most significant source regions in the 1980s, i.e., 20-30 years after peak usage. Also, re-emission of semi-volatile PAHs is significant for their distribution and LRTP. They reach the Arctic and Antarctic but do not necessarily accumulate there (no net import to high latitudes [Lammel et al., 2009]). PAH LRT is efficient despite relatively high reactivity in air. Processes determining the gas-particle distribution in air are considered to be key for this yet unexplained observation. Highly-resolved transport modelling including a dynamic aerosol sub-model can provide complementary evidence to understand PAH gas-particle partitioning [Lammel et al., 2009].

Air-sea exchange of semi-volatile substances allows for multiple cycles through the atmosphere and ocean. Oceanic transport enhances long-term meridional transport, as relatively fast currents exist along some continents (Africa and the Americas). Net northward transports prevail in the Northern Hemisphere oceans [Guglielmo et al., 2009]. On the other hand, transfer of contaminants from surface waters to the deep sea by both deep water formation and sinking with sedimenting particulate matter (biological pump [Dachs et al., 2002; Guglielmo et al., 2009]) may slow down long-range transport and suppress a contaminant’s mobility. Full consistency with regard to the
definition of the accessible environment has not been achieved among different models, for example about the question of whether or not burial in the deep sea should be considered as an irreversible removal from the environment [Scheringer et al., 2003; Wania and Daly, 2002].

4.3.2. Applications of POP transport models at regional scale

Following the prevailing large-scale circulation, receptor regions are generally located 'downwind' of areas of major usage of POPs. E.g., the Northern Pacific Ocean is expected to receive long-range transport form East Asia [Huang et al., 2007; Semeena et al., 2006], the Arctic from Europe and (less) from North America [AMAP, 2004; Huang et al., 2007; Iversen, 1996] as confirmed by monitoring (see C2 2.2.3). In contrast to zonal transport and transport from mid to high latitudes, interhemispheric transport is less significant. All transport can be subject to considerable interannual variability [AMAP, 2004; Huang et al., 2007; Iversen, 1996].

A number of studies of POP long-range transport and source-receptor relationships have performed for Europe, North America, and Southeast Asia on a regional scale. Transboundary transport of selected POPs within the European region is evaluated on regular basis in the framework of EMEP activity in support of the CLRTAP POP Protocol [Gusev et al., 2006; Gusev et al., 2007; Gusev et al., 2008; Gusev et al., 2009b]. These studies, for example for B(a)P and PCDD/Fs, have shown the significance of the transboundary transport between the European countries and of the contribution of intercontinental transport to the pollution levels. The assessment was carried out using the nested MSCE-POP model [Gusev et al., 2005b, EMEP Report 5/2005] and officially submitted national data on POP emissions of European countries. Examples of spatial distribution of annual total deposition fluxes of B(a)P and PCDD/Fs within the EMEP region are shown in Figure 4.7.

**Figure 4.7.** Spatial distribution of annual deposition fluxes of B(a)P (a), g/km²/y, and PCDD/Fs (b), ng TEQ/m²/y, calculated for 2007. [Adapted from Figure 3.27 and 3.32 in Gusev, A., et al. [2009a], Modelling of heavy metals and persistent organic pollutants: New developments, EMEP/MSC-E Technical Report 1/2009, July 2009, Meteorological Synthesizing Centre – East, Moscow, Russian Federation.]

Comparison of modelling results for B(a)P against the data of the EMEP monitoring network showed reasonable agreement with measurements. In particular, for almost 80% of the monitoring sites the deviations between computed and observed annual mean air concentrations were about or less than a factor of two (Figure 4.8).
Figure 4.8. Comparison of measured and calculated annual mean air concentrations of B(a)P for 2007, ng/m³. [Adapted from Figure 3.10 in Gusev, A., et al. [2009a], Modelling of heavy metals and persistent organic pollutants: New developments, EMEP/MSC-E Technical Report 1/2009, July 2009, Meteorological Synthesizing Centre – East, Moscow, Russian Federation.]

These studies indicated that the contribution of transboundary transport to the deposition of B(a)P and PCDD/Fs from European anthropogenic emission sources exceeded 50% for almost half of the European countries. The contribution of distant sources, like North American emissions, to total annual PCDD/F deposition over Europe can be about 10-20%. In western European countries like Portugal, France, and the United Kingdom this contribution can be even larger. These studies also characterized the input of re-emission. It was observed that re-emission can be an essential source of pollution for the European region. In particular, the contribution of PCDD/F re-emission to deposition over the European countries was estimated to be in the range from 20% to 40%.

Another study of source-receptor relationships using the MSC-POP model was performed for the Northern Atlantic region [Gusev et al., 2005a, EMEP Report 12/2005] where the pollution by B(a)P and lindane was evaluated, and contributions of European and North American emission sources were estimated. It was shown that the input of North American emissions to the pollution of the open Atlantic and Arctic oceans was rather essential and comparable to the contribution of European emissions. In particular, relative contribution of B(a)P emissions from North America to deposition over the open Atlantic ocean in 1999-2000 was estimated to about 60%.

An example of model evaluation of source-receptor relationships using receptor models was presented in [Peng et al., 2007]. They evaluated source-receptor relationships of dioxins and dioxin-like PCBs using approaches, based on potential source contribution function (PSCF) and concentration-weighted trajectory (CWT) methods, and measurements of air concentrations made at three monitoring sites in different parts of Hong Kong in 2004. The methodology developed helped to determine the relative significance of potential emission sources and pathways in a large part of China. Particularly, emission sources in the northern part of China, most likely incineration, PVC industry, and leaded petrol-fuelled vehicles, were identified as the possible sources of air pollution, especially in winter. Pollution transported via southeast China was attributed to solid waste incineration. Additionally, unknown sources in the South China Sea were identified as possible sources of Hong Kong air pollution of the toxic substances.

Lagrangian transport models have been used to study the past distribution, fate and distribution of emissions of less-volatile POPs from known primary sources [Cohen et al., 2002] and for the regional and intercontinental location of primary and secondary sources on an event basis [Eckhardt et al., 2007] or based on trajectory statistics [Dvorská et al., 2009; Hsu et al., 2003; Kallenborn et al., 2007].
Trajectory statistics in combination with monitoring can be used to study the effectiveness of emission reduction measures taken on the regional and decadal scales [Dvorská et al., 2009].

4.3.3. New POPs: Modelling studies of long-range transport

It is clear that POPs that are currently identified under the UNECE CLRTAP and the Stockholm Convention are not the only organic substances with high persistence and potential for long-range transport. Therefore, both conventions contain provisions to add new substances. Identifying “new” POPs from among the chemicals in commerce and unintentional by-products of industry is an area of active research. Models can be highly valuable tools in this exercise, but they must be applied in a way that is appropriate to the task. Generally, the search for new POPs requires screening lists of substances based on structure only, i.e., without empirical information about physico-chemical properties and degradability. Thus, modelling must be done using properties estimated from quantitative structure-activity relationships (QSARs), which introduces additional uncertainty into the assessment. Often there is a lack of complete information about emissions, observed levels in the environment, and sometimes physico-chemical and degradation data to support a simulative study. As an additional challenge, there is an unknown uncertainty inherent in extrapolating models from the relatively few well-studied POPs where simulative modelling studies have been performed to substances with very different properties, and because new processes or parameterisations may need to be included.

In particular, POPs modelling experience is largely limited thus far to non-polar substances. In order to improve modelling capabilities to quantify intercontinental transport and source-receptor relationships of polar and amphiphilic compounds, there is a need to evaluate parameterisations for these substance classes' surface and phase exchanges. Additional processes, yet incompletely understood, may be significant for these substance classes' cycling. E.g., non-volatile substances can be transferred from surface seawater to air with sea spray when accumulated in surface films [Qureshi et al., 2009].

Screening and/or ranking of new chemical substances with respect to their long-range transport potential and persistence is done in many regulatory instruments using defined half-life criteria. Particularly, screening criteria used in the CLRTAP and Stockholm Conventions are based on the following four properties: LRTP, persistence, toxicity and bio-accumulation. The first two properties are important characteristics identifying the ability of a chemical to be transported over long distances and be subject to intercontinental transport. For instance, the screening criterion of LRTP used both in CLRTAP and the Stockholm Convention is $T_{1/2}^{\text{air}} > 2$ days [see, e.g., Decision 1998/2 of the Executive Body for CLRTAP UNECE, 1998]. For numerical indication of this parameter numerous metrics may be used.

However, models offer more detailed information on LRTP and persistence. Multimedia POP fate models are able to evaluate LRTP with allowance for all processes removing a pollutant from the atmosphere: degradation, dry and wet deposition and gaseous exchange. Similar to this, persistence can be evaluated with allowance for degradation in various media and exchange between them. Additionally, model calculations allow evaluating LRTP using distance-related metrics, which characterize the ability of pollutants to undergo long-range transport in a more direct way, and overall persistence (Pov) as a metrics of persistence. Multimedia models with zero spatial resolution provide additional information about the medium of most efficient transport (air or water), and the dependence of persistence on whether emissions are to air, water or soil. The OECD Overall Persistence and Long-range Transport Assessment Tool (The OECD Tool) is a zero-spatial dimension multimedia model that was recently recommended for screening assessment and hazard ranking of chemical substances [Wegmann et al., 2009].

It should be stressed however that different models will provide different outcomes in description of LRTP and persistence. In order to make the metrics of LRTP and persistence valuable parameters to be used for identifying new POPs to be covered by the Aarhus Protocol and the Stockholm Convention, the differences between different metrics and POP models were (and are still) to be mapped. To reveal the differences in the evaluation of LRTP and Pov resulting from application...
of different models a number of model intercomparison studies were performed as summarized in Section 4.4.1.

With spatially resolved models even more information is available, including the dependence of LRTP and Pov on geographical location of emission sources and/or variability of meteorological parameters. Studies of these dependencies have so far focused on one or a few specific chemicals and give in addition spatial distribution of chemicals emitted from conventional point emission sources. This information can support the negotiation process on inclusion of the considered substances to international environment-protection activities.

To contribute to the preparatory work for the review of the Protocol on POPs to the CLRTAP Convention, EMEP/MSC-E has developed specific methodology based on the application of spatially resolved models for the evaluation of LRTP and persistence of POPs [Gusev et al., 2009b]. The methodology was applied to the evaluation of LRTP and Pov for 20 substances, 18 of which were considered as POP-candidates within CLRTAP and/or the Stockholm Convention, and two (B(a)P and HCB) were used as “benchmark substances” of regional and global concern, respectively.

For the evaluation of LRTP of substances two numerical parameters - half-life of a substance in the atmosphere $T_{1/2}^{\text{air}}$ and transport distance $T_{D0.001}$ - were used, where $T_{1/2}^{\text{air}}$ was the time by which the mass of the considered pollutant in the atmosphere is reduced to half of the initial mass, and $T_{D0.001}$ was determined as an average distance at which concentration of the pollutant drops 1000 times compared with the atmospheric concentration at the source. It should be noted that the variability of meteorological parameters can play an essential role in the evaluation of LRTP. The illustration of this dependence was presented in [Gusev et al., 2009b] through the example of evaluation of two LRTP metrics ($T_{1/2}^{\text{air}}$ and TD) by the MSCE-POP model for 20 legacy and new POPs. An empirical relation between the $T_{1/2}^{\text{air}}$ and TD derived on the basis of model simulations of POP transport from the point sources at four geographical locations is shown in Figure 4.9. The non-linear relationship between TD and $T_{1/2}^{\text{air}}$ can be explained by the increasing influence of tortuosity of wind trajectories for large values of $T_{1/2}^{\text{air}}$. The values of $T_{1/2}^{\text{air}}$ and TD calculated by the model for different substances and source locations can be used for evaluation of the effective wind speed.

![Figure 4.9](image)

**Figure 4.9.** The dependence of $T_{D0.001}$ on $T_{1/2}^{\text{air}}$ obtained in the MSCE-POP model simulations for 20 new and legacy POPs and the approximation by an empirical relation. [Reprinted from Figure 2.25 in Gusev, A., et al. [2009a], Modelling of heavy metals and persistent organic pollutants: New developments, EMEP/MSC-E Technical Report 1/2009, July 2009, Meteorological Synthesizing Centre – East, Moscow, Russian Federation.]

Evaluation of persistence was performed using three metrics: half-lives in the environmental media $T_{1/2}^{\text{soil}}$ and $T_{1/2}^{\text{water}}$ and the overall persistence, Pov, expressed as total environmental half-life $T_{1/2}^{\text{env}}$. The $T_{1/2}^{\text{env}}$ computation took into account degradation processes in all media including inter-compartmental mass exchange. To evaluate these parameters, simulations with the conventional emission source located in Europe were made by means of the MSCE-POP model. In addition, to examine the dependence of LRTP on emission source location, model simulations for sources located in North America, China, and Japan were performed. According to the estimates of LRTP given in
Figure 4.10, the considered substances can be split into two groups: substances cycling regionally (with TD close to that for B(a)P) and substances cycling globally (with TD close to that for HCB).

![Graph showing half-life in air (T1/2) and transport distance (TD) for various substances.]

**Figure 4.10.** Results on LRTP evaluation: (a) – half-life in air, (b) – transport distance. [Reprinted from Figure 1.9 in Gusev, A., et al. [2009b], *Persistent Organic Pollutants in the Environment*, EMEP Status Report 3/2009, June 2009, Meteorological Synthesizing Centre – East, Moscow, Russian Federation.]

The importance of the evaluation of the overall persistence was illustrated for the example of PCP and β-endosulfan [Gusev et al., 2009b]. Particularly, it was shown that, in spite of the fact that half-lives in soil of these two substances were comparable (60 days for PCP and about 50 days for β-endosulfan) and the half-life in water for β-endosulfan (40 days) was larger than that for PCP (about 2 days), the half-life in the environment for PCP was much larger than for β-endosulfan. This fact is conditioned by the differences in intermedia exchange for these chemicals. PCP is mainly accumulated in soil where it is subject to slow degradation. In addition, β-endosulfan degrades in the air much faster than PCP. Hence, β-endosulfan, being re-volatilized to the atmosphere from soil and water due to intermedia mass exchange, is subject to fast degradation in this medium. This rapid degradation leads to the substantial difference in the calculated values of the Pov for these two substances. The results of the Pov evaluation for the 20 considered substances are presented in Figure 4.11, in which group of substances with high Pov can be distinguished. These substances are expected to undergo multi-hop transport within the Northern Hemisphere.

![Graph showing overall persistence (Pover) for various substances.]

**Figure 4.11.** Results of Pov evaluation for 20 substances. [Reprinted from Figure 1.10 in Gusev, A., et al. [2009b], *Persistent Organic Pollutants in the Environment*, EMEP Status Report 3/2009, June 2009, Meteorological Synthesizing Centre – East, Moscow, Russian Federation.]

As a contribution to environmental risk assessment of substances, global scale transport models have been applied in an evaluative fashion to quantify the LRTP and total environmental persistence (or residence time, Pov). Studies using a spatially and temporally resolved transport model show that total environmental lifetime and long-range transport potential are not intrinsic substance properties, but depend strongly on time, location and modal split of emission into the environment. E.g., the mean total environmental lifetime of DDT applied in agriculture in the 1980s was considerably longer than in the 1970s and 1990s, and the lifetime of DDT exceeds the one of γ-HCH under most emission scenarios, but not under all [Leip and Lammel, 2004; Semeena and Lammel, 2004].
2003]. A set of indicators has been developed to exploit 3D non-steady state model predictions of substance distributions evolving over time for derivation of measures of LRTP [Leip and Lammel, 2004]. Although it is clear that LRTP and Pov are not intrinsic properties of chemical substances in the general sense, there is a strong incentive to evaluate these hazard properties in a defined model system under 'standard' environmental conditions such that they can be treated as “pseudo-intensive” properties to allow substances to be ranked in a relative way [Mackay, 2001]. This is the approach taken in the OECD Pov and LRTP Screening Tool, for example by Wegmann et al [2009].

After a POP is included into an international legislation, a lot of information is needed for evaluation of compliance and the effectiveness of the legislation. In particular, the information on current contamination levels (concentrations and deposition fluxes), source-receptor relationships (transboundary transport between various countries and intercontinental transport), trends of contamination and projections for the future is required. Such information can be obtained on the basis of an integrated approach using monitoring, modelling and emission data. This approach includes refinement of emission inventories, evaluation of monitoring data and model development based on the comparison of monitoring and modelling results, and reporting modelling results in line with monitoring data. More detailed discussion on this approach is given in Section 4.5.

4.3.4. Influence of climate variability and climate change on transport pathways and levels of persistent pollutants

As discussed in detail in Chapter C1, there are many possible effects of climate change on the intercontinental transport of POPs. These include changes of wind fields, distribution of atmospheric constituents (atmospheric particles, reactive species), efficiency of removal processes (degradation, dry and wet deposition), characteristics of underlying surfaces (e.g., changes of land use, shifting of zones), seawater currents, and extent of snow/ice cover. POPs are characterized by a wide range of physical-chemical properties among which the most important with respect to the climate change are volatility, phase partitioning, and intermedia cycling. Additionally, most of processes governing their global dispersion are temperature dependant. Therefore projected future changes of climate (e.g. increasing of air temperature) might have essential effect on the distribution of both new and legacy POPs on the global scale. A comprehensive review of possible effects of climate change on the long-range transport of contaminants, including POPs, to the Arctic was given in [AMAP, 2004; Leip and Lammel, 2004; Macdonald et al., 2005; Semeena and Lammel, 2003]. The study discusses potential changes in atmospheric circulation analysing temporal variations of the Arctic Oscillation (AO) index. It is noted that under positive AO conditions, especially in winter, atmospheric transport of POPs from eastern North America and Western Europe to the Arctic may become more rapid. At the same time these conditions may increase the removal of POPs with enhanced precipitation, and thus change the balance between the atmospheric and oceanic transport pathways, especially for particle associated POPs and those with low Henry’s law constants.

POPs cycling’s response to climate change is particularly difficult to anticipate as the key chemical properties, volatility, phase partitioning, and degradation kinetics, are all sensitive to temperature and hydrological change [Macdonald et al., 2005]. For example, under warming conditions volatilisation from surface compartments may increase the fraction of POPs in air, while increased cloud cover and ozone concentrations may weaken or strengthen, respectively, the chemical sink of POPs in air, i.e. reaction with the hydroxyl radical. Thus these changes may increase the contribution of intercontinental transport of POPs. At the same time, as predicted by climate models, temperature difference between the polar and equator regions may become lower and the thermodynamic forcing toward the poles may decrease. Models are essential for understanding of POP transport and fate, however there still exist significant uncertainties in the description of processes and input data to produce realistic predictions of changes in pollution transport due to potential climate changes.

A few studies have used models to study the possible effects of climate change on the fate and transport of POPs. MacLeod et al [2005b] modelled the variability in PCB concentrations in the atmosphere using model parameterisations of BETR Global representing 40 different years, and looked for correlations between modelled concentrations and the North Atlantic Oscillation (NAO) Index.
Modelled concentrations at some locations were correlated with NAO index, and there was some evidence that similar correlations could be seen in monitoring data from sites in North America and Europe. Later, Lamon et al. [2009] used BETR Global parameterized with environmental conditions forecast for the years 2080-2100 under the IPCP’s A2 climate scenario and compared results to a present day scenario. They found increased intercontinental transport of PCBs as a result of enhanced wind speeds in the A2 scenario compared to present conditions, and identified the potential for higher emissions of semi-volatile substances to air from primary sources driven by higher temperatures. The potential for higher temperatures to mobilize POPs from primary or secondary sources to air as a result of climate forcing is also highlighted by evidence of positive correlations between concentrations of HCHs, HCB and lighter PCBs in air and NAO index [Ma et al., 2004].

An interesting aspect of the relationship between climate forcing and POPs was investigated in another study by Ma et al. [2005]. They explored the hypothesis that endothermic evaporation of DDT and toxaphene from soils in the southern United States might account for a large-scale cooling trend observed in that region during the last century. Their calculations indicated that pesticide evaporation may have contributed to the cooling trend, but that the contribution was an order of magnitude smaller than that required to account for the entire range of temperature variability that was observed.

4.4. Intercomparison of POP intercontinental transport models

4.4.1. POP model intercomparison studies

Intercomparison studies are useful instruments to analyze performance of the developed models, their uncertainties and deficiencies, and to elaborate recommendations for their further development. A number of intercomparison studies for the POP models with different complexity and different goals were performed recently. Some of these studies compared models, inter alia, with respect to their results concerning long-range transport potential (LRTP) and overall persistence (Pov). Besides these, a number of other model intercomparison studies were directed at LRTP and Pov issues [Fenner et al., 2005; Wania and Dugani, 2003]. These studies have proven that multimedia box models can be used for these ranking purposes, and that different box models show rather comparable rankings.

A number of studies were performed to compare how different types of POP models simulate POP fate and transport in different media. The inter-comparison of the EVn-BETR and DEHM-POP described in [Hansen et al., 2006] attempted to compare two models representing two different types of the POP models. The study was devoted to modelling α-HCH and compared seasonally averaged air, soil and water concentrations and distribution patterns within the European region. The analysis of particular removal processes showed noticeable differences between the descriptions of atmospheric advection processes used in the considered models. Further, the difference in the results due to the use of averaged rain rates in EVn-BETR instead of intermittent rain events was revealed. Generally there is a good agreement between distribution patterns calculated by the two models. However, atmospheric levels predicted by the EVn-BETR model were higher than those calculated by the DEHM-POP model. The differences were attributed to a less-effective advective algorithm used in EVn-BETR compared to that in DEHM-POP. It was also mentioned that ocean currents can be a possible mechanism for transporting α-HCH away from Europe.

More detailed analysis of the agreement between box and spatially resolved models was undertaken by Lammel et al. [2007]. In this study three multimedia mass-balance box models (MBMs), namely SimpleBox, ChemRange and MPI-MBM and one non-steady state multicompartment chemistry-atmospheric transport model MPI-MCTM were compared. The study attempted to compare compartmental distribution, overall environmental residence time and a measure for the long-range transport potential for DDT, γ-HCH, atrazine and methyl parathion. It was pointed out that MBM models tended to underestimate atmospheric transport velocity as a consequence of the neglection of temporal and spatial variability of meteorological parameters. The easy-to-use rapid box models could be “turned in” to better match the results of the comprehensive MCTM. Box models will continue to play an important role for rapid screening of the great number of potentially persistent organic pollutants and other persistent chemicals to be identified within
REACH. Besides, it was concluded that there is good agreement between the two types of models with respect to the LRTP-ranking of chemicals.

The EMEP intercomparison study of POP models [see Hollander et al., 2008] was initiated in 2002 in accordance with the recommendations of the Executive Body for the LRTAP Convention. The main aim of the study is to exchange scientific experience between different groups of POP modellers in order to improve understanding of POP fate in the environment and to evaluate the uncertainties of POP modelling. Twelve models were included in the intercomparison study. During this study various aspects of POP modelling were analyzed, in particular, physico-chemical properties of selected POPs and their uncertainties, parameterisations of main processes determining POP behaviour in various environmental compartments, estimates of concentrations of PCBs in media and their intermedia fluxes. Additionally, ranking of model estimates of the Pov and LRTP for 14 chemicals representing a wide range of POP physico-chemical properties was compared.

The results of the intercomparison study allowed evaluation the uncertainties of modelling due to the differences in physico-chemical parameters used. Assuming that the uncertainty of each particular parameter is characterized by the scattering of its values between the models, the uncertainty of MSCE-POP model output can be evaluated as 20% at maximum. Maximum uncertainties are caused by differences in degradation rates in the environmental media and in octanol/air and octanol/water partitioning coefficients.

For evaluation of LRTP of the chemicals the outflow of the pollutant from the calculation domain is crucial. One of the reasons for differences in the evaluation of this parameter by models of different types is spatial resolution [see also Lammel et al., 2007]. In POP transport models, air flows reflect dynamic atmospheric conditions, including wind speed variability and episodic transport events, whereas in box models climatologic states, i.e., long-term average are used, which even out the effect of episodic transport events. The above influence of resolution on model output leads to higher differences in evaluation of LRTP between models than those in Pov. In particular, this is illustrated by the high correlations between LRTP rankings obtained by more highly resolved models MSCE-POP, G-CIEMS, and EVN-BETR, on one hand, and between rankings obtained by box models SimpleBox and OECD Tool, on the other hand.

4.4.2. HTAP intercomparison of POP models

The HTAP intercomparison of POP models is aimed to support the development of better understanding of the intercontinental transport of air pollutants in the Northern Hemisphere. Similar to the activity of other modelling groups within the HTAP intercomparison this study for POPs includes a series of source-receptor simulations (SR1 and SR8). These simulations are aimed to investigate the response of pollution levels on the global scale to the emission perturbation in the selected four HTAP source regions, namely, Europe (EU), North America (NA), East Asia (EA), and South Asia (SA). These regions of the globe and the Arctic are considered as the receptors in the analysis of modelling results.

The three models that were included in this intercomparison represent multimedia box models (SimpleBox), spatially resolved multimedia box models (BETR-Global), and multimedia chemical transport models (MSCE-POP). Thus these models are different in the approaches applied to describe pollutant transport and in the representation of environment compartments and spatial resolution used. Particularly, the MSCE-POP and the BETR-Global are spatially resolved models operating with spatial resolution 2.5x2.5 and 15x15 degrees, correspondingly. The SimpleBox is the generic MBM which has no spatial resolution but allows nesting of regional and global domains.

Several POPs with different physico-chemical properties were selected for the evaluation of intercontinental transport in the SR1 and SR8, namely, three PCB congeners (PCB-28, PCB-153, and PCB-180) and α-HCH. They are characterized by significant long-range transport potential and residence times in the atmosphere and other compartments. In particular, half-life of PCB-28 in the atmosphere based on the data on degradation rate can be about 10 days, while for other selected PCBs it can be up to several months. α-HCH and PCB-28 are present in the atmosphere mostly in gaseous phase while other two heavier PCB congeners have appreciable fractions in the particulate phase.
Following the requirements of HTAP model intercomparison the model simulations and analysis of source-receptor relationships were performed for the year 2001. The source-receptor experiments were comprised of the base case model run and four model runs with 20% reduced annual emission for each of the chemical in each of NA, EU, SA and EA. The model spin-up for the prior period of time was performed using historic emissions in order to take into account the influence of secondary emission sources. For the evaluation of PCB intercontinental transport the “maximum” scenario of the global PCB emission inventory [Breivik et al., 2007] for the period 1930-2100 was selected. Long-range transport of α-HCH was evaluated using the global emission inventory compiled by [Li and Bidleman, 2003]. Each of the models used its own scenario of historic emission for the spin-up simulations based on these inventories.

The spatial distribution of α-HCH and PCBs emissions on the global scale following these emission inventories is essentially non-uniform (Figure 4.12). It can be seen that for PCBs major emission sources are located in European and North American regions, while the contribution of other regions is lower. In the case of α-HCH the highest emissions were in South Asia whereas in other regions they are smaller, especially in North America. To focus attention on the differences between models, rather than on differences in location of emissions, additional SR experiments (presented below) were performed for the equally-distributed emission of an arbitrarily defined amount between the four HTAP source regions.

![Figure 4.12. Spatial distribution of annual emission of α-HCH emission (t/y) for 2000 [Li and Bidleman, 2003] (upper panel) and of PCB-153 emission (t/y) for 2001 [Breivik et al., 2007] (lower panel).](image)

**Base case simulations results and comparison with measurements**

The spatial patterns of surface air concentrations for 2001 obtained by the spatially resolved BETR-Global and MSCE-POP models are given in Figure 4.13. In general, the models provide consistent estimates of air concentration distribution on an annual level, and major transport pathways of selected POPs. The areas of elevated concentrations reflect the major source regions and transport pathways. The modelled air concentrations show the prevalence of α-HCH transport from the EU and the SA regions, which affects downwind and surrounding regions. For PCB-28 more marked evidence of transport from the EU and the NA regions to the Arctic and to the EA region over Eurasia can be seen. Heavier PCBs are characterized by weaker transport from the NA to the EU and to the Arctic and from the EU to other regions.
Figure 4.13. Spatial distribution of modelled annual mean air concentrations of \( \alpha \)-HCH, PCB-28, 153, and 180 (pg/m\(^3\)) obtained by BETR-Global (upper row) and MSCE-POP (lower row) models.

Differences in illustrated spatial patterns of air concentrations can be explained by the effect of several factors: differences in spatial pattern of emissions, models resolution, and modelling approaches.

Modelling results of base case simulations of two models BETR-Global and MSCE-POP were compared with available measurements of EMEP and AMAP monitoring networks. The scatter plots in Figure 4.14 illustrate the level of agreement between the modelled and measured annual mean air concentrations of selected POPs. On the whole better agreement for both models is found for the PCB-153, PCB-180, and \( \alpha \)-HCH. For these chemicals, most of the predicted air concentrations are within a factor of 3 of the observed levels.

Larger discrepancies (a factor of 4 and higher) are obtained for PCB-28, especially for the monitoring sites in Kosetice (the Czech Republic), Rorvik and Aspvreten (Sweden). The models overestimate the air concentrations measured there, which may reflect uncertainties of PCB-28 emission estimates and its spatial distribution used in the model simulations. At the same time both models provide reasonable agreement with measurements of remote sites in the Arctic. Significant underestimation of observed PCB-153 and PCB-180 in air by the BETR-Global can be noted for the Kosetice site. This might be the effect of low spatial resolution used in the model and the necessity to use finer resolution modelling to better resolve measured levels of pollution in Central Europe, where ongoing sources are indicated by the emission inventory.
Figure 4.14. Comparison of BETR-Global and MSCE-POP model predictions with annual mean air concentrations of α-HCH, PCB-28, PCB-153, and PCB-180 observed at monitoring sites of the EMEP and AMAP networks in 2001. Dashed lines show the area of agreement within a factor of 3.

Evaluation of source-receptor relationships

Figure 4.15 shows the effect of regional emission reductions on the annual mean POP concentrations as the average of the three models, and the range in variability between the models. In most cases the largest effect on the pollution levels results from a change in local emissions (6-16%). Variations of responses to the emission perturbation can be seen in the receptor regions as well as between the selected POPs. The differences are mainly caused by the uneven spatial distribution of emissions (different relative contributions of the source regions to the total emission) and the effect of prevailing transport pathways. Particularly, for α-HCH the most marked effect on concentrations in the receptor region (decrease from 2% to 13%) results from the reduction of SA emissions, which have the largest contribution to the total emission. Similar influence is obtained by the models for PCB pollution levels due to the changes of emissions in the EU region. The lowest effect results from the reduction of α-HCH in the EA and the NA, and for PCBs in the EA due to their relatively low contributions to the total emissions. It should be noted that emission perturbations were applied only to the anthropogenic emissions while the emission of secondary sources was not perturbed.

In general, the models are quite consistent in simulating the changes in air concentrations in response to regional emission changes. In most of the cases the difference between the mean response and the model estimates are within a factor of 2-3. In some cases, however, especially when the effect of emission changes is low, these differences are higher. The BETR-Global model provides generally larger decreases of concentrations in response to emission reduction, which indicates more pronounced atmospheric transport of pollution as in the eastward direction and northward to the Arctic. Among the reasons for this might be the lower spatial resolution of BETR-Global model in
comparison to the MSCE-POP model. The smallest effect of emission changes in most of the cases is predicted by the SimpleBox model.

![Figure 4.15.](image)

Figure 4.15. Relative decreases (in %) of annual mean surface air concentrations in the receptor regions due to 20% emission reductions in four HTAP regions. The bars represent the average change for the models compared. The whiskers show the maximum and minimum estimates of response to the emission reduction obtained by the models.

The influence of emission reduction for the selected source-receptor pairs, representing the zonal transport of pollution in the eastward direction and meridional transport to the Arctic, is shown in Figure 4.15. The strongest SR relationships for PCBs can be seen for the pairs EU->SA and EU->EA (4-5% decrease of concentrations). Other pairs (NA->EU, EA->NA, and SA->EA) of S-R relationships are comparatively weaker (about 1% and lower). For α-HCH the strongest S-R relationship is obtained for the pair SA->EA (about 6%). Arctic pollution is mostly sensitive to the changes of emissions in the EU (for all selected POPs) followed by the NA (for PCBs) and the SA (for α-HCH). Comparing the results for PCB congeners, generally higher response to the emission changes can be noted for PCB-28 (especially for MSCE-POP and SimpleBox) than for the heavier congeners (PCB-153, PCB-180) in cases of NA->EU, EA->NA, EU->SA, and EU->EA pairs. PCB-28 is more volatile and its long-range transport can be more efficient compared to less volatile heavier PCB congeners. At the same time, as shown in Figure 4.16, the Arctic region is almost equally sensitive to the changes in emissions of all three congeners.
**Source attribution**

The contribution of emissions originated from the HTAP regions to the pollution levels in each receptor region is shown in Figure 4.17, using the example of results of the BETR-Global and MSCE-POP models. Relative contributions of HTAP source regions were obtained by extrapolating the changes due to 20% emission reduction up to 100% assuming a low level of non-linearity in the applied modelling approaches. Both models show rather consistent predictions of the HTAP source region contributions to the concentrations and deposition. The largest contribution for most of the selected POPs in general is from local emissions, especially for those regions with higher emissions (NA and EU for PCBs, SA and EU for α-HCH). Among the distant sources for PCBs, the emissions of the EU and NA dominate, while for α-HCH the SA is the most significant. Greater differences between the models can be seen for α-HCH compared to the estimates for PCBs. This is likely due to differences in the interpretation of the α-HCH emission inventory information. The BETR-Global model predicts stronger influence of the SA due to its higher contribution to the total α-HCH emission. Additionally, differences in model setup for the spin-up period may affect results. For PCBs, for which the emission inventory is more detailed than for α-HCH, both models provide more consistent predictions especially for the contributions of four HTAP regions.

Along with the contribution of HTAP source regions the diagrams present the contribution of other sources which include anthropogenic emissions in other regions and the contribution of secondary emission sources. This group of sources can essentially contribute up to almost 50% in the Arctic region. The contribution of other sources is generally more significant in the MSCE-POP
model results. However, it should be noted that estimates of the re-emission contribution have larger uncertainties and therefore the deviations between the model estimates of re-emission are higher.

**Figure 4.17.** Estimates of contributions from different emission source regions (Other sources: emission in other regions and secondary emissions) to annual mean surface air concentrations (pg/m³) of α-HCH, PCBs (28, 153, 180) over five receptors (NA, EU, SA, EA, and the Arctic) obtained by the two models BETR-Global (BG) and MSCE-POP (MP).

*Source-receptor experiments with uniformly distributed emissions*

Additional experiments were performed with the aim to estimate the relative importance of emission changes in the HTAP source regions for the selected receptors. For this purpose an arbitrary amount of annual emission of selected POPs (100 kg/y) was evenly distributed within the four source
regions so that all the regions had the same mass emitted. It was assumed that there was no emissions outside these regions and environmental compartments were uncontaminated at the beginning of model simulations. Similar model runs as in the SR1 and SR8 experiments were performed with 20% emission perturbations in the HTAP source regions for 2001. In this experiment one-year model simulations show mostly the influence of anthropogenic emission sources of the current year and contribution of secondary sources is minimized.

The effect of the emission reduction on surface air concentrations for particular pairs of sources and receptors is shown in Figure 4.18. In contrast with the estimates given in Figure 4.16 the results of this experiment show mostly the same level of response to emission changes for all the pairs (about 1.5%-2%). Slightly more significant effect is obtained for the closest pair of regions SA->EA (2-3%).

\[ \text{Effect of 20\% emission reduction} \]

\[ \text{Concentration change, \%} \]

\[ \text{S-R relationship} \]

\[ \text{Effect of 20\% emission reduction} \]

\[ \text{Concentration change, \%} \]

\[ \text{S-R relationship} \]

\[ \text{a-HCH} \quad \text{PCB-28} \quad \text{PCB-153} \quad \text{PCB-180} \]

**Figure 4.18.** Relative decreases (in \%) of annual mean surface air concentrations due to 20% decrease of emissions for the selected source-receptor pairs in an experiment with equally distributed emissions. The bars represent the average change for the models compared. The whiskers show the maximum and minimum estimates obtained by the models. The changes are shown for the source-receptor relationships between the selected four HTAP regions (a) and between these regions and the Arctic (b).

Comparing the results for different POPs, it can be seen that for more volatile $\alpha$-HCH and PCB-28 the response is generally higher, reflecting more efficient atmospheric transport of them. Longer time simulations would likely show a larger effect of differences in physico-chemical properties of these POPs. The pollution of the Arctic region, in the case when the HTAP source regions have the same level of emissions, is more sensitive to changes in emissions in the EU region (about 5-6\%). The slightly lower response to the 20\% emission reduction can be seen for the pairs NA->AR and EA->AR (about 4\%), and SA->AR is weakest (about 2\%).
Estimates of source attribution based on the results of these additional model simulations were performed extrapolating the effect of 20% emission changes in the HTAP source regions up to the 100%. The relative importance of the distant and local emission sources for the selected five receptors is shown in Figure 4.19a. The averaged (for the selected POPs) contributions to the surface air concentrations obtained by the two models BETR-Global and MSCE-POP are presented. The highest contribution of foreign sources is obtained for the EA (about 25%) followed by the NA and EU (about 20%), while the lowest contribution is for the SA (about 10%). Differences between the estimates of contributions provided by the models are not large, however, the contributions of domestic sources are typically larger in the MSCE-POP model results.

The source attribution for the Arctic based on the modelling results of BETR-Global and MSCE-POP is given in Figure 4.19b. Both models provide consistent contributions of the HTAP source regions to the air concentrations over the Arctic. They indicate higher influence of the EU and NA emissions, particularly, about 30% in case of the BETR-Global, and 40% and 20%, in case of the MSCE-POP model. The EA contributes about 25%, while the lowest contribution belongs to the SA region (5-10%). The BETR-Global model predicted two-times stronger influence of the SA emissions on the pollution levels in the Arctic region.

![Figure 4.19](image-url)  
**Figure 4.19.** Estimates of contributions of foreign and own emissions to air concentrations over receptor regions averaged for the selected POPs (a), and contributions of HTAP source regions to air concentrations in the Arctic regions obtained by the BETR-Global (BG) and MSCE-POP (MP) models.

The results of the modelling experiments with uniform emission distribution in comparison to the results of SR1-SR8 experiments show that the receptor regions are sensitive to the distribution of emissions between the HTAP source regions. Particularly, prevailing α-HCH emissions in the SA
region and PCB emissions in the EU region increases the effect of emission changes in them on the receptor regions.

4.5. Status of the integrated approach and future outlook

One of the fundamental challenges of environmental science is to explain the occurrence of pollutants in the environment at locations far from sources. Confronting this challenge requires a quantitative model that can describe the pathways for transport of the pollutant away from source regions, and deposition in target regions. This model must then be used to integrate empirical information about emissions, physico-chemical properties of the substance and monitoring data, and demonstrate that these diverse types of information provide a consistent picture of the overall system of chemical and the environment. A complete, self-consistent description of chemical properties, emissions, transport pathways and environmental concentrations provides a quantitative basis for making regulatory decisions designed to reduce environmental and human exposure in regions remote from sources.

The task of the assessment of environmental contamination by POPs is complicated by a number of factors connected with peculiarities of POP’s fate in the environment. These are the wide range of physico-chemical properties of POPs, their ability to accumulate in environment media, and intermedia exchange. The persistence of POPs in the environment means that contamination levels can be determined not only by current but also by historical emissions.

Assessment of environmental pollution by POPs should generally provide the following information:

- primary and secondary emissions to air and other media and their trends,
- estimates of spatial and temporal contamination trends based on monitoring and modelling,
- attribution of sources of pollution at global and regional scales,
- predictions of future pollution levels based on future emission scenarios,
- estimates of the effect of future climate changes on the pollution levels.

At the global scale, the PCBs are best characterized in terms of such an integrated understanding. For these substances we have a spatially and temporally resolved global emission inventory and the most complete time-series of monitoring data for any POPs. The physico-chemical properties of the PCBs are among the best characterized of any POPs. With this basis, global-scale environmental fate and transport models are able to describe concentrations and trends of PCBs at a variety of monitoring sites in the Northern Hemisphere. However, even in this “best case”, the monitoring data are still fragmentary, and cover only a small fraction of the global environment. Monitoring is strongly biased towards Eastern North America and Northern Europe. Asia and the entire Southern Hemisphere are not well characterized in terms of long-term trends.

At the regional scale, trajectory models can be used to interpret monitoring data and identify likely source regions for episodic long-range transport events that result in high concentrations. Studies of this type provide compelling evidence of the contribution of distant sources to pollutant burdens.

Within the framework of this integrated approach to understanding environmental pollution, models can be used to guide new observations and experiments that will reduce uncertainties in the overall picture. Models can and should be used as a basis for formulating hypotheses about source-receptor relationships that can be tested with field studies. Expanding the availability and scope of monitoring data, and continued work on emissions inventories and physico-chemical properties will allow more insight to be gained from modelling studies, and improve our ability to more rapidly understand the behaviour of emerging POPs. Thus, models are useful tools not only for the evaluation of levels and trends but also for other purposes, like the development and improvement of emission inventories and the planning and organization of monitoring networks and field measurement campaigns.
Modelling of POP long-range transport and fate is therefore essential to assembling a complete and self-consistent understanding of the problem of environmental pollution. When a consistent, integrated picture can be assembled, the models are then useful for analysing future contamination based on the scenarios of future emissions under different regulatory strategies and possible changes in climate.

Although POP pollution has been studied for many years, considerable gaps in knowledge of POP fate and governing processes still exist. Application of models for assessment purposes requires input information on physico-chemical properties of POPs, their emissions, and geophysical information that are subject to many uncertainties. Besides, model description of the processes governing POP fate in the environment are often simplified and/or insufficiently investigated. As a consequence, validation of models against existing measurements and their further improvement is needed. Monitoring can help to further develop models especially in areas where certain gaps in knowledge exist. In particular, specially designed field studies and monitoring experiments can provide valuable information for further development of modelling approaches and thus improve understanding of POP fate and decrease uncertainties in assessment.

Taking into account an integrated approach to the evaluation of POP contamination is of importance to further improve the assessment of environmental contamination by POPs and to reduce the overall uncertainty of the assessment. There is essential potential for complementing and integrating of the monitoring, development of emission inventories, and modelling of POP long-range transport and fate within the assessment. The EMEP work under CRLTAP is comprised of activities involved in monitoring of pollution levels, pollutant emission levels determination, modelling of long-range transport and estimating source-receptor relationships. Closer integration of these activities is of importance for further improvement of pollution assessment. For this purpose the integrated monitoring-modelling approach to assessment of environment contamination is now being developed within EMEP. It includes several stages that allow identification of gaps in knowledge in modelling approaches and available emissions, improve the models and emission inventories used in the framework of assessment, and thus to refine the assessment products: estimates of contaminations levels, source-receptor relationships, trends, and projections. A schematic representation of integrated monitoring-modelling assessment is given in Figure 1.2. The figure illustrates the information flows between assessment components. The key point in the approach is the feedback provided through comparison of monitoring data with modelling results to the three activities within the frame of contamination assessment: monitoring, emissions and modelling.

The initial stage of the assessment may include compilation or development of emission inventories, carrying out monitoring of POP concentrations, and application of one or several models to estimate pollution by selected POPs. Specific attention is given to the analysis of agreement between the modelling results and obtained measurements. This stage can be based on a complex comparison of spatial and temporal variations of modelled and observed data, analysis of disagreement cases applying backward trajectories. Additionally, receptor modelling can be applied to identify possible sources of pollution of the studied regions. Results of the analysis generally indicate how well the model or ensemble of models predicts the observed levels of pollution. Besides, the results can be used to characterize the representativity of the monitoring sites, indicate model errors and the necessity to improve model parameterisations or understanding of processes governing POP fate, and gaps in emission information with respect to its spatial distribution and completeness of coverage of source categories.

Further stages of the assessment can be devoted to the reduction of identified uncertainties. Additional monitoring experiments and field campaigns can be organised to improve understanding of processes and subsequently to refine models parameterisation. Completeness and uncertainties of available emissions should be analyzed and scenarios of possible emissions should be elaborated. Improvement of POP emission inventories using more detailed description of intra-annual variations, source categories, inter-annual variations of emissions on global and regional scales permits to provide more detailed information about pollution trends and source-receptor relationships. Based on this information and revised model parameterisation the evaluation of POP pollution can be repeated to obtain refined assessment products.
Further progress in this direction is connected with the application of new methodologies for the investigation of pollution. Particularly, temporary or long-term passive sampling campaign with dense spatial coverage and different allocation of samplers, e.g. rural, sub-urban, urban areas, can provide valuable information on the extent of the range of pollution. Additionally, new types of samplers can bring more detailed information on pollution, e.g., measurements of deposition and emission fluxes. Further development of direct or indirect assimilation of measurements in modelling of POP fate can also reduce uncertainties of predictions of spatial and temporal trends.

It should be mentioned also that for the effective implementation of the integrated monitoring-modelling approach combined efforts of experts in monitoring, emission inventories and modelling are required.

4.6. Findings and Recommendations

**Modelling approaches for evaluation of POP transport.**

**FINDINGS:**

1. At present, there exists a set of POP fate models that describe the system of chemical and environment with widely varying levels of detail. These include multimedia box models, trajectory models, and spatially resolved multicompartment chemistry transport models. The different models reflect different design decisions and different applications – from screening of a large number of substances with respect to their long-range transport potential and environmental persistence to the detailed evaluation of pollution levels and trends and source-receptor relationships.

2. Models are intensively applied within various international bodies (LRTAP Convention, the Stockholm Convention, OSPAR, HELCOM, AMAP, etc.) to support the negotiation process on the evaluation of pollution levels for legacy substances and for inclusion of new ones.

3. The main processes governing intercontinental transport of POPs at relatively short time scales (monthly or annual basis) are atmospheric transport, gas-particle partitioning, degradation in the atmosphere and deposition. Similar to other pollutants, atmospheric flows are the primary pathway for spreading of POPs over long distances, however over longer time scales transport by ocean currents becomes important. Phase partitioning in the atmosphere, temperature dependence of POP physical-chemical properties and processes governing their transport are essentially important for the description of intercontinental transport of POPs. Thus model assessment of POP atmospheric transport requires taking into account dynamics of aerosols and interaction of POPs with atmospheric reactive species.

4. For POPs that have been cycling in the environment for decades the exchange of POPs between the atmosphere and different types of underlying surfaces, with subsequent accumulation in environmental media and re-emission, and transport in ocean currents play an important role in determining levels in locations remote from sources.

**RECOMMENDATIONS:**

1. Results from POP fate and transport models should be used to support the implementation of international conventions and bodies (CLRTAP, Stockholm Convention on POPs, AMAP, HELCOM, OSPAR, etc.).

2. Further work on the development and improvement of model parameterisation of gaseous exchange between the atmosphere and underlying surfaces and improving information about degradation in all the environmental media is needed. Particularly, for correct simulation of POP environmental levels in soil and seawater, further refinement of POP phase partitioning in these media and the uptake/release of POPs by vegetation is important.
3. In order to improve a model's capabilities to understand and predict intercontinental transport and source-receptor relationships of polar and amphiphilic compounds, there is a need to evaluate parameterisations for these substance classes' surface and phase exchanges.

4. The experience gained in studies of aerosol long-range transport and atmospheric chemistry are of importance for modelling of POPs as POPs can be present in the atmosphere both in gaseous and particulate phases and are subject to degradation through reactions with atmospheric reactants. For this reason the sharing of information and close co-operation in studies of intercontinental transport of various species is beneficial.

**Evaluation of POP intercontinental transport and source-receptor relationships.**

**FINDINGS:**

1. Modelling studies of POP long-range transport at global (intercontinental transport) and regional (transboundary transport) scales have been performed for a subset of legacy POPs (PAHs, PCBs, PCDD/Fs, HCHs, DDT) and new POPs (brominated flame retardants and fluorinated acids). For most of these POPs a significant role of intercontinental transport was indicated.

2. Existing models have been evaluated against available empirical information about physico-chemical properties of non-polar POPs, emissions and measured concentrations in the environment. Evaluation of modelling results reveals reasonable agreement between available measurements and model predictions of POP concentrations in the atmosphere. Deviations between the modelled and observed concentrations for most of the studied POPs are typically within a factor of three to four or better, however, in some cases the differences can be substantial indicating essential uncertainties both in emission inventories and in modelling approaches.

3. Studies of the global dispersion of POPs show the prevalence of intercontinental transport with westerly winds within the Northern Hemisphere. Transport of POPs to the Arctic region is also indicated. For example, modelling indicates that PCBs in air in the Arctic originate mostly in Europe and North America and have been transported via the Northern Atlantic. A significant contribution from Asian sources of HCH on other parts of the world is indicated in model studies. Despite partly very long residence times in air, most POPs are not well mixed on large spatial scales, but rather their concentration level in air is determined mostly by atmospheric transport, which is episodic in nature.

4. Regional studies of POP long-range transport showed important contributions of distant sources (through intercontinental transport). In particular, more than 50% of the PCBs deposited to the Great Lakes were attributable to distant emission sources. For α-HCH, important influence was observed for emissions in Asia due to trans-pacific transport. North American sources can have noticeable contributions to pollution of Europe for PCDD/Fs and B[a]P.

5. Evaluation of source-receptor relationships for POPs is more difficult than for other air pollutants because of the significance of secondary sources (re-emission, multi-hopping potential). Evaluation of re-emission can be subject to significant uncertainties as it depends on historical emissions and requires simulations of long time periods. The role of secondary sources increases as primary emissions decrease or cease as a result of emission control measures.

6. HTAP model experiments designed to evaluate and quantify POP intercontinental transport showed concentrations and deposition in receptor regions to be sensitive to changes in POP emissions on the global scale. Contamination levels in the receptor regions are most sensitive to emission reductions in regions with high emission rates;
thus, 20% emission reduction in Europe and North America (for PCBs) and in South Asia (for α-HCH) had the greatest influence on receptor regions, including the Arctic. Model simulations performed for the selected POPs showed that the contribution of intercontinental transport to the pollution levels in the HTAP receptor regions can reach 30%.

RECOMMENDATIONS:

1. Further studies revealing the role of the secondary sources and quantifying their contribution to long-range transport and pollution levels are required for better description of the source-receptor relationships for POPs. For this purpose additional modelling experiments for POPs within the HTAP multi-model intercomparison should be performed.

2. For further model development and evaluation of model performance with respect to evaluation of re-emissions more measurements of POP levels in surface media and air-surface exchange is needed.

3. Studies of source-receptor relationships for POPs are subject to high uncertainties, and thus require extension of available monitoring information (long-term trends, global scale monitoring campaigns, etc.) for the improvement of modelling approaches and refinement of model estimates of intercontinental transport. In this respect sharing of measurements and providing the access to the data of monitoring networks is of importance.

Evaluation of new substances.

FINDINGS:

1. Both mass balance models and multicompartment chemistry transport models can be used to support evaluation of the environmental hazards associated with new substances. These models evaluate LRTP and environmental persistence of chemicals taking into account main environmental processes such as media exchange and degradation (multimedia approach).

2. Studies using a spatially and temporally resolved transport models show that total environmental lifetime and long-range transport potential are not intrinsic substance properties, but depend strongly on time, location and modal split of emission into the environment. However, models can be formulated with generic assumptions about environmental conditions so that metrics of overall lifetime and long-range transport can be calculated that are pseudo-intensive properties of substances. These metrics can be used for preliminary ranking of environmental hazard in chemical screening assessments.

3. Comparison of ranking of chemicals with respect to their LRTP and persistence in the environment obtained by different models show reasonable agreement.

4. The results of model evaluation of new substances are used in the negotiation process as supporting information for revision of the POP Protocol under CLRTAP. In particular, metrics of LRTP and environmental persistence derived from multimedia models are recognized to be relevant for the evaluation of new substances by the Task Force on POPs.

RECOMMENDATIONS:

1. Wider use of approaches for the evaluation of new substances based on the application of multimedia POP models of different complexity along with half-life criteria is recommended.

2. Close co-operation with the ECHA (European Chemical Agency) in the framework of EC Regulation REACH (Registration, Evaluation, Authorization and restriction of
Chemicals) for obtaining necessary data on physical-chemical properties of industrial chemicals and emissions estimates for the evaluation of new chemicals candidates to POPs is recommended.

Integrated approach to the evaluation of POP contamination.

FINDING:

1. Separate consideration of emission data and the results of evaluation of POP pollution levels by monitoring and modelling cannot provide sufficient information on POP contamination and leads to considerable uncertainties. There is essential potential to complement and integrate monitoring activities, development of emission inventories, and modelling of POP long-range transport and fate within the assessment.

RECOMMENDATIONS:

1. The potential for emissions, models and monitoring data to be combined within an integrated approach to improve understanding intercontinental transport of POPs should be further exploited. As a first step toward this end, comprehensive studies that include emission inventories, modelling and comparison to field data for priority substances, from the point of view of importance of intercontinental transport, including legacy and new POPs should be compiled within the TF HTAP.

2. Compilation of available expert estimates of POP emissions is necessary, as a first step for the Northern Hemisphere, and subsequently for the global scale, taking into account requirements of the modelling community. POPs may cycle and undergo intercontinental transport even decades after phase-out. During and after emission control measures implementation, source types other than those from intended use, e.g., leaks from storage and illegal use, may be significant.

3. Existing regional (EMEP, AMAP) and global monitoring programmes (GAW of the WMO) should be invited for closer cooperation with respect to monitoring POPs. Particularly, it is of importance to consider possibilities for global scale monitoring of POPs in framework of WMO activities.

4. The modelling community should develop the necessary basis for an integrated approach, comprising available modelling approaches including back trajectory analysis, adjoint modelling, and high time resolution in order to capture the episodic nature of atmospheric transport under present-day and future climate parameters’ state and variabilities.

5. An expert group on integrated approach should be created under the TF HTAP to coordinate the activities of emissions determination, monitoring, and modelling communities.

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Chapter 5
Impacts of long-range transport of persistent organic pollutants on human health and ecosystems

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5.1. Overview of impacts of POPs

The ubiquity of POPs globally has led to global impacts of POPs on human health and ecosystems. While the prevalence of POPs in the environment is generally greater in areas where they are emitted, they can be transported over very long distances, as has been detailed in previous chapters. This long-range transport of POPs results in impacts of POPs on ecosystems and human health both near the source and far away.

POPs can negatively impact the health of humans and animals. The toxicity of many POPs has been well established, while some POPs are also known or suspected carcinogens. Many POPs also cause developmental abnormalities. Some POPs also have impacts that are unique to wildlife. These core concepts surrounding the health and environmental impacts of POPs are introduced below and are described in more detail in Sections 5.2 and 5.3.

5.1.1. Toxicity

Exposure to POPs has been linked to adverse health outcomes in people and animals. The degree of toxicity, however, varies widely from one substance to another. The target organs of toxicity also vary among POPs. For example, DDT acts primarily on the nervous system, while heptachlor has shown effects in animal studies on the liver, kidney, immune system, and nervous system. The exposure pathway (food, water, air, etc.) can also impact how effectively a POP is absorbed which, in turn, affects the toxicity of the substance.

The toxicity of a POP is established in two different ways: through controlled laboratory studies or through associations between measured POPs concentrations and specific health outcomes, either in people or in wildlife. The LD₅₀ is defined as the dose of a toxin, generally expressed per unit body weight that is necessary to kill 50% of the members of a tested population in a controlled study. This measure describes the toxicity due to an acute exposure to a substance for a given species. The LD₅₀, however, does not take into account lower-dose chronic exposures, which is the more relevant toxicity pathway for POPs.

To determine cumulative impacts due to chronic exposures, inferences must be drawn, relating observed health or ecosystem outcomes to measured concentrations of POPs. For example, exposure to POPs was correlated with population declines in several marine mammal species in the St. Lawrence River [Ritter et al., 1996]. Similarly, Dewailly et al. [2000] suggested that exposure to organochlorines could lead to increased risk of decreased immune function, as evidenced by ear infections, in Inuit infants. An association between elevated blood serum concentrations of POPs and prevalence of diabetes has also been found [Lee et al., 2006].

5.1.2. Developmental and reproductive effects

POPs have been shown to have effects on the development of foetuses and children and on the reproductive capacity of mature animals. Developmental effects occur due to exposure to POPs early in an animal or human’s development – often in utero or via milk. Concentrations of POPs in breast milk are often especially elevated due to the high fat content of the milk and the lipophilic nature of most POPs. Exposure to some POPs has caused embryo- and fœtotoxicity [AMAP, 2004]. A study on neonatal mouse brain development showed that exposure to some POPs at specific critical periods can cause disruption in adult brain function [Eriksson, 1997]. Neurodevelopmental effects have also been observed in humans, with noted negative impacts on cognitive development in children whose mothers were exposed to high levels of PCBs in the years up to and including pregnancy [U.S. EPA, 2002].
These developmental effects are intertwined with the effects of POPs on reproduction. Because some POPs can act as endocrine disruptors, they can interfere with the proper development and function of the reproductive system. The most studies of these effects are the estrogenic and antiestrogenic effects of various POPs [AMAP, 2004]. POPs can interfere with the proper development of reproductive organs, leading to effects that may not be evident until maturity. For example, embryonic exposure of alligators to POPs (especially DDE, a degradation product of DDT), is believed to have caused reproductive impairment and physical abnormalities in alligators [Guillette et al., 1999; U.S. EPA, 2002]. Endocrine disruptors are also implicated in thyroid and immune system impacts [AMAP, 2004].

5.1.3. Carcinogenicity

Many POPs have been associated with the development of tumours and are considered to be mutagenic or carcinogenic. POPs can interfere with processes at the cellular level. For example, a number of POPs, including PFOS and PFOA, are thought to cause proliferation of peroxisomes, which are a type of cellular organelle, found mainly in the liver and kidney [AMAP, 2004]. Peroxisome proliferation is thought to be a cause for tumour promotion via increased oxidative stress. POPs may also interfere with intercellular communication, which can also then lead to tumour promotion [AMAP, 2004; Trosko and Ruch, 1998]. Several PAHs are known mutagens which initiate and promote tumours; most other POPs are not mutagenic, though many are strong tumour promoters [AMAP, 2004].

The carcinogenicity of a POP is most often determined through laboratory studies. Much like tests for toxicity, tests for carcinogenicity may involve exposure of laboratory animals to the substance in question, followed by examination for tumours. Tests for mutagenicity can be performed in vitro, including establishing a substance’s ability to bind to DNA [AMAP, 2004; Kriek et al., 1998] and other methods. Observed links between measured concentrations of POPs in humans and animals and prevalence of cancers have also demonstrated the carcinogenicity of various substances. The high prevalence of unusual cancers in beluga whales in the Gulf of St. Lawrence combined with high measured POPs concentrations have suggested that POPs may be causing cancer in these marine mammals.

5.1.4. Effects unique to wildlife

While many POPs act similarly in both humans and wildlife, there are some effects of POPs that are unique to wildlife. One of the best known examples of this is the thinning of birds’ eggshells due to DDT. Among other effects is the increase in bone brittleness in fish due to toxaphenes [AMAP, 2004]. These effects on wildlife are discussed further in Section 5.2.

5.1.5. Relation to other assessments of POPs transport

This summary of the effects of long-range transport of POPs is primarily based on several recent assessments of POPs transport. The Arctic Monitoring and Assessment Programme (AMAP) has produced two especially relevant assessments in recent years: AMAP Assessment 2009: Human Health in the Arctic [AMAP, 2009], and AMAP Assessment 2002: Persistent Organic Pollutants in the Arctic [AMAP, 2004]. The Joint WHO/Convention Task Force on the Health Aspects of Air Pollution released Health Risks of Persistent Organic Pollutants from Long-Range Transboundary Air Pollution [Task Force on the Health Aspects of Air Pollution, 2003] in 2003 examined the health impacts from transported POPs and the susceptibility of various POPs to long-range transport. The Canadian Arctic Contaminants Assessment Report II of the Canadian Northern Contaminants Program included an assessment [Van Oostdam, 2003] of human health impacts due to the transport of pollutants, especially POPs, to the Arctic.

This chapter aims to summarize these previous assessments and examine the results of the HTAP analysis in Chapters 2-4 in light of these assessments.

5.2. Impact of POPs on ecosystems

Measureable concentrations of POPs have been detected in ecosystems both near the primary emissions source and far away. Many POPs have established biological effects in the animal species
that partially comprise an ecosystem in a given area. The two main approaches for identifying and estimating the risks for possible effects of POPs on ecosystems were described by AMAP [2004]. The first approach involves comparing observed levels of POPs in species to known detrimental levels, from laboratory and other studies. The second approach attempts to link subtle changes in biomarkers due to exposure to POPs. Both of these approaches are described in more detail by AMAP [2004]. Given POPs’ lipophilicity, bioaccumulation plays a large part in determining animals’ exposure to POPs. Bioaccumulation is described in detail in section 5.2.1.

5.2.1 Bioconcentration, bioaccumulation, and biomagnification

The concentrations of POPs in animals are often greater than the concentration of POPs in the animal’s nearby environment or the animal’s food. The processes by which this occurs are called bioconcentration, bioaccumulation, and biomagnification. The accepted definitions of these terms were set out by Gobas and Morrison [2000]. Bioconcentration is the uptake of a chemical by an aquatic organism through respiration and dermal absorption, resulting in a greater concentration of the substance inside the organism than in the water. Bioaccumulation is the process by which the concentration of a chemical is greater in an aquatic organism than that in water, due to all exposure routes, including through diet, respiration, and dermal absorption. Through biomagnification, the concentration of the substance in the organism exceeds that of the organism’s diet. A consequence of biomagnification is that the concentration of the substance increases at some or all steps in a food chain [Norstrom, 2002].

The ability of a chemical to bioaccumulate is one criterion by which it may be judged to be a POP [Norstrom, 2002]. Indeed, most of the substances covered by the Stockholm Convention, or their metabolites, have been shown to biomagnify; the only exception to this is endrin [Norstrom, 2002]. This biomagnification is an important aspect of the impacts of POPs, since this largely determines the dose to which an animal or a person is exposed.

Bioconcentration, bioaccumulation, and biomagnification of POPs occur primarily as a result of their lipophilicity. POPs are generally more soluble in fats and non-polar solvents than in water; the ratio of a POP’s equilibrium concentration in the octanol phase to its concentration in the aqueous phase of an octanol-water system is called its octanol-water partitioning coefficient, $K_{OW}$. (Octanol is used as a representative of fats and non-polar solvents in general.) Some POPs have very high values of $K_{OW} \geq 100,000$, readily leading to bioconcentration in aquatic organisms. Similarly, the octanol-air partitioning coefficient, $K_{OA}$, can play an important role in biomagnification in food webs containing air-breathing animals, including humans [Kelly et al., 2007]. The greater amount of fat in animals at higher trophic levels than in the animals they consume leads to an increase in the concentration of POPs at each step in a food chain, which is also known as biomagnification.

5.2.2 Measurement of POPs in ecosystems

Most measurements of POPs in biota come from intensive studies, with long-term sustained monitoring relatively rare. There is some sustained monitoring of POPs in animals in Western Europe and North America [GMP-WEOG, 2008], with the most thorough monitoring occurring under the umbrella of AMAP. More detailed information on these programs is given in [GMP-WEOG, 2008].

Some recent studies of POPs in ecosystems are summarized below.

Western Airborne Contaminants Assessment Project (WACAP)

The Western Airborne Contaminants Assessment Project (WACAP) is unique in that it involved measuring the concentrations of and investigating the sources and impacts of atmospherically transported contaminants at remote sites located over a large latitudinal range (i.e. the US/Mexican Border at 29 °N to the Arctic Alaska at 68 °N). All sites were located in US national parks where organic contaminants are not used or produced; however, the project included sites for which regional source contributions were large (e.g. Sequoia National Park, which is downwind from agricultural and population centres) as well as ones where there were essentially no regional source contributions (e.g. the national parks in Arctic and sub-Arctic Alaska). WACAP results also indicated that contaminant contributions from trans-Pacific sources, although certainly present, are small.
relative to the contributions from regional agricultural and industrial sources in the western US. Thus, observed impacts in non-Alaska WACAP parks can be primarily attributed to regional contaminant sources while observed impacts in Alaskan WACAP parks can be attributed to contaminants associated with long-range atmospheric transport.

WACAP assessed the potential effects of atmospherically transported pollutants on the health of fish in WACAP lakes and on piscivorous birds and mammals. Impacts on fish health were primarily assessed by comparing pollutant concentrations in individual fish to macrophage aggregate density, occurrence of plasma vitellogenin in male fish, and occurrence of testis abnormalities (indicating intersex). Although signs of contaminant impacts on reproductive and immune functioning were observed at some parks in the study, none were observed in fish from Alaskan lakes, suggesting that contaminant burdens associated solely with long-range atmospheric transport are not having measurable impacts on Alaskan fish.

The potential for atmospherically transported contaminants to affect food webs was ascertained by comparing contaminant concentrations in individual fish to contaminant threshold levels developed for piscivorous birds and mammals, including mink, river otter, and belted kingfisher. The concentrations of legacy organochlorine pesticides (i.e. DDT and metabolites, chlordane-related compounds, and dieldrin) and PCBs did not exceed wildlife health thresholds in Alaskan parks although they did in a handful of cases at other parks where regional sources had significant contributions. In contrast, the highest whole fish total mercury concentrations in the study were measured in Arctic Alaska and these values regularly exceeded wildlife health criteria.

The concentrations of atmospherically transported pollutants were also compared to human health thresholds for cancer for fish consumption for both recreational and subsistence fishers. Dieldrin concentrations exceeded threshold values for subsistence fishers at the Alaskan parks and all other parks except Olympic and Glacier. Dieldrin concentrations also exceeded the thresholds for recreational fishers in several individual fish in the study, but none were from Alaskan parks. Threshold exceedances were rarely observed for other atmospherically transported compounds; however, mainly because their threshold values were lower than those of dieldrin (not because their concentrations were lower). Mercury concentrations also exceeded contaminant health threshold values for human consumption in the Alaskan parks.

**FINDING:** WACAP results indicate that atmospherically transported organic contaminants can impact the health of fish in remote ecosystems and that they can reach concentrations in fish that exceed health threshold values for consumption by both piscivorous wildlife and humans. However, these impacts and exceedances were not observed at Alaskan parks where the contaminant load is due solely to long-range atmospheric transport (and not influenced strongly by regional sources).

**RECOMMENDATION:** The WACAP final report contains a thorough summary of recommendations and conclusions from the study. While further investigations into the impacts caused by mercury were given high priority over organic contaminants, the deposition of current-use pesticides and current-use brominated flame retardants continue to increase, and special attention should also be paid to them.

**POPs in Antarctica**

Human habitation in Antarctica has been limited to a relatively small number of explorers, tourists, scientists, and research support staff; nonetheless, organic contaminants have been detected in Antarctica since the 1960s. High contaminant concentrations have been measured in the vicinity of research stations which have historically dumped waste onto the land and into the sea. However, there is also evidence that semi-volatile contaminants are migrating to Antarctica via long-range atmospheric transport. The Southern Ocean sea pack is thought to act as a sink for atmospherically transported contaminants in winter, releasing contaminants to marine ecosystems during spring and summer when the sea ice breaks up and melts. Glacier melt associated with climate change, particularly on the Antarctic Western Peninsula, has been proposed as a current source of atmospherically derived DDT-
related compounds to marine ecosystems. A current review of contaminant concentrations, patterns, and trends measured in Antarctic biota is provided by Corsolini [2009].

A number of authors have expressed concern that Antarctic organisms could be more impacted by low contaminant concentrations than temperature species and that health threshold values established for temperate species may not be valid for them. These arguments are based on hypotheses that metabolic pathways for detoxifying xenobiotics are not as well developed in Antarctic species, that slow metabolic rates cause contaminants to reside in Antarctic organisms for longer periods, that high fat storage followed by dramatic fat losses (for example, during molting) result in increased exposure of and impact by contaminants, and that risks are enhanced by the extreme environments and the corresponding extreme physiological responses demonstrated by Antarctic organisms.

Only a handful of studies have been conducted that directly address the hypothesis that Antarctic organisms are more sensitive to contaminants than temperature organisms; a review is provided in Antarctic Ecosystems: Environmental Contamination, Climate Change, and Human Impact, published in 2005. In attempts to induce contaminant detoxification in Antarctic benthic fish species, Focardi et al. [1992a; 1992b] found that compared to temperate fish, the induction activities of Antarctic fish were very low and that induction was significantly delayed in them, presumably due to slow metabolic rates caused by cold temperatures. These results suggest that contaminants may reside in Antarctic fish for long periods of time before being metabolized and/or excreted, which could result in an increased toxicological effect. Bustnes et al. [2006; 2007] determined that organochlorines delayed reproduction and reduced foetal growth in south polar skuas even when measured concentrations were lower than health thresholds values established for temperate species of aquatic birds.

Studies have not been conducted to directly address whether or not atmospherically transported contaminants are impacting Antarctic wildlife. However, a few studies have compared the concentrations of biomarkers, which are used to indicate contaminant exposure and response, in Antarctic organisms exposed to atmospherically derived contaminants only (at reference sites) to those that could be experiencing higher-level exposure. Miller et al. [1999] showed that biomarker concentrations were 37 times higher in fish collected from Winter Quarters Bay, which is near McMurdo Station and considered the most polluted site in Antarctica, than in fish collected from a reference site in Antarctica. Biomarker concentrations were also measured in resident Adélie penguins and compared to those in the migratory south polar skua; results indicated that resident Antarctic sea birds experience lower levels of contaminant exposure than those that spend time in northern climes. Bustnes et al. [2006; 2007] aimed to determine if organochlorine accumulation in south polar skua was mainly occurring in Antarctica or elsewhere; their work suggested that most of the total accumulation of contaminants occurred elsewhere but that HCB and mirex accumulation could be occurring at an Antarctic breeding site. Overall, these results suggest that if atmospherically derived contaminants are currently having impacts on wildlife in Antarctica, those impacts are small compared to those caused by research station activities or contaminant exposure outside of Antarctica.

FINDING: There is currently no strong evidence that Antarctic organisms or ecosystems are being impacted by organic contaminants associated solely with long-range atmospheric transport (and not associated with human activities at research bases). There are reasons to believe, however, that Antarctic organisms are more susceptible to the effects of organic contaminants than temperate organisms, though more research is clearly needed in this area.

5.3. Impact of POPs on human health

In order to assess the impact that long-range transport of POPs can have on human health, a general overview of the known exposure pathways and health effects of POPs is given. This discussion covers POPs in general, with a particular focus on POPs that are known to be especially susceptible to long-range transport.

5.3.1. Exposure pathways

The main ways in which people can be exposed to POPs are through food, water, ambient air, and indoor air. Of these methods of exposure, intake through food is generally the largest exposure
route; in most areas, over 90% of total exposure to POPs estimated to come from the diet [Liem et al., 2001]. This is especially true in remote areas where nearly all POPs are the result of long-range transport. The exposure route through food is primarily a result of bioaccumulation and biomagnification (Section 5.2).

Humans eat many meats and animal products from species in which POPs have a tendency to bioaccumulate. Foods that can have especially high concentrations of POPs include fish, marine mammals, game, and milk [Liem et al., 2001]. Exposure to POPs is therefore strongly linked to diet, and diets containing foods with elevated POPs concentrations generally result in higher body burdens of POPs. Some of these links were established by studying the diets of sport fishermen near the Great Lakes of the US and Canada. Studies from the 1970s and 1980s indicated that frequent consumers of Great Lakes fish had higher blood serum PCB concentrations than unexposed populations; those who consumed the greatest amount of fish from the Great Lakes had blood serum PCB levels four times those of the unexposed population [Humphrey, 1976; Humphrey, 1988a; b; 1989; U.S. EPA, 2002].

The link between diet and exposure leads to larger health effects of POPs in populations with diets with high POPs concentrations. Some of the largest exposures to POPs occur in those who consume the most fish and game, which includes many of the native people of the Arctic. Fish and wild game comprise a large fraction of the diet of many of the native peoples of northern Canada, Alaska, Greenland, and Scandinavia. This diet combined with the transport of POPs to the Arctic, outlined in Sections 1, 2, and 3, make human exposure to POPs in the Arctic an area of special concern. Several studies examining POPs in Inuit mothers indicate that the relatively high blood levels of dioxin-like PCBs in Inuit mothers are due to the traditional/country diet.

**FINDING: The traditional Arctic diet combined with the transport of POPs to the Arctic make human exposure to POPs in the Arctic an area of concern.**

In a comparison of breast milk from Inuit mothers in northern Quebec and Caucasian mothers in the same region, the concentrations of PCBs in Inuit breast milk were roughly 5 times those of the nearby Caucasian mothers and roughly double those of women in industrial areas farther south [Dewailly et al., 1989; Halsall, 2001]. With almost no local sources of PCBs in the northern regions, it could be concluded that the Inuit diet was leading to the increased POPs concentrations. The concentrations of POPs in breast milk have also been examined in other studies. Due to the high fat content in breast milk, POPs can be passed from a mother to her child via breast milk. Some work has suggested that the exposure of breastfed infants to PCDDs, PCDFs, and PCBs per unit body weight can be one to two orders of magnitude greater than that of adults [Liem et al., 2001].

Though less relevant from a long-range transport perspective, acute exposures to POPs can occur for several reasons. Workers involved in pesticide production or application can be exposed to POPs occupationally. The risk of occupational exposure is higher in developing countries where some POPs are in greater use in agriculture. Exposure to unintentionally produced POPs, such as dioxins and furans, can result from chemical fires or accidents and from waste incineration. Indoor exposure to POPs from non-food sources can also occur from consumer products. For example, humans can be exposed to PBDEs, which are used as flame retardants, through many household products such as polyurethane foam in furniture cushions. While these can be the dominant routes of exposure for some individuals, for most people the dominant exposure route is through the diet [Liem et al., 2001].

As noted in Section 5.1.1, most exposures to POPs (with the exception of occupation exposures or industrial accidents) are chronic, low-level exposures. Daily intakes of PCBs, DDT, and chlordanes in Arctic diets are generally on the order of tens of micrograms per day, or less. These daily exposures are much smaller than these substances’ acutely toxic doses [Ritter et al., 1996], but the bioaccumulation of these POPs in the human body makes the effects of cumulative exposure the most important effects. The health effects due to low-level cumulative exposures are more difficult to determine than are the health effects due to acute exposures. The long timescales for effects, the low concentrations of contaminants, and the presence of confounding variables, such as other POPs, make conclusions about the health effects due to cumulative exposures to POPs much more difficult to reach than conclusions about acute exposures. To determine human health effects due to acute
exposures, short-term laboratory tests can suffice, while finding the effects of long-term exposures can require environmental sampling and epidemiology over long periods of time [U.S. EPA, 2002].

5.3.2. Human health impacts

As introduced in Section 5.1, there are many effects of POPs on human health. This section discusses these health impacts, focusing primarily on the effects due to cumulative low-level exposure, rather than acute exposure, of POPs that readily undergo long-range transport. In areas where long-range transport dominates exposure to POPs, the main effects of concern are those that affect reproduction and long-term survival, effects which are generally seen at a late stage of exposure and which can be difficult to ascertain [AMAP, 2004]. A summary of health effects of POPs, adapted from an AMAP assessment [2004], is given in Table 5.1.

Table 5.1. Overview of toxic properties of POPs. ↓ = suppression or decrease; ↑ = induction or increase. [Adapted from Table 3.1 of AMAP (2004), AMAP Assessment 2002: Persistent organic pollutants in the Arctic, Arctic Monitoring and Assessment Program, Oslo, Norway.]

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Reproductive/developmental effects</th>
<th>Neurotoxic effects</th>
<th>Immune effects</th>
<th>Cancer</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldrin/dieldrin</td>
<td>↓ Reproduction</td>
<td></td>
<td>Suppresses immune system</td>
<td>Non-mutagenic. Increased liver tumors</td>
<td></td>
</tr>
<tr>
<td>Chlordanes</td>
<td>↓ Reproduction</td>
<td></td>
<td>Suppresses immune system</td>
<td>Non-mutagenic tumor promoter</td>
<td></td>
</tr>
<tr>
<td>DDT and metabolites</td>
<td>Egg-shell thinning in bird eggs. ↓ Reproduction</td>
<td></td>
<td>Suppresses immune system</td>
<td></td>
<td>Adrenal cortex hyperplasia</td>
</tr>
<tr>
<td>HCBz</td>
<td>Fœtotoxic. Teratogenic. ↓ Reproduction</td>
<td></td>
<td>Suppresses immune system</td>
<td>Non-mutagenic tumor promoter</td>
<td>↑ Porphyria</td>
</tr>
<tr>
<td>α-HCH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Non-mutagenic tumor promoter</td>
</tr>
<tr>
<td>β-HCH</td>
<td>Estrogenic</td>
<td></td>
<td>Suppresses immune system</td>
<td>Non-mutagenic tumor promoter</td>
<td></td>
</tr>
<tr>
<td>γ-HCH (lindane)</td>
<td>Estrogenic and antiestrogenic. ↓ Reproduction</td>
<td></td>
<td></td>
<td></td>
<td>Non-mutagenic tumor promoter</td>
</tr>
<tr>
<td>Mirex</td>
<td>↓ Reproduction</td>
<td></td>
<td>Suppresses immune system</td>
<td>Non-mutagenic. Induces tumors</td>
<td></td>
</tr>
<tr>
<td>Toxaphenes</td>
<td>Fœtotoxic. ↓ Reproduction</td>
<td></td>
<td>Suppresses immune system</td>
<td>Mutagenic, potent carcinogen. Inhibits GJIC</td>
<td>↑ Bone brittleness in fish. Adrenal hypertrophy</td>
</tr>
<tr>
<td>Endosulfan</td>
<td>Fœtotoxic. ↓ Reproduction</td>
<td></td>
<td>Suppresses immune system</td>
<td>Non-mutagenic</td>
<td></td>
</tr>
</tbody>
</table>
Table 5.1. (cont’d) Overview of toxic properties of POPs. ↓ = suppression or decrease; ↑ = induction or increase [Adapted from AMAP, 2004].

<table>
<thead>
<tr>
<th>POPs</th>
<th>Reproductive/developmental effects</th>
<th>Neurotoxic effects</th>
<th>Immune effects</th>
<th>Cancer</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCDD/Fs and nPCBs and metabolites</td>
<td>Fœtotoxic. Deformities. ↓ Reproduction</td>
<td>Permanent changes in learning, behaviour, memory (nPCB)</td>
<td>Non-mutagenic tumor promoters. Affects GJIC</td>
<td>↑ Porphyria</td>
<td></td>
</tr>
<tr>
<td>PCNs</td>
<td>Embryotoxic. ↓ Reproduction</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PBDEs</td>
<td>Estrogenic and antiestrogenic</td>
<td>Permanent changes in learning, behaviour, memory</td>
<td>Suppresses immune system</td>
<td>Non-mutagenic</td>
<td></td>
</tr>
<tr>
<td>PFOS/PFOA</td>
<td>↓ Reproduction</td>
<td></td>
<td></td>
<td>Non-mutagenic, tumor promoter. ↑ Peroxisome proliferation. Inhibits GJIC</td>
<td></td>
</tr>
</tbody>
</table>

Developmental and reproductive effects

Some of the mostly strongly established effects of POPs on human health result from prenatal exposure and exposure during infancy. These include neurodevelopment, reproduction and sexual development, and immune system development. The connections between individual POPs and the immune system are discussed in the other health outcomes section.

There is strong evidence of impacts of POPs on the development of the brain and nervous system of laboratory animals. Exposure to a low-dose mix of toxic substances, including several POPs, in neonate mice during a certain critical period of brain development, has led to disruption in adult brain function [AMAP, 2003]. Similar periods in human brain development occur throughout the third trimester of pregnancy and the first two years of life [AMAP, 2003]. Exposure to POPs through the umbilical cord and through breast milk can therefore cause developmental impacts in fetuses, neonates, and infants.
One class of POPs for which there is a relatively large amount of data on neurodevelopmental effects is PCBs. Studies of PCB effects resulting from fish in the Great Lakes [Schwartz et al., 1983; Stewart et al., 1999], dairy products in the Netherlands [Koopman-Esseboom et al., 1994], and background concentrations in North Carolina [Rogan et al., 1986] have helped link PCB exposure and neurodevelopment. Higher cord serum concentrations of PCBs were associated with lower weight and smaller head circumference, though effects were not seen in the low-exposure North Carolina study [Rogan et al., 1986]. PCB exposures have also been related to lower birth weight and possibly shorter duration of pregnancy [Van Oostdam, 2003]. Studies in Russia have linked PCBs in mothers’ serum to premature births, stillborn births, and birth defects [Dudarev, 2006; 2007].

The neurodevelopmental effects of POPs, particularly PCBs, have been seen in behavioural outcomes. Exposure to PCBs was associated with decreased behavioural function, such as reflexes and activity levels, in several studies [Huisman et al., 1995; Rogan et al., 1986; Stewart et al., 2000]. Poorer visual recognition memory in infants was observed in studies in Michigan and upstate New York [Darvill et al., 2000; Jacobson et al., 1990; Jacobson et al., 1992; Jacobson et al., 1985]. Decreased intellectual function at 4 and 11 years of age was related to prenatal PCB exposure in the Michigan Great Lakes study [Jacobson et al., 1990; Jacobson and Jacobson, 1996], while similar results were found at 42 months in the Netherlands [Patandin et al., 1999]. These outcomes were all specifically associated with prenatal exposure to PCBs, rather than exposure through breast milk [Van Oostdam, 2003]. The main theory on how PCBs affect neurodevelopment involves the effect of PCBs on thyroid hormone homeostasis [Porterfield and Hendry, 1998; Van Oostdam et al., 2005].

The effects of POPs on the human reproductive system are not yet well understood. Stronger effects have been seen in animals than in humans. Several POPs have shown hormone-disrupting behaviour in laboratory studies [AMAP, 2009], which is indicative of potential to alter reproductive development. In work by Kelce et al. [1995], exposure of rats male rats to $p,p'$-DDE, a DDT metabolite, at weaning led to delayed onset of puberty, while exposure of adult male rats led to reduced seminal vesicle and ventral prostate weights. 2,3,7,8-TCCD (or TCDD) has also been shown to alter sexual development in male rats [Mably et al., 1992]. Evidence is emerging of effects of POPs on sexual development of humans. In a study of the effects of DDE on male development, Longnecker et al. [2002] related maternal serum DDE concentrations to male genital abnormalities. Though results were inconclusive, instances of cryptorchidism, hypospadias, and polythelia were greater in boys born to mothers with high serum DDE concentrations than in boys born to mothers with low serum DDE concentrations. The results of a study of the Y:X chromosome distribution in human sperm [Tiido, 2006] suggested that POPs may alter the male/female birth ratio. Dudarev (2006) [2006] showed associations between PCB concentrations in maternal blood and sex ratios of newborns. Conclusive evidence for a causal relationship between POPs and male/female ratios is still lacking, however [AMAP, 2009]. Some work has also suggested a link between maternal serum PCB concentrations and low birth weight, premature births, stillbirths, and menstrual irregularities [AMAP, 2009].

Carcinogenicity

The degree of carcinogenicity varies widely from one POP to another. While there is strong evidence of carcinogenicity for some POPs, there are varying amounts of evidence of carcinogenicity for others. Additionally, genetics are believed to play a role in the relationship between contaminants and cancer, making some groups and individuals more susceptible to the effects of POPs [AMAP, 2009]. The interplay between genes and contaminants, such as POPs, is believed to be the main origin of environmentally caused cancers; more detail on these interactions, including emerging science, is given in the AMAP Assessment 2009: Human Health in the Arctic [2009]. The carcinogenicity categories of several POPs according to the International Agency for Research on Cancer (IARC) are given in Table 5.2.

Long-range transport of dioxins, furans, and dioxin-like PCBs is important for human exposure [Task Force on the Health Aspects of Air Pollution, 2003], and there is evidence of carcinogenicity for some of these POPs. One known carcinogen is TCDD, while several other compounds of this class are tumour promoters [AMAP, 2004; Task Force on the Health Aspects of Air...
Pollution, 2003]. TCDD and dioxin-like PCBs have been shown to interfere with intercellular communication, which is thought to lead to cancer formation, while several compounds from this class also react with DNA [AMAP, 2004]. The health effects of PCBs are thought to be caused by all congener classes, including both dioxin-like and non-dioxin-like PCBs [Task Force on the Health Aspects of Air Pollution, 2003].

Table 5.2. IARC carcinogenicity ratings for several POPs. See http://monographs.iarc.fr/ENG/Classification/index.php

<table>
<thead>
<tr>
<th>POP</th>
<th>IARC classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,3,7,8-TCDD</td>
<td>1</td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td>1</td>
</tr>
<tr>
<td>PCBs</td>
<td>2A</td>
</tr>
<tr>
<td>Toxaphene</td>
<td>2B</td>
</tr>
<tr>
<td>Chlordane</td>
<td>2B</td>
</tr>
<tr>
<td>Heptachlor</td>
<td>2B</td>
</tr>
</tbody>
</table>

1 = carcinogenic to humans
2A = probably carcinogenic to humans
2B = possibly carcinogenic to humans

Several polycyclic aromatic hydrocarbons (PAHs) are known to be carcinogenic. Benzo[a]pyrene, or BaP, and 7,12-dimethylbenz[a]anthracene, or DMBA, are known mutagens that initiate and promote tumours [AMAP, 2004]. There is evidence of carcinogenicity for many other PAHs and mixtures of PAHs, with most of these effects resulting from inhalation. The risk of lung cancer from long-range transport of PAHs, however, is currently thought to be small [Task Force on the Health Aspects of Air Pollution, 2003].

Van Oostdam et al. [2005] discuss toxaphene as a priority contaminant in the Canadian Arctic. Not a single compound, toxaphene is actually a mixture of nearly 700 chlorinated terpenes [U.S. EPA, 2002]. Toxaphene is classified as a possible carcinogen (IARC group 2B), given the strong evidence for carcinogenicity in animals and inadequate evidence in humans [Ritter et al., 1996]. Toxaphene has also been shown to interact with DNA in in vitro studies, indicating a potential for tumour formation [Van Oostdam et al., 2005]. It is, therefore, difficult to assess the role of toxaphene transport in cancer formation given the inconclusive data on toxaphene carcinogenicity.

Chlordane has also been identified as a priority contaminant in the Arctic [Van Oostdam et al., 2005]. Chlordane is a mixture of up to 120 similar compounds, with five or six major isomers [Van Oostdam et al., 2005]. Heptachlor is a breakdown product and constituent of chlordane [Task Force on the Health Aspects of Air Pollution, 2003]. Long-range transport of both of these are thought to be mainly of concern for infants and those consuming Arctic country diets, though mostly for non-cancer health reasons [Task Force on the Health Aspects of Air Pollution, 2003; Van Oostdam et al., 2005].

There appear to be differences in the carcinogenicities of α-, β-, and γ-HCH. There is evidence of carcinogenicity in animals of α-HCH, though evidence is limited for β- and γ-HCH. Additionally, evidence is limited for carcinogenicity in humans for all three isomers [IARC, 1987; Task Force on the Health Aspects of Air Pollution, 2003]. There is evidence that all three varieties are non-mutagenic tumour promoters [AMAP, 2004].

Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are known to promote liver tumours in rats [AMAP, 2004], though carcinogenicity in humans has not been established. These substances also inhibit intercellular communication and increase peroxisome proliferation [AMAP, 2004]. One study suggested a link between occupational PFOS exposure and bladder cancer, though other epidemiological research has not supported this finding [AMAP, 2009].
Other health outcomes

POPs vary considerably in their degree of toxicity and in their target organs and systems in the human body. This section focuses primarily on the human health effects of POPs that are known to be subject to long-range transport. Effects on the immune system are generally associated with prenatal and childhood exposure, so these immune system effects are tied to early development of the immune system [AMAP, 2009].

One class of POPs known to undergo long-range transport is dioxins, furans, and dioxin-like PCBs [Task Force on the Health Aspects of Air Pollution, 2003]. The toxicities of these compounds are often compared using a toxic equivalency factor (TEF), through which the toxicities of the individual substances are normalized to that of a reference dioxin. These substances have been shown to have negative impacts on the thymus, leading to immune suppression and a reduced resistance to infection and cancer [AMAP, 2004]. The immunotoxicity of coplanar PCBs is well established, though the effects of other PCBs on the immune system have not been investigated as thoroughly [AMAP, 2009]. Other endpoints that have been noted included endometriosis and hearing loss [Task Force on the Health Aspects of Air Pollution, 2003]. The toxicology of non-dioxin-like PCBs has been poorly characterized to date; the immunotoxicological effects of PCBs are likely caused by both the dioxin-like and the non-dioxin-like varieties [Task Force on the Health Aspects of Air Pollution, 2003]. Non-dioxin-like PCBs, however, are suspected neurotoxins [AMAP, 2004].

DDT and its metabolites, such as DDE, are rather prevalent in Arctic areas [U.S. EPA, 2002] due primarily to long-range transport. Some of the main toxicological health effects associated with DDT include immune suppression and reduced thyroid weight [AMAP, 2004].

Hexachlorobenzene (HCB) is one of the most stable POPs [U.S. EPA, 2002] and is readily transported globally. Most of the health effects of HCB have been associated with acute exposures [Task Force on the Health Aspects of Air Pollution, 2003]. A number of potential effects due to low-level exposures to HCB have been identified, including porphyria, especially in children [AMAP, 2004; Task Force on the Health Aspects of Air Pollution, 2003]. HCB is also thought to cause suppression of the immune system [AMAP, 2004].

In a study of the relationship between blood serum concentrations of POPs and prevalence of diabetes, a strong connection was seen between the two. Lee et al. [2006] included 2,016 United States adults in their study. The study authors used measurements of six POPs because of their high prevalence in the study population: PCB153, HpCDD, OCDD, oxychlordane, DDE, and trans-nonachlor. Prevalence of diabetes, which occurred in 217 of the study participants, was strongly positively associated with all six POPs, even after controlling for several possible confounding variables. The study also found that obesity and diabetes were associated with one another only in subjects with detectable blood serum concentrations of POPs.

Prenatal exposure to organochlorine compounds was related to the susceptibility to infections and immune status in Inuit infants by Dewailly et al. [2000]. This study suggested a relationship between prenatal exposure to DDE, HCB, and dieldrin and middle-ear infections in 4- to 7-month-old infants. While suggesting a link between prenatal exposure and immune outcomes in infancy, this study did not find a link between postnatal exposure to organochlorines and ear infections. This study is especially relevant for long-range transport given that most Inuit exposure to POPs is the result of contaminants in the traditional diet due to long-range transport.

Additionally, there are a number of POPs for which the evidence for long-range transport or the evidence for cumulative human health effects is limited. For example, while the toxicity of pentachlorophenol has been well established, it is not known if long-range transport plays a significant role in human exposure [Task Force on the Health Aspects of Air Pollution, 2003]. Similarly, it is not known if long-range transport results in significant exposures to hexachlorocyclohexanes (HCH), while the health effects of HCH also remain uncertain. Heptachlor has shown health effects in animal tests, but conclusive evidence of long-term effects on humans have not been found. In contrast, the health effects of polycyclic aromatic hydrocarbons (PAHs) are somewhat well understood, but long-range transport of PAHs appears not to lead to substantial health impacts [Task Force on the Health Aspects of Air Pollution, 2003].
For some substances, such as the pesticides dieldrin, aldrin, and endrin, there is little data on the effects of long-term, low-dose exposures on humans, though effects on animals and acute effects on humans have been studied more thoroughly.

**FINDING:** Some POPs with the most clearly established health effects, such as PCBs, are also especially susceptible to long-range transport.

**RECOMMENDATION:** More research into the health effects of POPs for which long-range transport results in significant exposures, such as PBDEs, is needed.

### 5.3.3. Health impacts of POPs due specifically to long-range transport

Given the low concentrations of POPs that are sufficient for health impacts, a relatively small amount of epidemiological data on POPs in remote areas, and confounding influences of multiple POPs and other pollutants, ascertaining the health effects of long-range transport of POPs is a very challenging undertaking. Recent AMAP, CACAR, and WHO/CLRTAP assessments of the effects of the long-range transport of contaminants on the environment and human health are summarized here. The assessments have attempted to reach beyond just measurements of POPs concentrations and to actually relate those measured concentrations of POPs to tangible health impacts.

The AMAP 2009 assessment of human health in the Arctic concluded that current human exposure to contaminants negatively influences human health. Since most of the POPs in the Arctic are the result of long-range transport, it can be concluded that most of the health effects from POPs in the Arctic are also due to long-range transport.

Although a scarcity of data prohibits a thorough accounting of the effects of individual POPs on human health, PCBs were singled out in the AMAP 2009 assessment as a main contributor to POP-related health impacts. Negative effects from prenatal PCB exposure on human growth and gestation were noted. Studies in northern Quebec relating prenatal exposure to PCBs to cognitive impairments in children were also summarized. Evidence of a link between maternal PCB blood serum levels and adverse birth outcomes, such as low birth weight and stillbirths, arising from a Russian Arctic cohort study were also summarized. An influence of POPs on the sex ratio of newborns was also suggested. The links between POPs effects and genetics were discussed as an emerging area of research, though, to date, little is known about genetics in Arctic populations.

The AMAP 2002 assessment of contaminants in the Arctic raised some of the same concerns as the 2009 assessment. The 2002 assessment also pointed to PCBs as having the strongest evidence for health effects in the Arctic. Other dioxin-like POPs were also highlighted as being a matter of concern.

The Canadian Arctic Contaminants Assessment Report II [Van Oostdam, 2003] focused on the effects of contaminants in Arctic Canada. This assessment highlighted toxaphene as a POP of concern, since estimated exposures to toxaphene in the Canadian Arctic were in the same range at which effects on the immune system and on infant size had been observed. Exposures to chlordane were also estimated to be in the range in which health effects were expected to occur. This assessment also highlighted the work of Dewailly et al. [2000], linking prenatal exposure to organochlorines to increased infections in infancy as well as research showing a relationship between high maternal PCB blood serum levels in northern Quebec and low birth weight.

The Joint WHO/Convention Task Force on the Health Aspects of Air Pollution reported in 2003 on the health risks associated with many classes of POPs. This assessment discussed the health effects associated with various POPs as well as their potential for long-range transport. This report highlighted several POPs that are of concern or are potentially of concern with respect to long-range transport, especially DDT, HCH, dioxins, and PCBs. The combination of potential for long-range transport and an understanding of health effects for these POPs led to their being considered especially of concern. The task force also highlighted the need for a better understanding of the health effects and the long-range transport of other POPs.

From these recent assessments, several common themes emerged. First is the importance of new or emerging substances. Brominated flame retardants, such as polybrominated diphenylethers (PBDEs) and perfluorinated compounds, such as PFOS and PFOA, have been detected in remote
areas such as the Arctic. Other emerging compounds discussed in these assessments include halogenated phenols, such as pentachlorophenol (PCP), short-chain chlorinated paraffins (SCCPs), endosulfan, and polychlorinated terphenyls (PCTs). Assessments have cited the lack of information on health effects and long-range transport of these substances in calling for more research on these POPs. Related to these calls for more research are calls for increased monitoring. This would include both greater geographical coverage and a greater number of POPs and metabolites.

**FINDING:** Measureable health effects result from the long-range transport of POPs.

**RECOMMENDATION:** Research by the appropriate national and international bodies into the health effects of emerging substances is needed.

Another common point from these assessments is the need for a better understanding of how climate change will impact the long-range transport of POPs and how those changes will affect human health. With changing climate will likely come changes in the circulation and distillation of POPs. How these changes will affect human exposure and human health are not yet understood.

**FINDING:** The effects on exposure to POPs of changes in long-range transport resulting from changes in climate are not yet understood but may potentially be significant.

Finally, another theme that emerged from these assessments of POPs and human health is the impacts of mixtures of POPs. Given the ubiquity of many different POPs, humans are generally exposed to a large suite of substances, not just one pollutant. These POPs may affect human health differently in one another’s presence than they would separately. Understanding the effects of mixtures is especially important in remote areas without a local source of POPs. Without dominant local sources, no single substance dominates exposure. Some work on complex mixtures of POPs has been undertaken in the Greenlandic Inuit population, yet this has not been a large area of research to date [AMAP, 2009]. Given the different mechanisms by which POPs affect human health, markers for understanding the effects of mixtures are beginning to be determined [AMAP, 2009].

**5.4. Monitoring in human media**

In addition to the environmental monitoring of POPs outlined in Chapter 2, monitoring of POPs in human milk and blood and in biota also occurs. Monitoring in biota was discussed in Section 5.2. Monitoring in humans and biota is less common than monitoring in environmental media such as air. This monitoring has been most heavily concentrated in developed countries and the Arctic. Monitoring programs have consisted of a mix between sustained long-term monitoring and short-term snapshot studies. Generally, sustained monitoring of POPs in human media has only occurred in developed countries. A list of selected long-term monitoring programs for POPs in human media is given in Table 5-3. The AMAP program includes many national programs that feed into the AMAP process.

As part of the food component of the Global Environment Monitoring System (GEMS/Food), the WHO, in conjunction with UNEP, has collected data on the levels of contaminants in food and human milk since the 1970s. This program includes occasional monitoring of POPs in human milk. Four WHO surveys of POPs in human milk have been conducted since 1988, with different countries included in each survey. These surveys have measured concentrations of PCDD/PCDF and PCB in human milk. A number of individual studies of POPs in human milk and blood have also been performed, as discussed in Section 5.3.

Trends in POPs concentrations in human media are most readily available in areas with established long-term monitoring, such as in Western Europe and North America. Concentrations of PCCDs/PCCFs and dioxin-like PCBs have generally been declining across Western Europe since the 1980s [GMP-WEOG, 2008]. In spite of this decreasing trend, there remain areas of high exposure, such as the Arctic, that are still of concern [GMP-WEOG, 2008]. There is little information on long-term trends in POPs concentrations in human media outside of Western Europe, North America, and Japan. More information about the monitoring of POPs in human media, including the WHO surveys of POPs in human milk, can be found in the five regional reports on the Global Monitoring Plan under the Stockholm Convention [GMP-Africa, 2009; GMP-Asia-Pacific, 2008; GMP-CEE, 2008; GMP-GRULAC, 2009; GMP-WEOG, 2008]
FINDING: There is little information on long-term trends in POPs concentrations in food or human media in most of the world. Most of this long-term information is for developed countries only. Without such information, long-term trends in POPs concentrations in human media over most of the world cannot be established. Concentrations of PCCDs/PCCFs and dioxin-like PCBs have generally been declining across Western Europe since the 1980s.

Table 5.3. Selected long-term monitoring programs for POPs in human media [Based on information in GMP-CEE, 2008; GMP-WEOG, 2008].

<table>
<thead>
<tr>
<th>Program</th>
<th>Media</th>
<th>Coverage</th>
<th>Time period</th>
<th>POPs measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMAP</td>
<td>Blood</td>
<td>Arctic</td>
<td>1993-present</td>
<td>DDT, PCB, toxaphene, mirex, chlordane, dieldrin, heptachlor, HCB</td>
</tr>
<tr>
<td>US CDC</td>
<td>Blood</td>
<td>USA</td>
<td>1999-present</td>
<td>All 12 Stockholm Convention POPs</td>
</tr>
<tr>
<td>Uppsala</td>
<td>Milk</td>
<td>Sweden</td>
<td>1996-present</td>
<td>DDT, PCB, PCDD/PCDF, HCB, chlordane</td>
</tr>
<tr>
<td>Stockholm</td>
<td>Milk</td>
<td>Sweden</td>
<td>1970-present</td>
<td>DDT, PCB, HCB, chlordane</td>
</tr>
<tr>
<td>GerES</td>
<td>Blood, urine</td>
<td>Germany</td>
<td>1985-present</td>
<td>HCB, DDE, PCB</td>
</tr>
<tr>
<td>ESB</td>
<td>Blood</td>
<td>Germany</td>
<td>1984-present</td>
<td>HCB, PCB 153</td>
</tr>
<tr>
<td></td>
<td>Milk</td>
<td>Czech Republic</td>
<td>1990-present</td>
<td>All 12 Stockholm Convention POPs</td>
</tr>
</tbody>
</table>

5.5. Implications of HTAP analysis

The analysis of measurements, emissions, and modelling of POPs in Chapters 2, 3, and 4 have potential ramifications for human health and ecosystems. Viewing these chapters through the lens of impacts can shed important light on the past, present, and future of POPs and their effects on people and the environment.

Trends in atmospheric concentrations of POPs were discussed in Chapter 2. Concentrations in the Arctic, where local sources are minimal, are especially dependent on long-range transport. Trends in atmospheric concentrations of POPs were shown to vary from location to location and from substance to substance. Concentrations of lindane, for example, have shown decreases since the 1990s at the four Arctic stations discussed. This would suggest that reductions in emissions of lindane, which is regulated under the Stockholm Convention and the CLRTAP POPs protocol, have been effective in reducing the long-range transport of lindane. This would also suggest that health and ecosystem effects related to HCH should be on the decline. The persistence of POPs, however, could lead to a lag between the decrease in primary use / emissions and decreases in final health and ecosystem outcomes.

Long-term trends in atmospheric concentrations of other POPs have shown different patterns. As noted in Chapter 2, atmospheric concentrations of PBDEs increased between 2002 and 2005 at Alert, Canada. Concentrations of endosulfan at Alert have also been increasing since 1993. Endosulfan and PBDEs are both currently in widespread use. These increases in transport of in-use POPs suggest that significant long-range transport of these substances will continue. While the health and ecosystem impacts of many of these in-use POPs are not well understood, sustained or increasing transport may lead to increased impacts. Continued re-emission of POPs can continue long after primary emission, as outlined in Chapter 3. That such POPs will be transported globally for the
foreseeable future underscores the importance of understanding the health and ecosystem impacts of in-use and emerging POPs.

The trends in atmospheric concentrations of PCBs and HCB discussed in Chapter 2 indicate the importance of climatic changes in determining exposure to POPs. While PCB emissions have generally been declining, concentrations of PCBs measured at Zeppelin showed increasing trends from 2003 to 2006. This may be due at least in part to a reduction in sea ice cover near Spitsbergen, resulting in increased volatilization of PCBs from the ocean. Climatic changes can alter the effectiveness of control strategies and international agreements in their attempts to protect human health and the environment. As discussed in Chapters 1, 2, 3, and 4, climate change can affect the primary emission, re-emission, and transport pathways of POPs. Given the complex effects of various aspects of climate on individual POPs, the net effect that these impacts will have on human and ecosystem exposure to POPs still remains uncertain, but could impact the effectiveness of reductions in POPs emissions.

The HTAP model simulations described in Chapter 4 elucidated some important source-receptor relationships for POPs. The effects of PCB emissions from North America and Europe on the Arctic were highlighted, as was the transport of γ-HCH from South Asia to other regions. This highlights the importance of different POPs in different parts of the world: for example, industrial products in industrial areas, and pesticides in agricultural areas. The source apportionment calculations in Chapter 4 suggest that in a given region, some POPs may come from mostly local sources, while others come largely from distant sources. The health and ecosystem impacts could conceivably be attributed based on these source apportionment calculations, with the added complexity of exposures to a mixture of POPs from local and distant sources. This source apportionment is also suggestive that both local emissions and long-range transport are important in determining POPs concentrations, and, therefore, their impacts on ecosystems and health.

The importance of in-use and emerging POPs has been highlighted by all sections of this assessment. As more laboratory and environmental measurements become available and as modelling matures further, understanding of the impact of transport of these substances on human health and ecosystems will improve.

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Chapter 6
Summary

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6.1 Importance of Persistent Organic Pollutant long-range transport as an exposure pathway

POPs, by definition, are hazardous to human health and wildlife. Given their persistence in the environment, atmospheric long-range transport (LRT) of POPs constitutes an important pathway for the wide distribution of POPs, leading to human exposure and ecosystem impacts. For many POPs the main route of human exposure is through food, adding complexity to the overall risk assessment of POPs.

The extent of LRT depends critically on the chemical and physical properties of the individual POPs. Some long-lived POPs are effectively transported on a global scale, often through a succession of deposition and re-emission processes ("multi-hopper"). In some remote areas, such as the Arctic, LRT is nearly completely dominant, while regional emissions are dominant in other areas.

6.1.1 Findings

The main processes governing intercontinental transport of POPs at relatively short time scales (monthly or annual basis) are atmospheric transport, gas-particle partitioning, degradation in the atmosphere and deposition. Similar to other pollutants, atmospheric flows are the primary pathway for spreading of POPs over long distances. For POPs which have been cycling in the environment for decades, the exchange of POPs between the atmosphere and different types of underlying surfaces which leads to the accumulation of pollutants in environmental media and subsequent re-emission, and transport in ocean currents play important roles in determining levels in locations remote from sources.

The Hemispheric Transport of Air Pollution (HTAP) multi-model experiments, which were designed to evaluate and quantify intercontinental transport, showed concentrations and deposition to be sensitive to changes in POP emissions on the global scale. Due to incompleteness in key information, like global emission inventories, the HTAP multi-model experiments had to be limited to PCBs and HCHs as representative POPs; hence, only partly covering the very large variation of physical and chemical characteristics of POPs. The contamination levels in the receptor regions are most sensitive to emission reductions in regions with high emission rates; thus, 20% emission reduction in Europe and North America (for PCBs) and in South Asia (for α-HCH) had the greatest influence on receptor regions, including the Arctic. Model simulations performed for the selected POPs showed that contribution of intercontinental transport to the pollution levels in the HTAP receptor regions can reach almost 30%.

Modelling indicates that PCBs in air in the Arctic originate mostly in Europe and North America. A significant contribution from Asian sources of HCH on other parts of the world is indicated in model studies. The distribution of emissions and use of POPs also affects their transport. For example, α-HCH presently is emitted very little from North America; hence, North American emissions have little effect on concentrations of α-HCH in other regions. Changes in emissions of α-HCH from South Asia, however, impact other regions appreciably, given the pervasive use of α-HCH in that region. Similarly, while transport of α-HCH from North America to the Arctic is negligible, transport of various PCB congeners from North America to the Arctic is appreciable. These results suggest that the dominant source region for a given receptor region can vary from one POP to another.

6.1.2 Recommendation

- POPs present global-scale risks that require the TF HTAP to consider broadening its geographical scope and membership to include regions outside of the United Nations Economic Commission for Europe (UNECE).
6.2 Importance of monitoring

Monitoring and measurements have provided important information about the prevalence of POPs in the environment and their transport around the globe. Both intensive field studies and sustained monitoring have helped elucidate the transport and fate of POPs. While measuring the concentration of POPs in air has been the most widely employed technique, measurements in other media, such as water and soil, or in human media, wildlife, and food, also have shed light on the prevalence of POPs in the environment and the exposure of humans and animals to POPs.

6.2.1 Findings

6.2.1.1 Atmospheric monitoring

Long-term air monitoring programmes provide temporal trends with a time span of approximately 15 years, which are important for the analysis of POP LRT and the effect of emission changes in different regions of the globe. The UNECE region has several long-term monitoring programmes on POPs, but other regions are presently sparsely covered.

The spatial coverage and resolution of air monitoring programmes have increased considerably due to the adoption of passive air sampling methods. Passive air sampling campaigns for various POPs performed under the Long-range Transboundary Air Pollution (LRTAP) and Stockholm conventions provide essential information on spatial variation of pollution levels on global and regional scales. Atmospheric monitoring programmes provide good spatial coverage of the atmospheric concentration of most POPs and also for semi-volatile organic compounds, though few air monitoring programmes include measurements of these compounds in precipitation, from which deposition can be estimated.

6.2.1.2 Other media

Other than air, there are limited measurements and few organized monitoring programmes for POPs concentrations in other media, e.g. precipitation, dry deposition, ocean, snow, soil and vegetation (such as that under HELCOM for the Baltic Sea region). Air-surface interaction studies are limited to a few groups of compounds, e.g. PCBs, HCHs and some organochlorine pesticides. Oceanic measurements have been mainly collected via one-time cruise-based studies. There is evidence showing more polar compounds can be transported over long distances via ocean currents. For multi-hoppers and swimmers, ocean water is also an important partitioning medium, a sink or a source.

6.2.2 Recommendations

Observations of POPs in air, deposition and other media will continue to be a basis for our understanding of prevalence of POPs. That understanding allows evaluation of models for risk assessment and for policy abatement measures.

6.2.2.1 Other media

There is little information on long-term trends of POPs concentrations in food or human media, or in many other media relevant for human exposure, in most of the world. Sustained monitoring of POPs geared toward a more accurate understanding of human and ecosystem exposure to POPs, in media such as air, water, soil, and food, would give a more accurate depiction of the POPs to which humans are actually exposed. Similarly, long-term sustained monitoring in human media, such as blood and breast milk, is needed to understand how POPs impact human health and to understand how policies to reduce the emissions of POPs actually reduce LRT and protect health.

6.2.2.2 Maintaining and developing measurements

Existing atmospheric and precipitation monitoring programmes for POPs need to be continued to provide temporally- and spatially-resolved concentrations and deposition information. To understand how transport and concentrations of these pollutants change with time, the sampling and analytical methods of these programmes should remain consistent over time, ensuring that results generated remain comparable.
Passive air sampling programmes should be sustained to ensure the ability to develop temporal trends and can be expanded to cover regions where measurements are currently not available. Further development of cost-effective passive air sampling techniques to include measurements of more and new polar compounds is important for understanding their transport patterns and evaluating the need to control these substances.

Integrated monitoring of various media within the same vicinity is essential for understanding partitioning processes that influence transport and estimating flux for model validation and parameterization. It is recommended that existing air monitoring programmes measure POPs in other media at the same location, e.g. soil, water, snow and precipitation, to assess air-surface interactions. It is also important to develop an inventory of POPs in major reservoir compartments, such as soil and ocean water, in order to assess secondary emissions and subsequent transport, especially for legacy POPs that are showing a shift from primary to secondary sources. Additionally, there is a need for sustained measurements of POPs in ocean water to gain a better understanding of the transport behaviour of swimmers and multi-hoppers. Finally, monitoring of POPs in wild animals (in particular fish), food, and human media would allow for a more thorough understanding of exposure to POPs and their impacts on human health and ecosystems.

6.3 Modelling POP transport and fate. Importance of processes understanding.

At present, there exist a set of POP fate models that describe the system of chemical and environmental interaction with widely varying levels of detail. These include multimedia box models, trajectory models, and spatially resolved multi-compartment chemistry transport models. The different models reflect different design decisions and different applications to a large number of substances with respect to their LRT potential and environmental persistence, to the detailed evaluation of pollution levels and trends and source-receptor relationships.

Models are intensively applied within various international bodies (LRTAP Convention, the Stockholm Convention, OSPAR, HELCOM, AMAP, etc.) to support the negotiation process on the evaluation of pollution levels for legacy substances and for inclusion of new ones.

6.3.1 Findings

Existing POP models have been evaluated against empirical information about the physical and chemical properties of non-polar POPs, emissions and measured concentrations in the environment. Evaluation of modelling results reveals reasonable agreement between available measurements and model predictions of POP concentrations in the atmosphere. Deviations between the modelled and observed concentrations for most of the studied POPs are typically within a factor of three to four or better. However, in some cases the differences can be substantial, indicating essential uncertainties both in emission inventories and in modelling approaches.

The ability to measure and model POPs in the environment relies on a foundation of basic scientific knowledge of the physical and chemical properties of POPs. Partitioning and movement of POPs within a medium and among media depend also on a number of other key processes, such as dynamics of the media, decay processes and exchange processes between media.

The knowledge of POP abundances and chemodynamics in morphologically heterogeneous compartments (e.g. soil and snow) is very limited. 'Aging' of chemicals in soil, effects of snow sintering, and parameterisation of other environmental processes are not well understood. The same is true for biodegradation in soil and the ocean, which for many POPs are the most significant sink processes.

Uncertainties in the physical and chemical properties (e.g. Henry’s Law constants, vapour pressures, and octanol-water and octanol-air partition coefficients) of some POPs and semi-volatile organic compounds, and the lack of such measurements for new and emerging chemicals, render the understanding of air-surface exchange processes and the role that they play in LRT difficult.
In order to understand the impact of climate change on the inter-media exchange and LRT of chemicals, there is a need to improve estimates of temperature- and salinity-dependent physical and chemical properties, especially for new and emerging chemicals for which such information is lacking.

6.3.2 Recommendations

- Further work on the development and improvement of model parameterisation of gaseous exchange between the atmosphere and underlying surface and improving information about degradation in all the environmental media is needed. Particularly, for correct simulation of POP environmental levels in soil and seawater, further refinement of POP phase partitioning in these media and the uptake of POPs by vegetation is also important.

- In order to improve the model's capabilities to understand and predict intercontinental transport and source-receptor relationships of polar and amphiphilic compounds, there is a need for evaluated parameterisations for these substance classes' surface and phase exchanges.

- Extend descriptions of soil-air partitioning that go beyond the simplified KOA approach, taking into account the quality of organic matter, various types of chemical interactions of the chemical substance with organic matter, carbonaceous geosorbents and mineral matter, and its dynamics (which includes 'aging' of the substance in the soil).

- Improve measurements and modelling of physical and chemical properties, especially for Henry's Law constants (HLCs). Work to eliminate or minimize experimental artefacts in their determination, expand the data base for HLCs as functions of temperature and salinity and measurements of HLCs for emerging chemicals of concern.

- Develop techniques to provide better speciation of the “truly dissolved” and “truly gaseous” fractions of semi-volatile organic compounds so more accurate gas exchange estimates can be made. Revisit the surface microlayer in water bodies as an accumulation and exchange reservoir for POPs.

- Improve estimates of mass transfer coefficients to reduce the uncertainty in gas flux estimates. Extend models to include water surfaces with broken ice for applications in polar regions.

- Apply micro-meteorologically based experimental techniques to determine gas exchange fluxes for comparison to model estimates.

- Continue using chiral components as markers of different types of sources, as indicators for climate effects on diagenesis in soil and as tracers of LRT of POPs. Expand the availability of reference materials for chiral molecules, e.g., soils, sediment and biota.

- Characterize technical products of POPs pesticides (e.g., HCH, chlordane, heptachlor, DDT, dicofol, toxaphene) as starting points for understanding emission sources.

- Improve estimates of soil-air and water-air fractionation to understand how these processes alter compound ratios from source to sink.

- Use compound ratios in combination with other tracers (e.g., enantiomers, isotopes and combustion markers) to distinguish sources.

6.4 Primary and secondary emissions of POPs. Importance of air-surface exchange.

Knowledge of primary and secondary sources of POP emissions to the environment is essential to support policy activities to reduce the contamination of environment and to understand, quantify, and predict the source-receptor relationships.

Soils and seawater are major reservoirs for POPs and sources of secondary emissions to the atmosphere. The movement of POPs between the air and various surface media is a very important step between the original emission of POPs and their ultimate fate.
6.4.1 Findings

Significant advances have been made with respect to the development of emission inventories for some POPs in the last decades. Emission inventories were developed for DDT, HCB, HCHs, PAHs, PCBs, PCDD/Fs, and PFOS on global scale. Additionally, for some POPs there exist regional emission inventories, namely, for Europe, North America and China. Currently, the data on emissions of most legacy POPs and some new POPs are being reported and compiled under the LRTAP and Stockholm Conventions. Besides the emission inventories, there exist soil residue inventories (i.e., for HCH isomers on a global scale and toxaphene in the United States).

Development of emission inventories on a global scale is a challenging work. Information on usage and emission sources of POPs worldwide is lacking. The data collected for inventory work vary in quality and show large spatial and temporal gaps. Not every country keeps records or has a reporting mechanism, while in others information is proprietary. In this case, the application of gap-filling methodologies (the use of surrogates) is needed.

Emission inventories of all POPs are affected by essential uncertainties associated with the applied emission factors. Improvement of the emission factors as well as the understanding of the activity patterns is highly required. A higher distinction between different kinds of processes and their application conditions in different countries is also needed.

Many POP substances have direct emissions, not only to air, but also to other environmental media (soil, freshwater and seawater).

Although the emission inventories should include both primary and secondary emissions, most of the available POP emission inventories quantify primary emissions only. The emitted POPs tend to accumulate in environmental reservoirs, such as soil and water bodies, and re-emit to the atmosphere forming the secondary emissions, which, in the future, may supersede the primary emissions. Thus projections of future POPs emissions without considering the secondary emissions will be incomplete, or may be misleading in some cases.

Evaluation of the source-receptor relationships for POPs is more difficult than for other air pollutants, because of the significance of the secondary emission sources (re-emission and multi-hopping potential). Evaluation of re-emission can be subject to essential uncertainties, as it depends on the historical emissions and requires simulations of long time periods. In addition, the fate of POPs in soil, seawater, and vegetation is not sufficiently understood. The role of secondary sources means that POPs may cycle and undergo intercontinental transport even decades beyond phase-out of primary use and releases. During and after application of emission control measures, source types other than those regulated (e.g., leaks from storage and illegal use), may become significant.

Scientists concerned with risk assessment most often request the cumulative toxicity of the emissions, described by the concept of toxicity equivalence factors (TEF), to allow risk assessment of exposure to complex mixtures of different chemicals, such as dioxins and furans. Environmental modellers on the contrary, are increasingly requesting information on the emissions of individual POP constituents (isomers, congeners), due to their different fates in the environment. For POPs that are emitted into the environment as spatially and temporally variable mixtures, it is considered a great challenge to provide reliable emission estimates of individual isomers and congeners. This is clearly limiting the possibilities for modellers to evaluate the regional and global source-receptor relationships to very few POP compounds.

6.4.2 Recommendations

- Although global emission inventories for some of the POPs are available at present, further work on elaboration of emission inventories for other POPs and reducing uncertainties of available inventories is needed.

- Inventories of POPs emissions and their projections require the inclusion of secondary sources. Thus, it is recommended that emission inventories being developed take into account the historical substance releases into the environment.
Dynamic models, which include both the description of relevant air-surface exchange processes and reflect the life-time of POPs in the environment, need to be applied to estimate the contribution of secondary emissions. It is also recommended that the temporal (diurnal, seasonal) distribution or variation of emissions of POPs be taken into account.

There is a need for further measurements and characterization of the emissions of particular POPs at the sources of release and including the mode of release.

To evaluate secondary emissions, the inventories of POP residues in the environmental reservoirs (soil and ocean, in particular), are needed, not only for POPs used in the agricultural sector (pesticides), but also for industrial POPs (chemical products like PCBs and unintentional releases like dioxins). Observations of POPs content in soil and seawater are required to evaluate the residues of these POPs.

For industrial chemicals, such as the PCBs and the PBDEs, it would be desirable to conduct further experiments that aim to quantify emissions from key usage categories, since reliable empirical data are generally lacking. Specifically, there seems to be a need for further studies that aim to improve the understanding between atmospheric emissions of PCBs and temperature. Temperature dependency will be a key question for the future, to account for climate change.

The relative importance of PCB emissions due to unintentional formation needs further investigation and clarification with respect to the regional and global mass balance for individual PCB congeners. In addition to the general need for improved emission characterisation, additional environmental concentration measurements in air, soil, and water on a global scale, from which trends can be derived, are needed to allow comparison with modelling and serve as a check on emission totals.

For assessment of the success of the international regulations concerning POPs (i.e., the Protocol on POPs to the LRTAP Convention and the Stockholm Convention), emission inventories as well as future baseline projections on a global scale are required. An ultimate goal can be to present emission data and future baseline projections at least for all considered POPs in a format suitable for decision makers, who aim to develop cost-effective control measures.

Development and improvement of emission inventories for POPs needs further strengthening through international collaboration and the exchange of information.

6.5 Emerging substances, screening

As new chemical substances are introduced into commerce, and as new information is learned about existing substances, the ability to quantify to the long-range transport potential (LRTP) and the impacts of these emerging POPs is crucial. Environmental observations, process-oriented field and lab research and modelling all play important roles in this screening process. The results of model evaluation of new substances are used in national and international risk management as supporting information to take appropriate action. In particular, metrics of LRTP and environmental persistence derived from multimedia models are recognized to be relevant for the evaluation of new substances and their POPs characteristics by the Task Force on POPs and under the auspices of the Stockholm convention (POPRC).

6.5.1 Findings

Both mass balance models and multi-compartment chemistry transport models can be used to support the evaluation of environmental risk associated with new substances. These models evaluate LRTP and environmental persistence of chemicals, taking into account main environmental processes such as media exchange and degradation (multimedia approach). Comparison of the ranking of chemicals with respect to their LRTP and persistence in the environment obtained by different models showed reasonable agreement among their predictions.

To evaluate the potential of a substance to undergo LRT, numerical evaluation of LRT metrics is required. Various metrics for quantifying the LRT of substances have been proposed and can be classified either as transport-oriented or target-oriented metrics. These metrics are typically
calculated with the help of multimedia POP models (OECD Pov and LRTP Screening Tool, SimpleBox, Impact2002, ELPOS, ChemRange, BETR-Global, MSCE-POP, etc.). The choice of a particular metric strongly depends on model design. Multimedia POP models permit the inclusion of complex fate processes of POPs in the environment.

6.5.2 Recommendations

- There is a need to conduct process research and adapt measurement and analytical techniques to target ‘new’ POPs. Transport models will need to be parameterized for these chemicals and new emission inventories developed. The European Chemical Agency (ECHA) collects key data on physical and chemical properties and production volumes of industrial chemicals under the framework of EU Regulation REACH (Registration, Evaluation, Authorization and restriction of Chemicals). Co-operation and exchange of such data with the ECHA will be a valuable basis for the evaluation of new chemicals and POPs candidates to be subject to national, regional and global measures, particularly under the global Stockholm Convention where modelling is expected to play an increased role in future.

- There is also a need to continue screening efforts (based on monitoring/modelling activities) and research to identify new chemicals with POP-like characteristics for further consideration.

- Research by the appropriate national and international bodies into the health effects of existing and emerging substances is needed. Among the new or emerging substances, polybrominated diphenylethers (PBDEs) and perfluorinated compounds, such as PFOS and PFOA, have been detected in remote areas, e.g., the Arctic. Other emerging compounds discussed include halogenated phenols, such as pentachlorophenol (PCP), short-chain chlorinated paraffins (SCCPs), endosulfan, and polychlorinated terphenyls (PCTs). However, the lack of information on health effects and LRT of these substances necessitates more research on these POPs.

6.6 Integrated approach

An integrated approach to better understand LRT and fate of POPs in the environment is based on integrated use and analysis of monitoring, emission, and modelling data for evaluation of POP contamination. An integrated approach to POPs assessment requires cooperation and congregation of experts from different backgrounds.

6.6.1 Findings

This assessment and several other assessments have demonstrated that an integrated approach can successfully be applied to POPs even if the coverage of emission data, observations and model processes is incomplete. The added value comes from (1) the increased analytical capability for establishing risk for human health and the environment and (2) the uncertainty analysis, which identifies where improvement in data and process understanding is most needed to improve the overall analytical capability.

6.6.2 Recommendations

- TF HTAP should continue to move in this direction and promote collaboration among these groups of experts and related programmes.

- Initial steps of this integration include giving attention to the analysis of agreement between spatial and temporal variations of modelled and observed data. Results of the analysis can characterize the representativeness of the monitoring sites, indicate model errors, show the necessity to improve model parameterizations or the understanding of processes governing POP fate, and identify gaps in emission information with respect to its spatial distribution and completeness of coverage of source categories.

- Further stages of integration can be devoted to the reduction of identified uncertainties. Additional monitoring experiments and field campaigns can be organised to improve understanding of processes and subsequently to refine model parameterization. Completeness and uncertainties of available emissions should be analysed and emission scenarios should be elaborated. Model
predictions based on the developed emission inventories provide consistent information on the pollution variations in space and time and contributions of particular sources and source categories to the pollution levels. Nesting approaches developed in a number of contemporary global models permit linking the assessment of pollution on global, regional, and local scales. Models are useful for analysing future contamination based on the scenarios of future emissions under different regulatory strategies and possible changes of climate.

- Expand large-scale monitoring of POPs in air and soil to validate LRT and surface exchange models for the study of the environmental behaviour of legacy chemicals and those of emerging concern.
- Observations jointly with multi-compartment models allow assessment of global source strengths for POPs, for which inventories are incomplete or erroneous. The complexity of POPs environmental exposure routes to humans and ecosystem requires additional key information in all media, but the assessment of intercontinental transport of POPs requires monitoring with global coverage and field studies of specific processes related to LRT, such as surface air exchange.
- Assessment of environmental contamination by POPs is a challenging task due to the large variability of physical and chemical properties and the complexity of fate processes in the atmosphere, soil, seawater, vegetation, etc. Thus, monitoring of POPs concentrations in one or several compartments may not provide sufficient information on which to base appropriate policy decisions. Additionally, the occurrence and quantities of POPs in various environmental compartments is not only determined by current levels of emission, but also by historical loadings that have accumulated in environmental media and the ability of these chemicals to cycle between compartments and be redistributed. Hence, the development of emission inventories requires the use of multi-compartment models that account for primary and secondary emissions.

### 6.7 Effects of climate change

The interaction of climate with POPs has recently become an area of concern mainly due to (1) climate change may alter the desire or need to use POPs; (2) trends in POPs established by repetitively sampling any environmental compartment (air, water, biota, soil, vegetation) can be impacted by climate variables and thus needs to be considered before such trends can be interpreted in the context of emission controls; 3) exposure of populations and individuals within ecosystems can be altered by changes in any or all of the pathways leading to that population/individual and, (4) climate change can affect the vulnerability of populations to chemical exposure.

#### 6.7.1 Findings

Climate change has the potential to affect all POPs pathways in the atmosphere, hydrosphere, cryosphere, biosphere, and soil. There is evidence that climate change phenomena, e.g., elevated temperatures and sea-ice reduction, and extreme climate events, such as forest fires, flooding and glacial melting, will remobilize POPs previously deposited in sinks, e.g., forest soils and vegetation, ocean and lake sediments and glaciers. There is a need to estimate the amount of POPs that would be re-released by foreseeable climate change conditions by developing residue inventories through measurements in potential sinks.

#### 6.7.2 Recommendations

- Climate interactions with POPs and the connection between climate and variable meteorology should be considered in the collection and interpretation of data sets to assess spatial and temporal trends for POPs and source-receptor relationships. Further investigations are needed to understand and quantify climate-induced perturbations of POPs in multi-compartment environments and the impact of increased extreme climate events.
- In order to understand the impact of climate change on the inter-media exchange and LRT of POPs, there is a need to improve estimates of temperature and salinity dependent physical and
chemical properties and minimize experimental artefacts in their determination, especially for
new and emerging chemicals, where such information is lacking.

- For the investigation of the effect of climate change on POP fate in the environment, scenarios of
  future climate change for a sufficiently large period of time are required.

6.8 Concluding Remarks

POPs and POP-like chemicals are a unique group of toxic pollutants, having negative impacts
on ecosystems and human health spanning from years to several decades. They may be transported
over long distances via the atmosphere or the oceans and have the ability to partition to and from
various environmental media.

National and international regulations have reduced the production, consumption and release
to the environment of a number of POPs (like HCHs, DDT and other organochlorine pesticides,
dioxins/furans). Inventories of use and releases of such regulated substances generally confirm the
policy effectiveness. Due to the slow decay rate of POPs, these regulated substances will nevertheless
remain for a long time in the environment (legacy POPs). In some cases, declining time trends of
some substances (e.g., technical HCH) indicated a response to international controls. However, other
POPs showed slow or no significant decline in air in response to control, e.g., p,p’-DDT at the Arctic
stations of Alert and Pallas.

Existing air monitoring efforts should be continued to generate long-term trends to assess the
effectiveness of international control initiatives (POPs protocol and the Stockholm convention). It is
noteworthy that a non-declining atmospheric trend at remote locations may not necessarily indicate
ineffectiveness of control. The time required for the target chemical to reach a specific receptor region is
influenced by the relative locations of the source and the receptor, the chemical’s transport pathways and
its physical and chemical properties. Proper interpretation of temporal trends requires an understanding
of these influencing factors which can be estimated using appropriate transport models.

For the prediction of POP LRT, the coordinated use of multimedia modelling, monitoring
of POP content and trends in environmental media, refinement of the understanding of both primary
and secondary emissions, as well as POPs degradation and transformation processes are essential.
For this purpose, the development and use of an integrated approach for the evaluation of POP fate
and source-receptor relationships on a global scale is required. In addition to the understanding of
LRT, crucial information is also needed on the human exposure routes through air and food and the
risk of such exposure. The integrated approach will also assist in identifying new POP candidates
for policy measures.

Taking into account the complexity of POP pollution evaluation it is important to strengthen
collaboration and the exchange of information on scientific and research activity among various
international programmes and bodies.
### Table A.2.1. Major ongoing air monitoring programs

<table>
<thead>
<tr>
<th>Monitoring programme</th>
<th>Abbreviation</th>
<th>Region of interest</th>
<th>No. of sites</th>
<th>Period</th>
<th>Sampling method</th>
<th>Monitored compounds *</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arctic monitoring and Assessment Programme</td>
<td>AMAP</td>
<td>Arctic</td>
<td>12 (includes 8 NCP sites)</td>
<td>1993 - present</td>
<td>active/ non-directional</td>
<td>PCBs, HCB, HCHs, chlordanes, DDTs Additional compounds at 8 NCP-operated sites (see below).</td>
</tr>
<tr>
<td>Northern Contaminants Program (Canada) (Part of AMAP)</td>
<td>NCP</td>
<td>Arctic</td>
<td>8 (part of AMAP)</td>
<td>1992 - present</td>
<td>active/ non-directional</td>
<td>PCBs, DDTs, PAHs, PentaCB, mirex, chlordanes, HEPT, HEPX, PeCB, HCB, HCHs, endrin, aldrin DIEL, ENDO 2002-present : PBDEs Nov 2000 – Feb 2001: PCDD/Fs 2006-present, Alert station: PFCs</td>
</tr>
<tr>
<td>European Monitoring and Evaluation Programme</td>
<td>CLRTAP-EMEP</td>
<td>Europe</td>
<td>18 in 2007 (includes 3 AMAP sites)</td>
<td>1991 - present</td>
<td>active/ non-directional (12 sites with air and precipitation measurements and 6 sites with air measurements only)</td>
<td>As of 2007: PCBs, DDTs, chlordanes, HCB, PAHs, HCHs, HEPT, DIEL</td>
</tr>
<tr>
<td>Global Atmospheric Passive Sampling network</td>
<td>GAPS</td>
<td>Global</td>
<td>52 (current operation) 95 (since inception)</td>
<td>2004 - present</td>
<td>passive [PUF-disk/ XAD/ sorbent impregnated PUF (SIP)]</td>
<td>PCBs, chlordanes, DDTs, HEPT, HEPX, HCHs, DIEL, PBDEs, ENDO 2005: PCNs 2009 at 20 sites: PFCs</td>
</tr>
<tr>
<td>Monitoring programme</td>
<td>Abbreviation</td>
<td>Region of interest</td>
<td>No. of sites</td>
<td>Period</td>
<td>Sampling method</td>
<td>Monitored compounds</td>
</tr>
<tr>
<td>----------------------</td>
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</tr>
<tr>
<td>Integrated Atmospheric Deposition Network (US &amp; Canada)</td>
<td>IADN</td>
<td>Great Lakes</td>
<td>8 (3 in Canada, 5 in U.S.A)</td>
<td>1990 – present</td>
<td>active/ non-directional</td>
<td>PCBs, chlordanes, ENDO, HCHs, DDTs, HEPT, HEPX, aldrin, endrin, DIEL, HCB, MIREX, PAHs 2002-present: PBDEs 1995-2005 at Lake Ontario, Canada only: Toxaphene</td>
</tr>
<tr>
<td>National Air Pollution Surveillance (Canada)</td>
<td>NAPS</td>
<td>Canadian Urban</td>
<td>18 stations</td>
<td>1969 to present</td>
<td>active/ non-directional</td>
<td>PCP, HCB, PAHs, PCBs, PCDD/Fs, PBDEs</td>
</tr>
<tr>
<td>Monitoring Network in the Alpine Region for Persistent and other Organic Pollutants</td>
<td>MONARPOP</td>
<td>European Alpine regions</td>
<td>3 active air monitoring stations (out of 40 sites)</td>
<td>2004 – present</td>
<td>active/ directional (3 stations); passive (SPMD)</td>
<td>PCBs, DDTs, HCB HEPT, DIEL, aldrin, endrin, mirex, PCDD/Fs, HCHs, PAHs, PBDEs</td>
</tr>
<tr>
<td>National Dioxin Air Monitoring Network (U.S. EPA)</td>
<td>NDAMN</td>
<td>USA</td>
<td>34</td>
<td>1998 – 2004</td>
<td>active/ non-directional</td>
<td>PCDD/Fs, co-planar PCBs</td>
</tr>
<tr>
<td>New Jersey Atmospheric Deposition Network</td>
<td>NJADN</td>
<td>USA</td>
<td>9</td>
<td>1997-2001</td>
<td>active/ non-directional</td>
<td>PCBs, PAHs, DDTs, HCHs, ENDO, aldrin, DIEL</td>
</tr>
<tr>
<td>Xarxa de Vigilància i Previsió de la Contaminació Atmosfèrica</td>
<td>XVPCA</td>
<td>Catalonia (Spain)</td>
<td>28</td>
<td>1994 – present</td>
<td>Active</td>
<td>PCDD/Fs, 2003-present:PAHs, co-planar PCBs</td>
</tr>
<tr>
<td>National POPs monitoring network (MONET)</td>
<td>MONET</td>
<td>Central and Eastern Europe, Central Asia, Africa and Pacific Islands, Europe</td>
<td>3 (Pacific Islands) 157 (Central and Eastern Europe) 26 (Africa) and 17 (Central Asia) 55 (Europe and Central Asia)</td>
<td>2006-2007 2006-present 2008-2010 2009-2010</td>
<td>passive (PUF-disk); active/non-directional (at Kosetice)</td>
<td>PAHs, PCBs, HCHs, DDTs, HCB, PeCB At selected sites: dioxins</td>
</tr>
<tr>
<td>Monitoring programme</td>
<td>Abbreviation</td>
<td>Region of interest</td>
<td>No. of sites</td>
<td>Period</td>
<td>Sampling method</td>
<td>Monitored compounds</td>
</tr>
<tr>
<td>--------------------------------------------------------------------</td>
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</tr>
<tr>
<td>Chinese POPs Soil and Air Monitoring Program (SAMP), Phase I</td>
<td>SAMP-I</td>
<td>Chinese rural, urban</td>
<td>97 (4 background, 24 urban, and 69 rural)</td>
<td>2005-2007</td>
<td>passive (PUF-disk)</td>
<td>PCBs, chlordane, DDTs, HEPT, HEPX, HCHs, DIEL, ENDO, PAHs, PBDEs</td>
</tr>
<tr>
<td>Chinese POPs Soil and Air Monitoring Program (SAMP), Phase II</td>
<td>SAMP-II</td>
<td>Chinese urban and background</td>
<td>12 urban and 4 background</td>
<td>2008-present</td>
<td>Active /non-directional</td>
<td>PCBs, chlordane, DDTs, HEPT, HEPX, HCHs, DIEL, ENDO, PAHs, PBDEs</td>
</tr>
<tr>
<td>Spanish Monitoring Programme on POPs</td>
<td>PNA-COP</td>
<td>Spain</td>
<td>12 EMEP sites</td>
<td>2008-present</td>
<td>Passive (PUF-disk)</td>
<td>PCDD/Fs, non-/mono-ortho- and majority PCBs, DDTs, HCB, HCH, PBDEs</td>
</tr>
<tr>
<td>The UK Toxic Organic Micro Pollutants (TOMPs) programme</td>
<td>TOMPS</td>
<td>UK</td>
<td>6</td>
<td>1991-present</td>
<td>Active/ non-directional</td>
<td>PCDD/Fs, PCBs, PAHs</td>
</tr>
<tr>
<td>National Dioxins Program (Australia)</td>
<td>-</td>
<td>Australia</td>
<td>10</td>
<td>Sep 2002 – Aug 2003</td>
<td>Active/non-directional</td>
<td>PCDD/Fs, co-planar PCBs</td>
</tr>
</tbody>
</table>

DDTs = dichlorodiphenyldichloroethane isomers, DIEL = dieldrin, ENDO = endosulfan, PeCB = Pentachlorobenzene, HCB = hexachlorobenzene, HCHs = hexachlorocyclohexanes, HEPT = heptachlor, HEPX = heptachlor epoxide, PAHs = polycyclic aromatic hydrocarbons, PCBs = polychlorinated biphenyls, PCDD/Fs = polychlorinated dibenzo-p-dioxins and furans, PentaCB = pentachlorobenzene, PCNs = polychlorinated naphthalenes, PCP = pentachlorophenol, PFC = perfluorinated compounds
<table>
<thead>
<tr>
<th>Time period</th>
<th>Location</th>
<th>Brief description of the study</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>December 1992 -</td>
<td>Tagish, Yukon (60º20'N, 134º12'W) in the western Canada.</td>
<td>Weekly high-volume air samples were analyzed for OCPs. High concentrations of HCHs, DDT, and chlordanes were attributed to Trans-Pacific transport from eastern Asia.</td>
<td>Bailey et al. [2000]</td>
</tr>
<tr>
<td>January 1995</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1993-2005</td>
<td>Multiple sites in the North American and European Arctic</td>
<td>PCNs were measured by high volume and passive sampling. Results showed much higher concentrations in the European Arctic. Profiles showed the presence of PCNs from evaporative and combustion sources.</td>
<td>Bidleman et al. [2010]</td>
</tr>
<tr>
<td>December 5, 1994 -</td>
<td>Signy Island (South Orkney Islands, 60º72'S, 45º60'W) in Antarctica</td>
<td>PCBs and OCPs in air were measured over a time period of 17 weeks. Air concentrations were comparable to those in the Arctic. Long-range atmospheric transport from South America was identified as potential sources.</td>
<td>Kallenborn et al. [1998]</td>
</tr>
<tr>
<td>April 2, 1995.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1996-1997</td>
<td>2 reference sites, 2 rural sites, 5 urban sites, and 1 industrial site.</td>
<td>Background air concentrations were measured for PCDD/Fs, PCBs, and OCPs at 10 sites in New Zealand by using high-volume samplers. It was one of few studies conducted in the southern hemisphere.</td>
<td>Buckland et al. [1999]</td>
</tr>
<tr>
<td>June-July 2000</td>
<td>Izana Atmospheric Observatory in Teide (Tenerife Island, 28º18’N, 16º29’W; 2367 m.a.s.l.)</td>
<td>Air concentrations of PCBs and OCPs were found uniform in the free troposphere, and no significant differences were observed between samples with air masses originated from different directions.</td>
<td>Van Drooge et al. [2002]</td>
</tr>
<tr>
<td>Week 51, 1999 -</td>
<td>Bjørnøya (Bear island, 74º30’N, 19º00’E)</td>
<td>OCPs and PCBs were measured with a high-volume air sampler once a week in summers and once every two weeks in winters. Several atmospheric long-range transport episodes were identified and characterized.</td>
<td>Kallenborn et al. [2007]</td>
</tr>
<tr>
<td>Week 28, 2003</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>August 14 - 30, 2001</td>
<td>At ground and in the mid-troposphere above the Lower Fraser Valley, British Columbia, Canada</td>
<td>OCPs were concurrently measured on both ground levels and in the mid-troposphere above the Lower Fraser Valley during the Pacific 2001 flights. Higher concentrations of α-HCH in the mid-troposphere than ground levels indicated Trans-pacific transport from Asia to North America.</td>
<td>Harner et al. [2005]</td>
</tr>
<tr>
<td>September 21 -</td>
<td>Island Gotska Sandön in the Baltic Proper</td>
<td>Air measurements were conducted for PBDEs and PCBs in a central island in the Baltic Sea. Atmospheric transport and depositions of PBDEs and PCBs were investigated.</td>
<td>ter Schure et al. [2004]</td>
</tr>
<tr>
<td>November 11, 2001</td>
<td>i) West Antarctic Peninsula and southwest Adelaide Island (ca. 69ºW, 68ºS)</td>
<td>OCPs were measured with a high-volume air sampler in the austral winter (September 7 - October 26) 2001 and summer (January 7 - March 14) 2002. Elevated concentrations of heptachlor coincided with air masses originated from lower latitudes.</td>
<td>Dickhut et al. [2005]</td>
</tr>
<tr>
<td></td>
<td>ii) Close to Palmer Station and southwest Anvers Island (64.7ºS, 64.0ºW)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table A.2.2. cont’d. Independent Long-Range Transport Studies

<table>
<thead>
<tr>
<th>Time period</th>
<th>Location</th>
<th>Brief description of the study</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>March 15 - May 30, 2002</td>
<td>Cheeka Peak Observatory (48.3 N, 124.6 W; 480 m.a.s.l.) in western US.</td>
<td>Air samples were collected with high-volume air samplers over two and half months in the western US. Elevated concentrations of anthropogenic SOCs measured were related to possible Trans-Pacific events identified by modeling.</td>
<td>Killin et al. [2004]</td>
</tr>
<tr>
<td>2002 - 2003</td>
<td>Saint Helena (16°S, 5.45°W) in the south Atlantic</td>
<td>PCB background air concentrations were monitored with a high-volume air sampler. Air masses were predominantly (~ 99%) oceanic during the sampling period and there was not much variability in PCB concentration. The PCB levels in Saint Helena truly represented background concentration for the South Atlantic.</td>
<td>Gioia, R. and Jones, K.C., (personal communication, 2010)</td>
</tr>
<tr>
<td>2003 - 2006</td>
<td>Hedo Station Observatory on Okinawa, Japan (26.8° N, 128.2° E, 60 m.a.s.l.), Cheeka Peak Observatory in Washington State (48.3° N, 124.6° W, 500 m.a.s.l.), Mary’s Peak Observatory in Oregon’s Coast Range (44.5° N, 123.6°W, 1249 m.a.s.l.), and Mt. Bachelor Observatory in Oregon’s Cascade Range (43.9° N, 121.7° W, 2763 m.a.s.l.)</td>
<td>High-volume air samples were collected in various time periods at one Asian site, and three sites in the western US. Trans-Pacific transport and regional atmospheric transport from the western US were investigated for OCPs, PAHs, PCBs, and fluorinated compounds.</td>
<td>Primbs, et al. [2007; 2008a; 2008b]; Genualdi et al. [2009a; 2009b]</td>
</tr>
<tr>
<td>November 4, 2003 - January 30, 2004</td>
<td>A coastal site off northern Victoria Land (74°42’6.3”S, 164°06’52”E)</td>
<td>OCPs were sampled with a high-volume air sampler in the austral summer 2003-2004. Seasonal variation of HCHs and low ratios of α/γ-HCH may suggest long-range transport inputs from agricultural regions.</td>
<td>Cincinelli et al. [2009]</td>
</tr>
<tr>
<td>August 2004 - August 2005</td>
<td>Open Indian Ocean</td>
<td>PCBs and OCPs were analyzed in 12 air samples collected over the Indian Ocean. High PCBs at remote islands were attributed atmospheric transport inputs from a large military base and waste combustion. High concentrations of OCPs were related to air masses originated from continental sources.</td>
<td>Wurl et al. [2006]</td>
</tr>
<tr>
<td>April 2 - May 23, 2005</td>
<td>Waliguan Baseline Observatory (36°17’N, 100°154’E, 3816 m.a.s.l.) in China</td>
<td>OCPs and PBDEs were measured at the elevated Global Atmospheric Watch (GAW) station. High air concentrations of γ-HCH, DDTs, and PBDEs were attributed to long-range transport inputs from neighbor countries.</td>
<td>Cheng et al. [2007]</td>
</tr>
</tbody>
</table>
### Table A.2.2. cont’d. Independent Long-Range Transport Studies

<table>
<thead>
<tr>
<th>Time period</th>
<th>Location</th>
<th>Brief description of the study</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>October 2005 - April 2008</td>
<td>Balong Mountain along provincial road 303 (30°38.63’-31°05.08N’, 102°53.74’-104°02.93'E, 507-4485 m.a.s.l.)</td>
<td>Passive air sampling of PCBs and OCPs along a mountain transit in the Tibet-Qinghai Plateau showed that atmospheric transport inputs from populated Chengdu plain were likely major sources in this remote region.</td>
<td>Liu et al. [2010]</td>
</tr>
<tr>
<td>2006 - 2007</td>
<td>Aspvreten (58°80’N, 17°40’E), Sweden, and Pallas (68°00’N, 24°14’E), Finland</td>
<td>Air samples were collected with high volume samplers at two remote stations during winter 2006-2007. Atmospheric concentrations of PCDD/Fs over the Baltic Sea were found closely related to air mass origin. Major source regions of PCDD/Fs were traced by analyzing stable air mass trajectories.</td>
<td>Sellström et al. [2009]</td>
</tr>
<tr>
<td>October 2006 - February 2008</td>
<td>Nam Co Station in the Tibetan Plateau (30°46.44’N, 90°59.31’E, 4730 m.a.s.l.)</td>
<td>By using a flow-through sampler, air concentrations of PCBs, PAHs, and OCPs were measured on a monthly basis. High levels of OCPs were attributed long-range transport inputs from South of the Himalayas.</td>
<td>Xiao et al. [2010]</td>
</tr>
<tr>
<td>June 19 - 29, 2007 and February 11 - 21, 2008</td>
<td>Schneefernerhaus observatory (47°25.0’N/10°58.9’E, 2670 m.a.s.l.) in the Alps.</td>
<td>High volume air samples were taken for 2 weeks in each of the summer 2007 and winter 2008. Measurements of PAHs, chlorobenzenes, and DDTs were higher in winter than summer, but similar levels were found for HCHs and PCBs. Air concentrations of OCPs, PCBs, and PAHs in the free troposphere over Europe were comparable to those in the Arctic.</td>
<td>Lammel et al. [2009]</td>
</tr>
<tr>
<td>July 2007 - June 2008</td>
<td>At 16 sites in the Tibetan Plateau (28°21.633’-36°23.637N’, 80°05.654’-97°08.624’E, 2720-4740 m.a.s.l.)</td>
<td>A number of OCPs, PCBs and PBDEs were found in remote sites across the Tibetan Plateau by using passive air samplers, which were possibly influenced by long-range atmospheric transport inputs.</td>
<td>Wang et al. [2010]</td>
</tr>
<tr>
<td>November 6, 2007 - April 8, 2008</td>
<td>Sao Vicente island in Cape Verde (14.9 °N, 24.9 °W)</td>
<td>PCB background air concentrations were monitored with a high-volume air sampler. Air masses came predominantly (~ 95%) from the African continent. Congener profiles in the Sao Vicente island was found similar to those on the continent.</td>
<td>Gioia, R. and Jones, K.C. (personal communication, 2010)</td>
</tr>
</tbody>
</table>
Table A.2.3. Air Sampling Techniques Used by Monitoring Programs for POPs and POP-like Chemicals

<table>
<thead>
<tr>
<th>Technique</th>
<th>Approximate Sampling Rates</th>
<th>Examples of Sampling Media</th>
<th>General Sampling Time</th>
<th>Descriptions and Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Active (pumped)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Non-directional</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>High-volume (HiVol)</td>
<td>8-80 m$^3$/h</td>
<td>Particulates: Glass Fiber Filter (GFF) or Quartz Fiber Filter (QFF)</td>
<td>Several hours to 1 week</td>
<td>Used by most air sampling programs as listed in Table C2.1. Conventional method for air monitoring of POPs usually consists of a high-volume pump that draws air through a cartridge with a GFF/QFF to collect particles followed by a gas-phase sampling medium to absorb gaseous POPs. Can generate POPs concentrations in gas and particle phases quantitatively. Expensive to operate, require continuous power supply and constant maintenance. Short sampling time enables the tracking of high concentration episodes.</td>
</tr>
<tr>
<td>Low-volume (LoVol)</td>
<td>0.06 – 3 m$^3$/h</td>
<td>Same as HiVol</td>
<td>Several hours to several weeks</td>
<td>Construction same as HiVol with a low-volume pump. Longer time-integrated samples are required for chemical detection. Can quantitatively generate average POPs concentrations in gas and particle phases over the long sampling period.</td>
</tr>
</tbody>
</table>
Table A.2.3. cont’d. Air Sampling Techniques Used by Monitoring Programs for POPs and POP-like Chemicals

<table>
<thead>
<tr>
<th>Technique</th>
<th>Approximate Sampling Rates</th>
<th>Examples of Sampling Media</th>
<th>General Sampling Time</th>
<th>Descriptions and Characteristics</th>
</tr>
</thead>
</table>
| Directional | 1 LoVol (3 m³/h) coupled with 1 HiVol (8 m³/h) | LoVol with XAD cartridge and HiVol with GFF and PUFs | 3- to 4- months | Used at 3 meteorological stations located at the summits of the Alps, representing the highest elevation sites under MONARPOP. Four sampling cartridges collect air from different regions in different directions operated remotely based on daily meteorological trajectory forecasts. [Offenthaler et al., 2009]

Advantages: 1) can identify source regions with high POP concentrations or greater transport potential to receptor; 2) representative average concentrations through continuous sampling in seasonal and source-region-specific resolution, 3) small number of samples generated through continuous sampling.

Disadvantages: 1) unable to track short time events of higher concentration and their origin, 2) need to redefine source regions and require large air volumes for detectability. Pre-defined large-distant source regions may lead to seldom events, insufficient air volumes sampled and difficulties in forecasting of air masses coming from that region. Results may also be bias by the impact from the region in between. Difficult to study the influence of specific long-distant air transport (e.g. trans-Atlantic air transport to the Alps). 3) Wrong trajectory forecasts may lead to air sampled by the wrong filter. |
Table A.2.3. cont’d. Air Sampling Techniques Used by Monitoring Programs for POPs and POP-like Chemicals

<table>
<thead>
<tr>
<th>Technique</th>
<th>Approximate Sampling Rates</th>
<th>Examples of Sampling Media</th>
<th>General Sampling Time</th>
<th>Descriptions and Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Passive</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PUF-disk based</td>
<td>~3-4 m³/d</td>
<td>PUF disk; Sorbent-Impregnated PUF (SIP) disk</td>
<td>3 to 6 months</td>
<td>PUF or SIP-disk housed in 2 dome-shaped shelters. SIP-disks are composed of PUF-disk impregnated with finely ground XAD resin. Gas-phase POPs are sequestered by diffusion. Sampling rates estimated by using depuration compounds spiked onto sampling medium. PUF or SIP-disk requires no power supply, and is easy to operate. Provide semi-quantitative, seasonally-integrated results of mainly gas-phase concentrations [Pozo et al., 2006; Shoeib and Harner, 2002; Shoeib et al., 2008].</td>
</tr>
<tr>
<td>XAD-based</td>
<td>~1 m³/d</td>
<td>XAD</td>
<td>1 year</td>
<td>XAD-filled stainless steel mesh cylinder suspended in an inverted galvanized steel can with an open bottom. Gas-phase POPs are sequestered by diffusion. Sampling rates determined through field calibration studies, controlled wind, tunnel experiments, and flow field simulations [Wania et al., 2003]. XAD passive sampler requires no power supply, and is easy to operate. Provide semi-quantitative, annually-integrated results of mainly gas-phase concentrations.</td>
</tr>
<tr>
<td>SPMD</td>
<td>2-8 m³/d</td>
<td>low-density polyethylene tubes filled with triolein</td>
<td>6 months to 1 year</td>
<td>Used by MONARPOP at 40 sites at 7 levels of elevations on the Alps. Low-density polyethylene tubes filled with triolein that accumulates POPs via diffusion.</td>
</tr>
<tr>
<td>Flowthrough Air Sampler (FTAS)</td>
<td>3 – 60 m³/h (depends on windspeed)</td>
<td>PUF</td>
<td>Several weeks to 1 month</td>
<td>Used by NCP at Alert, Nunavut. Consists of a horizontally oriented, aerodynamically shaped, stainless steel flow tube mounted on a post with ball bearings allowing it to turn into the wind with the help of vanes. A series of PUF plugs sequester POPs from the air fed through the flow tube. Air volume sampled calculated using windspeeds recorded by a vortex wind sensor on top of the sampler. Quantitative (gas-particle-phase) concentrations calculated with breakthrough correction using frontal chromatography theory. [Xiao et al., 2007; 2008; 2009].</td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>Author</th>
<th>Journal</th>
<th>Region of interest</th>
<th>Sampling Date</th>
<th>Sampling matrix</th>
<th>Compounds monitored</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gioia, R et al</td>
<td>ES&amp;T, [2008b], 42, 1416–1422</td>
<td>North &amp; South Atlantic</td>
<td>2008</td>
<td>Air over oceans</td>
<td>PCBs</td>
</tr>
</tbody>
</table>
**Table A.2.4. cont’d.** Examples of papers detailing POPs in Air or Water in/over oceans

<table>
<thead>
<tr>
<th>Author</th>
<th>Journal</th>
<th>Region of interest</th>
<th>Sampling Date</th>
<th>Sampling matrix</th>
<th>Compounds monitored</th>
</tr>
</thead>
</table>

*DDTs = dichlorodiphenyltrichloroethane isomers, PAHs = polycyclic aromatic hydrocarbons, PCBs = polychlorinated biphenyls, PCDD/Fs = polychlorinated dibenzo-p-dioxins and furans, PFC = perfluorinated compounds*
Table A.2.5. Examples of Air-Water Gas Exchange Studies for SOCs, Large Lakes and Oceans.

<table>
<thead>
<tr>
<th>Location</th>
<th>Year</th>
<th>Chemicals</th>
<th>Findings</th>
<th>Reference</th>
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</thead>
</table>
| Lake Michigan, U.S.A. | 1994-1995 | PCBs, \textit{trans}-nonachlor | • Seasonal and spatial variability in PCB fluxes, deposition to volatilization.  
• Results for flux direction and magnitude depends on choice of HLCs.  
• Volatilization of \textit{trans}-nonachlor. | Miller et al., [2001]; Totten et al., [2003]; Zhang et al., [1999] |
| Lake Michigan, U.S.A. | 2001      | PCBs                 | • Deposition within ~40 km of Milwaukee.  
• Volatilization at further distances over open lake. | Wethington and Hornbuckle, [2005]|
• Main sources to the lake: wastewater treatment plant discharges, atmospheric deposition <1%.  
• Main losses: volatilization and outflow. | Peck and Hornbuckle, [2004]|
• Significant Clausius-Clapeyron (CC) relationship, $\log C_{\text{air}} = m/T + b$. | James et al., [2001]|
| Lake Superior, U.S.A. - Canada | 1988-1992 | PCBs                 | • Seasonal variability in fluxes, mainly volatilization except near-equilibrium or deposition in early spring. | Hornbuckle et al., [1994]|
| Lake Superior, U.S.A. - Canada | 2002-2003 | HCB, $\alpha$-HCH    | • Directly measured fluxes using micrometeorological technique.  
• Volatilization fluxes measured in 75% of events. | Perlinger et al., [2005]|
• Significant CC relationships.  
• Volatilization removes 2-6% of toxaphene in the lake annually. | Jantunen and Bidleman, [2003]; James et al., [2001]|
| Lake Ontario, U.S.A. - Canada | 1993      | $\alpha$-HCH         | • Volatilization of $\alpha$-HCH in summer-early fall, deposition or near-equilibrium in other seasons.  
• Mass loss similar to advection and wet deposition input. | Ridal et al., [1996; 1997]|
<p>| Lake Ontario, U.S.A. - Canada | 2003      | Perfluorinated compounds | • Main sources were inflow from Lake Erie and wastewater treatment plants, dominant loss occurred via outflow through the St. Lawrence River; atmospheric deposition and volatilization were minor. | Boulanger et al., [2005]|</p>
<table>
<thead>
<tr>
<th>Location</th>
<th>Year</th>
<th>Chemicals</th>
<th>Findings</th>
<th>Reference</th>
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</table>
| Great Lakes, U.S.A. - Canada | 1993-1996 | toxaphene                  | • Volatilization from lakes Superior and Huron, deposition into lake Ontario in all seasons. Volatilization from Michigan in summer-fall and deposition in winter-spring. Volatilization from Erie in all seasons except fall, when deposition occurred.  
  • Modeling suggests that Superior and Michigan were atmospheric sinks for toxaphene until ~1980, when flux reversed to volatilization.  
  • Volatilization estimated to account for 70% of annual loss from Superior. | Swackhamer et al., [1999]   |
| Great Lakes, U.S.A. - Canada | 1990s, modeling | PCBs                      | • Gas exchange (volatilization) dominates over precipitation and dry particle deposition.  
  • Great Lakes are a net source of PCBs to the atmosphere.                                                                                                                                  | Meng et al., [2008]         |
| Great Lakes, U.S.A. - Canada | 1990s and 2000 | HCHs, chlordane, dieldrin | • Seasonal and by-lake variability in HCH and dieldrin fluxes, deposition to volatilization.  
  • Air-water equilibrium or volatilization of chlordanes.                                                                                                                               | Jantunen et al., [2008b]   |
| Taihu Lake, China         | 2004-2005  | HCHs, chlordane, DDTs, endosulfan-I | • Volatilization of α-HCH and chlordanes.  
  • Sources to the lake: HCHs in contaminated sediments, discharge of chlordane from manufacturing plants.  
  • Significant CC relationships.  
  • Deposition of DDTs and endosulfan-I                                                                                                                                                    | Qiu et al., [2008]          |
| Lake Baikal, Russia       | 1991       | PCBs, HCHs, HCB, DDTs, chlordane, toxaphene | • Deposition of HCHs, DDTs, toxaphene, near-equilibrium or deposition of chlordanes and HMW PCBs, volatilization of LMW PCBs, HCB.                                                                 | McConnell et al., [1996]    |
| South China Sea           | 2005       | HCHs, DDTs, chlordane, endosulfan-I | • Near-equilibrium of α-HCH at all sites except near Vietnam, where volatilization was estimated; deposition of γ-HCH.  
  • Deposition of α-HCH in the region 15 years earlier.  
  • Generally volatilization of p,p′-DDE; deposition of DDTs and chlordane near land and volatilization in open-ocean areas.                                                | Zhang et al., [2007]        |
| Mediterranean Sea         | 2001-2002  | PCBs, HCB, HCHs, DDTs      | • High dissolved concentrations in coastal waters and surface microlayer.  
  • PCBs in marine waters, influenced by coastal run-off, volatilized and became a secondary source to the coastal atmosphere.                                                             | García-Flor et al., [2005; 2009] |
### Table A.2.5. cont’d. Examples of Air-Water Gas Exchange Studies for SOCs, Large Lakes and Oceans.

<table>
<thead>
<tr>
<th>Location</th>
<th>Year</th>
<th>Chemicals</th>
<th>Findings</th>
<th>Reference</th>
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</table>
| Aegean Sea        | 2005        | PBDEs                 | • Investigations at Izmir Bay, a coastal site. BDE 209 the most abundant congener in air and water.  
• Volatilization of BDE 28 and deposition of other congeners.  
• Fluxes by dry particle deposition generally an order of magnitude higher than gas exchange. | Cetin and Odabasi, [2007a; b]       |
| Baltic Sea        | 1999        | PCBs                  | • Tendency for volatilization of LMW PCBs; could not be determined with 95% confidence due to uncertainties in HLCs. Deposition of PCB 180.                                                                | Bruhn et al., [2003]              |
| Baltic Sea        | 1997-1998   | HCHs                  | • Near-equilibrium, with events of volatilization or deposition, depending on air mass origins.                                                                                                          | Wiberg et al., [2001]            |
| Baltic Sea        | 1970-2000, modeling | HCHs                | • Atmospheric deposition accounted for 80-96% of HCH loadings to the northern Baltic, with the remainder by river flow. Seasonal cycles of α-HCH deposition or volatilization predicted. | Breivik and Wania, [2002a; b]     |
| Kattegat Sea      | 1998-1999   | PCBs, HCHs            | • Volatilization of PCBs, with deposition of some congeners during colder parts of the year. Deposition of α- and γ-HCHs.                                                                               | Sundqvist et al., [2004]          |
| North Sea         | 2004        | phthalates            | • Deposition of dibutyl- and benzylbutyl phthalate, volatilization of di-(2-ethylhexyl) phthalate.                                                                                                          | Xie et al., [2005]                |
| White Sea         | 1999        | γ-HCH, endosulfan-I    | • Deposition of endosulfan-I, volatilization of γ-HCH.                                                                                                                                                  | Weber et al., [2006]              |
| Atlantic Ocean    | 1998-2001   | PCBs, PCDD/Fs         | • Gas exchange dominates over particle dry deposition for all PCBs and LMW PCDD/Fs.  
• Particle deposition dominates for HMW PCDD/Fs  
• Relative contribution of particle deposition increased in regions of high marine aerosol/dust transport | Jurado et al., [2004a; 2004b]      |
| Atlantic Ocean    | 2005        | PCBs                  | • Significant CC relationships over the South Atlantic.  
• No significant CC relationships over North Atlantic off Africa and Europe; air concentrations controlled by advection of contaminated air masses.  
• PCBs close to air-water equilibrium in South Atlantic, deposition in North Atlantic off Africa and Europe. | Gioia et al., [2008b]             |
<table>
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<tr>
<th>Location</th>
<th>Year</th>
<th>Chemicals</th>
<th>Findings</th>
<th>Reference</th>
</tr>
</thead>
</table>
| Atlantic Ocean                 | 2005  | PAHs                             | • Elevated PAH concentrations in air off the northwest coast of Africa, possibly from biomass burning, emerging oil industry and natural sources.  
• No significant CC relationships.  
• Volatilization of anthracene and phenanthrene, near-equilibrium for fluoranthene and pyrene, in remote open-ocean areas.  
• For anthracene and phenanthrene, depletion by OH radicals comparable to sea-to-air volatilization fluxes. | Nizzetto et al., [2008]         |
| Atlantic Ocean                 | 2001  | PCBs, HCB, HCHs                  | • Diurnal cycling of PCB air concentrations over South Atlantic, daytime concentrations higher by factors of 1.5-2.5.  
• Wind speed and temperature not controlling influences.                        | Jaward et al., [2004]           |
| Atlantic Ocean, Norwegian Sea | 1999-2001 | HCHs                             | • Deposition of α-HCH in the temperate-tropical North Atlantic and near-equilibrium or deposition above 40°. Variable flux direction (deposition to volatilization) in the temperate-tropical South Atlantic and deposition below -50°.  
• Variable flux direction (deposition to volatilization) for γ-HCH in the North Atlantic - Norwegian Sea above 40° and deposition in all other Atlantic regions. | Lakaschus et al. [2002]; Schreitmüller and Baßchminter, [1995] |
| North Atlantic, Eastern Arctic Ocean | 2004 | PCBs                             | • Relative abundance of PCBs in seawater increased with latitude for LMW and decreased for HMW congeners.  
• Deposition of PCBs in the Arctic.  
• Increased air concentrations and higher deposition in marginal ice zone, where melting snow and ice may have released PCBs into the air. | Gioia et al., [2008a]            |
| North Atlantic, Eastern Arctic Ocean | 2004 | PCBs, HCB, HCHs, chlordanes      | • Deposition of α-HCH at 75% of sites, near equilibrium in rest. Deposition of γ-HCH at all sites.  
• Deposition of cis-chlordane at all sites. Deposition of trans-chlordane at about half the sites, near equilibrium at rest.  
• Near equilibrium of HCB at 80% of sites, deposition near Europe.  
• No correlation of atmospheric concentrations with temperature. | Lohmann et al., [2009]          |
| Eastern Arctic Ocean           | 1996  | HCHs                             | • Near-equilibrium for α-HCH and deposition for γ-HCH                                                                                   | Harner et al., [1999]          |
| Eastern Arctic Ocean, North Sea Norwegian Sea | 2004 | phthalates, musk compounds       | • Deposition of all phthalates except for di-(2-ethylhexyl) phthalate, which was near equilibrium in the Norwegian Sea and Arctic Ocean, and volatilizing off the coast of Norway.  
• Volatilization of polycyclic musks in the North Sea and deposition in the Arctic | Xie et al., [2007a; 2007b]       |
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<th>Location</th>
<th>Year</th>
<th>Chemicals</th>
<th>Findings</th>
<th>Reference</th>
</tr>
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</table>
| Bering-Chukchi Seas          | 1993, 1988 | HCHs                             | - Exchange direction of $\alpha$-HCH reversed, from deposition in 1988 to near-equilibrium or volatilization in 1993, due to decline in air concentrations.  
- Exchange direction of $\gamma$-HCH was deposition in 1988 and near-equilibrium or deposition in 1993. | Jantunen and Bidleman, [1995]; Sahsuvar et al., [2003]                                                                   |
| Western Arctic Ocean         | 1994       | HCHs                             | - Exchange direction of $\alpha$-HCH was volatilization in the Beaufort Sea and near-equilibrium in the northern Canada Basin; $\gamma$-HCH was depositing in both regions.  
- Higher air concentrations of $\alpha$-HCH were found over open water than in ice-covered regions. | Jantunen and Bidleman, [1996]; Sahsuvar et al., [2003]                                                                   |
| Arctic Ocean                 | 1993-1999  | $\gamma$-HCH, endosulfan-I       | - Deposition of endosulfan-I over all regions of the Arctic Ocean.  
- Deposition of $\gamma$-HCH in most regions.                                                                                     | Weber et al., [2006]                                                      |
| Canadian Archipelago, southern Beaufort Sea | 1999 and 2008 | HCHs                             | - Exchange directions were volatilization for $\alpha$-HCH, near-equilibrium or deposition for $\gamma$-HCH and deposition for HCB.  
- Significant CC relationships in some cases.  
- Higher $\alpha$-HCH in air accompanied ice breakup.                                                                                  | Jantunen et al., [2008a]; Su et al., [2006]; Wong et al., [2011] |
| Canadian Archipelago         | 1993       | HCHs, HCB, chlordanes, toxaphene, endosulfan-I | - Seasonal variations in exchange for HCHs, HCB, chlordanes, endosulfan-I, dieldrin and toxaphene, with flux reversals for some chemicals.  
- Volatilization of HCHs and deposition of other OCPs during ice-free periods.                                                      | Hargrave et al., [1997]                                                 |
| Antarctica                   | 2003-2004  | HCB, HCHs                        | - Deposition of both chemicals in the Ross Sea.  
- Near-equilibrium of $\alpha$-HCH during early January in coastal seas of Antarctic Peninsula, deposition during other months of the austral summer. Deposition of $\gamma$-HCH in all summer months. | Cincinelli et al., [2009]; Dickhut et al., [2005]                                                                   |
| South Atlantic and Antarctica| 1997       | $\alpha$-HCH                     | - Near-equilibrium from -40-60° and deposition further south.                                                                                                                                    | Jantunen et al., [2004]                                                 |
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Appendix B of Chapter 2
Observations and Capabilities – Modelling Studies related to Observations

Approaches to model the effect of mountains as POP convergence zones

Already the first studies on POP accumulation in mountains speculated about the reasons and mechanisms that lead to the observed higher loads in elevated regions. Blais [1998; 2001] and Donald [1998] attributed higher concentrations of SOCs at high altitudes to high precipitation, low temperatures and glacial runoff.

More recently Frank Wania and his researchers chose a modelistic approach towards the mechanisms of enhanced POP deposition in mountains. They hypothesized that mountain cold trapping of POPs is mainly driven by the temperature dependency of a given compounds’ susceptibility to efficient precipitation scavenging. Partitioning of POPs into condensed phases increases at lower temperatures (and, hence, with the altitudinal temperature lapse). A stronger partitioning of the chemicals to atmospheric particles, rain droplets and snowflakes at lower temperatures makes wet deposition more efficient in transferring the organic contaminants from the atmosphere to the Earth’s surface [Daly et al., 2007; Wania and Westgate, 2008].

Based on the results of a multicompartment fate and transport model parameterized for mountain systems, Wania and Westgate [2008] concluded that substances with equilibrium partitioning coefficients at 25 °C between water and air from 10^{3.5} to 10^{5.5} and between atmospheric particles and air from 10^{8.5} to 10^{11} are most likely to be subject to mountain cold trapping (a large number of POPs fall within these ranges). Such substances remain in the vapor phase at higher valley temperatures, but are scavenged efficiently at the lower temperatures prevailing at higher altitudes. This implies that substances subject to mountain cold-trapping are approximately two orders of magnitude less volatile than substances that experience global cold-trapping (e.g. while lighter PCBs get preferentially trapped at higher latitudes, the heavier PCBs are particularly prone to mountain cold-trapping). The authors found a good agreement between model and field studies, with the exception of those studies that rely on sample media such as plant foliage for which precipitation is not the dominant deposition pathway. The observed altitudinal concentration increases of compounds that are particle-bound at all temperatures along a mountain slope may be the result of more efficient atmospheric wash-out due to precipitation increases with altitude in some mountain regions.

Wania and Westgate [2008] concluded that, both in polar and mountain cold trapping, temperature-dependent phase partitioning plays a crucial role for POPs input. Nevertheless, these processes are controlled by different mechanisms and affect different chemicals. Polar cold-trapping is caused by the temperature dependent partitioning between the Earth’s surface and atmosphere (grasshopper effect). In the case of mountain cold trapping the temperature dependence of partitioning between the various atmospheric components (gas phase vs. particles, rain droplets and snowflakes) is important. The authors assume that the different scale of the transport distances along latitudinal and elevation gradients is the key issue underlying these differences: unlike POP deposition across polar regions, downward fluxes to mountainous terrain have to occur rapidly before the contaminated air has passed over the mountain range. Wet deposition of particles being the most efficient transfer process, those POPs which – under the temperature lapse encountered during the mountain passage – transit from gaseous into particulate phase are most susceptible to mountain cold-trapping.

Based on their suggested mechanisms of contaminant cold-trapping in mountains, Wania and Westgate [2008] expect (i) a higher deposition of susceptible POPs in humid than in arid mountain ranges, (ii) largest altitudinal deposition gradients in mountains with precipitation rate increases with altitude and in mountains with higher temperature differences between valley and summit. Consequently, high mountain ranges in the humid temperate zone should be most susceptible to the enrichment of such organic contaminants at higher elevations.
Modelling soil-air exchange and emissions

Many small-scale models have been developed to predict volatilization of pesticides following application to farm fields, and early work has been reviewed [van der Berg et al., 1999]. Some models such as PEARL (Pesticide Emission Assessment at Regional and Local Scales) [Leistra and Van den Berg, 2007], and PRZM-3 (Pesticide Root Zone Model Version 3) [Suarez, 2005] incorporate volatilization from soil as part of larger models of fate and transport of pesticides in soil and water. Most simulations of soil-air exchange [e.g., Cousins et al., 1999; Harner et al., 2001; Leistra and Van den Berg, 2007; Meckone and Bennett, 2003] have been carried out using isothermal models, mostly based on the approach of Jury et al. [1983]. These assume vertical migration of the chemical by diffusion through air- and water-filled pore spaces, leaching and (in some models) bioturbation in a multilayered soil compartment and a transfer through an air boundary layer at the soil surface. Some models provide for non-isothermal simulations, which involve consideration of heat and moisture as well as pesticide vapour transport in the soil and incorporate short-term meteorological measurements [2000a; Reichman et al., 2000b; Scholtz et al., 2002a; 2002b; Scholtz and Bidleman, 2006].

In order to model emissions of pesticides on large scales (global and regional), a Simplified Gridded Pesticide Emission and Residue Model (SGPERM) [Li et al., 2000] was developed and used to compile several inventories for both emissions to air and residues in soil for several pesticides, such as α-HCH [Li et al., 2000] and β-HCH [Li et al., 2003] on a global scale, toxaphene in the USA [Li, 2001; Li et al., 2001], and endosulfan in China [Jia et al., 2009], which have described the pesticides in both air and soil simultaneously.

A large number of field-scale measurements of pesticide fluxes have been made over the last three decades, but only a few situations have been described in which both measurements and models have been brought together to assess fluxes and/or ground-level air concentrations. In some cases the agreement is generally good [Jia et al., 2010; Leistra and Van den Berg, 2007; Li and Ren, 2009; Scholtz et al., 2002b; Scholtz and Bidleman, 2006], but not in others [Wolters et al., 2003]. A monitoring program, Chinese POPs Soil and Air Monitoring Program (Chinese POPs SAMP), especially designed for soil-air exchange study, was carried out in China in 2005-2007, in which both air and soil samples were concurrently collected across China and the assessments of soil-air exchange for PCBs were published [Li et al., 2010; Ren et al., 2007; Zhang et al., 2008] and presented in Section C.2.4.2.2. Model applications on large spatial scales, limited to DDT, have achieved qualitative agreement between observations and predictions [i.e. trends, gradients Schenker et al., 2008; Stemmler and Lammel, 2009].

Models do not reflect the large spatial variation of SOC levels in soil. This reflects the limited understanding of the parameters determining spatial and temporal variabilities of degradability in soil, but may be partly explained by an uncertain spatial representativeness of experimental soil data. Apart from microbiological species availability, soil hydrology (e.g. flooding, freezing, thawing) may introduce non-linearities not represented by models.

To fingerprint source-receptor relationships, soil-air exchange fluxes and soil-air FFs or FRs have been predicted in a large-scale atmospheric transport model for OCPs. The modelled spatial pattern of FRs reflects the soil-air exchange dynamics on a continental or global scale. In a modelling assessment on global atmospheric transport and fate of γ-HCH (lindane) in 2005 using the global-scale CanMETOP (Canadian Model for Environmental Transport of Organochlorine Pesticides), the model simulated annual global soil-air FRs of lindane exhibit a pattern showing net deposition (FR < 1) in cold northern territories and the Tibetan plateau, and net volatilization (FR > 1) in most low to mid latitudes under mild and warm conditions in the Northern Hemisphere [Zhang et al., 2008]. Given that the chemical has been banned in most countries, this spatial pattern highlights potential sources of secondary emission and receptors of lindane across the Northern Hemisphere.

Multimedia fugacity models can be classified as "transport-oriented" and "target-oriented". Transport-oriented models describe the potential for transport in air and/or water with simultaneous exchange with soil, water and vegetation, while target-oriented models describe the percentage of
emitted substance that migrates to surface media in selected target regions as a consequence of transport and subsequent deposition. Outputs of these models include metrics of long-range transport potential (characteristic travel distance = CTD and spatial range) and overall persistence (P_{OV}) [Fenner et al., 2005]; Scheringer et al., 2010. Target-oriented models include Globo-POP and BETR. An output of Globo-POP is the Arctic Contamination Potential (ACP), the mass of chemical in the arctic physical [Brown and Wania, 2008; Wania, 2003; 2006] or physical-biological [Czub et al., 2008] environments divided by the mass or emission in the global environment. BETR estimates the transfer efficiency (TE), the ratio of mass deposition flux from air to surface media to the continuous mass release flux in the source region [MacLeod and Mackay, 2004]. Multimedia models are reviewed and compared by Fenner [2005] and Scheringer [2010].

Globo-POP groups compounds within the 'chemical space' as explained in Chapter C1 (Figure C1-1) Many SOCs are 'multimedia' chemicals which are transported by both air and water currents and accumulate in soil and water. For these substances, soil-air and water-air exchanges are critically important, and these processes are included in the OECD Screening Tool for the P_{OV} and CTD of chemicals [Scheringer et al., 2010; Wegmann et al., 2009].

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Appendix C of Chapter 2
Observations and Capabilities – Air Monitoring Programs

European Monitoring and Evaluation Programme (EMEP)

The European Monitoring and Evaluation Programme (EMEP) is a scientifically-based and policy-driven programme under the 1979 CLRTAP for international co-operation to solve transboundary air pollution problems. Parties to EMEP perform systematic collection, analysis and reporting of air and precipitation monitoring in the context of long-range atmospheric transport (LRAT) at regional background sites across Europe through EMEP in close collaboration with a broad network of scientists and national experts. With the extension of the CLRTAP by the 1998 Aarhus Protocol on POPs, monitoring data for POPs in air and deposition at background sites have been reported to EMEP since 1999. However, the EMEP database also includes historical data for POPs dating back to 1991. As comparable measurement data are essential for regional assessments, measurements under EMEP are coordinated by a Chemical Coordinating Centre (EMEP/CCC). The EMEP/CCC recommends methods for monitoring, chemical analysis, quality assurance, data validation and reporting as well as data storage activities to EMEP parties. EMEP monitoring data for POPs are summarized in annual reports from the EMEP/CCC [e.g., Aas and Breivik, 2009], available through EMEP’s homepage (http://www.emep.int) and by direct access to the database (http://ebas.nilu.no/). EMEP performs integrated analysis of POPs transport by incorporating monitoring data with EMEP-developed emission inventories for selected POPs (Chapter C3) and transport models (Chapter C4) [Gusev et al., 2009].

Kosetice Observatory – Multimedia Monitoring under EMEP – Seasonality, Sources and Trends

The Kosetice observatory of the Czech Hydrometeorological Institute located in the southern Czech Republic (N49°35´; E15°05´) is the only EMEP site where POPs are being determined in other environmental matrices in addition to air and deposition. The samples of ambient air, wet deposition, surface water, sediment, soil and biota, as the key components of the environmental system, have been collected for the last 20 years at this station.

Typical seasonality in the atmospheric concentrations of POPs can be seen in Figs. 1-5. The polycyclic aromatic hydrocarbon (PAH) levels show a characteristic pattern (Fig. 1) prompted by higher occurrence of these compounds in the cold seasons when they are produced by various combustion processes. The highest atmospheric levels of PAHs found in January and February were as much as three orders of magnitude higher than the lowest ones measured in July and August.
PCB and OCP concentrations displayed a very different profile (Figs. 2-5). Most of these compounds were banned in Europe and their maxima are not connected to their production or seasonal application. They are present in the atmosphere due to volatilization from the old deposits (soils, sediments, wastes) or due to LRAT from the regions where they are still being applied. In agreement with this hypothesis, elevated levels of organochlorines are observed in summer when increasing temperatures enhance evaporation of these compounds. Even though this seasonality is not as well pronounced as it is in the case of PAHs, it can still be detected for PCBs in Fig. 2, and for pesticides in Figs. 3 - 5.
Figure 3. Hexachlorobenzene (HCB) and Pentachlorobenzene (PeCB) in ambient air (ng m⁻³), Kosetice observatory, 1996-2008 (weekly sampling).

Figure 4. Hexachlorocyclohexanes (HCHs) in ambient air (ng m⁻³), Kosetice observatory, 1996-2008 (weekly sampling).
Annual median air concentrations were calculated for all subgroups (PAHs, PCBs, HCB, HCHs and DDTs) and resulting values were compared to evaluate the long-term trends for each group of compounds and the period of 1996-2008 (Fig. 6). While PAH levels have been quite stable in the last decade, PCBs showed generally decreasing trends. Pesticides fluctuated showing highest atmospheric concentrations in two periods immediately following major floods in 2007 and 2002.
Monitoring data from Kosetice can be used for an assessment of sources and distribution processes, and for validation of long-range transport and environmental fate models (Fig. 7).

Figure 7. Distribution of ground source loadings for HCB in two time periods (1997-99 and 2004-06) derived from the air mass back trajectory analysis. The dark green colour depicts areas with the lowest contribution to HCB levels measured in Kosetice, whereas dark red depicts areas of the highest contribution.

The integrated monitoring program allows for comparison of the long-term trends of the POP levels in various matrices. The atmospheric samples are most homogenous due to efficient mixing of air. On the other hand, they are most variable in time due to the fast response of the atmosphere to any changes in point and diffusive sources. The moss or needle samples respond very well to current atmospheric levels of POPs. The sediment and soil samples offer long-term records of POP contamination because they act as efficient sinks of POPs. However, we need to be aware that matrices with high accumulation potential can also turn from sinks to sources of POPs.

As can be seen in Fig. 8, time-related trends of POPs vary between compounds and matrices. For PCBs, significantly decreasing trend was observed not only for air, needles and moss, but also for sediment and soil. In contrast, decreasing trends were not significant for pesticides in most of the matrices.

Long-term data from multimedia sampling can also be used for evaluating various environmental models.
The Arctic Monitoring and Assessment Programme (AMAP) and the Northern Contaminants Program (NCP)

AMAP is an international organization established in 1991 to implement components of the Arctic Environmental Protection Strategy (AEPS). The primary function of AMAP is to advise the governments of the eight Arctic countries (Canada, Denmark/Greenland, Finland, Iceland, Norway, Russia, Sweden and the United States) on matters relating to threats to the Arctic region from pollution, and associated issues. AMAP is responsible for measuring the levels, and assessing the effects of anthropogenic pollutants in all compartments of the Arctic environment, including humans; documenting trends of pollution; documenting sources and pathways of pollutants; examining the impact of pollution on Arctic flora and fauna, especially those used by indigenous people; reporting on the state of the Arctic environment; and giving advice to Ministers on priority actions needed to improve the Arctic condition. AMAP has completed its most recent assessment report with respect to three subject areas: POPs, contaminants and human health, and radioactivity in 2009 [AMAP, 2009a; b; 2010a; b].

As part of AMAP, Canada operates the NCP which conducts research in the Canadian Arctic with regard to human health; contaminant fate, levels and trends; education and communication of contaminants information in the North. NCP’s organic pollutant air monitoring program features the longest time series for atmospheric POPs at the North American Arctic station of Alert (Canada). The most recent results of the NCP program will be summarized in the Canadian Arctic Contaminants Assessment Report (CACAR) III to be completed in 2011/2012.

Additional information including assessment reports and publications can be found in the:
AMAP website: [http://www.amap.no/](http://www.amap.no/)
Norwegian Arctic and Antarctic Stations

Atmospheric monitoring of POPs in atmospheric samples is already ongoing for more than 15 years at the Norwegian Atmospheric monitoring site “Zeppelin mountain” (Ny-Ålesund, Svalbard). Important scientific results on the fate and distribution properties of selected POP contaminants in the Arctic atmosphere have been derived from this unique data set. However, no comparable long-term monitoring information is available from Antarctica. Thus, as a part of the new scientific atmospheric program for the Norwegian Antarctic station “Troll” at Dronning Maud Land, the Norwegian Institute for Air Research (NILU) has established a long term atmospheric POP monitoring program based upon identical analytical methods, sampling strategies and selected target POP compounds as applied for the Arctic “Zeppelin mountain” atmospheric monitoring station in Ny-Ålesund. A set of 33 polychlorinated biphenyl (PCB) congeners and 14 organochlorine pesticides (HCHs, chlordanes, and DDT derivatives) have been quantified in high volume air samples from both stations. The first year-around atmospheric POP monitoring on the Antarctic continent (Troll station) has been completed for 2007. A first critical evaluation of the data and a comparison with the simultaneously collected POP contamination levels from high volume air samples from the “Zeppelin mountain” station revealed surprising concentration and pattern differences (Table 1).

Table 1. Comparison of POP concentration ranges [min. – max. pg/m³] in air samples from Zeppelin (Arctic) and Troll (Antarctica) during the sampling period 2007.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Zeppelin air</th>
<th>Troll air</th>
</tr>
</thead>
<tbody>
<tr>
<td>SUM PCB (33 congeners)</td>
<td>7 - 70</td>
<td>0.2 - 3</td>
</tr>
<tr>
<td>SUM hexachlorocyclohexanes (HCH)</td>
<td>7 - 20</td>
<td>0.3 - 5</td>
</tr>
<tr>
<td>SUM chlordanes (trans-/ cis chlordane and nonachlor)</td>
<td>0.2 - 4</td>
<td>0.1 - 1</td>
</tr>
<tr>
<td>SUM dichloro- diphenyl- trichloro ethane derivatives (p,p’- and o,p’-DDT, DDD, DDE)</td>
<td>0.2 - 2</td>
<td>0.1 - 1</td>
</tr>
<tr>
<td>Hexachlorobenzene (HCB)</td>
<td>3 - 11</td>
<td>15-30</td>
</tr>
</tbody>
</table>

Distinct differences in POP pattern and level distributions have been identified. PCB levels seem higher in Arctic atmospheric samples as well as pesticides like HCH isomers and DDT derivatives (Table 1). Cyclodiene pesticides (e.g. chlordanes) are slightly lower in concentrations in Antarctic samples, whereas HCB is found in higher levels for Antarctic ambient air. A combination of available emission and application inventories as well as meteorological back trajectory modelling will be applied in order to identify atmospheric transport properties, seasonal distribution patterns and potential source regions on the southern hemisphere.

The Toxic Organic MicroPollutants (TOMPs) Air Monitoring Programme

The Toxic Organic MicroPollutants (TOMPs) air monitoring programme has been running continuously since 1991. This programme has successfully provided long-term ambient air concentration data for a number of sites, both urban and rural, and is vital in providing an assessment of the successful implementation of a number of pollutant reduction measures and the UK’s obligations under a number of international agreements. The TOMPs network is funded by the UK Department for Environment Food and Rural Affairs (DEFRA), and provides concentration and long-term trend data for ‘dioxins’ (PCDD/Fs), PAHs and PCBs within the U.K. The network was set up in 1990 and is managed by Lancaster University (LU). There are six sites including; Manchester (urban), London (urban), High Muffles (rural), Hazelrigg (semi-rural), Weybourne (rural/coastal) and
Auchencorth Moss (rural). Sampling is carried out using High Volume samplers with PUF plugs and GFFs to trap vapour and particle phase chemicals, respectively. The sites are operated continuously, sampling between 300 m$^3$ and 600 m$^3$ per week, changing the filters and PUFs fortnightly to avoid sample breakthrough.

Further details of the network can be found at http://www.lec.lancs.ac.uk/research/chemicals_management/tomps.php

**MONARPOP**

MONARPOP was started in 2004 by an initiative of ministries and institutes in Austria, Germany, Italy, Slovenia and Switzerland (see http://www.monarpop.at/ and Offenthaler et al. 2008). The main objective of the project is to monitor POPs and other organic pollutants with respect to their long-range transport to remote regions in the Alps, prevalent source directions of their origin, the regional distribution of loads within the area of the Alps, the variation with altitude, an assessment of present pollutant stocks bound in forests of this region and possible biological effects of the detected loads. The project aims to provide information to decision makers and to establish a tool for future assessments of the success of the Stockholm Convention.

Remote alpine sites (40) have been chosen in Austria, Germany, Italy, Slovenia and Switzerland. In addition, seven altitude profiles with several subplots were selected to investigate the vertical variation of POP-levels. Air and deposition is sampled continuously and year-round at three sites above the timberline at mountain summits. The input of POPs and other organic pollutants is examined by measuring their concentration in air (with direction-specific active and with passive sampling devices), in deposition and needle samples. The present load of POPs in mountainous woodland ecosystems is estimated from needle, humus and topsoil concentrations. The sampled material is screened for detoxifying metabolic activities and dioxin-like effects (AhR-response). The air and deposition monitoring at the three alpine summits continues which secures a related future contribution to the “Effectiveness Evaluation” of the Stockholm Convention.

**Integrated Atmospheric Deposition Network (IADN)**

The Integrated Atmospheric Deposition Network (IADN) has been in operation since 1990, under the guidance of an implementation plan signed in that year, to monitor for the atmospheric loadings of toxic chemicals to the North American Great Lakes. The first implementation plan committed the United States and Canada to work cooperatively towards the initiation of the IADN. Agencies involved in IADN are The U.S. Environmental Protection Agency (U.S. EPA) and Environment Canada’s Science and Technology Branch.

IADN is specifically called for in Annex 15 of the Great Lakes Water Quality Agreement (GLWQA). In Canada, these activities are delivered federally through the Great Lakes program, and activities delivered at the provincial level are described in the Canada-Ontario Agreement (COA). The mandate for IADN also resides in Section 112(m) of the U.S. Clean Air Act Amendments of 1990 (CAA). The U.S./Canada Binational Great Lakes Toxics Strategy (BGLTS), signed in 1997, calls for monitoring of the atmospheric deposition of toxic chemicals to the Great Lakes basin. Many of the "challenges" in the BGLTS are directly related to IADN capabilities and goals.

The goals of IADN are to determine, with a specified degree of confidence the atmospheric loadings and trends (both spatial and temporal) of priority toxic chemicals to the Great Lakes and its basin on a biennial basis. Acquire quality-assured air and precipitation concentration measurements,
with attention to continuity and consistency of those measurements, so that trend data are not biased by changes in network operations or personnel. Finally, to help determine the sources of the continuing input of those chemicals.

**The National Air Pollution Surveillance (NAPS)**

The National Air Pollution Surveillance (NAPS) Network was established in 1969 as a joint program of the federal and provincial governments to monitor and assess the quality of the ambient air in Canadian urban centres.

Air quality data for sulphur dioxide (SO₂), carbon monoxide (CO), nitrogen dioxide (NO₂), ozone (O₃) and total suspended particulates (TSP) are measured at over 152 stations in 55 cities in the ten provinces and two territories. Various statistics derived from the measurements and comparisons with the National Air Quality Objectives prescribed under the Canadian Environmental Protection Act are published in annual data reports. For Canada’s national Smog (Ground-Level Ozone) Management Program, data for nitric oxide, nitrogen oxides and volatile organic compounds (VOCs) are being collected. The NAPS database has been expanded to include ozone observations from Canadian and U.S. rural monitoring locations in order to allow analysis of regional ozone episodes.

Measurements of PM10 (suspended particles with aerodynamic diameters less than 10 micro meters) and PM2.5 have been made at Canadian sites since 1984. Sample filters are analyzed for 50 elements (including toxic metals such as arsenic, lead and mercury) 14 inorganic and organic anions and 11 inorganic cations.

Since 1988, the Centre has been developing and applying improved techniques for measuring potentially toxic air contaminants. Measurements of VOC (aromatics, aldehydes and ketones) and semi-volatile organic compounds (PAHs, dioxins and furans) are now carried out at 40 urban and rural locations in Canada. The data have formed the principal ambient air exposure data base for 14 Canadian Environmental Protection Act (CEPA) Priority Substances List (PSL) assessments.

**Global Atmospheric Passive Sampling (GAPS) Network**

The Global Atmospheric Passive Sampling (GAPS) Network is in its 6th sampling year and is the only global-scale program that contributes information on air concentrations of POPs to the Global Monitoring Plan (GMP) of the Stockholm Convention on POPs. The Stockholm Convention, negotiated under the auspices of the United Nations Environment Programme (UNEP), established a globally binding framework initially targeting a group of POPs which includes several organochlorine pesticides [aldrin, chlordane, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, toxaphene, and dichlorodiphenyltrichloroethane (DDT)], PCBs, and polychlorinated dibenzo-p-dioxins and -furans. Under Article 16 (Effectiveness Evaluation) of the Convention, monitoring data on core media (air and human tissues) is required to assess effectiveness of control measures on POPs and for investigating their regional and global transport. The Guidance Document for a Global Monitoring Programme for POPs, produced by UNEP, encourages the use of passive samplers as a cost-effective means for filling data gaps and producing spatially resolved data for POPs.

Results from GAPS contributed to several regional reports of the first Global Monitoring report presented at COP4. In some cases the GAPS results were the only data for a particular region. In addition to addressing data gaps for POPs on a global scale, the GAPS team is also involved in capacity building and technology transfer to other regions wishing to implement a passive sampling program for POPs.

**MONET**

Passive air samplers (PAS) were recommended by the Preliminary Ad-hoc Technical Working Group for the Global Monitoring Plan of the Stockholm Convention as a suitable tool for the global monitoring of POPs in ambient air. At the EMEP station of Kosetice, PAS were deployed in parallel with high volume air samplers to monitor for atmospheric POPs since 2003. This practice allowed for the field calibration of PAS for both gas and particle phase chemicals. Five years of PAS data are showing the same seasonal fluctuations and temporal trends as those obtained by high volume air sampling.
Based on these positive results, a national POPs monitoring network was established in the Czech Republic (MONET-CZ) employing the PAS technique. In 2004, a number of sites in the vicinity of various sources (chemical, petrochemical and cement industry, traffic, domestic heating) were monitored to evaluate their impacts and pollution trends. Redundant sites were omitted in 2005, and new source types were added (municipal, medical and danger waste incinerators, remediation technologies). A new set of 15 background sampling sites was included in cooperation with the Czech Hydrometeorological Institute. This set consisted of mountain sites along the Czech borders to evaluate the impact of transboundary transport in this region. The new design of the MONET network containing 37 sites (including 15 backgrounds) was introduced and initiated in January, 2006. It has been maintained since, collecting thirteen 28-day samples every year from each site.

In terms of seasonality, winter maxima were typically observed for PAHs. Concentrations of DDTs were consistently highest in the fall. Seasonal maxima of HCHs varied from site to site. Interestingly, HCB concentrations were higher in winter rather than summer suggesting that combustion sources (seasonal residential heating) were more significant than summer evaporation from diffusive secondary sources. No clear temporal trends have been observed yet.

As Central, Southern and Eastern Europe is the region with a lack of data on atmospheric POPs, three screening campaigns were organized between 2006 and 2008 (MONET-CEECs). The operational philosophy was the same as for the model network in the Czech Republic: 5-20 sampling sites were selected per country (according to the size of each country) and monitoring was conducted for 5 months. Industrial, agricultural, urban and rural sites were included together with the background sites. The goal was not only to determine the background levels but also to provide information on the extent of pollution. In addition to the Central and Eastern European Countries (CEEC), 26 sites from the African continent (MONET-AFRICA) and 21 sites from the Central Asia (former Soviet Union countries as part of MONET-CEECs) were monitored in 2008 and 3 sites from the Pacific Islands between 2006 and 2007 (MONET-PIs).

The ambient air monitoring activities in the CEEC, Central Asia, Africa and Pacific Islands driven by RECETOX (Research Centre for Toxic Compounds, Masaryk University, Czech Republic) report results under the common name of the “MONET networks”. RECETOX is the nominated Regional Center of the Stockholm Convention for the region of CEEC. For many participating countries, MONET activities generated their first dataset on the atmospheric levels of POPs. To carry these activities beyond the first screening, best candidates for background monitoring have to be selected in every region, and resources must be sought to make the program sustainable.

It has been recognized that knowledge on Western European POP levels would greatly improve the understanding of the CEEC data. Although Western Europe is formally a part of the WEOG (Western Europe and Others Group) region, the rest of Europe reports under the CEEC. It is desirable to harmonize the monitoring activities in both parts of Europe to gain systematic information on the levels and trends of the atmospheric pollution in this continent.

EMEP stations participating in MONET activities seem to be the best candidates for long-term background monitoring in many CEE countries (Czech Republic, Estonia, Latvia, Moldova, Slovakia, Slovenia). An agreement has been made between RECETOX and EMEP to organize a follow-up study as a joint activity of these partners. MONET stations from the previous campaigns were complemented by new stations from Western Europe to provide a good geographical coverage (Fig. 9 – MONET-EUROPE). Local partners participating in previous campaigns are encouraged to use this opportunity to become a part of the international network and build their own capacity. The goal is to maintain sustainable PAS monitoring at the majority of sites. That would greatly improve the understanding to the sources, fate and transport of POPs in Europe and provide rich information for the modelling databases. At the same time, it would create necessary synergies between the Stockholm Convention and Convention on Long-Range Transboundary Air Pollution.
Substantial geographical differences currently exist in monitoring capacity to contribute comparable atmospheric POP data for evaluating the effectiveness of the Stockholm Convention. Such differences in capacity within and between regions provide opportunities for regional capacity building focused on the capability to detect regional trends. As the regional centres should play a role in coordination efforts, RECETOX is ready to extend its support to other regions. To ensure long term sustainability and comparability of results, it is recommended that new programs grow from strategic partnerships with existing programs, and benefit from their experiences. This approach has already been applied in the MONET-AFRICA and MONET-PIs campaigns and RECETOX is prepared to take on an active role as a strategic partner in the follow up studies.

Capacity building has been an important aspect of the MONET networks. RECETOX Summer School of Environmental Chemistry and Ecotoxicology organized in cooperation with the Secretariat of the Stockholm Convention annually since 2005 provided a platform for training of scientists participating in the MONET networks and other interested individuals.

Understanding that monitoring data will only serve the purpose of effectiveness evaluation when they are available and accessible for interpretation and visualization, RECETOX has developed the Global Environmental Assessment and Information System GENESIS. It is a tool for collection, aggregation, processing, and visualization of environmental data; as well as a tool for assessing effects and associated risks. The aim is to build a sophisticated interactive system capable of identifying links between the quality of the environment and the public health status. RECETOX offers this tool to assist in the development and maintenance of the network of databases containing monitoring information.

More information on the MONET networks can be found in the following references [Dvorská et al., 2008; Holoubek et al., 2007a; 2007b; Klánová et al., 2007a; b; Klánová et al., 2008a; 2008b; 2008c; Klánová et al., 2009; Komprda et al., 2009].
Other Monitoring Programs

New Jersey Atmospheric Deposition Network (NJADN):
http://www.state.nj.us/dep/dsr/njadn/fullreport.pdf

Xarxa de Vigilància i Previsió de la Contaminació Atmosfèrica (XVPCA):
http://mediambient.gencat.net/eng/el_medi/atmosfera/informacio_on_line/dades.jsp

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## Appendix D

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