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Concentrations and levels of POPs from long-range transboundary air pollution in freshwater fish and sediments

Norwegian Institute for Water Research
– an institute in the Environmental Research Alliance of Norway

REPORT

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Abstract

This report gives an overview of recently observed levels of selected POPs in freshwater fish and sediments from North America, Europe and circumpolar Arctic, related to long-range transport based on data from some central surveys. It is shown that there is a general lack of coordinated monitoring or regional surveys that focus on POPs in the freshwater environments for which LRTAP is a major source. Methodological differences in sampling, analytical methods and reporting makes comparison among results from the different projects very difficult. There are very few sites with trend data, but they generally show decreasing levels of legacy POPs. Levels of some new substances, such as brominated flame retardants (PBDE) and PFAS, are probably rising. There is an urgent need to establish systematic long-term monitoring of new POPs in background areas, and coordinated international surveys with harmonized methodology and reporting. This report also shows that multimedia models are tools that can be used for an initial screening of organic substances. Their results are robust and give reliable information on persistence, the potential for long range transport and partitioning between compartments.

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1. Persitente organiske forbindelser (POPer)	1. Persistant organic pollutants (POPs)
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CONVENTION ON LONG-RANGE
TRANSBOUNDARY AIR POLLUTION

INTERNATIONAL COOPERATIVE PROGRAMME ON
ASSESSMENT AND MONITORING OF ACIDIFICATION
OF RIVERS AND LAKES

Concentrations and levels of POPs from long-range transboundary air pollution in freshwater fish and sediments

ICP Waters Programme Centre
Norwegian Institute for Water Research
Oslo, December, 2005

Preface

The International Cooperative Programme on Assessment and Monitoring of Rivers and Lakes (ICP Waters) was established under the Executive Body of the Convention on Long-Range Transboundary Air Pollution at its third session in Helsinki in July 1985. The Executive Body also accepted Norway's offer to provide facilities for the Programme Centre, which has been established at the Norwegian Institute for Water Research, NIVA. Berit Kvæven, Norwegian Pollution Control Authority (SFT), has led the ICP Waters programme.

The main aim of the ICP Waters Programme is to assess, on a regional basis, the degree and geographical extent of the impact of atmospheric pollution, in particular acidification, on surface waters. Twenty-two countries in Europe and North America participate in the programme on a regular basis.

ICP Waters is based on existing surface water monitoring programmes in the participating countries, implemented by voluntary contributions. The monitoring sites are generally acid sensitive and pollution sensitive. The ICP site network is geographically extensive and includes long-term data series (more than 15 years) for many sites. The programme conducts yearly intercalibrations on chemistry and biology.

This report is an assessment of POPs in the aquatic environment. Methods for monitoring of POPs was a topic for discussion at the ICP Waters Workshop in Zakopane in 1998. Even if the ICP Waters network is well suited for POPs monitoring the work is still in its initial phase, and a regional assessment on POPs cannot be based on ICP Waters data, therefore other data sources have been utilized.

The aim of the report has been to identify data sources relevant for giving a regional overview of POPs in the aquatic environment related to long-range transboundary air pollution and by doing this, get an idea of the amount of existing data and identify challenges for mapping POPs pollution attributed to LRTAP. The report reveals that our future challenge is to harmonize monitoring of POPs in freshwater ecosystems.

The results will serve as a possible input to the review of the POPs protocol in 2006.

Eirik Fjeld has been responsible for the assessment of POPs in the environment, while Anne Christine Le Gall has been responsible for the chapter on multi-media modelling.

We thank members of the ICP Waters Task Force meeting and our reviewers Jaakko Mannio, SYKE, Finland and Dixon Landers, EPA, USA for valuable comments.

Oslo, December 2005
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Contents

Summary

The aim of this report is to give an overview of the occurrence of selected POPs in the aquatic environment in Europe and North America as a possible input to the review of the POPs protocol in 2006.

This report gives an overview of the recent levels of selected POPs in freshwater fish from North America, Europe and circumpolar Arctic, related to long-range transport based on data from some central surveys. It is shown that there is a general lack of coordinated monitoring or regional surveys that focus on POPs in the freshwater environments for which LRTAP is a major source. Methodology regarding sampling, analytical methods and reporting makes comparison between results from the different projects very difficult. The results from the assessment confirms previous studies indicating that global distillation processes (grasshopper-effect) leads to elevated concentrations of contaminants in fish from arctic and alpine areas and that levels are increased in background areas not affected by local pollution.. This shows that the issue has an important relevance for ICP Waters.

There are very few sites with trend data, but they generally show decreasing levels of legacy POPs. Levels of some new substances, such as brominated flame retardants (PBDE) and PFAS, are probably rising.

This report also shows that multimedia models are tools that can be used for an initial screening of organic substances. Their results are robust and give reliable information on persistence, potential for long range transport and partitioning between compartments.

An important recommendation from this report is that there is an urgent need to establish systematic long-term monitoring of new POPs in background areas, and coordinated international surveys with harmonized methodology and reporting.

1. Introduction

Of all the pollutants released into the environment every year by human activity, persistent organic pollutants (POPs) are amongst the most dangerous. For decades these highly toxic chemicals have killed and sickened people and animals by causing cancer and damaging their nervous, reproductive and immune systems. They have also caused uncounted birth defects.

The definition of a POP is a chemical that remains intact in the environment for long periods, becomes widely distributed geographically, accumulates in the fatty tissue of living organisms and is toxic to humans and wildlife. POPs circulate globally and can cause damage wherever they travel.

A variety of transport processes are dispersing POPs throughout the global environment (Figure 1). POPs undergo atmospheric transport either in the gas phase, sorbed to suspended particles or in cloud water. Due to their semivolatile nature, some POPs readily shift their distribution between gas phase and condensed phase in response to environmental changes in temperature and phase composition.

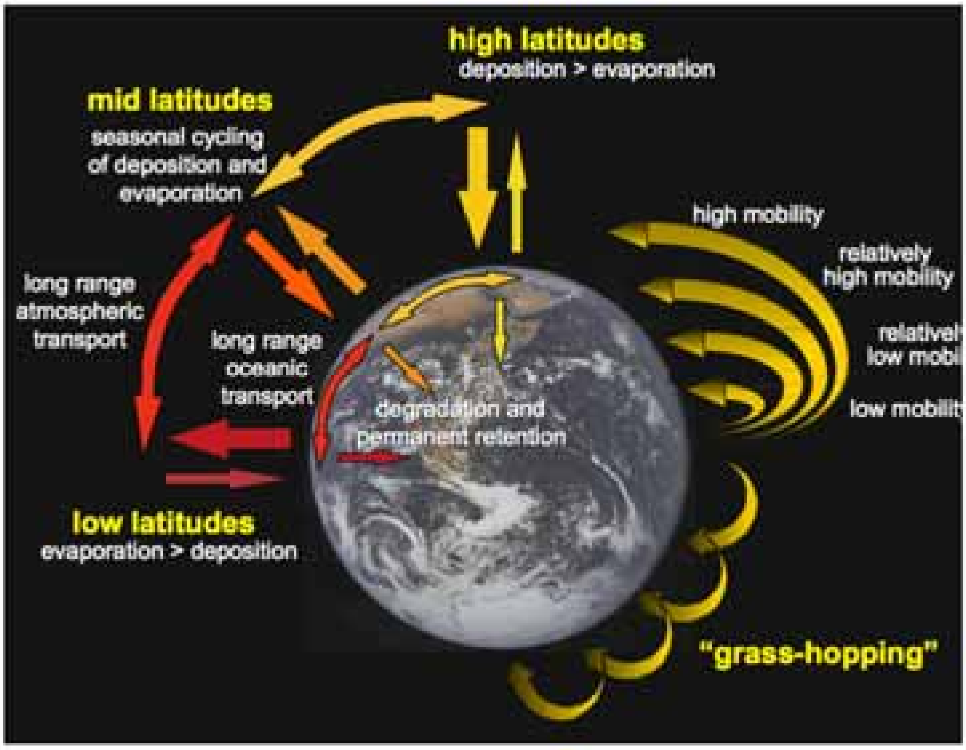

Figure 1. *Illustration of the principles governing the long range transport behaviour of POPs, that can reversibly exchange between the atmosphere and the Earth's surface. From UNEP/GEF (2003)*

Through a repeated process of evaporation and deposit, they can be transported through the atmosphere to regions far away from the original source. This "cold condensation" process can transport POPs from warm to cold regions, such as the Arctic and alpine areas (Wania and

Mackay 1993 and 1996; Blais et al. 1998; Grimalt et al. 2002). Because the less volatile POPs are being retained more efficiently close to the source, is there a compositional shift in the deposition of POPs towards more volatile compounds with increasing distances and decreasing temperatures. This phenomenon, called "global distillation" favours the transport of the more volatile POPs to high latitudes and altitudes (Wania and Mackay 1993 and 1996).

Regulation of emission of POPs to the environment is covered in several international Conventions. The largest one is the global UNEP Stockholm Convention covering 12 of the most well known harmful POPs. The UNECE LRTAP Convention covering Europe and North America covers 16 harmful substances. The OSPAR and HELCOM Conventions are marine Conventions that cover emissions that can affect the Atlantic sea, the North Sea and the Baltic Sea. POPs are also regulated under the EU Water Framework Directive.

The aim of this report is to give an overview of the occurrence of selected POPs in the aquatic environment in Europe and North America as a possible input to the review of the POPs protocol in 2006.

In greater detail, this assessment report aims to:

- Identify substances relevant for the work of ICP Waters and the LRTAP Convention with regard to:
    - physiochemical characteristics
    - atmospheric transport mechanisms and potential for LRT
    - associated international conventions, protocols or directives
- Review case studies and central data sets to obtain a picture of:
    - Levels in freshwater fish on a regional scale
    - Spatial gradients: lowland–alpine, south–north
    - Time trends – examples from fish and sediments
- Review multimedia models as tools for initial screening of organic substances.
- Give recommendations on future monitoring by:
    - Defining high priority substances
    - Identifying susceptible areas or ecosystems

2. International agreements on POPs

2.1 The POPs protocol under the LRTAP Convention

The Executive Body adopted the Protocol on Persistent Organic Pollutants on 24 June 1998 in Aarhus (Denmark) and the protocol entered into force 23 October 2003. It focuses on a list of 16 substances that have been singled out according to agreed risk criteria. The substances comprise 11 pesticides (including DDT, aldrin, dieldrin, lindane, hexachlorobenzene and heptachlor), 2 industrial chemicals (hexabromobiphenyl and PCBs) and 3 by-products or contaminants (dioxins/furans, hexachlorobenzene and polyaromatic hydrocarbons).
The ultimate objective is to eliminate discharges, emissions and losses of POPs.

The 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, hexaclorobenzene, PCBs). Finally, the Protocol severely restricts the use of DDT, HCH (including lindane) and PCBs. The 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.

***Table 1**. Substances regulated by the POPs protocol under the LRTAP Convention. (A: banned for production and use; B: restriction of the use; C: reduce emission)*

Aldrin	A
Chlordane	A
Chlordecone	A
DDT	B, C
Dieldrin	A
Dioxins/Furans	C
Endrin	A
HCB	C
HCH (incl Lindane)	C
Heptachlor	B
Hexabromobiphenyl	A
Hexaclorobenzene	B
Mirex	A
PAH	C
PCBs	B, C
Toxaphene	A

2.1.1 Health Effects of Persistent Organic Pollutants

The Task Force on Health (TF Health) reviewed health risks of several persistent organic pollutants, and identified those where long-range transport contributed significantly to exposure and health risks. The assessment process involved expert review of accumulated evidence and a series of working group meetings, conducted between May 2000 and May 2002 (WMO, 2003). The risks associated with the following groups of substances were reviewed: pentachlorophenol (PCP), DDT, lindane (γ-HCH), hexachlorobenzene (HCB), heptachlor, polychlorinated dibenzodioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs). The conclusions related to health hazard characterization and to the assessment of health implications relative to LRTAP of this group of pollutants were presented in TF Health reports to Working Group on Effects. The TF Health also performed a short hazard assessment for polychlorinated terphenyls (PCTs), polybrominated diphenylethers (PBDEs), polybrominated dibenzodioxins and furans (PBDD/Fs), short chain chlorinated paraffins (SCCPs) and Ugilec, identifying main gaps of information necessary for risk assessment.

2.2 The Stockholm Convention

The Stockholm Convention organized under UNEP is a global treaty to protect human health and the environment from persistent organic pollutants (POPs). In implementing the Convention, Governments will take measures to eliminate or reduce the release of POPs into the environment.

The 2001 Stockholm Convention on Persistent Organic Pollutants (POPs) entered into force on 17th May 2004 marking the start of an international effort to reduce and eliminate 12 particularly toxic POPs for reduction and eventual elimination. This group, the so called "dirty dozen", comprise the compounds aldrin, chlordane, DDT, dieldrin, endrin, dioxin, furans, heptachlor, hexachlorobenzene, mirex, polychlorinated biphenyls (PCBs), and toxaphene. They fall into three categories: pesticides, industrial chemicals, and unintended by-products of combustion and industrial processes.

The aims of the Stockholm convention are to:

- Reduce or eliminate the carcinogenic chemicals known as dioxins and furans, which are produced unintentionally as by-products of combustion.
- Assist countries in malarial regions to replace DDT with increasingly safe and effective alternatives. Until such alternatives are in place, the Convention allows governments to continue using DDT to protect their citizens from malaria; a major killer in many tropical regions.
- Support efforts by each national government to develop an implementation plan.
- Measure and evaluate changes in the levels of POPs in the natural environment and in humans and animals in order to confirm whether the Convention is indeed reducing releases of POPs to the environment.
- Establish a POPs review committee for evaluating additional chemicals and pesticides to be added to the initial list of 12 POPs.
- Finalise guidelines for promoting "best environmental practices" and "best available techniques" that can reduce and eliminate releases of dioxins and furans.

In addition to banning the use of POPs, the treaty focuses on cleaning up the growing accumulation of unwanted and obsolete stockpiles of pesticides and toxic chemicals that contain POPs. Recently, five new candidates of POPs that have been proposed to be included in the Stockholm Convention, as they are recognized to fulfil the screening criteria in the Convention. These are the brominated flame retardants of the group pentachlorodiphenyl ethers (PBDEs; the technical mixtures called penta-BDE) and hexabromobiphenyl (HxBB), the pesticides Chlorodecone and Lindane (γ-HCH), and the perfluorinated compound perfluorooctane sulfonate (PFOS).

3. Selected substances and their characteristics

3.1 Selected substances

According to the UNEP POPs Convention (the Stockholm Convention) and the Aarhus protocol, the following criteria should be fulfilled to classify a substance as a long range atmospheric transboundary POP:

- Environmental persistence (half life in water > 2 months, half life in sediments and soils > 6 months)
- Subject to long-range atmospheric transport (half life in air > 2 days)
- Potential for biomagnification (bio-accumulation factor for aquatic species > 5000, or log K_{OW} > 5 (log K_{OW}: logarithm of the octanol-water partition coefficient)
- Environmental adverse effects

There are many different groups of POPs that have a long range transport potential. For the purpose of this report and for practical considerations, a selection must be made. This report will therefore primarily consider the substances or group of chemicals given in Table 2. Among these are the "Dirty Dozen" addressed by the Stockholm Convention, the substances addressed by the LRTAP Convention and a few others selected on their basis on their persistence, toxicity, LRT potential, their present use, and availability of relevant data on their environmental occurrence. The structural formulas of the different group of POPs are shown in Figure 2 and Figure 3.

Table 3 lists the common names of the substances and their CAS numbers (unique identifiers for chemical substances, registered by Chemical Abstracts Service, http://www.cas.org/). Also listed are the substances vapour pressures, their octanol water partition coefficients and their Henry Law's constants. These three physiochemical properties are important for their environmental dispersal and accumulation in living organisms.

The vapour pressure of a substance (defined as the pressure of the vapour of the substance at equilibrium with its condensed form) determines to a large extent its tendency to transfer to and from the atmosphere (or other gaseous environmental phases). The vapour pressure also determines the speciation of the substance in the atmosphere (gaseous vs. particulate). Although the vapour pressure of the POPs in Table 3 seems low, their extremely low water solubility causes them to partition significantly to the atmosphere when present in surface waters. The vapour pressures of the POPs in Table 3 vary by several orders of magnitudes. Hence, there are large differences in their tendencies to escape to the atmosphere and in their potential for long range atmospheric transport.

The octanol-water partition coefficient (K_{OW}) is a useful indicator of a substance's environmental partitioning from water into natural organic phases. Poorly metabolised, neutral non-polar organic substances, such as POPs, tend to accumulate in organic matter and particulary in fatty tissues (lipids) of organisms. Hence their concentrations are often relatively high in particles rich in organic matter and they bioconcentrate in animals fatty tissues. The bioconcentration factor of a substance (the ratio of the concentration inside an organism to the concentration in the surrounding environment) is closely related to its water octanol-water partition coefficient. In many instances *n*-octanol serves not only as an appropriate surrogate for fatty tissues in organisms, but also for humic matter in soils and sediments and other naturally occurring organic phases. The octanol-water partition coefficient for the substances in Table 3 varies by several orders of magnitude, and reflects important differences in their potential for bioconcentration. Within a component group with several congeners, such as PCBs, dioxins and PBDEs, the K_{OW} generally increases with the degree of halogenation.

The Henry's law constant describes the equilibrium partitioning behaviour of a chemical between water and air phases, and it is therefore an important descriptor of atmospheric-water surface exchange.

Table 2. *List of substances considered by the LRTAP Convention, the Stockholm Convention and substances assessed in this report.*

CLRTAP	Stockholm Convention	Assessed in this ICP Waters report
Aldrin	Aldrin	X
Chlordane	Chlordane	X
Chlordecone		
DDT	DDT	X
Dieldrin	Dieldrin	X
Dioxine/Furane	Dioxine/Furane	X*
Endrin	Endrin	X
HCB		X
HCH (incl Lindane)		X
Heptachlor	Heptachlor	X
Hexabromobiphenyl		
Hexaclorobenzene	Hexachlorobenzene	X
Mirex	Mirex	X
PAH		X
PCBs	PCBs	X
Toxaphene	Toxaphene	X
		SCCP
		PFOS
		PBDE

* Concentrations not reviewed in this report

***Table 3.** Name of selected substances, their type of use/origin, CAS number, octanol-water partition coefficient (log K_{OW}) vapour pressure and Henry's Law constant.*

common name of substance	type/origin	CAS reg. no.	log K_{OW}	Vapour pressure (25°C) mm Hg	Henrys law const. atm m3/mol (25°C)	reference
aldrin	P	309-00-2	6.50	1.20 x 10^{-4}	4.4 x 10^{-5}	EPI Suite, 2004
endrin	P	72-20-8	5.20	3 x10^{-6}	6.36 x 10^{-6}	EPI Suite, 2004
dieldrin	P	60-57-1	5.40	5.89 x 10^{-6}	6.36 x 10^{-6}	EPI Suite, 2004
chlordane	P	57-74-9	6.16	9.75 x 10^{-6}	4.86 x 10^{-5}	EPI Suite, 2004
DDT	P	50-29-3	6.91	1.6 x10^{-7}	8.32 x 10^{-6}	EPI Suite, 2004
heptachlor	P	76-44-8	6.10	4 x 10^{-4}	2.94 x 10^{-4}	EPI Suite, 2004
mirex	P, I	2385-85-5	5.28	3 x 10^{-7}	8.11 x 10^{-4}	EPI Suite, 2004
toxaphene	P	8001-35-2	5.9 (median)	6.69 x 10^{-6} (20°C)	6 x 10^{-6}	EPI Suite, 2004
hexachlorobenzene	P, I, U	118-74-1	5.73	1.8 x 10^{-5}	1.7 x 10^{-3}	EPI Suite, 2004
PCBs	I	various	4.3-8.26	1.6-0.003 x 10^{-6}	0.3 x 10^{-4} to 1 x 10^{-7}	ECERG, 2005
dioxins and furans	U	various	5.60-8.20	2-0.007 x 10^{-7}	1 x 10^{-4} to 2 x 10^{-6}	ECERG, 2005
Lindan	P	58-89-9	3.72	4.2 x 10^{-5}	5.14 x 10^{-6}	EPI Suite, 2004
PBDE	I	various	4.28-9.9 (a)	3.85 x 10^{-3} to <10^{-7}		UNEP/GEF, 2003a
SCCP	I	various	4.39-8.69	3.3 x 10^{-4} to 6.0 x 10^{-8} (20°C)		EC, 2000
PFOS	I	1763-23-1	-	-	-	
PAH	U	various	4.79-8.20	0.0051 to 0.0015 x 10^{-9}		UNEP/GEF 2003a

,P = Pesticide; I = Industrial compound; U = Unintended by-product

a) for tri-hepta kongeners: log K_{OW}: 5.74-8.27, Braekwelt et al. 2003

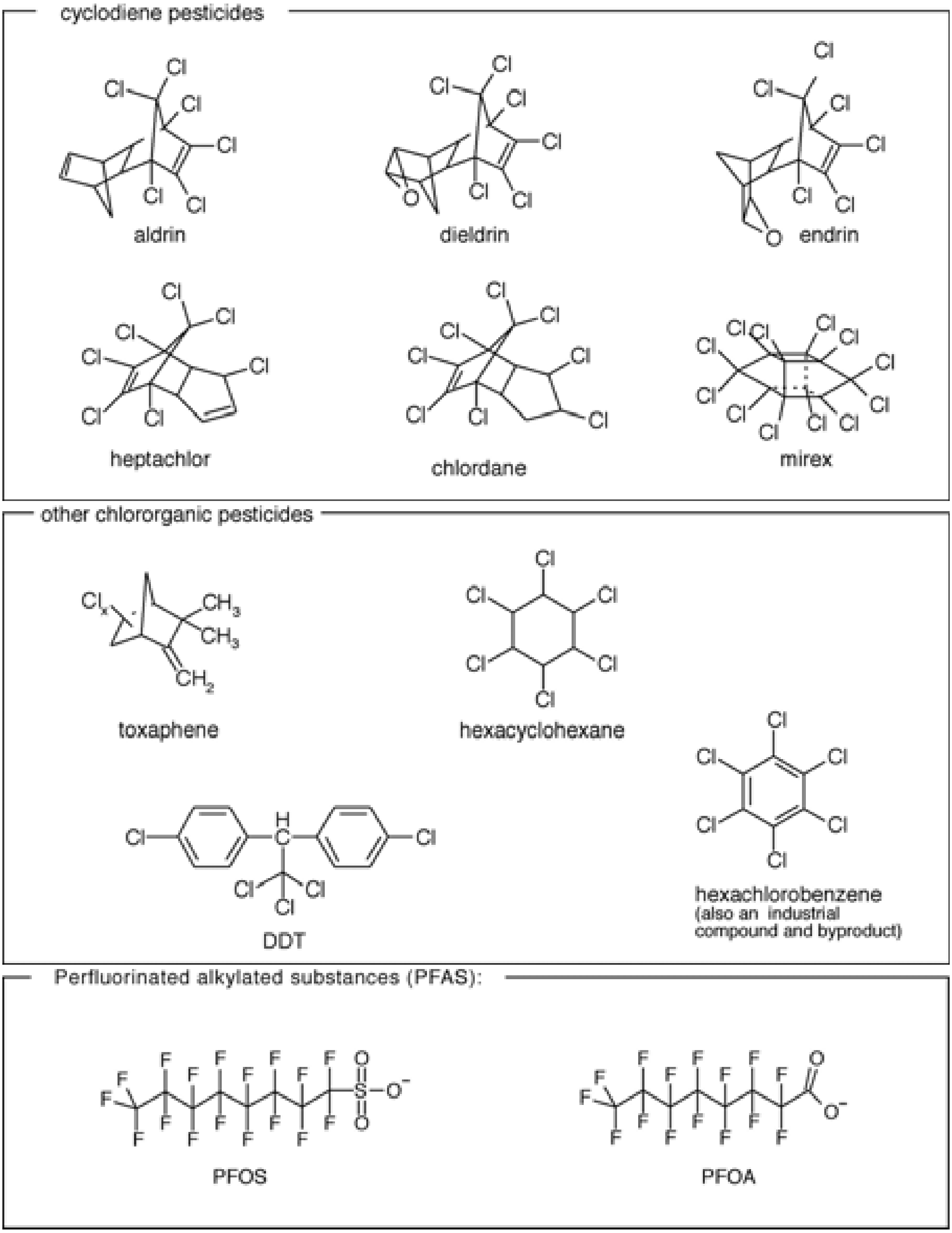

Figure 2. *Structural formulas of different group of POPs.*

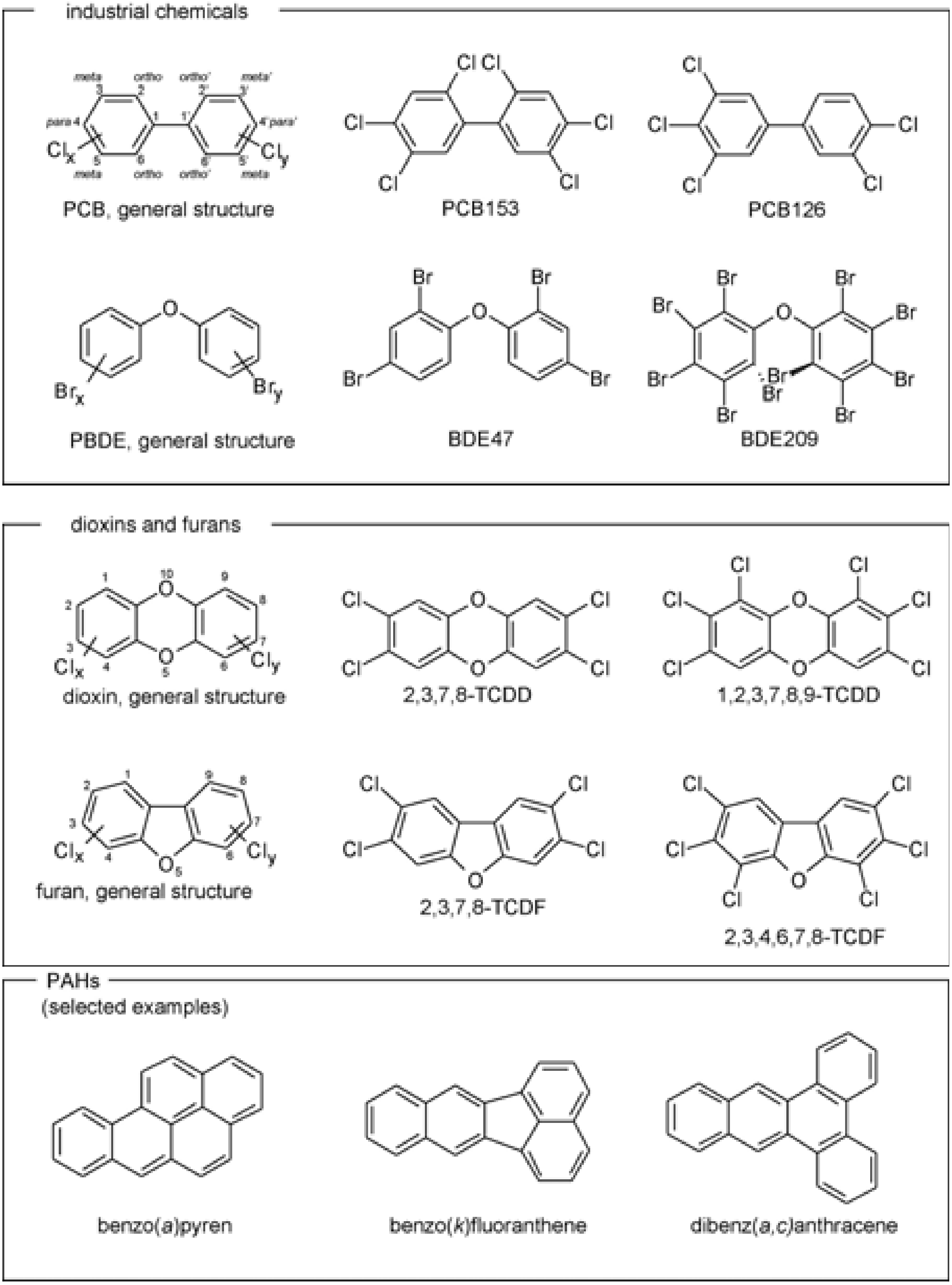

Figure 3. *Structural formulas of different group of POPs.*

3.2 Characterization of the substances

In the following discussion we will give a short description of the substances with emphasis on their use and potential for long range atmospheric transport. For a brief account on their toxicity, see (UNEP/GEF 2003a).

3.2.1 Aldrin and dieldrin

Aldrin and dieldrin are two closely related pesticides belonging to the cyclodiene group and their commercial production started in the late 1940s and early 1950s. They were widely used throughout the world up to the early 1970s as soil insecticides to control rootworms, beetles and termites and disease vectors such as mosquitoes and tsetse flies (UNEP/GEF 2003a).

In the environment and in living organisms aldrin is quickly oxidized to dieldrin which is a very persistent substance. Volatilisation from moist soils and water surfaces is expected to be an important fate process for both of aldrin and dieldrin, based upon their vapour pressures and Henry's Law constants. Due to the high vapour pressure of aldrin it is expected to exist solely in the vapour-phase in the ambient atmosphere, whereas dieldrin will exist in both the vapour and particulate phases. Because of its persistence and semivolatile nature, dieldrin has a high potential for long range atmospheric transport.

3.2.2 Endrin

Endrin is a pesticide of the cyclodiene group, and was introduced in 1951. It is a stereoisomer[1] of dieldrin. It has been used as an insecticide on field crops such as cotton, maize, sugarcane, rice, and cereals. It has also been used to control grasshoppers and termites in non-cropland and as a rodenticide to control voles and mice. The use of endrin was prohibited in most developed countries in the 1970s and 1980s.

Endrin is regarded as a highly persistent pesticide when applied to soils or leached to natural waters. Volatilization from moist soils and water surfaces is expected to be an important fate process, based on its vapour pressure and Henry's Law constant. In the atmosphere it is expected to exist in both particulate and vapour phases.

3.2.3 Chlordane

Chlordane is a pesticide of the cyclodiene group and was introduced in 1945. It has been used as a broad-spectrum insecticide for treating field crops, especially corn, and controlling cockroaches, ants, termites and other household pests. The technical product chlordane refers to a complex mixture of different chlordane isomers[1], other chlorinated compounds and by-products. The most abundant constituents are *cis*- and *trans*-chlordane, heptachlor, and *trans*- and *cis*-nonachlor (Dearth and Hites, 1991). By the mid-1970s severe restrictions were in place on the use of chlordane in most developed countries, but it has been used extensively in

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[1] An isomer is one of two or more forms of a chemical compound which have the same number and type of each atom but a different arrangement of atoms. Stereoisomers are isomers where the atoms are bonded by the same sequence of bonds but having different three-dimensional structures which are not interchangeable.

some developing regions up to the late 1990s and it is still used in some nations for controlling termites.

Chlordane is highly persistent in soils and natural waters. Volatilization from moist soils and water surfaces is expected to be an important fate process for both, based on its vapour pressure and Henry's Law constant. In the atmosphere, it is expected to exist in both particulate and vapour phases.

3.2.4 Heptachlor

Heptachlor is a pesticide of the cyclodiene group, and was first introduced in the early 1950s as a general insecticide on field crops, such as corn, cereals and cotton. Later, the use was confined almost exclusively to the control of soil insects and termites. The use of heptachlor was banned or severely controlled in most developed countries in the 1970s and 1980s, but the production did not cease before 1997.

Heptachlor is metabolised in soils, plants and animals to the toxic and persistent compound heptachlor epoxide. Heptachlor is persistent when applied to soils or leached to natural waters, and volatilisation from moist soils and waters is expected to be an important fate process. It is expected to exist in both particulate and vapour phases in the atmosphere.

Heptachlor is one of the active compounds in technical chlordane, and the metabolite heptachlor epoxide is therefore often calculated into the sum of chlordane compounds when their environmental presence is reported.

3.2.5 Mirex

Mirex is a compound of the cyclodiene group, with its commercial manufacturing starting in the late 1950s. It was used as an insecticide for controlling ants and termites, but was also used extensively as a flame retardant (trade name: Dechlorane) in plastics, rubber, paint, paper and electrical goods. By the late 1970s severe restrictions were in place on the use of mirex in most developed countries, but it is still used in some nations for controlling termites.

Mirex is extremely persistent in the environment, and volatilization from moist soils and waters is expected to be an important fate process. Based on its rather small vapour pressure, mirex in the ambient atmosphere is expected to exist mainly in the particulate phase with a lesser proportion of it in the vapour phase.

3.2.6 Toxaphene

Toxaphene is a complex mixture of more than 670 compounds called polychlorinated bornanes and camphenes. Toxaphene has been in use since 1949 and was the most widely used insecticide in the USA in 1975, primarily on cotton, cereals, and vegetables. It has also been used to control ectoparasites such as lice, ticks and mites in livestock, and to kill unwanted fish in lakes. The use of toxaphene was banned or severely controlled in most developed countries in the 1970s and 1980s, but it was still commonly used in some nations in the late 1999s (U.S. EPA 2002).

Toxaphene can be very persistent in soils and water under aerobic conditions, and volatilisation from moist soils and waters is expected to be an important fate processes. In the atmosphere it is expected to exist in both particulate and vapour phases.

3.2.7 Hexachlorobenzene

Hexachlorobenzene (HCB) was first introduced in 1945 as a fungicide on grain crops. It is also generated as a by-product or impurity in the manufacture of several chlorinated industrial chemicals and during electrolytic chlor-alkali and magnesium production. Waste incineration (low temperature burning) may also emit HCB in the flue gases. The use of HCB as a fungicide was banned or severely controlled in most developed countries in the 1970s and 1980s.

HCB is persistent in the soils and waters, and volatilization from moist soils and water surfaces is expected to be an important fate processes. In the atmosphere it is expected to exist in both particulate and vapour phases.

Hexachlorobenzene is one of several chlorobenzenes of environmental concern. Pentachlorobenzene, and sometimes also other lower chlorinated benzenes, may be calculated into the sum of chlorobenzenes when their environmental presence is reported.

3.2.8 Dichlorodiphenyltrichloroethane (DDT)

DDT is the abbrevation of the obsolete chemical name dichlorodiphenyltrichloroethane. The commercial production of the insecticide DDT started in 1945, after it was used successfully to control insect-borne diseases during World War II. For many years it was one of the most widely used insecticides in agriculture and forestry – as well as for controlling disease vectors, such as mosquitoes and tsetse flies. The worldwide use of DDT declined during the 1960s due to increased insect resistance, development of alternative pesticides, and environmental considerations. DDT was banned during the 1970s and 1980s in most developed countries, but its use continues in some parts of the world, especially in tropical regions to control malaria.

DDT is considered to be very persistent in soils and natural waters under aerobic conditions, and volatilization from moist soils and water surfaces is expected to be an important fate process. In the atmosphere it is expected to exist in both particulate and vapour phases. DDT slowly breaks down or metabolized in soils, sediments and animals to the less acute toxic, but persistent compounds DDE (dichlorodiphenyldichloroethylene) and DDD (dichlorodiphenyl-dichloroethane).

3.2.9 Hexachlorocyclohexane (HCH) and lindane

HCH exists as several isomers, and its γ-isomer (lindane) was recognized as an insecticide in the early 1940s. Lindane became one of the most widely used insecticides in the world, used as a broad-spectrum insecticide for use in agriculture and forestry, and for controlling ectoparasites such as lice, ticks and mites. Commercially, HCH has been sold in two principal formulations: technical HCH, which is a mixture of mainly α-HCH (55-80%), β-HCH (5-14%), and γ-HCH (8-15%), and lindane, which is basically pure γ-HCH. The use of HCH became banned or restricted during the 1970s and 1980s in many developed countries, but its use continues in some parts of the world. HCH is not regulated by the international UNEP POP convention, but is addressed by the 1998 Aarhus Protocol on POPs under the LRTAP Convention. The EU recommends that its production and uses should be confined to a minimum and it will ultimately be phased out by the end of 2007 at the latest.

Lindane and HCH are relative persistent in soils and waters, with half-lives generally greater than 1 year. Their bioconcentration factors are smaller than those of the other organochlorines because of their moderately low lipophilicity. However, the individual isomers differ somewhat in their physiochemical characteristics, and therefore, there are differences in their environmental persistence, dispersal mechanisms, and accumulation in biota. β-HCH is more lipophilic than the α- and γ-HCH, and it also has the lowest vapour pressure and Henry's law constant. It is the most persistent isomer, and shows a higher bioconcentration factor than the other two. α-HCH has the greatest potential for long range atmospheric transport due to its higher vapour pressure. Volatilisation from wet soils and water surfaces is expected to be important fate processes for α- and β-HCH, whereas the volatilisation rate for β-HCH is expected to be low due to its small Henry's law constant. The three isomers are expected to exist in both particulate and vapour phases in the atmosphere.

3.2.10 Polychlorinated biphenyls (PCBs)

The commercial manufacture of PCBs started in 1929, and they have been used extensively in a variety of industrial products and applications because of their chemical inertness, heat resistance, are non-flammable, have a low vapour pressure and high dielectric constant. They have been used in transformers and capacitors, in heat transfer and hydraulic systems, as paint additives, in carbonless copy paper and in plastics. There are 209 possible chlorinated biphenyls (referred to as congeners[2]), but only about 130 are likely to be found in commercial products. The worldwide production peaked in the 1970s, but most developed countries banned or severely controlled PCB production and application of it the late 1970s and 1980s. However, there are still large quantities that remain in use or exist in waste products.

The environmental persistence of PCBs generally increases with an increase in the degree of chlorination. Mono-, di- and trichlorinated biphenyls biodegrade relatively rapidly, tetrachlorinated biphenyls biodegrade slowly, and higher chlorinated biphenyls are resistent to biodegradation. Volatilization from soils and water surfaces appears to be important fate processes. Low chlorinated PCBs volatilize more readily than the higher chlorinated congeners. The vapour pressure of PCBs generally decreases with an increase in the degree of chlorination. Higher chlorinated PCBs are therefore more likely to exist in the particulate phase in the atmosphere than the lower chlorinated PCBs.

3.2.11 Dioxins and furans

Dioxins and furans are a common name for polychlorinated dibenzo-p-dioxins (PCDDs) and chlorinated dibenzofurans (PCDFs). They have up to 8 chlorine atoms, and dioxins may have 75 possible congeners and furans may have 135 different congeners. They are formed as

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[2] Congener is a term in chemistry that refers to one of many variants or configurations of a common chemical structure.

unintentional by-products during combustion processes involving chlorine, such as waste incineration, combustion of oil and coal, metallurgical processes, Portland cement production, chlorine bleaching of pulp and paper, and in chemical manufacturing.

PCDDs and PCDFs are persistent in soils and waters, and they have high bioconcentration factors. Volatilization from wet soils and water surfaces appears to be important fate processes only for the less chlorinated congeners. These are also more likely to exist in both the vapour and the particulate phases in the atmosphere than the more chlorinated congeners.

The levels of dioxins and furans in freshwater fishes will not be reviewed in this report, as they usually have not been included in the type of large scale surveys we have based our assessment on.

3.2.12 Polybrominated diphenylethers (PBDEs)

Polybrominated diphenylethers (PBDEs) belong to a family of related compounds that are used as flame retardants. There are 209 possible brominated diphenylethers (congeners), and the different congeners are numbered according to the IUPAC system used for numbering PCBs. The commercial production of PBDEs as flame retardants started in the early 1960s, and they were widely used in a broad range of commercial and household products, such as textiles, polyuretane foams, plastics and rubbers. The technical PBDEs are produced in three principal formulations with different degrees of bromination: penta-BDE (five bromine atoms), octa-BDE (eight bromine atoms), and deca-BDE (fully brominated with 12 bromine atoms) but they also contain other PBDEs . The use of penta- and octa-BDEs was forbidden within the EU since 2004, while deca-BDE will be phased out in 2006 unless risk assessment results demonstrate that this is unnecessary. The USA has prohibited significant new use and import of penta- and octa-BDE since 2005. deca- and octa-BDE was included in November 2005 on a list of chemicals proposed for inclusion in the Stockholm Convention on Persistent Organic Pollutants.

PBDEs are very persistent in soils and waters. Penta- and octa-BDE have high bioconcentration factors, whereas deca-BDE has been regarded as non-bioavailable. Recent studies have shown that this congener may also accumulate in humans and animals (Jakobsen et al. 2003, Lindberg et al. 2004) and that fish (carp) can metabolise it to other lower brominated congeners (Stapleton et al. 2004). It can also be dehalogenated under aerobic conditions (Gerecke et al. 2005). Volatilisation from wet soils and water surfaces are expected to be important fate processes for tetra- to penta-congeners, whereas the estimated Henrys Law’s constants for the higher brominated congeners are too low for volatalisation to be an important environmental process. In the atmosphere, the tetra- to penta-congeners are likely to exist in both the vapour and particulate phases, whilst the higher brominated congeners are likely to be present only in the particulate phase.

3.2.13 Polycyclic aromatic hydrocarbons (PAHs)

PAHs are a group of compounds that consist of two ore more fused aromatic rings. They are built up of carbon and hydrogen, and do not contain any other constituents. PAHs are formed during incomplete combustion of organic materials. They are released to the environment by both human and natural processes, such as residential burning of wood, burning and processing of fossil fuels, primary aluminium production (in particular Söderberg technology), forest fires and volcanoes.

The environmental persistence of PAHs increases with their molecular weight. High molecular weight PAHs are regarded as very persistent in soils, sediments and natural waters. Their vapour pressure and Henry's Law constant decrease with molecular weight, and volatilization from wet soils and water surfaces is expected to be an important fate process for PAHs of low and medium molecular weight (up to four rings). The low and medium molecular PAHs are expected to exist in both vapour and particulate phases in the atmosphere, whilst the heavier compounds are likely to be present only in the particulate phase.

3.2.14 Short chained chlorinated paraffins (SCCPs)

Short chained chlorinated paraffins (SCCPs) are chlorinated straight-chain hydrocarbons (n-alkenes), with a carbon chain length between 10 and 13. Their chlorine content ranges from 30% to 70% on a weight basis. SCCPs have been used industrially as cutting oils in metal working, high pressure lubricating oils, flame retardants, plasticizers and corrosion inhibitors.

They are regarded as persistent in the environment, and the vapour pressure values, Henry's law constants and atmospheric half-life values are in the same range as those of other persistent organic pollutants and imply a significant potential for long-range atmospheric transport. SCCPs are highly lipophilic substances, and they are known to bioconcentrate in aquatic organisms.

The use of SCCPs is regulated in the EU because if their adverse environmental properties and it has been added to a list of priority hazardous substances.

3.2.15 Perflourinated alkylated substances (PFAS)

Perfluorinated alkylated substances (PFAS) are a group of substances built up of a completely fluorinated alkyl chain with a functional group at one end. This is usually an alcohol, a sulfonyl or carboxylic group. These compounds are chemically stabile products with both hydrophobic and lipophobic properties, and have been used in a wide variety of industrial products and applications, such as soil- and stain-resistant coatings for textiles and leathers, floor polishes, grease- and oil-resistant coatings for paper products, fire-fighting foams, mining and oil well surfactants, metal plating and electronic etching baths (Renner 2001). They have also been used to produce fluoropolymers to provide non-stick surfaces on cookware and waterproof, breathable membranes for clothing.

Among the different PFASs, perfluorooctanyl sulfonate (PFOS) and perfluorooctanoic acid and its salts (PFOA) have recently gained much attention as environmental contaminants, and they are now recognized as ubiquitous organic contaminants. The production of PFOS in the USA was voluntarily phased out in 2000, and in November 2005 it was included on a list of chemicals proposed for inclusion in the Stockholm Convention on Persistent Organic Pollutants. Because of the high priority of PFOS in international environmental legislation, we will concentrate on the occurrence of this substance in this report.

PFOS is extremely persistent in the environment, and no apparent biodegradation occurs under aerobic or anaerobic conditions. As a lipophobic substance, it does not accumulate in lipid-rich tissue, but binds to proteins in blood and liver. Its octanol-water partition coefficent is not measurable, but it bioconcentrates in aquatic organisms because of its protein binding properties. Due to its low vapour pressure and low air-water partition coefficient, it is not expected to volatilize readily. It is therefore assumed to be transported in the particulate phase in the atmosphere.

4. Environmental levels and trends

There is a huge volume of data on the environmental occurrence of POPs, and an open literature survey from 1992–2002 has shown more than 20 000 references relate to POPs in water, according to UNEP/GEF (2003a). However, the data are characterised as "often patchy, and typically the result of one-off studies rather than systematic, comparable and long-term monitoring". It is also often difficult to systematically compare data from different studies "because the measuring and reporting protocols vary widely in the published data". Such obstacles make it difficult to fully utilize the information found in these studies.

During recent years several international assessment reports and reviews of persistent toxic substances in the environment have been published. The Arctic Monitoring and Assessment Programme (AMAP) has produced two definitive assessment reports (AMAP 1998 and 2004). Within the UNEP Chemicals, there has been one global report and twelve regional assessment reports, addressing persistent toxic substances (see: UNEP Chemicals/GEF 2003 and references therein). A concise review of health risks of POPs from LRTAP has been made by Joint WHO/Convention Task Force on Health Aspects of Air Pollution (2003). These reports and reviews have been useful sources for information and references for this report.

Except for the Arctic, few broad assessments have been made with a focus on the occurrence and effects of POPs in surface waters attributed to LRTAP. The main effort has been on waters in agricultural, industrialised or urban areas, with significant influence from local pollution sources. Due to difficulties of separating the influence of local and long range atmospheric transported pollutants, we have in this report chosen not to concentrate on data from some well-studied areas and locations strongly affected by local pollution, such as the Great Lakes in North America, and large European waterways such as the Danube River and Rhine River. However, we have included some surveys from large river basins in North America, as these show the concentration range from reference sites to strongly contaminated sites.

We want to emphasise that this review are not meant to be a comprehensive collection of data on LRTAP POPs in freshwater environment, but represent examples selected on basis of their availability and relevance. We have chosen to give a broad overview of the recent levels of selected POPs in freshwater fish from North America, Europe and circumpolar Arctic, based on data from some central surveys and selected case studies from pristine areas and upland waters, such as:

Arctic
Arctic Monitoring and Assessment Program (AMAP), reporting environmental levels in the circumpolar Arctic.

Europe
The EU project EMERGE. Data on sediments and biota in alpine lakes. Miscellaneous national data on geographical distribution and trends, such as Nordic data from the environmental monitoring programmes of Sweden and Norway. Scottish sediment data from Lochnagar (Rose et al. 2001) reporting trends in deposition of selected POPs.

North America

In the USA, the BEST program of the USGS has been monitoring environmental contaminants and their effects on fish in several large river basins. Recent reports provide information on POPs in fish from the basins of the Mississippi River (Schmitt 2002), Yukon River (Hinck et al. 2004a), Columbia River (Hinck et al. 2004b) and Rio Grande (Schmitt et al. 2004). The data tables in these reports give the summary statistics of the POP levels based on several species from each station, and there is not sufficient information here to break these statistics down on each species. Hence, we present the concentration of POPs in fish from these surveys as pooled data from several species.

An area in northeast Canada, outside the Arctic and Great Lakes area, from northern Alberta to Labrador, was assessed by a recent study by Muir et al. (2002a and b). This survey was conducted as a part of the TSRI program (Toxic Substances Research Initiative). The survey studied levels of POPs in fish, food webs and sediments in 34 lakes, and dated sediment samples reveal the historical deposition trends. Some of the lakes had direct human impacts that are significant in the interpretation of the results, but the majority were generally remote from urban areas and permanent settlements. The Northern Contaminants Program (Fisk et al. 2003), reported environmental levels in the Canadian Arctic.

In water bodies with LRT as the major source of the POPs discussed here, the concentrations in water are extremely low, often beyond the detection limits. This is further complicated by the fact that there has been a diversity of analytical protocols and methods in use at different laboratories, and the methods have evolved rapidly through times. Hence, compiling reliable information of the concentration of POPs in water is often complicated, and we have therefore focused on documenting the levels in freshwater fish and sediments.

The sample matrices vary somewhat between the different surveys. The BEST surveys have used homogenized whole fish, after having taken out sub samples of liver, gonads, bile, blood etc. for other analyses. The TSRI program used whole fish, whereas the NRC and AMAP used muscle samples (NCR also used muscle samples with skin). The liver is commonly used in burbut, a cod-like freshwater fish, because it has a large lipid-rich liver (often 30–45% lipids), which effectively accumulates lipophilic pollutants.

Often, when comparing accumulation of lipophilic contaminants, the concentrations are normalized to the lipid content of the samples. This reduces the variability related to differences in lipid content and renders possible a more direct comparison of samples of different tissues or species. However, such normalization was not feasible with the current data, as many of the surveys reported only the sample concentrations on a wet weight basis, without any possibilities to match these with the respective lipid content. Nor could more elaborate adjustments for fish size, age and trophic position be made, as this also would require access to more detailed datasets than the summary statistics often published in the survey reports. This also makes it difficult to perform correct statistical significance tests for differences in concentrations between regions or species.

4.1 Recent levels and spatial distributions

All the concentrations in this chapter are given on a wet weight basis (denoted as w.w. in the captions) unless other is stated.

4.1.1 Cyclodiene pesticides in fish

Among the cyclodiene pesticides, their occurrence in the freshwater environment are in general best known for the chlordanes and for dieldrin. The other pesticides have been less frequently included in the surveys analysis program.

Statistics on the concentrations of chlordanes and dieldrin in fish, based on recent different surveys and programmes, are shown in Figure 4. The chlordane group seem in general to be the cyclodiene pesticide with the highest concentrations in fish, followed by dieldrin. Data on endrin and mirex are scarcer, but suggest that the concentrations of these pesticides are in general lower than both chlordane and dieldrin (see appendix, Table A1).

In fish from three large river basins (Rio Grande, Mississippi River, Colorado River), covering a large part the conterminous USA, the geometric means of chlordanes in fish from different sites were commonly about 30-40 ng/g (median values), whereas the range of the individual composite samples were <30–550 ng/g. The median concentrations for dieldrin in all the three surveys were <10 ng/g, while the range of individual samples was <10–29 ng/g. Median concentrations for mirex and endrin were also below detection limits (<10 ng/g), but the frequency of samples below the detection limits were considerably larger than for dieldrin. These three surveys represent sites with varying degree of human impact, from reference sites with no known local discharges of pollutants to significant polluted sites. Due to the rather high detection limits (10–30 ng/g), these surveys cannot provide exact information on the levels of cyclodiene pesticides in fish from sites without local pollution sources (recent background levels).

The TRSI study of Muir et al. (2003a) showed that the concentrations of chlordanes and dieldrin in fish from Canada, outside the Arctic and the Great Lakes area, were substantially lower than in fish from the BEST surveys in conterminous USA. Again, the chlordane concentrations were in general higher than the dieldrine concentrations. The median concentrations of chlordane in five of the best-represented species (lake trout, pike, walleye, whitefish and cisco) varied from 1.3 to 10.4 ng/g. Corresponding figures for dieldrin were 0.01 to 0.28 ng/g. The highest concentrations were found in lake trout, a lipid-rich top predator, with lower concentrations in the leaner species.

The concentrations of chlordanes reported in the arctic surveys, NCP (Fisk et al. 2003) and AMAP (1998), were comparable to those reported in the Canadian TSRI study (Muir et al., 2003a). The median concentrations in muscle fillets were 1.3–10.1 ng/g, with the highest concentrations in lake trout. Corresponding figures for dieldrin were substantially lower: 0.07–0.7 ng/g. For the liver samples of burbot, the median concentrations of chlordanes were about 24–27 ng/g, while the median dieldrin concentrations only were 2–6 ng/g. It is reasonable to assume that these concentrations represent recent regional background levels for fish from water bodies with LRTAP as their main pollution source. All the samples from the Yukon River Basin survey (BEST, Hinks et al. 2004) had median concentrations below detection limits that were relatively high compared to other studies (chlordane: 5 ng/g, dieldrin: 1 ng/g).

The concentrations of the other cyclodiene pesticides were in general considerably lower than chlordane and dieldrin. In burbot from the arctic, the liver concentrations of endrin and mirex were about 2–6 and 0.6 ng/g, respectively.

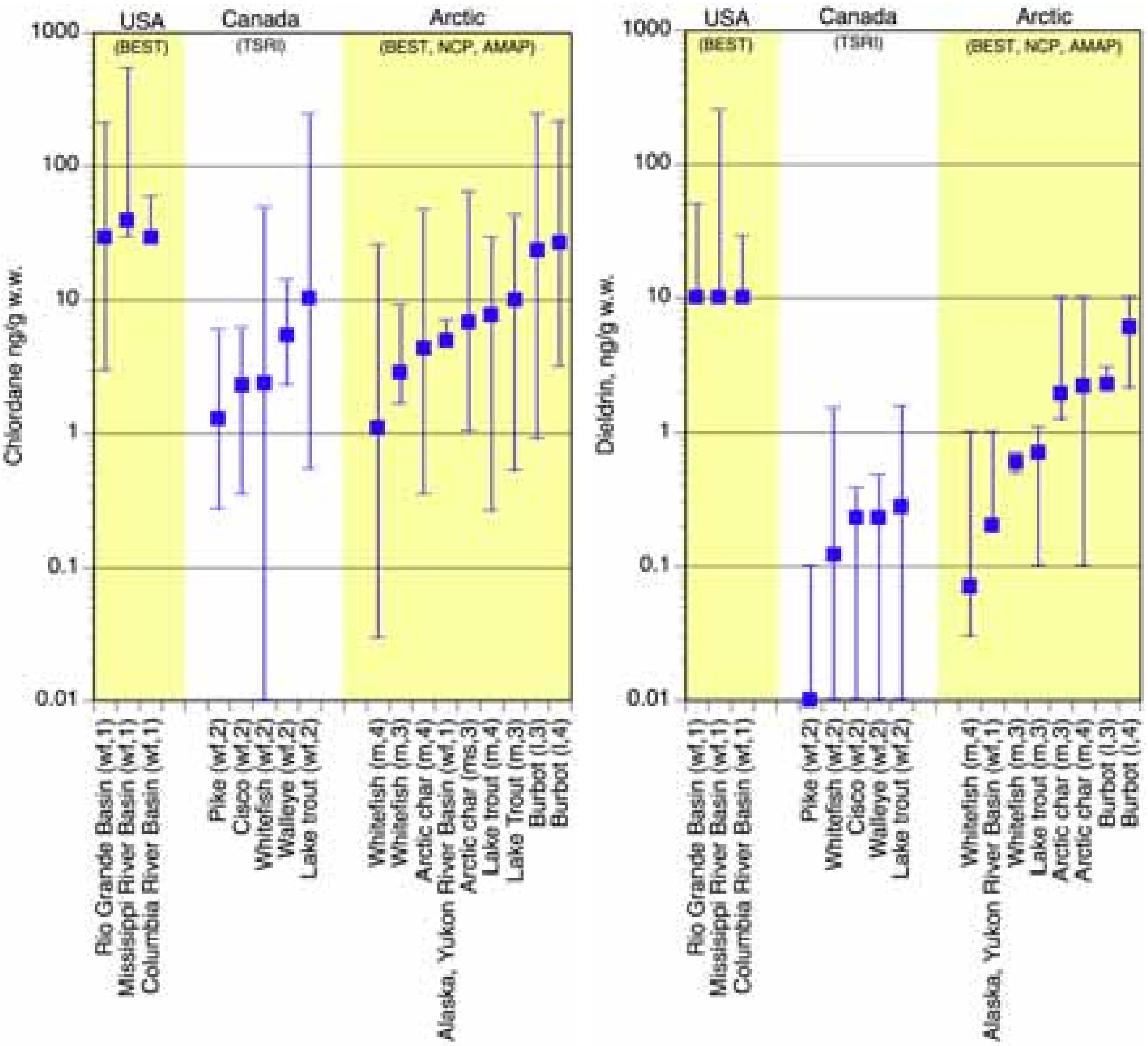

Figure 4. *Concentrations of chlordanes and dieldrin in freshwater fish. Median values: square symbols. Sample spread: vertical bars. The sample matrix and the data sources are coded in the category axis labels. Sample matrix: wf, whole fish; m, muscle; ms, muscle with skin; l, liver. Statistics for the BEST program are based on several species. Data sources (see appendix): 1, BEST; 2, TSRI; 3, NCP; 4, AMAP.*

4.1.2 Toxaphene and DDT

Toxaphene and DDT were, in general, the pesticides with the highest concentrations in freshwater fishes, and it is noteworthy that the toxaphene levels were of the same order in the arctic as in more temperate regions (Figure 5).

The DDT concentrations of fish samples from the large river basins in the conterminous USA (the BEST program) were commonly about 40–265 ng/g (medians), with a range of 10–11 100 ng/g. The median concentrations of toxaphene were lower than their relatively high detection limits, but were estimated to be <15 and <25 ng/g (substituted with half of the detection limits). The maximum toxaphene concentration was 8 300 ng/g, and was found in a fish sample from the Mississippi River basin.

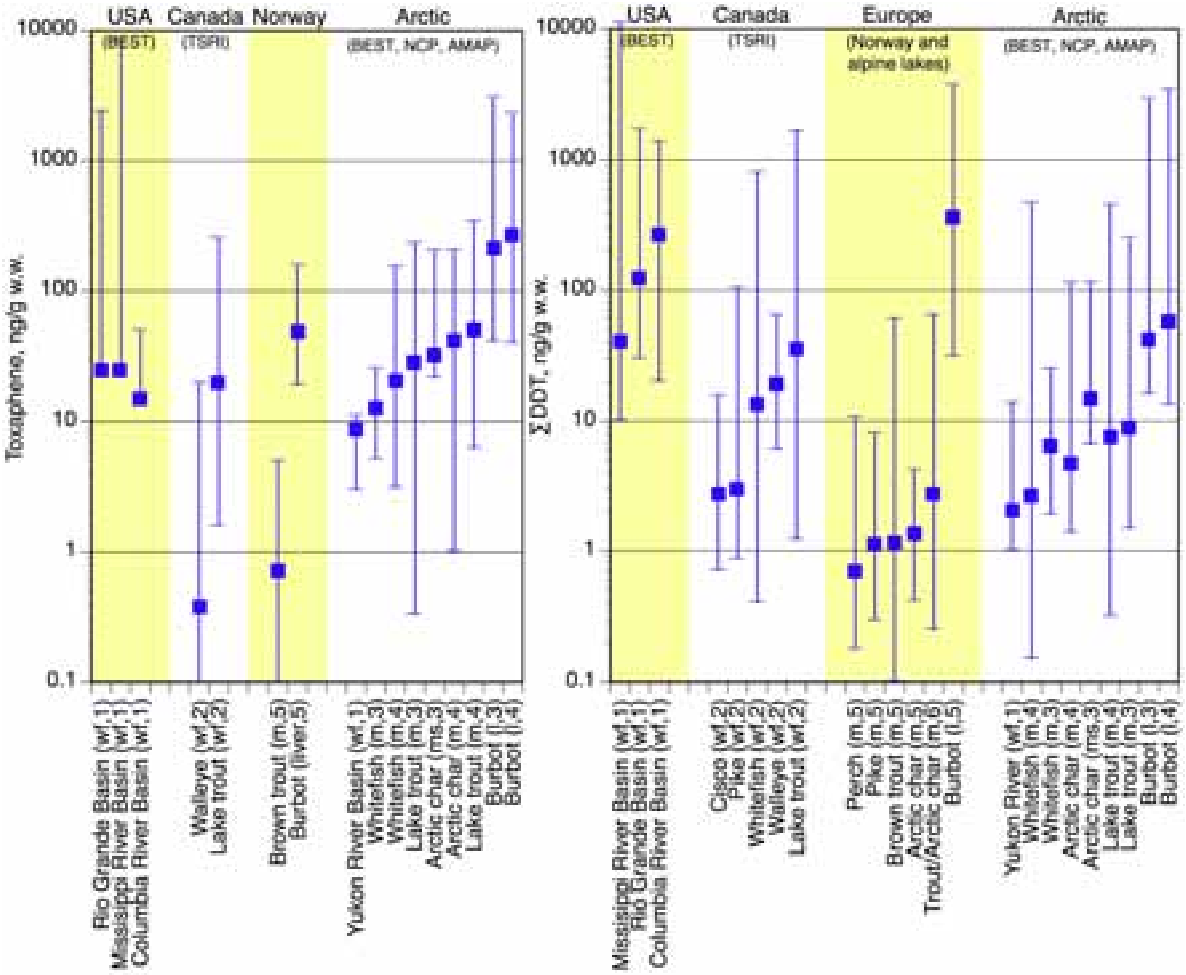

Figure 5. *Concentrations of toxaphene and DDT (sum of DDT and breakdown produkts) in freshwater fish. Median values: square symbols. Sample spread: vertical bars. The sample matrix and the data sources are coded in the category axis labels. Sample matrix: wf, whole fish; m, muscle; ms, muscle with skin; l, liver. Statistics for the BEST program are based on several species. Data sources (see appendix): 1, BEST; 2, TSRI; 3, NCP; 4, AMAP; 5: Norway, Fjeld et al. (2001); 6: European alpine lakes, Vives et al. (2004).*

In the Canadian TRSI study (Muir et al. 2003a), the DDT concentrations were significantly lower than in the BEST surveys, with median values between 2.7–34.7 ng/g and a total range of 0.4–1 642 ng/g. As with the cyclodiene pesticides, the highest concentrations were found in the piscivorous (fish eating), lake trout and walleye. The median toxaphene concentrations (and range) for lake trout and walleye were 19.8 ng/g (1.6–254 ng/g) and 0.37 ng/g (0.05–19.9 ng/g), respectively.

Fish from European alpine lakes (EMERGE project: Vives et al. 2004) and Norwegian lakes (Fjeld et al. 2001) had substantially lower DDT concentrations than fish from the above-mentioned BEST and TSRI surveys. The median concentrations in fish muscle tissue were between 0.7–2.7 ng/g, with a sample range of 0.1–65 ng/g. The alpine lake study showed a statistical association with lake altitude, interpreted by the authors as a cold condensation effect on airborn organic pollutants. The highest DDT muscle concentrations were found in fish from a lake in the French Pyrenees. For burbot from Norwegian lakes, the median liver concentration were 359 ng/g (range: 31–3702 ng/g), with decreasing concentrations along a south-north gradient. The relatively high DDT concentrations in burbot liver are related to their diet (fish consuming top-predator) and the high lipid content of their liver. Data on toxaphene were scarcer, but the Norwegian survey showed median concentrations (and range) for brown trout (muscle fillets) and burbot (liver) to be 0.7 ng/g (0.07–5 ng/g) and 48 ng/g ng/g (19–157 ng/g), respectively (sum of three different toxaphene congeners: Parlar no. 26, 50 and 62). The surveys were performed on lakes without known point sources of DDT and toxaphene, except for DDT in a few Norwegian lakes, and the median values can therefore be regarded as background levels for European alpine and Nordic regions.

In the arctic surveys, toxaphene was in general the POP with the highest concentrations. The median concentrations in fish tissue or whole fish were in the range of 8.5–50 ng/g, with a sample range of 0.3–344 ng/g. The highest concentrations were found in lake trout and arctic trout. The median DDT concentrations for the same surveys were 2–15 ng/g, with a sample range of 1-250 ng/g. The NCP and AMAP programs included analyses of burbot liver, and the concentrations of toxaphene were also here significantly higher than for DDT. The median (and sample range) of toxaphene and DDT in burbot liver were 208–267 ng/g (40–3050 ng/g) and 41–57 ng/g (14–3433 ng/g), respectively.

4.1.3 Polychlorinated biphenyls, PCBs

The PCB concentrations were, in general, within the same range as the DDT concentrations, and showed similar geographical variations (Figure 6). Highest levels were found in the conterminous USA, lowest levels in Scandinavia and European alpine lakes, and intermediate to high levels in Canada and the Arctic. The number of congeners reported varies between the surveys, from the so-called “Seven Dutch” and up to 103 congeners (Muir et al. 2001, referred to in the NCP program). However, the Seven Dutch congeners are considered to comprise 40–60 % of the occurring PCB mixture in the environment (de Voogt and Brinkman 1989), which is an acceptable percentage when we are comparing levels that differ with one to several orders of magnitude.

In the BEST surveys from large river basins in the conterminous USA, the median concentrations of the multispecies fish samples were commonly about 30–105 ng/g, with a sample range of 30–3 300 ng/g. The TSRI study (Muir et al. 2003a) showed that the PCB concentrations in fish from Canada, outside the Arctic and Great Lakes area, were clearly lower than in the BEST surveys, with median concentrations of individual fish samples about 2.4–37.7 ng/g and a sample range of 0.1–1003 ng/g. Again, the highest concentrations were found for the top-predators, walleye and lake trout, with median concentrations (and range) of 38 ng/g (7.6–123 ng/g) and 38 ng/g (1.4–1003 ng/g), respectively.

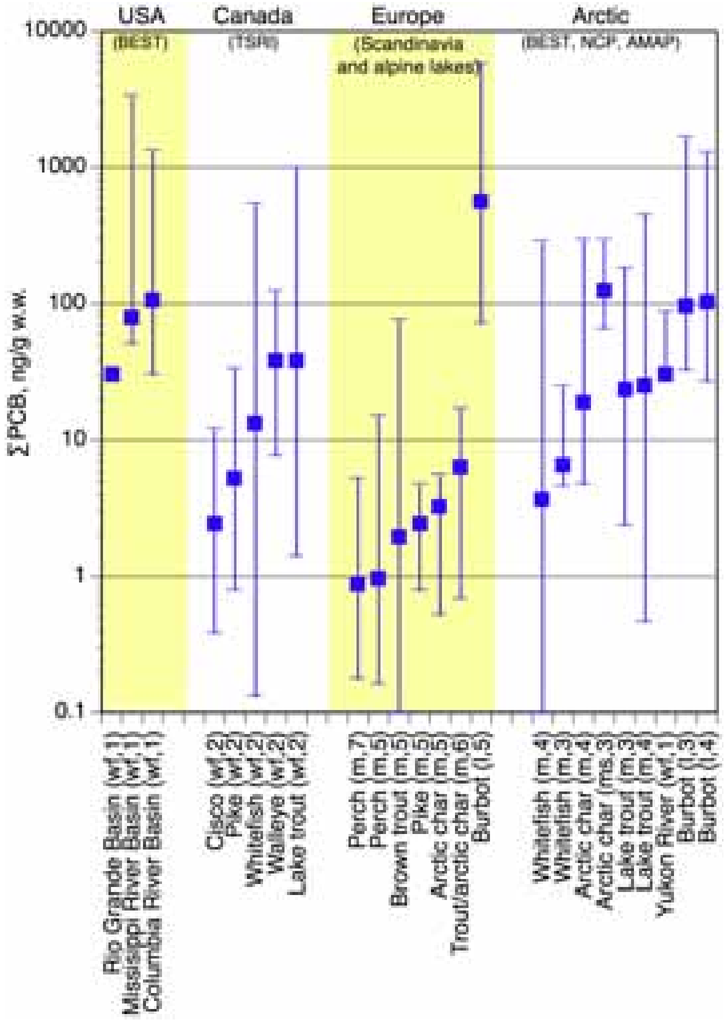

Figure 6. *Concentrations of PCB (sum of different congeneres) in freshwater fish. Median values: square symbols. Sample spread: vertical bars. The sample matrix and the data sources are coded in the category axis labels. Sample matrix: wf, whole fish; m, muscle; ms, muscle with skin; l, liver. Statistics for the BEST program are based on several species. Data sources (see appendix): 1, BEST; 2, TSRI; 3, NCP; 4, AMAP; 5, Fjeld et al. (2001); 6, Vives et al. (2004); 7 , Sternbeck et al. (2004).*

In Scandinavian (Fjeld et al. 2001, Sternbeck et al. 2004) and European alpine lakes (Vives et al. 2004), the median concentrations of PCBs in fish muscle tissue were between 0.9–6.3 ng/g, with a sample range of 0.1–76 ng/g. As for the DDTs, there was a statistical association between the concentrations of PCBs and altitude, interpreted by the authors as a cold condensation effect on PCB depositions. These surveys sampled lakes without known point sources of PCBs, with the exception for a few Norwegian lakes, and the median values can therefore be regarded as representative background levels for European alpine and Nordic regions. Norwegian data on PCBs in burbot liver (Fjeld et al. 2001) showed a median (and sample range) of 557 ng/g (72–5816 ng/g), but the levels in many of these populations were probably influenced by diffuse sources from populated and urban areas.

In the arctic surveys, the PCB concentrations in fish muscle and whole fish were, in general, elevated compared to data from the Scandinavian and European alpine lake surveys. The median concentrations varied between 3.7–125 ng/g, with a sample range 0.1–448 ng/g. The medians (and range) of PBC concentrations in burbot liver were 96–103 ng/g (27–1630 ng/g), i.e. somewhat lower than the levels from the Norwegian survey.

4.1.4 Chlorobenzenes and hexacyclohexane

The concentrations of chlorobenzenes (CBs) and hexacyclohexane (HCH) were in general relatively low and within the same range as the dieldrin concentrations. However, in the BEST surveys from the conterminous USA, all the samples of these POPs had concentrations lower than a rather high detection limit of 10 ng/g.

In the Canadian TSRI study (Muir et al. 2003a), the median concentrations (and sample range) of CBs and HCH in whole fish were 0.3–1.8 ng/g (0.01–10.4 ng/g) and 0.1–0.6 ng/g (0.01–52.5 ng/g), respectively.

Data on these two POPs in fish from European surveys are also scarce, but the Norwegian survey (Fjeld et al. 2001) and the European alpine lake survey (Vives et al. 2004) showed median concentrations (and sample range) in trout and arctic char to be about 0.3 ng/g (0.05–1.5 ng/g) for CBs, and about 0.2–0.3 ng/g (0.1–16 ng/g) for HCH. The concentrations in burbot liver from Norwegian lakes were substantial higher: 14.2 ng/g (1.9–24 ng/g) for CBs, and 7.5 ng/g (1-32 ng/g) for HCHs. The Norwegian survey (Fjeld et al. 2001) shows that higher concentrations in burbot liver as compared to brown trout and arctic char are related to the high lipid content of its liver and the food habits of this species (burbot is fish-consuming top predator).

In the arctic surveys, the median concentrations (and sample range) of CBs in fish were 0.02–2.03 ng/g (0.004–6.7 ng/g), whereas the corresponding statistics for HCH were 0.7–4.05 ng/g (0.1–5.1 ng/g). The concentrations in burbot liver from arctic lakes were about 6.3–12.3 ng/g (0.5–12.8 ng/g) for CBs, and 4–8 ng/g (1.5–50.4 ng/g) for HCH, which is comparable to those reported in the Norwegian survey (Fjeld et al. 2001).

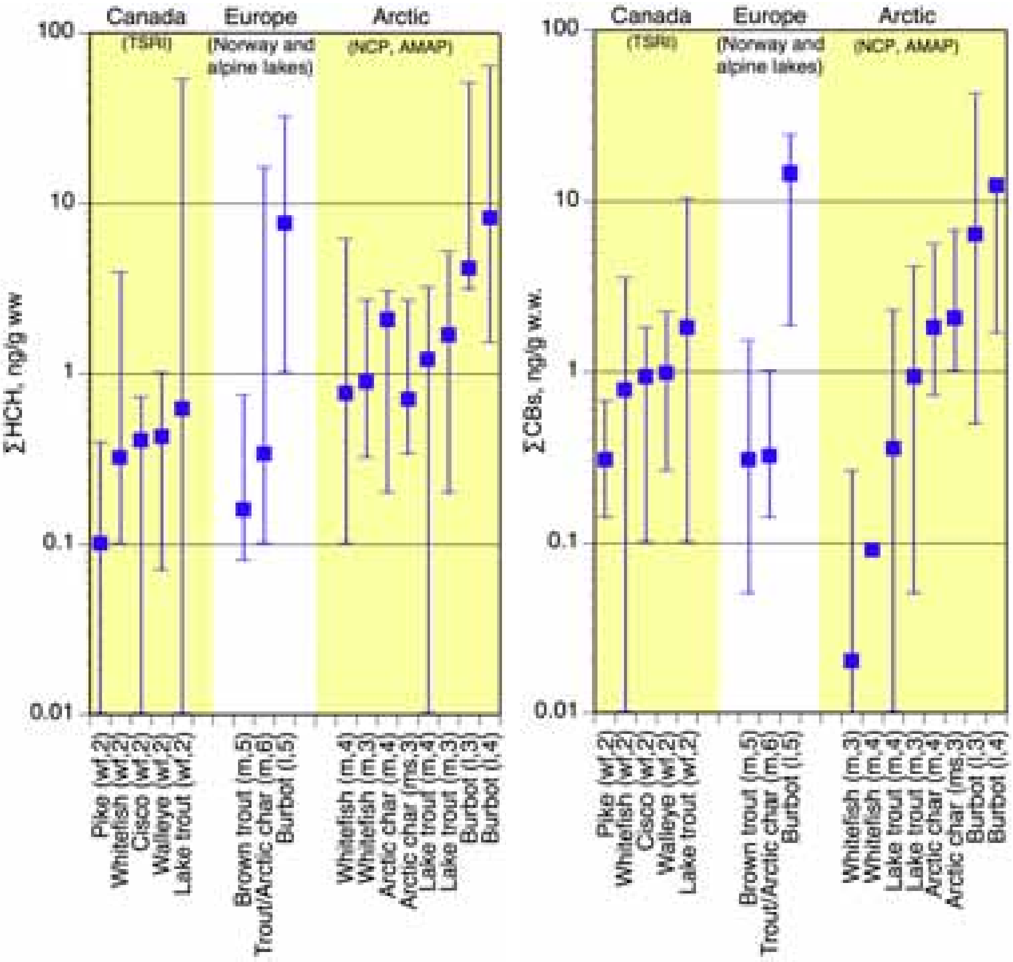

Figure 7. *Concentrations of hexacyclohexane (ΣHCH, sum of different isomers) and chlorobenzenes (ΣCBs, sum of compounds) in freshwater fish. Median values: square symbols. Sample spread: vertical bars. The sample matrix and the data sources are coded in the category axis labels. Sample matrix: wf, whole fish; m, muscle; ms, muscle with skin; l, liver. Statistics for the BEST program are based on several species. Data sources (see appendix): 1, BEST; 2, TSRI; 3, NCP; 4, AMAP; 5, Fjeld et al. (2001); 6, Vives et al. (2004).*

4.1.5 Polycyclic aromatic hydrocarbons, PAHs

Fish do not accumulate PAHs to any significant degree, but metabolise PAHs and excrete the metabolites. This lack of accumulation in fishes prevents exact determination of exposure using traditional analyses. An example of this is given by the EMERGE project on European alpine lakes. Despite of the large variability in the PAH concentrations in surface sediments of more than two orders of magnitude (12–7500 ng/g dw), which reflects different PAH loadings to the lakes, the PAH concentrations in fish liver (population means) only varied five-fold, from 8.8 to 44 ng/g ww (Vives et al. 2004) (Figure 8). Significant correlations between PAH concentrations in liver and lake sediments could not be detected. Adjusting for differences in the sediments organic content and lipids in liver did not change this picture.

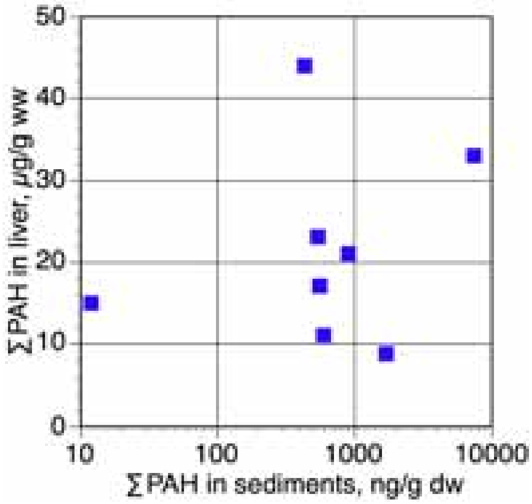

Figure 8. *Scatter plot of PAH concentrations in lake sediments (dry weight) and fish liver (population means, wet weight). Data from European alpine lakes and an arctic lake (Vives et al., 2004).*

4.1.6 Polybrominated diphenylethers, PBDEs

Although polybrominated diphenylethers (PBDEs) have been in use commercially as flame retardants since the mid 1970s, it is often mentioned as a “new” POP, and has only in the recent years been included in the more comprehensive environmental surveys. There are therefore far less data on PBDEs than on the other so-called “legacy” POPs.

We have used data from four different studies to illustrate the range in the concentrations of PBDEs in North America, and these show that the background levels and levels in exposed fish populations may differ by more than three orders of magnitude (Figure 9). A survey from the Columbia River system (Rayne et al. 2003) showed concentrations in the range of 1–72 ng/g, with the highest concentrations in whitefish from the mainstream river, and the lowest concentrations in nearby pristine watershed affected only by atmospheric deposition. More extreme variations were found in Washington State freshwater fish (Johnson and Olsson 2001, where concentrations varied from 1.4 ng/g in rainbow trout from a remote site to 1 250 ng/g in mountain whitefish from an urbanized river. From the northeastern USA, Dodder et al. (2003) have reported background concentrations in the range 6.9–18 ng/g and 65 ng/g in a lake close to a suspected source. From Lake Michigan, Manchester-Neesvig et al. (2001) have reported PBDE concentrations in lake trout in the range of 45–150 ng/g.

In European surveys, the background PBDE concentrations seem to be lower than for the North American studies. A study from Sweden on perch reports a median concentration (and range) of 0.1 ng/g (0.06–0.33 ng/g) (Sternbeck et al. 2004). Similar statistics for concentrations in remote alpine populations of trout and arctic char were 0.27 ng/g (0.07–1.1 ng/g) (Vives et al. 2004b). A study from Switzerland showed the median concentration (and range) of PBDEs in whitefish from lakes in populated areas to be 2.7 ng/g (1.6–7.4 ng/g) (Zennegg et al. 2003). The lakes were not affected by discharges from major point sources of PBDEs, and the authors suggested that atmospheric deposition was an important pathway.

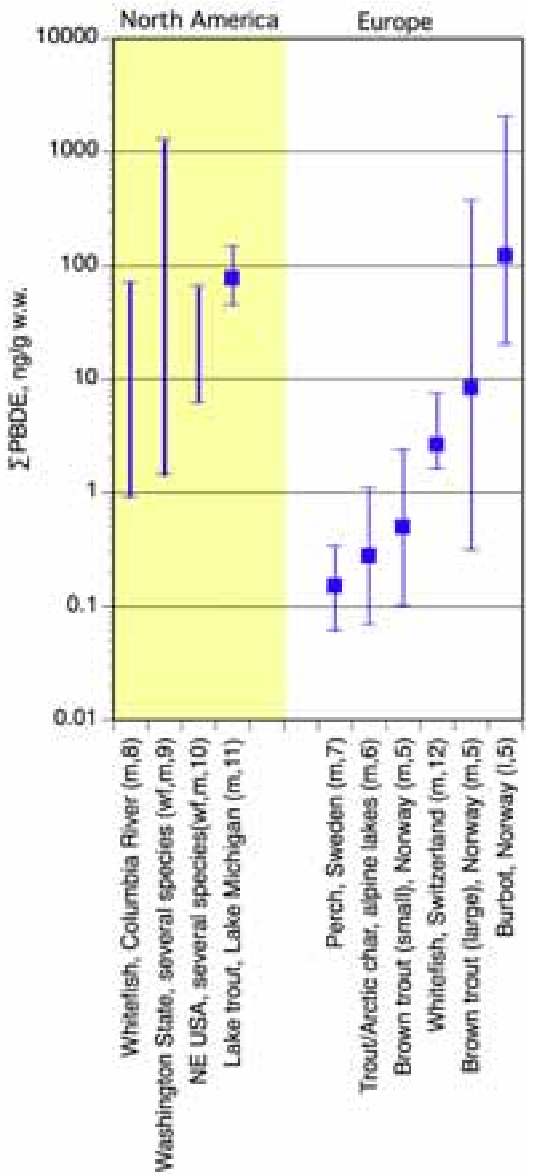

Figure 9. *Concentrations of PBDE (sum of different congeneres) in freshwater fish. Median values: square symbols (medians were not available for all surveys). Sample range: vertical bars. The sample matrix and the data sources are coded in the category axis labels. Sample matrix: wf, whole fish; m, muscle; ms, muscle with skin; l, liver. Statistics for the BEST program are based on several species. Data sources (see appendix): 5, Fjeld et al. (2001); 6, Vives et al. (2004); 7, Sternbeck et al. (2004); 8, Rayne et al. (2003); 9, Johnson and Olsson (2001); 10, Dodder et al. (2003), 11, Manchester-Neesvig et al. (2001); 12, Zennegg et al. (2003); 13, Mariussen et al. (2003).*

Norwegian studies on brown trout have found a median concentration in small invertebrate-feeding populations of 0.49 ng/g (range: 0.1–2.36 ng/g) (Fjeld et al. 2001), while the concentrations in large fish-eating populations were significantly higher with a median value of 8.3 ng/g (sample range: 0.3–367 ng/g) (Mariussen et al. 2003). Except for a population with the extremely high concentration, none of the others were affected by major local PBDE discharges. The median concentrations can therefore be regarded as background levels. The higher concentrations of PBDEs in the populations of large-sized fish compared to populations of small fish are probably a biomagnification effect. Analyses of burbot liver showed a median concentration of 121 ng/g (range: 20.3–1995 ng/g). Only the population with the extremely high PBDE concentration was affected by a major point source and the median concentration can therefore be regarded as a background value.

The data from the Norwegian national survey of POPs in freshwater fish (Fjeld et al. 2001) demonstrates a negative south-north trend in the PBDE concentrations (adjusted for differences in lipids) in fish populations from lakes without major point sources (Figure 10). It is likely that this spatial trend reflects a south-north decrease in atmospheric depositions of PBDEs.

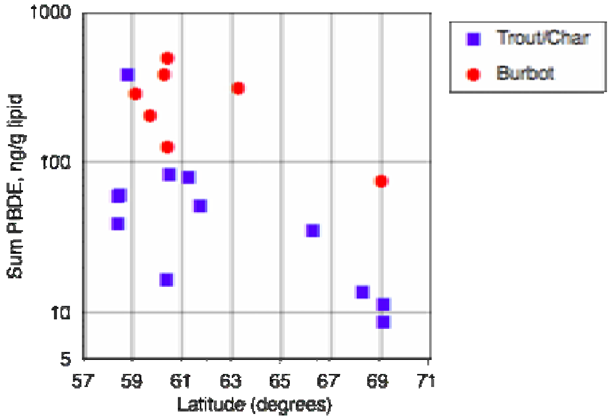

Figure 10. *PBDEs in fish populations (ng/g lipid) from Norway along a south-north gradient. Data from Fjeld et al. (2001).*

4.1.7 Short chained paraffins, SCCP

There are few recent studies on the occurrence of short chained paraffins, SCCP, in freshwater biota, especially from waters unaffected by local point sources.

Tomy et al. (1997) analyzed yellow perch and catfish from the Detroit River and found SCCP concentrations of 1100 and 300 ng/g, respectively (Figure 11). From western Lake Ontario, Muir et al. (2001) found mean SCCP concentrations in lake trout to be 59–73 ng/g and in carp to be 2600 ng/g.

Norwegian studies on brown trout and arctic char have found a median concentration of 6.0 ng/g, with a sample range of 2.7–22 ng/g (Fjeld et al. 2001). For samples of burbot liver, the median concentration was 153 ng/g, and the sample range was 86–1480 ng/g. The higher concentrations in burbot liver are caused by its high lipid content and the food habits of this species (fish-consuming top predator). These median values can be regarded as the background levels, as most of the populations – except those with the highest concentrations – were unaffected by local point sources.

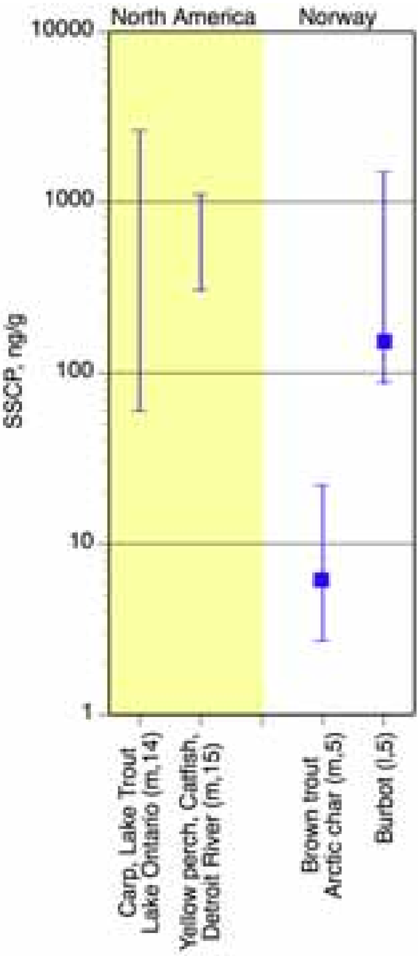

Figure 11. *Concentrations of short chained paraffins (SCCP) in freshwater fish. Median values: square symbols (medians were not available for all surveys). Sample range: vertical bars. The sample matrix and the data sources are coded in the category axis labels. Sample matrix: wf, whole fish; m, muscle; ms, muscle with skin; l, liver. Statistics for the BEST program are based on several species. Data sources (see appendix): 5, Fjeld et al. (2001); 14, Muir et al. (2001); 15, Tomy et al. (1997).*

4.1.8 Perfluorinated alkylated substances, PFAS

Research on the environmental occurrence of perfluorinated alkylated substances (PFAS) has been conducted mainly during the last years, although these chemicals have been in commercial use for about 50 years. Perfluorooctane sulphonate (PFOS) is commonly the dominating PFAS in freshwater fishes, and the liver seems to be a target organ where it accumulates in especially high concentrations. In Figure 12 we have presented a selection of some recent results from studies on the occurrence of PFOS in freshwater fishes.

From Lake Ontario, Martin et al. (2004a) reported PFOS concentrations in whole body homogenates of fish in the range of 46–450 ng/g, and it was shown that bioaccumulation was occurring at the top of the food web. Kannan et al. (2005) found a similar concentration range in the liver of fish from Lake Michigan waters (9–350 ng/g), and the data similary indicated a significant biomagnification of PFOS. From 20 inland lakes in New York State, Sinclair and Kannan (2005) reported that PFOS concentrations in fish liver ranged from 3 to 315 ng/g.

From two lakes in Arctic Canada, Martin et al. (2004b) reported PFOS concentrations in fish liver in the range of 5.7 to 50 ng/g.

In a survey of PFAS in the Nordic environment, Kallenborn et al. (2004) reported about PFOS concentrations in freshwater fish liver in the range of 8–432 ng/g, with the highest concentrations in fish caught in the vicinity of a sewage treatment plant. However, the concentrations in the edible parts of the fish seems to be significant lower, and a Norwegian survey (Fjeld et al. 2005) reported PFOS concentrations in muscle fillets in the range <0.002 ng/g to about 4 ng/g, with the lowest concentrations in brown trout from an alpine remote lake and the highest concentration in perch from a lake from a populated area.

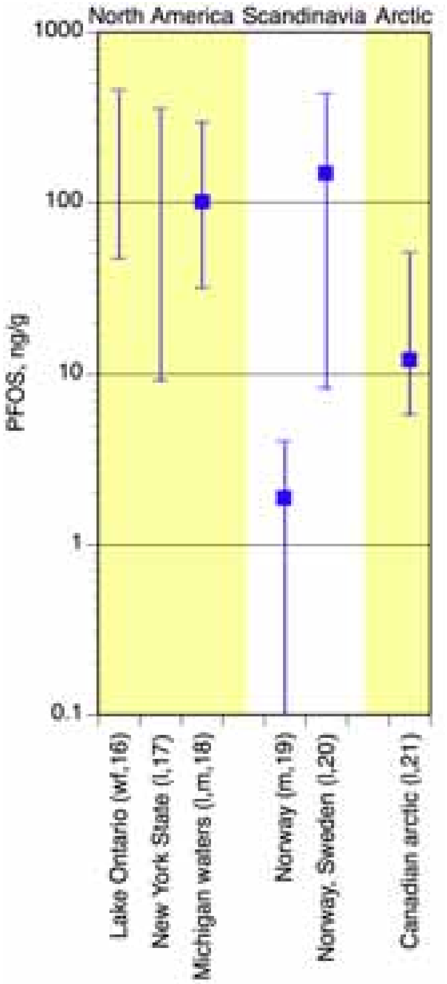

Figure 12. *Concentrations of perfluoroalkyl sulfonates (PFOS) in freshwater fish (various species). Median values: square symbols (medians were not available for all surveys). Sample range: vertical bars. The sample matrix and the data sources are coded in the category axis labels. Sample matrix: m, muscle; l, liver. Data sources (see appendix): 16, Martin et al. (2004a); 17, Sinclair and Kannan (2005); 18, Kannan et al. (2005); 19, Fjeld et al. (2005); 20, Kallenborn et al.(2004); 21, Martin et al. (2004b).*

4.2 Time trends

4.2.1 POPs in fish from Swedish reference lakes

There exists few long time series of POPs in freshwater fish from lakes with LRTAP as the only pollution source. However, the Swedish monitoring program for freshwater biota has produced some exemplary time series on legacy POPs in fish populations from different parts of the country (Bignert 2002). These time series are probably the world longest time series of their kind.

Analyses of long time series of PCB concentrations in pike from Lake Bolmen (1967–1997) and Lake Storvindeln showed significant decreasing yearly rates of about 5% and 4.5%, respectively (Figure 13). These two lakes are unaffected by local pollution sources, and they are situated in southern and northern Sweden, respectively. The recent levels in the southern lake are about two times higher than in the northern lake. These data, together with other time series on char and roach, indicate that the decreasing trend is levelling out, but the time series are too few to make any convincing conclusions for the latest decade.

Similar long time series of DDT concentrations showed significant decreasing trends from Lake Bolmen (1967–1997) and Lake Storvindeln (1968–1997) with yearly rates of about 9% and 8%, respectively (Figure 14). As for the PCBs, the DDT concentrations seemed to decrease with latitude, as the concentrations in fish from Lake Bolmen were approximately three times higher in than in Lake Storvindeln, even in 1998.

The concentrations of α-HCH in pike from Lake Bolmen (1988-1996) and Lake Storvindeln (1968–1996) showed significant decreasing mean trends of about 10% a year. A similar decreasing trend (11%) was found for lindane (γ-HCH) in pike from lake Bolmen , whereas the concentrations in pike from lake Storvindeln dropped from a level about 30 ng/g lipid in 1968–1988 to a level close to or below the detection limit (≈ 0.05 ng/g lipid) in 1995.

The concentrations of HCB in pike from Lake Storvindeln (1968-1998) decreased significantly with a mean rate of about 5% a year, whereas no significant trend was found for pike from Lake Bolmen. The decreasing trend for Lake Storvindeln seems to have leveled out the last ten years, as there was no significant change in the concentrations during this period.

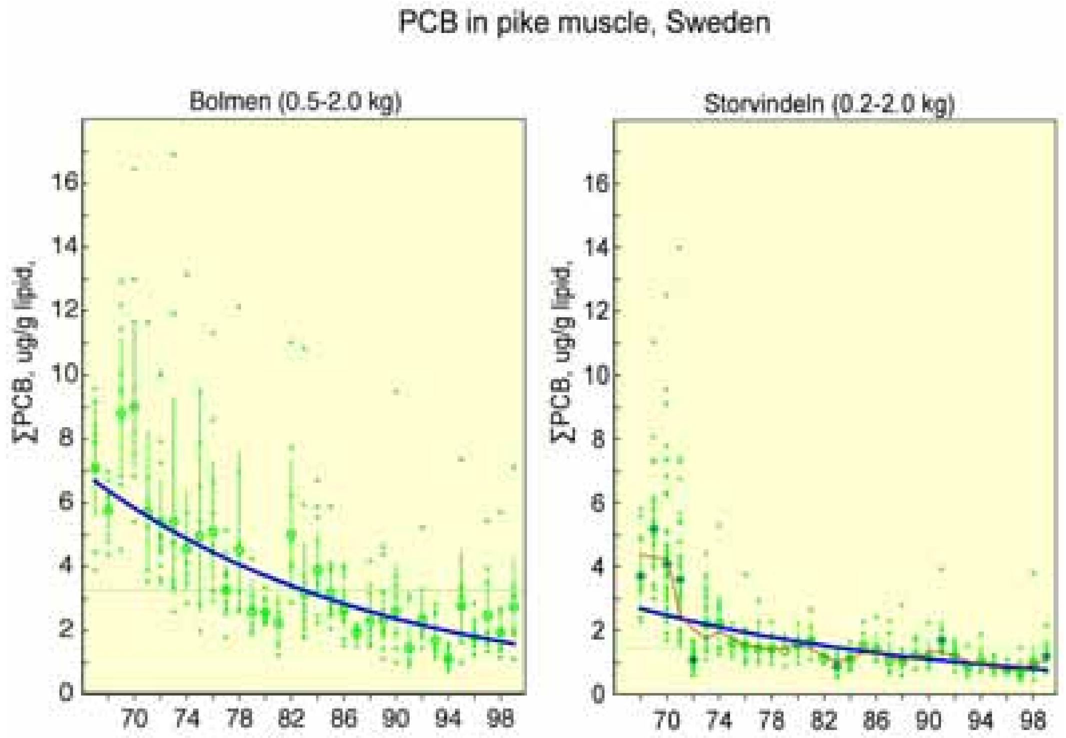

Figure 13. *Time series of PCBs in pike muscle (μg/g lipid) from Lake Bolmen (southern Sweden) and Lake Storvindelen (northern Sweden). Redrawn after Bignert (2002).*

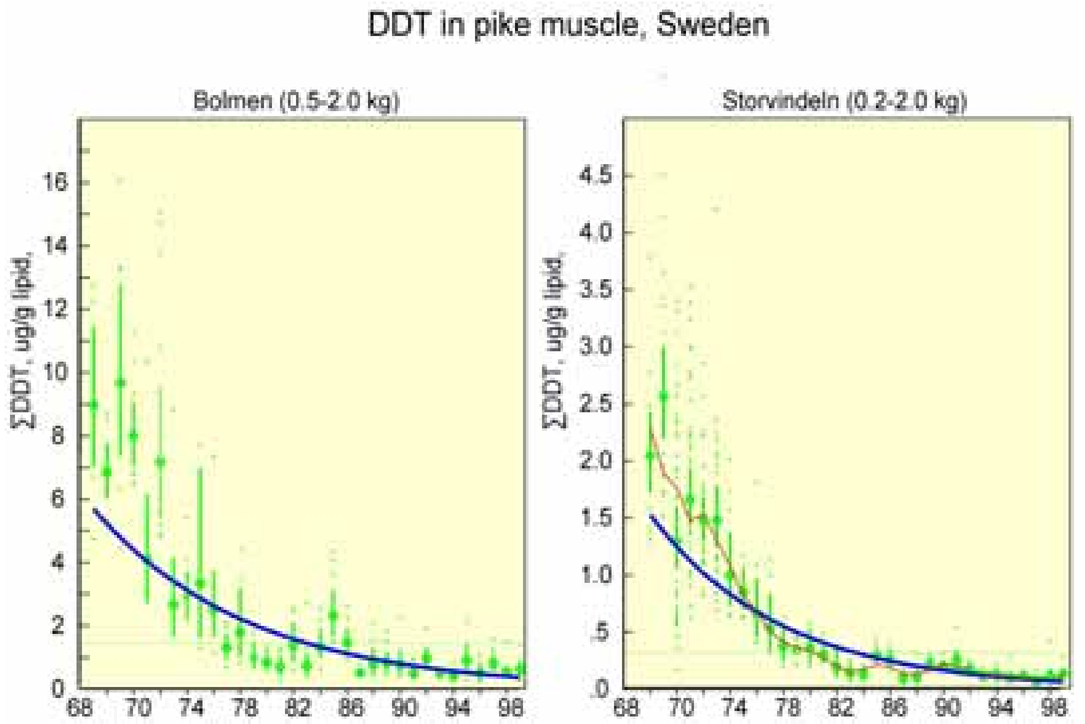

Figure 14. *Time series of DDT in pike muscle (μg/g lipid) from Lake Bolmen (southern Sweden) and Lake Storvindelen (northern Sweden). Redrawn after Bignert (2002).*

4.2.2 POPs in lake sediment cores

Sediment cores from remote lakes without local pollution sources can be used as an environmental archive for the study of atmospherically deposited pollutants. By dating the sediments, valuable information on time trends, current inputs and sources can be provided. In the following we have presented some results which illustrates this

In a study of the Scottish alpine lake Lochnagar, Rose et al. (2001), revealed the historical profile of toxaphene (Figure 15). This pesticide has never been in use in the UK. The profile showed a dramatic increase in the beginning of the 1960s, reached its maximum concentration around 1990, and decreased rapidly after this. The double-peaked profile correlates with the production in the former East Germany and the USA, and it suggests that the main pathways were atmospheric inputs from both east Europe and North America.

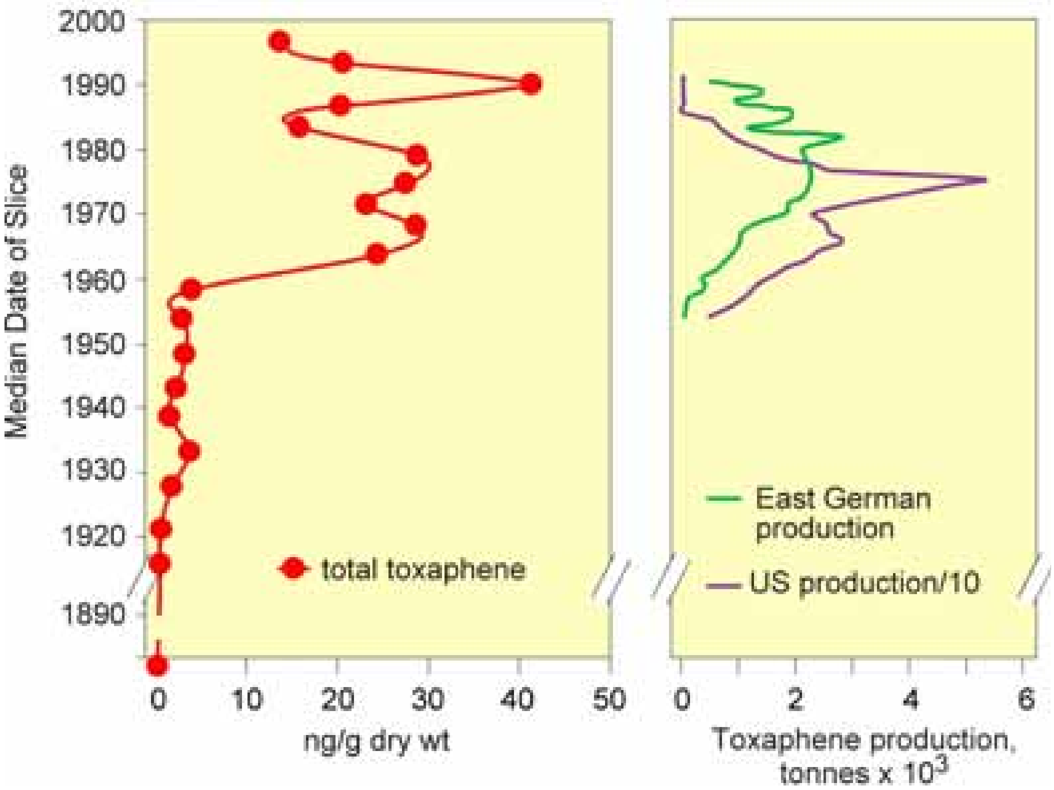

***Figure 15.** Concentration of toxaphene in dated sediments from Lake Lochnagar, Scotland (left panel) and the historical production of toxaphene (right panel). Redrawn after Rose et al. (2001).*

In a survey of Canadian lake sediments by Muir et al. (2002b), historical profiles of POPs in several lakes were revealed. Although the historical pattern differed in each core, some common features were apparent: a significant increase in the levels of PCBs and DDT generally began in the 1940s and maxima were reached in the 1970s in most cores. Examples on such historical profiles are given in Figure 16.

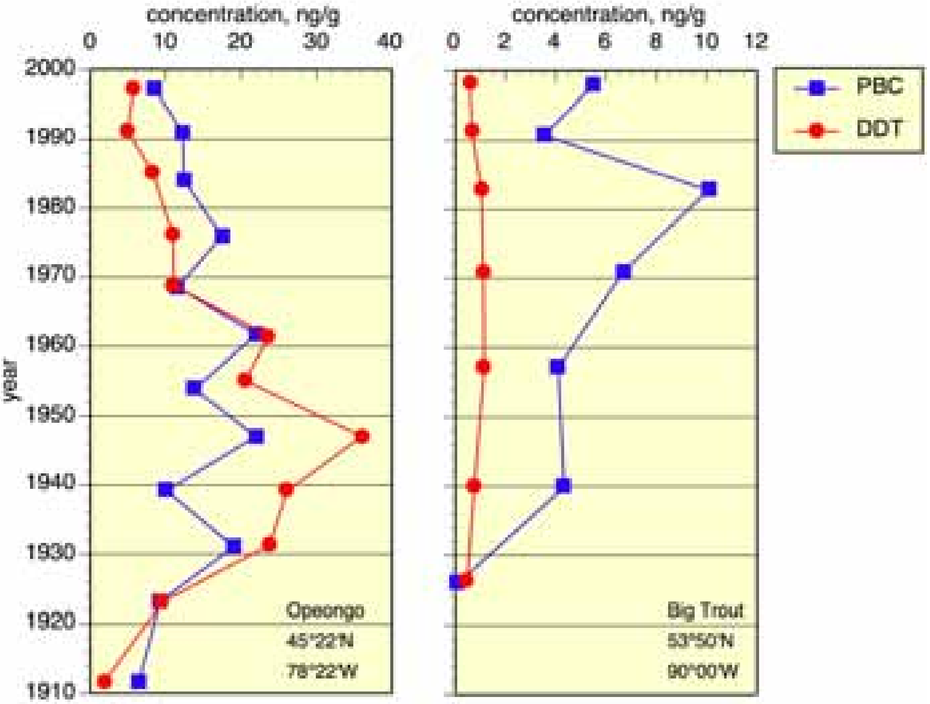

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Figure 16. *Concentration of ΣDDT and ΣPCBs in dated sediment cores form Canadian lakes without local pollution sources. Redrawn after Muir et al. (2002b).*

Brominated flame retardants of the type PBDEs were also analyzed in a selection of cores in the survey of Muir et al. (2002b). PBDEs were detected only in the recent sediment layers of all cores. An example of this is given in Figure 17, where we have plotted the fully brominated congener BDE-209 in a sediment core. BDE-209 was in general first detected in the sediment layers deposited in the 1970s, which corresponds to the years when the commercial use of PBDE started. In the sediment core presented in Figure 17, BDE-209 was found also in a deeper sediment layer, which may be due to more intensive bioturbation (mixing of the sediments due to the activity of bottom dwelling organisms) in this core than in the others. BDE-209 is highly sorbed to particles and thus susceptible to particle mixing.

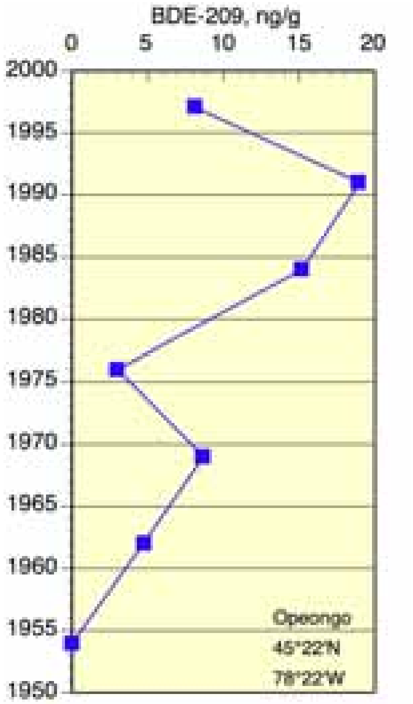

Figure 17. *Concentration of BDE-209 (a polybrominated diphenyl ether, a flame retardant) in dated sediment cores from Lake Opeongo (Ontario, Canada). Redrawn after Muir et al. (2002b).*

5. Environmental pathways and multimedia models

5.1 Aims of multimedia models

Currently the European Inventory of Existing Chemicals (INECS) contains about 100,000 substances of which about 20,000 are produced in amounts exceeding 10 tonnes/yr. Governmental organizations, scientific experts, and the Agenda 21 have demanded an acceleration of the assessment of these substances. There are a number of criteria that can be used for this assessment. According to the Stockholm Convention and the Aarhus Protocol, bioaccumulation, persistence, potential for long range transport and toxicity are the four main parameters to consider in order to evaluate whether the substance is to be classified as undesirable or not.

Many properties of the substance, the environment and living organisms that influence the fate of an organic substance once it has been emitted to the environment. These properties are too numerous for the human mind to deduce how the substance is going to behave.

It is possible, however, to measure the dispersion, toxicity, bioaccumulation or persistence in the field by analyzing samples taken in the environment. This approach is the only one that can be used to verify hypotheses about a pollutant's fate, but it has some major drawbacks. First, any sampling gives only an image of the situation that exists at one point in time and in space. Second, it is not possible to evaluate by these means the fate of a new substance or of a substance that has not been released for a long time. For new substances or for substances for which analytical techniques may not be available, sampling in the environment will not provide any information on substances fate in the environment.

Multimedia models have been designed to fill this gap of knowledge and understanding. Their aim is to evaluate the fate of compounds in the environment and to do it rapidly, for a wide range of chemicals and a wide range of environments, so that that the policy maker's demand may be satisfied. Thus, while representing as many processes as it is nowadays possible to do, these models calculate transfers of compounds between air, soil, water and living organisms, deduce the expected concentrations or the relative proportions between the compartments and calculate both persistence and potential for long range transport. They could therefore become useful in the framework of international protocols.

5.2 Multimedia models principles

Multimedia models are based on present understanding of exchange processes between solid, aqueous and gaseous phases. Although for some substances these processes may be very well described in the scientific literature there is a lack of experimental data for many substances and many environmental conditions. It is known, for instance, that most chemicals will adsorb differently onto sand and clay and that exchange processes are temperature dependent. The exact reasons as to why this is may however not be known or it may not be possible to translate them into mathematical equations.

Therefore to keep with their aims, multimedia models have been designed to be generic: the whole complex environment is usually described by a small number of homogeneous compartments, whose properties average the properties of the environment that is to be represented. Such a representation is not accurate but it remains realistic. Thus, it is possible to describe a state such as Ohio or Greece with only four compartments, one for the soil, one for the atmosphere, one for freshwater and one for its sediment as is done in EQC, one of the simplest multimedia models. This model requires relatively few parameters mainly: compartments dimensions, density, particle(s) concentrations, the organic content of each solid phase, advection rates in wind and water and the mass transfer coefficients that represent the net diffusion velocity of the substance between compartments (Mackay, 2001; Mackay et al., 1996a).

The substances are equally described by a small number of physico-chemical parameters. Some express the tendency to partition between phases (e.g., Henry law's constant, octanol-water partition coefficient Kow) whereas others express the molecular tendency to remain or to react in one compartment (e.g., half lives in the different compartments). This data may not always be available or may be known only with large uncertainties (e.g., Kow, half lives), but whether models are used or not, they are required to perform any assessment in the international legislative framework. Both the environment and the substance properties are likely to change in time. However, in order to keep the models simple and to reduce data requirement, most multimedia models are either designed to represent a state of equilibrium or a steady state. Mackay has defined four levels of modelling:

- Level I calculations assume steady state and equilibrium between phases in a close system in which there are no degradation processes. These types of models provide information about the compartments in which the substance partitions.
- Level II calculations also assume steady state and equilibrium but the system is open so that input to and output from the system are permitted. Degradation processes can be described. These types of models provide an approximate value of persistence and information on the main loss mechanisms.
- Level III calculations assume steady state but not equilibrium. Instead, they take into account diffusion processes within each phase. These processes potentially slow down exchanges between phases since they limit the concentrations of substances at the interfaces. These types of models give information on the relative importance of transport mechanisms, on persistence and on potential for long range transport. In level III calculations, results depend on the mode of entry: It must therefore be specified in which compartment the substance is emitted.
- Level IV calculations are dynamic calculations and the only ones that take temporal variations of the environment into account. These types of models provide information on concentrations evolution with time.

Whichever the level, all multimedia models are based on mass balance calculations:

Mass variation = inputs – losses – degradation

Inputs usually represent substance emission into the system. In Level III and IV models, results for persistence and long range transport potential depend on the compartment(s) that receives this emission. Inputs can also be an advected substance from outside the considered system. In such situations, no pollution issue can be solved solely by reducing local sources and solutions have to be sought at a global scale.

Losses can be by advection out of the compartment (such as transport by water or by air in and out of the considered compartment, burial in sediments, etc...). Advection out of a compartment leads to a lower threat around the source but it is really a displacement of the problem as long as the compound remains in the global environment. This is why long-range transport potential has been included as a criterion.

The degradation of a substance is understood to be a change of its chemical structure (and subsequently the CAS number that it is allocated). This can be caused by physico-chemical processes (e.g. hydrolysis, photolysis, atmospheric oxidation reactions, aqueous oxidation and reduction) or biological reactions (often by microbial organisms). Although in multimedia models, once a substance is degraded it is considered that it is "gone" from the environment, the model user must consider whether daughter compounds represent a new risk: some daughter compounds can be more toxic and more persistent than the substance itself (e.g. DDE from DDT).

In the models considered here, all degradation mechanisms are supposed to follow first order kinetics and concentrations can therefore be calculated using the following equation:

$$C = C_0\, e^{(-kt)}$$

C: Concentration
C_0: Initial concentration
k: degradation rate
t: time

Degradation rates (described by the degradation constant k or the half-life: $t_{1/2} = \ln 2/k$) range between hours and years and this influences the time the compounds remain in the environment. Often, degradation is slowest in soil and sediments and fastest in atmosphere. This means that a substance emitted in soil, if it has some affinity with particles, may have a greater persistence than if emitted in the atmosphere, where it may be degraded before it is deposited to soil and water. Such a mechanism is represented in Level III models, in which it is therefore important to specify the substance entry route in the environment.

5.2.1 Meaning of the results

Overall persistence, as calculated by multimedia models, gives an indication of the length of time a substance may remain in the global environment. This metric gives more complete information than the half-lives in each compartment since its calculation takes into account altogether the half lives in all compartments and the partitioning between them. There is a broad consensus for using this parameter as a descriptor of persistence. The impact of a substance far from its source can be considered with two types of models (Fenner et al., 2005)

- Target oriented models: They evaluate how much of the substance emitted reaches a target located far from the substance source. The targets can be lakes (as in the BETR model) or arctic zones (as in the GloboPOP model) (MacLeod et al., 2001; Wania and Mackay, 2000).
- Transport oriented models: the priority is given to the simulation of transport in the atmosphere and/or in water. This type of models calculates either the distance an emitted molecule may travel on an open scale (numbers of kilometers, e.g.: ELPOS, Caltox, SimpleBox) or on a closed scale (from 0 to 0.95. e.g.: ChemRange) (Beyer and Matthies, 2002; Den Hollander et al., 2004; McKone and Enoch, 2002; Scheringer, 2002).

Target oriented models are useful for gathering information on substances that are likely to be deposited after they have been transported. This deposition is often caused by temperature differences. At temperate climates, air temperatures are relatively high and the substance relatively volatile. It partitions significantly to the atmosphere in which it can travel towards regions where the temperature is lower. There, its volatility decreases and it is deposited to soil and water. If the temperature increases again (e.g. during the day or during the summer), the substance may again volatilize and be carried further in the atmosphere. This transport-deposition process can be repeated several times and the substance may progressively reach regions such as the arctic where the temperatures are low enough for the substances to be trapped. This is the grasshopper effect described by Wania and simulated by GloboPOP.

One main difference between target and transport oriented models is apparent for very volatile substances, such as CCl_4. These types of chemicals can travel over long distances in the atmosphere. This has been shown by field measurement and leads to a high potential for long range transport calculated by transport oriented models. However, since the volatility of this type of substance is very high, even at low temperature, they may not deposit again: Their potential for long range transport calculated by target oriented models would therefore be relatively low.

The potential for long range transport is calculated in a number of different ways by the different models. For instance, ELPOS calculates the characteristic travel distance (CTD) as the distance from the source at which the substance concentration has dropped from its initial concentration C_0 to C_0/e (Bennett et al., 1998). When the persistence and the CTD are calculated for emissions into air, it has been shown that in steady state conditions the following equation applies (Beyer et al., 2000):

CTD = Wind speed x Persistence x fraction of substance in air

Thus, CTD is a distance usually expressed in km, and can, for some compounds, be longer than the earth circumference. This implies that a molecule can go around the earth several times before it is deposited. This clearly implies a high potential for dispersion in the atmosphere.

For ChemRange, the potential for long range transport is called the spatial range and it is calculated as the percentage of the earth circumference over which 95% of the emitted substance can be found (Scheringer, 1996). The result ranges from 0 to 0.95.

From these definitions, it becomes clear that the potentials for long range transport of two models are expressed by numbers that cannot be directly compared. However, it has been shown that if substances are ranked by different models using different long range transport potential metrics, the ranking order is relatively constant from one model to the other (Fenner et al., 2005).

Multimedia models can also be used to evaluate into which compartment a substance tends to partition. Models give this information as concentration, as mass or as proportion of the total emitted substance in each compartment. These results are very dependent on compartment volumes and therefore must be interpreted with care.

5.2.2 Uncertainties in results:

Validation of multimedia model results is difficult because of their generic character: As explained earlier, the environment is described by average properties and it is therefore usually not possible to find a site in the real environment whose characteristics are closely described by the model. It is therefore unlikely to obtain field measurements that compare well with model results.

Moreover, most multimedia models simulate a steady state world with constant properties whereas in the actual world, substance releases are started and discontinued, seasons and temperature continuously cycle, and wind, river flows, oceanic currents and rain also vary continuously.

Yet, the results of multimedia models have been shown to represent well the tendencies observed for a number of compounds for which field measurements have been carried out (Mackay et al., 1996b; Muir et al., 2004; Pederson et al., 2001; Shen et al., 2004-2005). Moreover, the concordance between model results is also a support for their validity.

Modellers however acknowledge several sources of uncertainties in multimedia models (Beyer and Matthies, 2001; Hertwich et al., 2000; Leßmann, 2002; OECD, 2004):

- Uncertainties due to the limited knowledge of some processes that cannot therefore be represented. Such a source of uncertainty cannot be quantified and will be similar in most models.
- Uncertainties due to the modeller’s choice to represent or not some processes or to his choice of parameterisation. These uncertainties lead to differences between model results and are more or less important depending on the processes and on the substance. They are also difficult to quantify but they can be identified by comparing model results. Hence, different results are to be expected:
    - ⇨ for the most volatile substances between target oriented models and transport oriented;
    - ⇨ for water soluble substances between models that couple transport in air and in water (ChemRange) and those that do not (ELPOS);
    - ⇨ for particle bound substances between models that simulate degradation on aerosols and those that do not;
    - ⇨ for particle bound substances again between models that simulate degradation in sediment (ELPOS) and those that do not (ChemRange);
    - ⇨ for all substances between models with different compartment nature, sizes, and land to water area ratio.
- Uncertainties due to the environment’s natural variability. Again, these are difficult to quantify but can be evaluated by comparing results for different scenarios (e.g. different rain rates, temperature, emissions, wind and current speed…)
- Uncertainties due to uncertainties in input parameters. Theese can be quantified, if the input parameter uncertainty is known. As a result, most uncertainty analyses focus on this type of model uncertainty, which may lead to a narrow approach of uncertainties. Yet, these studies are useful and have shown the high dependency of the model results to a number of input parameters for which it would be necessary to improve the accuracy. For emission to air, the substance properties to which the calculation of long range transport potential is particularly sensitive are half lives in air, vapour pressure and water solubility. On the other hand, the evaluation of persistence is sensitive to half lives in air and in soil,

Kow and the vapour pressure (OECD, 2004). Unfortunately, large uncertainties are often associated to these parameters.

5.3 A suggestion on the use of multimedia model as a screening tools

Work and reflection about how to use multimedia models as screening tools in a legislative framework is on-going (Fenner et al., 2005; Klasmeier et al., 2005; OECD, 2004). Here, we present some suggestions on how relevant information can be obtained from these types of models. This is done with the help of a small series of chemicals arbitrarily selected out of the priority chemicals of the EU Framework Directive (1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, anthracene, benzo[a]pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, naphthalene and two polybrominated diphenyl ethers (BDE 15 and BDE 153)). A series of 4 chemicals listed as POPs by international conventions (CB 28, CB 180, a-HCH, HCB) are also included in the calculations. The results for these known POPs and for priority chemicals of the EU water framework directive can thus be compared.

The models can be used to evaluate the chemicals following two approaches:

1. How persistent and likely to be transported over long distance are the substances?
2. In which compartment are the substances likely to be found after their emission?

The two approaches are going to be treated one after the other, although the same model runs are used. The same data set is also used in both cases. Gathering the data is often the step that is the most time consuming.

5.3.1 The models used

In this example, calculations were carried out with two models: ChemRange and ELPOS (version 1.01). Both are Level III transport oriented models, but ChemRange uses a closed scale whereas ELPOS gives its results on an open scale. In ChemRange, environment compartments describe the whole earth (with 70% of its surface being water) whereas the size of ELPOS compartments are that of the generic regional distribution model of EUSES. Both models are extensively described in the literature and have been used in the OECD model intercomparison (OECD, 2004; Scheringer et al., 2004; Stroebe, 2003).

5.3.2 Data

Data given here (Table 4 and Table 5) have been gathered from various sources. Considering the number of sources for such data and the variability between them, it would probably be possible to obtain a different data set for these compounds. When the half-life in sediment was not available, the value was set equal to the half-life in soil. This is proposed as a working example and not as a reference data set. The environmental conditions used were the standard conditions of the two models (ELPOS and ChemRange). The emissions were set to 100 kg/d for all substances.

Table 4. Physico-chemical proprieties of test substances. Numbers in italics refer to the data source: 1: HSDB (http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB); 2: ASTDR (http://www.atsdr.cdc.gov/toxpro2.html#-P-); 3: Wania and Dugani, 2003; 4: INERIS (http://chimie.ineris.fr/en/index.php); 5: Mackay et al., 1992; 6: Klasmeier et al., 2005; 7: CAS registry. #: Value set equal to the soil half-life.

Substance name	**CAS**	**Molecular weight**		**Melting point**		**Log Kow**		**Kaw**		**Vapour pressure**	
		g/mol		**°C**				**-**		**Pa**	
1,2,3-trichlorobenzene	87-61-6	181	*1*	54	*1*	4.10	*1*	1.14E-01	*1*	2.80E+01	*1*
1,2,4-trichlorobenzene	120-82-1	181	*1*	17	*1*	4.02	*1*	1.43E-01	*1*	6.13E+01	*1*
anthracene	120-12-7	178	*1*	218	*1*	4.45	*1*	5.90E-04	*1*	3.56E-04	*1*
Benzo(b)fluoranthene	205-99-2	252	*2*	168	*2*	6.60	*1*	5.66E-03	*1*	6.67E-05	*1*
Benzo(k)fluoranthene	207-08-9	252	*1*	217	*1*	6.84	*1*	1.73E-05	*1*	1.29E-07	*1*
benzo[a]pyrene	50-32-8	252	*1*	179	*1*	5.97	*1*	4.66E-05	*1*	7.32E-07	*1*
naphthalene	91-20-3	128	*1*	80	*1*	3.30	*1*	1.89E-02	*1*	1.13E+01	*1*
BDE 15		328	*3*	58	*3*	5.48	*3*	1.68E-03	*3*	1.00E-02	*3*
BDE 153		644	*3*	162	*3*	7.08	*3*	1.38E-04	*3*	8.87E-06	*3*

Substance name	**Half-life air**	**k_{deg} air**		**Half-life water**	**k_{deg} water**		**Half-life sediment**	**k_{deg} sediment**		**Half-life soil**	**K k_{deg} soil**	
	days	**/days**		**days**	**/days**		**days**	**/days**		**days**	**/days**	
1,2,3-Trichlorobenzene	57.0	1.22E-02	*1*	150	4.62E-03	*4*	300	2.31E-03	#	300	2.31E-03	*4*
1,2,4-Trichlorobenzene	30.0	2.31E-02	*1*	148	4.70E-03	*1*	301	2.30E-03	#	301	2.30E-03	*1*
Anthracene	0.14	4.95E+00	*4*	150	4.62E-03	*4*	3000	2.31E-04	#	3000	2.31E-04	*4*
Benzo(b)fluoranthene	0.88	7.92E-01	*1*	15.2	4.57E-02	*5*	2440	2.84E-04	*5*	610	1.14E-03	*5*
Benzo(k)fluoranthene	0.46	1.51E+00	*5*	20.8	3.33E-02	*5*	1400	4.95E-04	#	1400	4.95E-04	*1*
Benzo[a]pyrene	0.05	1.51E+01	*5*	13.0	5.33E-02	*5*	2100	3.30E-04	*1*	309	2.24E-03	*1*
Naphthalene	2.50	2.77E-01	*1*	43.0	1.61E-02	*1*	18.0	3.85E-02	#	18	3.85E-02	*1*
BDE 15	5.00	1.39E-01	*3*	60.0	1.16E-02	*3*	240.0	2.89E-03	*3*	58	1.19E-02	*3*
BDE 153	46.3	1.50E-02	*3*	150.0	4.62E-03	*3*	600.0	1.16E-03	*3*	150	4.62E-033	*3*

Table 5. *Physico-chemical proprieties of POPs. Numbers in italics refer to the data source: 1: HSDB (http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB); 2: ASTDR (http://www.atsdr.cdc.gov/toxpro2.html#-P-); 6: Klasmeier et al., 2005; 7: CAS registry.*

Substance name	**CAS**	**Molecular weight**		**Melting point**		**Log Kow**		**Kaw**		**Vapour pressure**	
		g/mol		**°C**		**-**		**-**		**Pa**	
CB 28	7012-37-5	258	*7*	56	*7*	5.66	*6*	1.23E-02	*6*	2.70E-02	*6*
CB 180	35065-29-3	395	*2*	109	*2*	7.16	*6*	3.28E-03	*6*	1.08E-04	*6*
a-HCH	319-84-6	291	*1*	160	*1*	3.94	*6*	2.96E-04	*6*	2.45E-01	*6*
HCB	118-74-1	285	*1*	232	*1*	5.73	*1*	4.18E-02	*6*	1.49E-01	*6*

Substance name	**Half-life air**	**k_{deg} air**		**Half-life water**	**k_{deg} water**		**Half-life sediment**	**k_{deg} sediment**		**Half-life soil**	**K k_{deg} soil**	
	days	**/days**		**days**	**/days**		**Days**	**/days**		**days**	**/days**	
PCB-28	10.6	6.52E-02	*6*	229	3.02E-03	*6*	708	9.79E-04	*6*	417	1.66E-03	*6*
PCB-180	111	6.27E-03	*6*	2290	3.02E-04	*6*	7080	9.79E-05	*6*	41700	1.66E-05	*6*
a-HCH	120	5.78E-03	*6*	135	5.13E-03	*6*	2290	3.02E-04	*6*	135	5.13E-03	*6*
HCB	940	7.37E-04	*6*	1420	4.87E-04	*6*	14225	4.87E-05	*6*	1423	4.87E-04	*6*

5.3.3 Results

Using these data sets, both ELPOS and ChemRange were run for all substances. In order to obtain the most conservative results, Klasmeier et al. (2005) suggest that the models are run in turn with 100% emissions in soil, in water and in air. The persistence and long-range transport potential values retained are the maxima of the three scenarios. Often the persistence is greatest for emissions into soil whereas the greatest potential for long range transport is generally that obtained with 100% emission in air, as this is the most mobile medium.

5.3.4 Screening substances according to their persistence and potential for long range transport:

This is best done by plotting results on graphs. On Figures 1 and 2, the results are shown for the test and for the four known POPs as obtained by ChemRange and ELPOS respectively. The continuous line is the “volatility” line, which represents the maximum long-range transport potential for a given persistence, assuming transport in air only. Since in ChemRange, water transport is possible as well as air transport some very soluble substances could be found to the left of this line. With ELPOS, this is not possible since the model simulates transport just in one mobile medium at a time. Transport in air has been used to draw this line and to obtain the plotted values for the substances.

POPs are compounds with high persistence and high long-range transport potential. It is therefore logical to find the 4 POPs used in this example in the top right corner of the graphs, both for ELPOS and for ChemRange.

Two of the EU water Framework Directive substances, the two trichlorobenzene isomers, are found close to a-HCH and therefore might have characteristics that are close to that of POPs. ELPOS also suggests that BDE 153 might have long-range transport potential and persistence close to that of POPs.

Calculations show that a substance with a range greater than 35% is present in all grid cells in ChemRange. Therefore, this model predicts that both trichlorobenzene isomers may be found in most regions around the earth. ELPOS does not predict as clearly such a wide distribution.

The difference between the two models might be caused by the transport in water included within ChemRange and not within ELPOS.
Benzo(k)fluoranthene, benzo(b)fluoranthene, benzo(a)pyrene and anthracene have relatively low long range transport potential but are highly persistent. This may be a cause of concern, since it implies that these substances are likely to remain for long periods of time in soil, sediment or surface waters in areas close to their source.

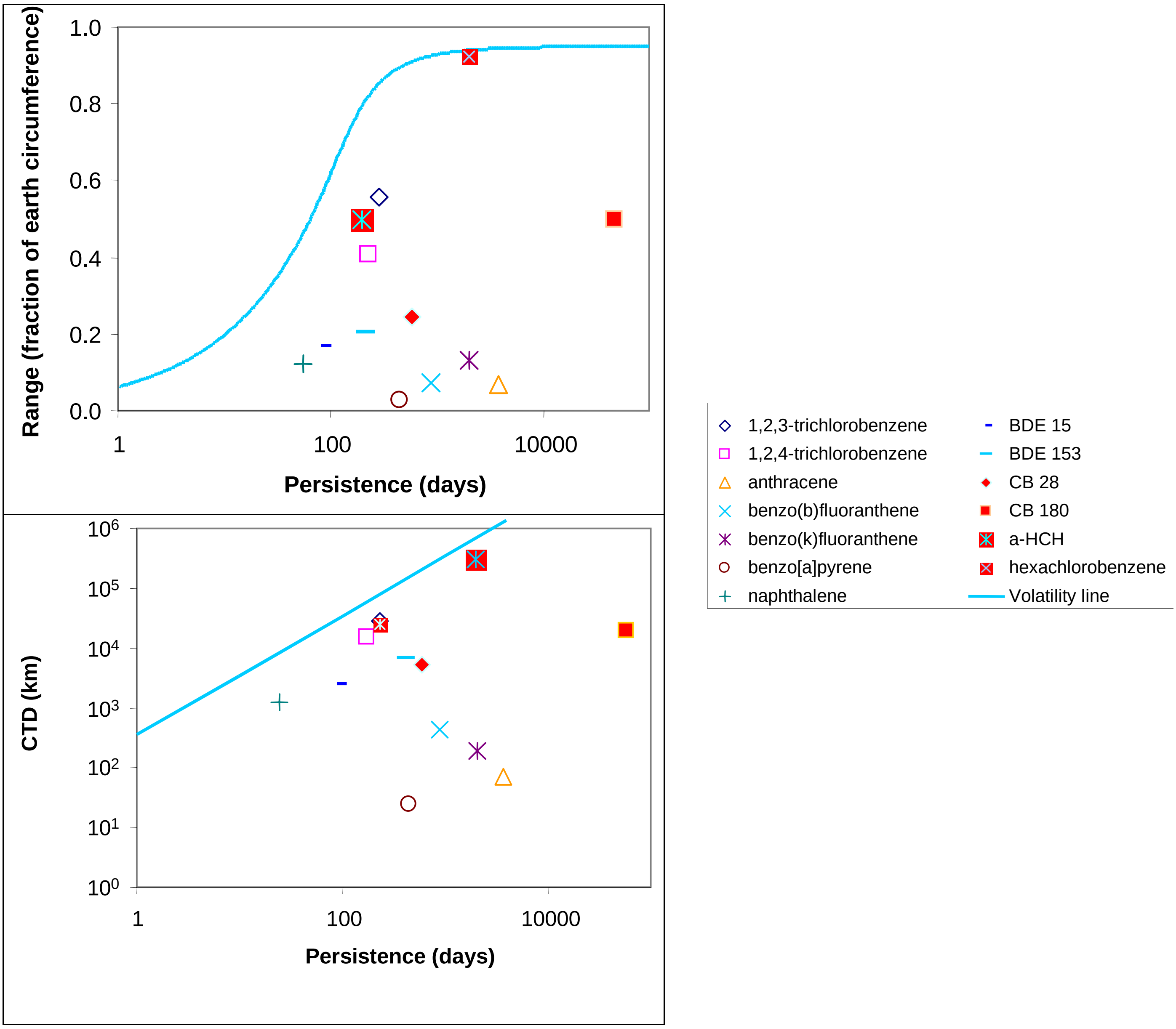

Figure 18.Spatial range for emission in air vs. maximum persistence for emission in air, soil or water obtained with ChemRange and ELPOS.

5.3.5 Screening according to proportions in different compartments:

Another way to take advantage of multimedia models is to consider the proportions of emitted substances that end up in each of the environment compartments. This can be done considering the results in Table 3.

Both models suggest that when benzo(b)fluoranthene, benzo(k)fluoranthene and benzo[a]pyrene are emitted to soil or to water, they remain in these compartments. When they are emitted to the atmosphere they are redistributed to all three compartments, the major part being trapped in soil. For four substances (anthracene, naphthalene, BDE 15 and 153), ELPOS results suggest that they tend to partition to soil if they are emitted to air whereas ChemRange results suggest that a large proportion is eventually found in water.

The two trichlorobenzene isomers and naphthalene tend to remain in the compartment in which they are emitted according to ChemRange, but ELPOS suggest that they migrate from water to air.

These differences between the two model results can easily be understood when the proportions of the water compartment in each are compared. In ELPOS, the volume of the water compartment represents 0.01% of the total environment and the area of the water surface represents 3% of the total area. In ChemRange the volume of the water compartment represents 2.3% of the total environment and its surface covers 70% of the globe. It is therefore expected that substances will be more likely to partition to water in ChemRange because of its larger water compartment. The question then is: What can we expect to happen in the real world?

It depends on the long-range transport potential: ChemRange may better describe the fate of a substance that is likely to reach the ocean, i.e. a substance with a large potential for long range transport. On the other hand, a substance likely to be transported only over land (i.e. only over short distances) would have its fate better described by ELPOS. Within the data set presented here, there are two substances with large potential for long range transport, i.e. the two trichlorobenzene isomers. For these substances, the ChemRange simulation should be considered when setting up legislation or evaluating their potential impact on the environment. Three other substances have a CTD greater than 1000 km. Depending where their sources are located, the use of ChemRange in the evaluation of their impact on the global environment may need to be considered.

Table 6. *Proportion of substances as calculated by ELPOS and ChemRange for three different scenarios : 100% to soil, 100% to water and 100% to the atmosphere. For ELPOS: the total % in aquatic compartment is the sum of the percentages in water and sediments; the percentages given are obtained when calculating persistence; CTD is that obtained with emission in air. For ChemRange: Range is the maximum value obtained between the three scenarios.*

	ELPOS					ChemRange		
	% in soil	**% in water**	**% in sediments**	**Total % in aquatic compartment**	**% in air**	% in soil	% in water	% in air
1,2,3-trichlorobenzene	CTD = 27877 km					Range = 36%		
Emission to soil	79%	0%	0%	0%	21%	87	2	12
Emission to water	9%	3%	2%	5%	86%	0	79	20
Emission to air	9%	0%	0%	0%	91%	0	8	92
1,2,4-trichlorobenzene	CTD = 14825 km					Range = 41%		
Emission to soil	83%	0%	0%	0%	17%	89	1	10
Emission to water	7%	5%	3%	9%	84%	0	88	12
Emission to air	8%	0%	0%	0%	92%	0	6	93
Anthracene	CTD = 70 km					Range = 20%		
Emission to soil	100%	0%	0%	0%	0%	99	1	0
Emission to water	2%	32%	66%	98%	0%	0	100	0
Emission to air	90%	1%	2%	3%	7%	42	38	20
Benzo(b)fluoranthene	CTD = 436 km					Range = 7%		
Emission to soil	100%	0%	0%	0%	0%	100	0	0
Emission to water	1%	2%	97%	99%	0%	0	99	0
Emission to air	68%	0%	16%	17%	16%	66	7	27
Benzo(k)fluoranthene	CTD = 188 km					Range = 5%		
Emission to soil	100%	0%	0%	0%	0%	100	0	0
Emission to water	0%	1%	99%	100%	0%	0	100	0
Emission to air	95%	0%	5%	5%	0%	95	3	1
Benzo[a]pyrene	CTD = 25 km					Range = 2%		
Emission to soil	100%	0%	0%	0%	0%	100	0	0
Emission to water	0%	4%	96%	100%	0%	0	100	0
Emission to air	92%	0%	7%	7%	1%	82	9	9
Naphthalene	CTD = 1244 km					Range = 9%		
Emission to soil	99%	0%	0%	0%	1%	98	2	1
Emission to water	1%	50%	2%	52%	47%	0	99	1
	1%	0%	0%	0%	98%	0	14	86
BDE 15	CTD = 2439 km					Range = 32%		
Emission to soil	100%	0%	0%	0%	0%	100	0	0
Emission to water	1%	13%	81%	94%	5%	0	100	0
Emission to air	11%	3%	16%	18%	70%	20	64	15
BDE153	CTD = 6814 km					Range = 8%		
Emission to soil	100%	0%	0%	0%	0%	96	4	0
Emission to water	19%	1%	77%	78%	3%	0	100	0
Emission to air	80%	0%	9%	9%	11%	0	30	69

5.4 Conclusions

Multimedia models are tools that can be used for an initial screening of organic substances. They are generic and therefore carry some uncertainties. However a number of comparisons with field measurements and intercomparison exercises between models suggest that their results are robust and give reliable information on persistence, potential for long range transport and partitioning between compartments.

The differences between results from different models can be explained by the differences in models formulations (e.g., compartment sizes and how processes are taken into account). It is essential to understand them when substance screening is carried out so that adequate models are used depending on both the user's aims and the substance behaviour in the environment.

Screening can be done by considering persistence, long range transport potential and substance partitioning between compartments.

In the example given in this chapter, only two transport oriented models were used. It may be interesting to complete the approach by running a target oriented model. Thus, substances that are likely to deposit to cold environments (i.e. arctic but also mountains) could be identified too.

Discussions to suggest methodologies to use these modelled criteria are on-going in different expert groups (e.g. OECD, EMEP-MSC-East). Eventually, multimedia models are bound to become useful and efficient tools that may speed up the process of organic compound assessment.

5.5 Acknowledgement

This work and the examples given therein have been largely inspired from discussions on-going within a working group set under the OECD. Therefore, it may be considered of each of the participants of this working group and co-authors of Fenner et al. (2005) has had an input to this chapter and these contributions are here gratefully thanked.

6. Conclusions and recommendations

This report has given a broad overview of the recent levels of selected POPs in freshwater fish from North America, Europe and the circumpolar Arctic, based on data from some central surveys. We have not included data from some well-studied areas and locations strongly affected by local pollution, such as the Great Lakes in North America, and large European waterways such as the River Danube and the River Rhine, because of the difficulties of separating the effects of local and long range atmospheric transported pollutants. However, we have included results from some surveys of large river basins in North America, as these show the concentration ranges from reference sites to sites strongly affected by upstream discharges.

The results from this assessment related to long-range transport of POPs show that

- There is a general lack of coordinated monitoring or regional surveys that focus on POPs in the freshwater environments for which LRTAP is a major source.
- There are many different projects focusing on POPs in freshwaters, however methodology regarding sampling, analytical methods and reporting makes comparison between results from the different projects very difficult or impossible.
- The general spatial pattern in concentrations is explainable in the light of global distilling processes, which leads to elevated concentrations of POPs in fish from arctic and alpine areas.
- The results from the assessment show that most POPs are found in all of the investigated remote ecosystems. However, we have not discussed these concentration levels in relation to possible biological effects.
- There are very few sites with trend data, but the one we have generally shows decreasing levels of legacy POPs (e.g., PCB, DDT, dioxins etc.).
- Levels of some new substances, such as brominated flame retardants (PBDE) and PFAS, are probably rising.

Based on the experience of making this assessment, it is very clear that there is an urgent need to establish systematic long-term monitoring of new POPs in background areas, and that coordinated international surveys with harmonised methods and reporting is needed to get a necessary overview of POPs in freshwater ecosystems.

- At present there are no international harmonized and agreed method how to monitor and map the levels of POPs in freshwaters.
- A recommendation for monitoring of POPs in freshwater should be made. This could be based largely on the protocols and methods that already are developed and established within the EU-programme EMERGE.
- Freshwater fish is the most sensitive organisms for monitoring POPs. Freshwater fish is also the most used organism international for monitoring and investigate POPs in surface waters.
- A monitoring programme should include new POPs (Chlorodecone, Lindane, PFAS, PBDEs) in addition to a selection of important legacy POPs.
- Alpine areas are well suited for monitoring of POPs from LRTAP. This shows that the present ICP Waters network is well suited for such monitoring.

This report also shows that multimedia models are tools that can be used for an initial screening of organic substances. Their results are robust and give reliable information on persistence, potential for long range transport and partitioning between compartments. Discussions to suggest methodologies for using these modelled criteria are on-going in different expert groups (e.g. OECD, EMEP-MSC-East). Eventually, multimedia models are bound to become useful and efficient tools that may speed up the process of organic compound assessment.

7. References

AMAP 1998. AMAP Assessment Report. Arctic Pollution Issues. Arctic monitoring and Assessment Programme (AMAP), Oslo, Norway xii+859 pp.

Bennett, D. H., McKone, T. E., Matthies, M., and Kastenberg, W. E. (1998). General formulation of characteristic travel distance for semivolatile organic chemicals in a multimedia environment. *Environmental Science & Technology* **32**, (24), 4023-4030.

Beyer, A., and Matthies, M. (2001). Long-range transport potential of semivolatile organic chemicals in coupled air-water systems. *Environmental Science and Pollution Research* **8**, (3), 173-179.

Beyer, A., and Matthies, M. (2002). Criteria for atmospheric long range transport and persistence of pesticides and industrial chemicals, **Rep. No. 7/2002**. UBA, Umweltbundesamt, Berlin, Germany. 244 p. Site internet: http://www.usf.uni-osnabrueck.de/projects/elpos

Beyer, A., Mackay, D., Matthies, M., Wania, F., and Webster, E. (2000). Assessing long-range transport potential of persistent organic pollutants. *Environmental Science & Technology* **34**, (4), 699 - 703.

Bignert, A. 2002. Comments concerning the national Swedish programme in fresh water biota 2001. Swedish Museum of Natural History, Contaminant Research Group. Report. 68 pp.

Blais JM, Schindler DW, Muir DCG, Kimpe LE, Donald DB, Rosenberg B. 1998. Accumulation of persistent organochlorine compounds in mountains of western Canada. Nature 395, 585-588.

Dearth, M. A., and Hites, R. A.1991. Complete analysis of technical chlordane using negative ionization mass spectrometry. Environ. Sci. Technol. 25, 245–254.

Den Hollander, H. A., Van Eijkeren, J. C. H., and van de Meent, D. (2004). SimpleBox 3.0: Multimedia mass balance model for evaluating the fate of chemical in the environment, **Rep. No. 601200003/2004**. RIVM, Bilthoven, the Netherlands.

Dodder, N.G., Strandberg, B., and Hites, R.A. 2002. Concentrations and spatial variations of polybrominated dipheny ethers and several organochlorine compounds in fishes from the Northeastern United States. Environ. Sci. Techn. 36: 146-151.

EC (European Commission). 2000. Alkanes, C10-13, chloro-. Editors: B.G. Hansen, S.J. Munn, G. Schoening, M. Luotamo, A. van Haelst, C.J.A. Heidorn, G. Pellegrini, R. Allanou, H. Loonen. EUR 190010 - European Union Risk Assessment Report Volume 4. Luxembourg: Office for Official Publications of the European Communities.

ECERG 2005. (Data compiled by the Environmental Organic Chemistry and Ecotoxicology Research Groups, Lancaster University) URL: http://www.es.lancs.ac.uk/ecerg/kcjgroup/modelling.html (last visited: Dec. 21 2005)

EPI Suite (version 3.12). 2004. Computer program. U.S. Environmental Protection Agency. URL: http://www.epa.gov/oppt/exposure/docs/episuitedl.htm (last visited Dec. 21. 2005)

Fenner, K., Scheringer, M., MacLeod, M., Matthies, M., McKone, T. E., Stroebe, M., Beyer, A., Bonnell, M., Le Gall, A. C., Klasmeier, J., Mackay, D., van de Meent, D., Pennington, D., Scharenberg, B., Suzuki, N., and Wania, F. (2005). Comparing estimates of persistance and long range transport potential among multimedia models. *Environmental Science & Technology* **Accepted**.

Fisk, A.T. K. E. Hobbs and D.C.G. Muir. (eds) 2003. Contaminant Levels and Trends in the Biological Environment, Canadian Arctic Contaminants Assessment Report II. Indian and Northern Affairs Canada. 202 .

Fjeld, E., Schlabach, M., Berge, J.A., Green, N., Eggen, T., Snilsberg, P. Vogelsang, C., Rognerud, S., Kjelberg, G., Enge, Dye, C. and Gundersen, H. Screening of a selection of new POPs, 2005. Brominated flame retardants, perfluorinated alkylated substances, irgarol, diuron, BHT and dicofol. Norwegian Pollution Control Authority, Report TA-2096/2005. 97 pp. (in Norwegian with English summary)

Gerecke A C, Hartmann P C, Heeb N V, Kohler H-P E, Giger W, Schmid P, Zennegg M and Kohler M. 2005. Anaerobic degradation of decabromodiphenyl ether. Environ. Sci. Technol. 39: 1078-1083.

Grimalt, J.O., Fernandez, P., Berdie, L., Vilanova, R., Catalan, J., Psenner, R., Hofer, R., Appleby, P.G., Rosseland, B.O., Lien, L., Massabuau, J.C. & Battarbee, R.W. 2001. Selective Trapping of Organochlorine Compounds in Mountain Lakes of temperate areas. Environ. Sci. Technol. 35: 2690 - 2697.

Hertwich, E. G., McKone, T. E., and Pease, W. S. (2000). A systematic uncertainty analysis of an evaluative fate and exposure model. *Risk Analysis* **20**, (4), 439-454.

Hinck, J.E., Bartish, T.M., Blazer, V.S., Denslow, N.D., Gross, T.S., Myers, M.S., Anderson, P.J., Orazio, C.E., and Tillitt, D.E., 2004, Biomonitoring of Environmental Status and Trends (BEST) Program: Environmental Contaminants and their Effects on Fish in the Yukon River Basin: U.S. Geological Survey, Columbia Environmental Research Center, Columbia, Missouri, Scientific Investigations Report 2004—5285, 87 pp.

Hinck, J.E., Schmitt, C.J.; Bartish, T. M., Denslow, N.D.; Blazer, V.S., Anderson, P .J.; Coyle, J.J., Dethloff, G.M. and Tillitt, D.E., 2004, Biomonitoring of Environmental Status and Trends (BEST) Program: Environmental Contaminants and their Effects on Fish in the Columbia River Basin: U.S. Geological Survey, Columbia Environmental Research Center, Columbia, Missouri, Scientific Investigations Report 2004–5154, 125 pp.

Jakobsson K, Thuresson K, Rylander L, Sjodin A, Hagmar L, and Bergman A. 2002. Exposure to polybrominated diphenyl ethers and tetrabrombisphenol A among computer technicians, Chemosphere 46: 709–716.

Johnson, A. and Olson, N. 2001. Analysis and occurrence of polybrominated diphenyl ethers in Washington state freshwater fish. Arch. Environ. Contam. Toxicol. 41: 339-44.

Kallenborn, R., Berger, U., and Järnberg, U. 2004. Perfluorinated alkylated substances (PFAS) in the Nordic environment. Nordic Council of Ministers, TemaNord 2004: 552. 112 pp.

Kannan, K., Tao, L., Sinclair, E., Pastva, S.D., Jude, D.J., and Giesy, J.P. 2005. Perfluorinated compounds in aquatic organisms at various trophic levels in a Great Lakes food chain. Arch. Environ. Contam. Toxicol. 48: 559-566.

Klasmeier, J., Matthies, M., Fenner, K., Scheringer, M., Stroebe, M., Beyer, A., Le Gall, A. C., MacLeod, M., McKone, T. E., Pennington, D., Suzuki, N., van de Meent, D., and Wania, F. (2005). Long-range transport potential and overall persistence in screening and assessment of organic chemicals. *Environmental Science & Technology* **in preparation**, 16+figures.

Leßmann, K. (2002). Probabilistic exposure assessment. Parameter uncertainties and their effect on model outputs. Diploma thesis, University of Osnabrueck, Osnabrueck, Germany. Site internet: http://www.usf.uos.de/~klessman/Parameter_Uncertainties_Lessmann.pdf

Lindberg P, Sellström U, Häggberg L, and de Wit CA. 2004. Higher brominated diphenyl ethers and hexabromocyclododecane found in eggs of peregrine falcons (Falco peregrinus) breeding in Sweden. Environ. Sci. Technol. 38: 93-96.

Mackay, D. (2001). Multimedia environmental models. The fugacity approach, second edition/Ed. Lewis Publishers, Boca Raton, USA. ISBN 1-56670-542-8.

Mackay, D., Di Guardo, A., Paterson, S., and Cowan, C. E. (1996a). Evaluating the environmental fate of a variety of types of chemicals using the EQC model. *Environmental Toxicology and Chemistry* **15**, (9), 1627-1637.

Mackay, D., Di Guardo, A., Paterson, S., Kicsi, G., and Cowan, C. E. (1996b). Assessing the fate of new and existing chemicals: a five-stage process. *Environmental Toxicology and Chemistry* **15**, (9), 1618-1626.

Mackay, D., Shiu, W. Y., and Ma, K. C. 1992. Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals,IV pp. Lewis Publishers, Boca Raton, USA. ISBN 0-87371-683-7.

MacLeod, M., Woodfine, D. G., Mackay, D., McKone, T., Bennett, D., and Maddalena, R. 2001. BETR North America: A regionally segmented multimedia contaminant fate model for North America. *Environmental Science & Pollution Research* 8, (3), 156-163.

Mariussen, E., Fjeld, E., Strand-Andersen, M., Hjerpset, M. and Schlabach, M. 2003. Spatial distribution of polybrominated diphenyl ethers in trout from Norwegian lakes. Organohalogen compd. 61: 69-72.

Martin, J.W., Smithwick, M.M., Braune, B.M., Hoekstra, P.F., Muir, D.C., and Mabury, S.A. 2004. Identification of long-chain perfluorinated acids in biota from the Canadian Arctic. Environ. Sci. Technol. 38: 373-80.

Martin, J.W., Whittle, D.M., Muir, D.C., and Mabury, S,A. 2004. Perfluoroalkyl contaminants in a food web from Lake Ontario. Environ. Sci. Technol. 38: 5379-5385.

McKone, T. E., and Enoch, K. G. (2002). CalTOX, A Multimedia Total Exposure Model Spreadsheet User's Guide Version 4.0, *Technical Report- Do Not Quote, Cite or Use for Regulatory Action*, Rep. No. LBNL-47399. Lawrence Berkeley National Laboratory. Site internet: http://eetd.lbl.gov/ied/era/

Muir D., Bennie D., Teixeira C., Fisk A., Tomy G., Stern G. and Whittle M. 2001. Short chain chlorinated paraffins: Are they persistent and bioaccumulative? ACS Symposium Series, 773: 184-202.

Muir, D. C. G., Teixeira, C., and Wania, F. 2004. Empirical and modeling evidence of regional atmospheric transport of currently used pesticides. *Environmental Toxicology and Chemistry 23,* (Special issue in honour of Don Mackay), 2421-2432.

Muir, D., R. Anderson, K. Drouillard, M. Evans, W. Fairchild, S. Guildford, D. Haffner, K. Kidd, J. Payne, M. Whittle 2002a. Biomagnification Of Persistent Organic Pollutants And Mercury In Canadian Freshwater Subsistence Fisheries And Food Webs. Toxic Substances Research Initiative Project #236 Final Report, National Water Research Institute, Environment Canada. 61 pp.

Muir, D., Douglas, M., Pienitz, R., Vincent, W., and Wania, F. 2002b. Sources, Long Range Transport and Impacts of New and Old POPs Inferred from Date lake Sediment Cores and Lake waters. Toxic Substances Research Initiative Project #206 Final Report, National Water Research Institute, Environment Canada. 52 pp.

Muir, D.C.G., G. Köch, J. Reist, and D. Bright. 2001a. Temporal trends of persistent organic pollutants and metals in landlocked char. In: Synopsis of Research Conducted Under the 2000/01 Northern Contaminants Program. S. Kalhok (ed.). Indian and Northern Affairs Canada, Ottawa. pp. 202–207.

OECD 2004. Guidance document on the use of multimedia models for estimating overall environmental persistance and long-range transport, *OECD environment directorate, joint meeting of the chemicals committee and the working party on chemicals, pesticides and biotechnology*, Rep. No. ENV/JM/MONO(2004)5, JT00160339. OECD, Paris, France. 83 p. Site internet: http://appli1.oecd.org/olis/2004doc.nsf/43bb6130e5e86e5fc12569fa005d004c/d5d405dd127503abc1256e5b00541567/$FILE/JT00160339.PDF

Pederson, B. M., Thibodeaux, L. J., Valsaraj, K. T., and Reible, D. D. (2001). Testing a multimedia compartmental model with monitoring data. *Environmental Toxicology and Chemistry* **20**, (9), 2114-2121.

Rayne, S., Ikonomou, M.G., and Antcliffe, B. 2003. Rapidly increasing polybrominated diphenyl ether concentrations in the Columbia River system from 1992 to 2000. Environ. Sci. Techn. 37: 2847-2854.

Renner, R. 2001. Growing concern over perfluorinated chemicals. Environ. Sci. Technol. 35: 154A–160A.

Scheringer, M. (1996). Persistence and spatial range as endpoints of an exposure-based assessment of organic chemicals. *Environmental Science & Technology* **30**, (5), 1652-1659.

Scheringer, M. (2002). Persistence and Spatial Range of Environmental Chemicals. New Ethical and Scientific Concepts for Risk Assessment, Wiley-VCH, Weinheim, Germany. ISBN 3-527-30527-0.

Scheringer, M., Salzmann, M., Stroebe, M., Wegmann, F., Fenner, K., and Hungerbuhler, K. (2004). Long-range transport and global fractionation of POPs: insights from multimedia modeling studies. *Environmental Pollution* **128**, (1-2), 177-188.

Schmitt, C.J., (ed). 2002, Biomonitoring of Environmental Status and Trends (BEST) Program: environmental contaminants and their effects on fish in the Mississippi River Basin: U.S. Geological Survey, Biological Science Report 2002-0004, 241 pp.

Schmitt, C.J., Dethloff, G.M., Hinck, J.E., Bartish, T. M., Blazer, V.S., Coyle, J.J., Denslow, N.D. and Tillitt, D.E., 2004, Biomonitoring of Environmental Status and Trends (BEST) Program: Environmental Contaminants and their Effects on Fish in the Rio Grande Basin: U.S. Geological Survey, Columbia Environmental Research Center, Columbia, Missouri, Scientific Investigations Report 2004—5108, 117 pp.

Shen, L., Wania, F., Lei, Y. D., Teixeira, C., Muir, D. C. G., and Bidleman, T. F. (2004-2005). Atmospheric distribution and long-range transport behavior of organochlorine pesticides in North America. *Environmental Science & Technology* **39**, (2), in press.

Sinclair, E. and Kannan, K. 2005. Perfluorinated compounds in the livers of fish and birds from New York State. SETAC 26th Annual Meeting in North America. Conference abstract. url: http://abstracts.co.allenpress.com/pweb/setac2005/category/?ID=57586 (last visited: 4. Dec. 2005)

Stapleton HM, Alaee M, Letcher RJ, and Baker JE. 2004. Debromination of the flame retardant decabromodiphenyl ether by juvenile carp (Cyprinus carpio) following dietary exposure. Environ Sci Technol. 38:8 A-9A.

Sternbeck, J., Kaj, L., Remberger, M., Palm, A., Junedahl E., Bignert, A., Haglund, P., Lindkvist, K., Adolfsson-Erici, M., Nylund, K., and Asplund. L. 2004. Organiska miljögifter i fisk från svenska bakgrundsområden. IVL Swedish Environmental Research Institute, IVL Report B 1576. 47 pp.

Stroebe, M. (2003). Chemrange code. Zurich, Switzerland.

Tomy, G.T., Stern, G.A., Muir, D.C.G., Fisk, A.T., Cymbalisty, D., and Westmore, J.B. 1997. Quantifying C10-C13 polychloroalkanes in environmental samples by high resolution gas chromatography/electron capture negative ion mass spectrometry. Anal Chem. 69: 2762–2771.

U.S. EPA. 2002. 2000 Toxic Release Inventory (TRI) Public Data Release Report. United States Environmental Protection Agency

UNEP/GEF (United Nations Environment Programme/ Global Environment Facility). 2003a. Regionally Based Assessment of Persistent Toxic Substances. Global report 2003. United Nations, Geneve, Switzerland. 207 pp.

Vives, I., Grimalt, J.O., Catalan, J., Rosseland, B., and Batterbee, R.W. 2004a. Influence of altitude and age in the accumulation of organochlorine compounds in fish from high mountain lakes. Environ. Sci. Technol. 38: 690–698.

Vives, I., Grimalt, J.O., Lacorte, S., Guillamón, M., and Barcelo, D. 2004b. Polybromodipenyl ether flame retardants in fish from lakes in European high mountains and Greenland. Environ. Sci. Technol. 38: 2338–2344.

Wania F, Mackay D. 1993. Global fractionation and cold condensation of low volatility organo-chlorine compounds in polar regions. Ambio 22, 10-18.

Wania F, Mackay D. 1996. Tracking the distribution of persistent organic pollutants. Environ Sci Technol 30, 390A-396A.

Wania, F., and Dugani, C. B. 2003. Assessing the long-range transport potential of polybrominated diphenyl ethers: A comparison of four multimedia models. *Environmental Toxicology and Chemistry* **22**, (6), 1252-1261.

Wania, F., and Mackay, D. 2000. The global distribution model. A non-steady state multi-compartmental mass balance model of the fate of persistent organic pollutants in the global environment, *Technical Report*. University of Toronto at Scarborough, Department of Physical and Environmental Sciences, Toronto, Canada. 21 p. Site internet: http://www.scar.utoronto.ca/~wania/reports/GloboPOP.pdf

Appendix A. Summary statistics

Summary statistics on the concentrations (ng/g wet weight) of persistent organic pollutants in freshwater fish. The statistics are given as median concentrations (and range) of reported sample concentrations. No/sites: number of samples/number of sites. The matrices are: carcass (c), whole fish (wf), muscle (m), muscle with skin (ms), liver (l).

References

1. BEST, Biomonitoring of Environmental Status and Trends Program. Rio Grande Basin: Schmitt et al., 2004. Mississippi River Basin: Schmitt, 2002. Columbia River Basin: Hinck et al., 2004. Yukon River Basin: Hinck et al,. 2004.
2. TSRI, Toxic Substances Research Initiative. Muir et al., 2002a.
3. NCP, Northern Contaminants Program. Fisk et al., 2003
4. AMAP, Arctic Monitoring and Assessment Programme. AMAP 1998.
5. Fjeld et al., 2001.
6. Vives et al., 2004.
7. Sternbeck et al., 2004.
8. Rayne et al., 2003.
9. Johnson and Olsson 2001.
10. Dodder et al., 2003.
11. Manchester-Neesvig et al., 2001.
12. Zennegg et al., 2003.
13. Mariussen et al., 2003
14. Muir et al., 2001.
15. Tomy et al., 1997.
16. Martin et al.. 2004a.
17. Sinclair and Kannan, 2005.
18. Kannan et al., 2005.
19. Fjeld et al., 2005.
20. Kallenborn et al., 2004.
21. Martin et al., 2004b.

					Dieldrin		Endrin		ΣChlordanes		Mirex	
Location	survey	species	Matrix	ref.	no/ sites	Conc. ng/g w.w	no/ sites	Conc. ng/g w.w	no/ sites	Conc. ng/g w.w c.	no/ sites	Conc. ng/g w.w
USA, Rio Grande Basin	BEST	several	wf	1	47/10	<10 (<10-50)	47/10	<10	47/10	30 (<30-210)	47/10	<10
USA, Missisippi River Basin	BEST	several	wf	1	163/47	<10 (<10-250)	163/47	<10 (<10-700)	163/47	40 (<30-550)	163/47	<10 (<10-80)
USA, Columbia River Basin	BEST	several	wf	1	64/16	<10 (<10-29)	64/16	<10	64/16	30 (<30-60)	64/16	<10
Arctic, Yukon River Basin	BEST	several	wf	1	31/10	<0.2 (<0.2-1)	31/10	<1.0	31/10	<5 (<5-7)	31/10	<0.3
Canada	TSRI	lake trout	wf	2	323/23	0.28 (0.01-1.59)			323/23	10.4 (0.54-244)	323/23	
Canada	TSRI	pike	wf	2	20/3	0.01 (0.01-0.10)			20/3	1.3 (0.27-5.9)	20/3	
Canada	TSRI	walleye	wf	2	60/3	0.23 (0.01-0.48)			60/3	5.4 (2.3-14)	60/3	
Canada	TSRI	whitefish	wf	2	89/11	0.12 (0.01-1.5)			89/11	2.39 (<0.01-49.1)	89/11	
Canada	TSRI	cisco	wf	2	47/11	0.22 (0.01-0.38)			47/11	2.3 (0.35-6.1)	47/11	
Arctic	NCP	lake trout	m	3	5/5	0.7 (0.1-1.1)			18/9	10.1 (0.52-42.9)		
Arctic	NCP	burbot	l	3	5/1	2.3 (2.2-3.11)			19/8	23.8 (0.9-248)	4/2	0.57 (0.35-0.59)
Arctic	NCP	arctic char	ms	3	9/3	1.95 (1.24-10.1)			9/3	6.8 (1.03-62.9)	9/3	0.14 (0.08-4.35)
Arctic	NCP	whitefish	m	3	2/2	0.6 (0.5-0.7)			5/3	2.9 (1.66-9.02)		
Arctic	AMAP	arctic char	m	4	11/10	2.26 (0.1-10)	2/2	0.125 (0.2-0.15)	9/9	4.38 (0.35-47.3)	3/3	0.77 (0.77-1)
Arctic	AMAP	lake trout	m	4	1/1	0.5		-	20/20	7.61 (0.26-30)		
Arctic	AMAP	burbot	m	4	2/2	6.03 (2.13-9.92)	1/1	4.38	13/12	26.7 (3.2-217)	3/3	0.69 (0.12-11.6)
Arctic	AMAP	whitefish	m	4	4/4	0.07 (0.03-1)	2/2	0.07 (0.07-0.07)	16/16	1.1 (0.03-25.9)		

					PCB		DDT		CBs		HCH	
Location	Survey	species	matrix	ref.	no/ sites	Conc. ng/g w.w	no/ sites	Conc. ng/g w.w	no/ sites	Conc. ng/g w.w	no/ sites	Conc. ng/g w.w
USA, Rio Grande Basin	BEST	several	wf	1	47/10	30	47/10	120 (30-1690)				
USA, Missisippi River Basin	BEST	several	wf	1	163/47	80 (50-3300)	163/47	40 (10-11100)				
USA, Columbia River Basin	BEST	several	wf	1	64/16	105 (30-1300)	64/16	265 (20-1390)				
Canada	TSRI	cisco	wf	2	47/11	2.4 (0.38-11.9)	47/11	2.7 (0.71-15.6)	47/11	0.93 (0.1-1.8)	47/11	0.4 (0.01-0.72)
Canada	TSRI	pike	wf	2	20/3	5.2 (0.8-33.5)	20/3	3 (0.86-105)	20/3	0.3 (0.14-0.67)	20/3	0.1 (0.01-0.39)
Canada	TSRI	whitefish	wf	2	89/11	13.3 (0.13-532)	89/11	13.5 (0.4-815)	89/11	0.78 (0.01-3.5)	89/11	0.32 (0.1-3.9)
Canada	TSRI	walleye	wf	2	60/3	38 (7.6-123)	60/3	19 (6.1-65)	60/3	0.97 (0.26-2.2)	60/3	0.42 (0.07-1)
Canada	TSRI	lake trout	wf	2	323/23	37.7 (1.4-1003)	323/23	34.7 (1.2-1642)	323/23	1.8 (0.1-10.4)	323/23	0.61 (0.01-52.5)
Sweden		perch	m	7	24/3	0.88 (0.174-5.28)						
Norway		perch	m	5	26/26	0.96 (0.16-15)	26/26	0.69 (0.18-10.7)				
Norway		brown trout	m	5	34/34	1.95 (0.1-75.8)	34/34	1.15 (0.1-61)	34/34	0.305 (0.05-1.5)	34/34	0.16 (0.08-0.74)
Norway		pike	m	5	13/13	2.42 (0.78-4.7)	13/13	1.1 (0.3-8)				
Norway		arctic char	m	5	9/9	3.18 (0.52-5.5)	9/9	1.32 (0.41-4.3)				
Europe, alpine	EMERGE	trout/arctic char	m	6	9/9	6.3 (0.68-17)	9/9	2.7 (0.25-65)	9/9	0.32 (0.14-1)	9/9	0.33 (0.1-16)
Norway		burbot	l	5	12/11	557 (72-5816)	12/11	359 (31-3702)	12/11	14.2 (1.85-24)	12/11	7.5 (1-32)
Arctic	AMAP	whitefish	m	4	17/20	3.65 (0.1-280)	17/20	2.65 (0.15-464)	1/1	0.09 (-)	9/9	0.75 (0.1-6.1)
Arctic	NCP	whitefish	m	3	5/4	6.6 (4.58-24.7)	5-4	6.43 (1.9-24.6)	3/2	0.02 (0.004-0.26)	5/4	0.89 (0.32-2.66)
Arctic	AMAP	arctic char	m	4	11/11	18.6 (4.72-290)	11-11	4.61 (1.37-114)	9/9	1.79 (0.72-5.5)	11/11	2.05 (0.2-3.03)
Arctic	NCP	arctic char	ms	3	9/3	125 (64.9-290)	9-3	14.8 (6.69-114)	3/3	2.03 (1-6.7)	9/3	0.7 (0.33-2.64)
Arctic	NCP	lake trout	m	3	19/10	23.2 (2.37-183)	19-10	8.9 (1.46-250)	11/7	0.93 (0.05-4.09)	19/10	1.68 (0.2-5.1)
Arctic	AMAP	lake trout	m	4	24/24	25.05 (0.46-448)	24/24	7.6 (0.32-458)	9/3	0.35 (0.01-2.3)	19/19	1.2 (0.01-3.17)
Arctic, Yukon River Basin	BEST	multispecies	wf	1	31/10	30.5 (30-87)	31/10	2 (1-14)				
Arctic	NCP	burbot	l	3	19/8	96.4 (32.2-1630)	19/8	41.3 (16.2-2850)	12/5	6.27 (0.49-41.6)	19/8	4.05 (3.07-50.39)
Arctic	AMAP	burbot	l	4	11/12	103.5 (26.9-1267)	12-13	57 (13.6-3433)	3/3	12.3 (1.68-12.8)	12/13	8.13 (1.53-63)

Location	Survey	species	matrix	ref.	Toxaphene	
					no/sites	Conc. ng/g w.w
USA, Rio Grande Basin	BEST	several	wf	1	47/10	25 (25-2400)
USA, Missisippi River Basin	BEST	several	wf	1	163/47	25 (25-8300)
USA, Columbia River Basin	BEST	several	wf	1	64/16	15 (15-50)
Canada	TSRI	walleye	wf	2	1/20	0.37 (0.05-19.9)
Canada	TSRI	lake trout	wf	2	5/83	19.8 (1.6-254)
Norway		brown trout	m	5	16/16	0.7 (0.07-5)
Norway		burbot	l	5	5/5	48 (19-157)
Arctic	AMAP	whitefish	m	4	61/13	20.4 (3.1-154)
Arctic	NCP	whitefish	m	3	-/4	12.7 (5.19-25.5)
Arctic	AMAP	arctic char	m	4		41.3 (1-203)
Arctic	NCP	arctic char	ms	3	27/3	31.75 (21.5-203)
Arctic	NCP	lake trout	m	3	-/10	28.5 (0.33-234)
Arctic	AMAP	lake trout	m	4	≈170/10	50.1 (6.2-344)
Arctic, Yukon River Basin	BEST	several	wf	1	31/10	8.5 (11-3)
Arctic	NCP	burbot	l	3	-/8	208 (40.8-3050)
Arctic	AMAP	burbot	l	4	91/10	267 (40.5-2301)

Area	Survey	species	matrix	ref.	PBDEs	
					no/sites	Conc. ng/g w.w
Coulombia River		whitefish	m	8	4/4	(0.9-71.8)
Washington State		multiple species	wf,m	9	14/6	(1.4-1250)
NE USA		multiple species	wf,m	10	6/4	(6.2-65)
Lake Michigan		lake trout	m	11	21/1	77 (44.6-149)
Sweden		perch	m	7	24/3	0.15 (0.06-0.33)
Europe, alpine	EMERGE	trout, arctic char	m	6	11/11	0.27 (0.069-1.1)
Norway		brown trout	m	5	13/13	0.49 (0.1-2.36)
Switzerland		whitefish	m	12	8/8	2.65 (1.6-7.4)
Norway		brown trout (piscivorous)	m	13	6/6	8.3 (0.3-367)
Norway		burbot	l	5	8/7	121 (20.3-1995)

Location	Survey	species	matrix	ref.	SCCP	
					no/sites	Conc. ng/g w.w
Lake Ontario		carp, lake trout	m	14	-	(59-2600)
Detroit River		yellow perch	m	15	-	(300-1100)
Norway		brown trout	m	5	14/14	6 (2.7-22)
Norway		burbot	l	5	6/5	153 (86-1480)

Area	Survey	species	matrix	ref.	PFAS	
					no/sites	Conc. ng/g w.w
Lake Ontario		multiple species	wf	16	4/1	(46-450)
New York State		multiple species	l	17	-/20	(9-350)
Michigan waters		multiple species	l,m	18	21/3	100 (32-297)
Norway		multiple species	m	19	5/5	1.85 (0.002-3.99)
Norway, Sweden		multiple species	l	20	8/2	146 (8.1-432)
Canadian Arctic		multiple species	l	21	6/1	12 (5.7-50)

Appendix B. Publications from ICP Waters

All reports from the ICP Waters programme from 1987 up to present are listed below. All reports are available from the Programme Centre. Publications from 2002 up to present can be found at http://www.iis.niva.no/ICP%2Dwaters

Manual for Chemical and Biological Monitoring. Programme Manual. Prepared by the Programme Centre, Norwegian Institute for Water Research. NIVA, Oslo 1987.

Norwegian Institute for Water Research, 1987. Intercalibration 8701. pH, Ks, SO_4, Ca. Programme Centre, NIVA, Oslo.

Norwegian Institute for Water Research, 1988. Data Report 1987 and available Data from Previous Years. Programme Centre, NIVA, Oslo.

Norwegian Institute for Water Research, 1988. Intercalibration 8802. pH, K_{25}, HCO_3, NO_3, SO, Cl, Ca, Mg, Na, K. Programme Centre, NIVA, Oslo.

Proceedings of the Workshop on Assessment and Monitoring of Acidification in Rivers and Lakes, Espoo, Finland, 3rd to 5th October 1988. Prepared by the Finnish Acidification Research Project, HAPRO, Ministry of Environment, October 1988.

Norwegian Institute for Water Research, 1989. Intercalibration 8903: Dissolved organic carbon and aluminium fractions. Programme Centre, NIVA, Oslo. NIVA-Report SNO 2238-89.

Note: Some reflections about the determination of pH and alkalinity. Prepared by the Programme Centre, Norwegian Institute for Water Research. Håvard Hovind, NIVA, Oslo October 1989.

Hovind, H. 1990. Intercalibration 9004: pH and alkalinity. Programme Centre, NIVA, Oslo. NIVA-Report SNO 2465-90.

Skjelkvåle, B.L. and Wright, R.F. 1990. Overview of areas sensitive to acidification: Europe. Programme Centre, NIVA, Oslo. Acid Rain Research Report 20/1990. NIVA-Report 2405-90. ISBN 82-577-1706-1.

Johannessen, M. 1990. Intercalibration in the framework of an international monitoring programme. Proceedings of the third annual Ecological Quality Assurance Workshop, Canada Centre for Inland Waters, Burlington Ontario. Programme Centre, NIVA, Oslo.

Norwegian Institute for Water Research, 1990. Data Report 1988. Programme Centre, NIVA, Oslo.

Norwegian Institute for Water Research, 1990. Data Report 1989. Programme Centre, NIVA, Oslo.

Proceedings for the 5th Meeting of the Programme Task Force Freiburg, Germany, October 17 -19, 1989. Prepared by the Umweltbundesamt, Berlin July 1990.

Hovind, H. 1991. Intercalibration 9105: pH, K_{25}, HCO_3, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K and TOC. Programme Centre, NIVA, Oslo. NIVA-Report 2591-91.

Norwegian Institute for Water Research, 1991. The Three Year Report. Summary and results 1987 – 1989: Results from the International Co-operative Programme on Assessment and Monitoring of Acidification in Rivers and Lakes. Programme Centre, NIVA, Oslo.

Norwegian Institute for Water Research, 1991. Summary of The Three Year Report 1987 – 1989. Programme Centre, NIVA, Oslo.

Scientific papers presented at the Sixth Task Force meeting in Sweden 23 - 24 October 1990. Swedish Environmental Protection Agency, Sweden, September 1991.

Seventh Task Force meeting of international Co-operative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes. Galway, Ireland. September 30 - October 3 1991. Proceedings.

Johannessen, M., Skjelkvåle, B.L. and Jeffries, D. 1992. International cooperative Programme on Assessment and Monitoring of Rivers and Lakes. In: Conference Abstracts, Intern. Conference on Acidic Deposition, Glasgow 16-21, sept. 1992, p. 449. Kluwer Academic Press.

Hovind, H. 1992. Intercalibration 9206: pH, K_{25}, HCO_3, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K, Al and DOC. Programme Centre, NIVA, Oslo. NIVA-Report 2784-92.

Norwegian Institute for Water Research, 1992. Data Report 1990. Programme Centre, NIVA, Oslo.

Norwegian Institute for Water Research, 1992. Evaluation of the International Co-operative Programme on Assessment and Monitoring of Acidification in Rivers and Lakes. Programme Centre, NIVA, Oslo.

Hovind, H. 1993. Intercalibration 9307: pH, k_{25}, HCO_3, NO_3 + NO_2, Cl, SO_4, Ca, Mg, Na, K, total aluminium, reactive and non-labile aluminium, TOC and COD-Mn. Programme Centre, NIVA,Oslo. NIVA-Report 2948-93.

Raddum, G.G. 1993. Intercalibration of Invertebrate Fauna 9301. Programme Centre, NIVA, Oslo. NIVA-Report SNO 2952-93.

Proceedings of the 9th Task Force Meeting in Oisterwijk, the Netherlands, November 1-3, 1993. Programme Centre, NIVA, Oslo.

Skjelkvåle, B.L., Newell, A.D, and Johannessen, M. 1993. International Cooperative Programme on Assessment and Monitoring of Rivers and lakes: Status and Results. In: BIOGEOMON - Symposium on Ecosystem Behaviour: Evaluation of Integrated Monitoring in small catchments. Prague, September 18-20, 1993. Czech Geological Survey, Prague 1993. s. 274-275.

Hovind, H. 1994. Intercomparison 9408. pH, k_{25}, HCO_3, NO_3 + NO_2, Cl, SO_4, Ca, Mg, Na, K, total aluminium, TOC and COD-Mn. Programme Centre, NIVA, Oslo. NIVA-Report SNO 3142-94.

Skjelkvåle, B.L., Newell, A.D., Raddum, G.G., Johannessen, M., Hovind, H., Tjomsland, T. and Wathne, B.M. 1994. The six year report: Acidification of surface water in Europe and North America. Dose/response relationships and long-term trends. Programme Centre, NIVA, Oslo. NIVA-Report SNO 3041-94.

Norwegian Institute for Water Research, 1994. Data Report 1991. Programme Centre, NIVA, Oslo.

Stoddard, J.L. and Traaen, T.S. 1994. The stages of Nitrogen Saturation: Classification of catchments included in "ICP on Waters". In: M. Hornung, M.A. Stutton and R.B. Wilson (eds.) Mapping and Modelling of Critical Loads for Nitrogen: a Workshop Report. Proceedings of a workshop held in Grange-over-Sands (UK), 24-26 October 1994. pp.69-76.

Hovind, H. 1995. Intercomparison 9509. pH, k_{25}, HCO_3, NO_3 + NO_2, Cl, SO_4, Ca, Mg, Na, K, total aluminium, aluminium-reactive and nonlabile, TOC and COD-Mn. Programme Centre, NIVA, Oslo. NIVA-Report SNO 3331-95. ISBN 82-577-2849-7.

Traaen, T.S. and Stoddard, J.L. 1995. An Assessment of Nitrogen Leaching from Watersheds included in ICP on Waters. Programme Centre, NIVA, Oslo. NIVA-Report SNO 3201-95.

Norwegian Institute for Water Research, 1995. Data Report 1992-93. Draft 1994. Part 1, Introduction and Chemistry. Programme Centre, NIVA, Oslo.

Norwegian Institute for Water Research, 1995. Data Report 1992-1993. Draft 1994. Part 2, Biology and Site-data. Programme Centre, NIVA, Oslo.

Raddum, G.G. 1995. Aquatic Fauna. Dose/response and long term trends. Programme Centre, NIVA, Oslo.

Raddum, G.G. 1995. Intercalibration of Invertebrate Fauna 9502. Programme Centre, NIVA, Oslo.

Raddum, G.G., and Skjelkvåle, B.L. 1995. Critical limits of acidification to invertebrates in different regions of Europe. *Water Air Soil Poll.* 85: 475-480.

Hovind, H. 1996. Intercomparison 9610. pH, K_{25}, HCO_3, NO_3 + NO_2, Cl, SO_4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC and COD-Mn. Programme Centre, NIVA, Oslo. NIVA-Report SNO 3550-96.

Newell, A.D, and Skjelkvåle, B.L. 1996. Acidification trends in surface waters in the International Program on Acidification of Rivers and Lakes. *Water Air Soil Poll.* 93:27-57.

Proceedings of the 10th Task Force Meeting in Budapest 1994. Prepared by the Programme Centre, NIVA, Oslo March 1996.

Norwegian Institute for Water Research, 1996. Programme Manual. Programme Centre, NIVA, Oslo. NIVA-Report SNO 3547-96.

Raddum, G.G. 1996. Intercalibration of invertebrate fauna 9603. Programme Centre, NIVA, Oslo.

Lükewille, A., Jeffries, D., Johannessen, M., Raddum, G.G., Stoddard, J.L and Traaen, T.S. 1997. The Nine Year Report. Acidification of Surface Water in Europe and North America. Long-term Developments (1980s and 1990s). Programme Centre, NIVA, Oslo. NIVA-Report SNO 3637-97.

Hovind, H. 1997. Intercomparison 9711. pH, K_{25}, HCO_3, NO_3 + NO_2, Cl, SO_4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC and COD-Mn. Programme Centre, NIVA, Oslo. NIVA-Report SNO 3716-97.

Johannessen, M., and Skjelkvåle, B.L. 1997. International Co-operative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes - ICP Waters; Programme objectives, organization and main results. In: Proceedings to "International Conference on management of Transboundary Waters in Europe" 22-25 September 1997 in Poland. Programme Centre, NIVA, Oslo. **ICP Waters Report 43/1997**.

Henriksen, A. and Posch, M. 1998. Critical loads and their exceedances for ICP Waters sites. Programme Centre, NIVA, Oslo. NIVA-Report SNO 3821-98, **ICP Waters Report 44/1998**.

Smith, D. and Davis, I. 1997. International Cooperative programme on Assessment and Monitoring of Acidification of Rivers and lakes: 8th Task Force Meeting, 1992. Can.Tech.Rep.Fish.Aquat.Sci. 2155: iv 68 p.

Summary of The Nine Year Report from the ICP Waters Programme. NIVA-Report SNO 3879-98, **ICP Waters report 46/1998**.

Raddum, G.G. 1998. Intercalibration 9804: Invertebrate fauna. NIVA-Report SNO 3912-98, **ICP Waters Report 47/1998**.

Larsen, S.E., Friberg, N. and Rebsdorf, Aa.. (eds.) 1999. Proceedings from the 12th Task Force Meeting in Silkeborg, Denmark, October 23-25, 1996. National Environmental Research Institute, Denmark 52 pp NERI Technical Report, No. 271

Hovind, H. 1998. Intercomparison 9812. pH, K_{25}, HCO_3, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC and COD-Mn. NIVA-Report SNO 3939-98, **ICP Waters Report 49/1998**.

Rosseland, B.O., Raddum, G.G. and Bowman, J. 1999. Workshop on biological assessment and monitoring; evaluation and models. NIVA-Report SNO 4091-99, **ICP Waters Report 50/1999**.

Hovind, H. 1999. Intercomparison 9913. pH, K_{25}, HCO_3, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC and COD-Mn. NIVA-Report SNO 4093-99, **ICP Waters Report 51/1999**.

Skjelkvåle, B. L., Andersen, T., Halvorsen, G. A., Raddum, G.G., Heegaard, E., Stoddard, J. L., and Wright, R. F. 2000. The 12-year report; Acidification of Surface Water in Europe and North America; Trends, biological recovery and heavy metals. NIVA-Report SNO 4208/2000, **ICP Waters report 52/2000.**

Stoddard, J. L., Jeffries, D. S., Lükewille, A., Clair, T. A., Dillon, P. J., Driscoll, C. T., Forsius, M., Johannessen, M., Kahl, J. S., Kellogg, J. H., Kemp, A., Mannio, J., Monteith, D., Murdoch, P. S., Patrick, S., Rebsdorf, A., Skjelkvåle, B. L., Stainton, M. P., Traaen, T. S., van Dam, H., Webster, K. E., Wieting, J., and Wilander, A. 1999. Regional trends in aquatic recovery from acidification in North America and Europe 1980-95. Nature 401:575- 578.

Skjelkvåle, B.L., Olendrzynski, K., Stoddard, J., Traaen, T.S, Tarrason, L., Tørseth, K., Windjusveen, S. and Wright, R.F. 2001. Assessment of trends and leaching in Nitrogen at ICP Waters Sites (Europe And North America). NIVA-report SNO 4383-2001, **ICP Waters report 54/2001.**

Hovind, H. 2000. Intercomparison 0014. pH, K_{25}, HCO_3, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC, COD-Mn. Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA-Report SNO 4281-2000, **ICP Waters Report 55/2000**.

Hovind, H. 2000. Trends in intercomparisons 8701-9812: pH, K_{25}, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K and aluminium - reactive and nonlabile, TOC, COD-Mn. NIVA-Report SNO 4281-2000, **ICP Waters Report 56/2000**.

Wright, R.F. 2001. Note on: Effect of year-to-year variations in climate on trends in acidification. NIVA-report SNO 4328-2001, **ICP Waters report 57/2001**.

Kvaeven, B. Ulstein, M.J., Skjelkvåle, B.L., Raddum, G.G. and Hovind. H. 2001. ICP Waters – An international programme for surface water monitoring. *Water Air Soil Poll.***130**:775-780.

Skjelkvåle, B.L. Stoddard J.L. and Andersen, T. 2001. Trends in surface waters acidification in Europe and North America (1989-1998). *Water Air Soil Poll.***130:**781-786.

Stoddard, J. Traaen, T and Skjelkvåle, B.L. 2001. Assessment of Nitrogen leaching at ICP Waters sites (Europe and North America). *Water Air Soil Poll*. **130**:825-830.

Raddum, G.G. and Skjekvåle B.L. 2000. Critical Load of Acidifying Compounds to Invertebrates In Different Ecoregions of Europe. *Water Air Soil Poll.* **130**:825-830.

Raddum.G.G. 2000. Intercalibration 0005: Invertebrate fauna. NIVA-report SNO4384-2001, **ICP Waters report 62/2001**.

Lyulko, I. Berg, P. and Skjelkvåle, B.L. (eds.) 2001. National presentations from the 16th meeting of the ICP Waters Programme task Force in Riga, Latvia, October 18-20, 2000. NIVA-report SNO 4411-2001. **ICP Waters report 63/001**.

Hovind, H. 2001. pH, K_{25}, HCO_3, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC, COD-Mn. Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA-Report SNO 4416-2002, **ICP Waters report 64/2001**.

Bull, K.R. Achermann, B., Bashkin, V., Chrast, R. Fenech, G., Forsius, M., Gregor H.-D., Guardans, R., Haussmann, T., Hayes, F., Hettelingh, J.-P., Johannessen, T., Kryzanowski, M., Kucera, V., Kvaeven, B., Lorenz, M., Lundin, L., Mills, G., Posch, M., Skjelkvåle, B.L. and Ulstein, M.J. 2001. Coordinated Effects Monitoring and Modelling for Developing and Supporting International Air Pollution Control Agreements. *Water Air Soil Poll.* **130**:119-130.

Raddum.G.G. 2002. Intercalibration 0206: Invertebrate fauna. NIVA-report SNO-4494-2002, **ICP Waters report 66/2002**.

Skjelkvåle, B.L. and Ulstein, M. 2002. Proceedings from the Workshop on Heavy Metals (Pb, Cd and Hg) in Surface Waters; Monitoring and Biological Impact. March 18-20, 2002, Lillehammer, Norway. NIVA-report SNO-4563-2002, **ICP Waters report 67/2002**.

Hovind. H. 2002. Intercomparison 0216. pH, K_{25}, HCO_3, NO_3 + NO_2, Cl, SO_4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC, COD-Mn. Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA-Report SNO 4558-2002, **ICP Waters Report 68/2002**.

Halvorsen, G.A, Heergaard, E. and Raddum, G.G. 2002. Tracing recovery from acidification - a multivariate approach. NIVA-report SNO 4564-2002, **ICP Waters report 69/2002**.

Jenkins, A. Larssen, Th., Moldan, F., Posch, M. and Wrigth R.F. 2002. Dynamic Modelling of Surface Waters: Impact of emission reduction - possibilities and limitations. NIVA-report SNO 4598-2002, **ICP Waters report 70/2002.**

Wright, R.F and Lie, M.C. 2002.Workshop on models for Biological Recovery from Acidification in a Changing Climate. 9-11 september 2002 in Grimstad, Norway. Workshop report. NIVA-report 4589-2002.

Skjelkvåle, B.L. (ed.). 2003. Proceedings of the 18th meeting of the ICP Waters Programme Task Force in Moscow, October 7-9, 2002. NIVA-report SNO 4658-2003, **ICP Waters report 71/2002**.

Raddum.G.G. 2003. Intercalibration 0307: Invertebrate fauna. NIVA-report SNO-4659-2003, **ICP Waters report 72/2003**.

Skjelkvåle, B.L. (ed). 2003. The 15-year report: Assessment and monitoring of surface waters in Europe and North America; acidification and recovery, dynamic modelling and heavy metals. NIVA-report SNO 4716-2003, **ICP Waters report 73/2003.**

Hovind, 2003. Intercomparison 0317. pH, K25, HCO3, NO3 + NO2, Cl, SO4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC, COD-Mn. Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA-report SNO 4715-2003, **ICP Waters report 74/2003.**

Raddum, G.G, et al. 2004. Recovery from acidification of invertebrate fauna in ICP Water sites in Europe and North America. NIVA-report SNO 4864-2004, **ICP Waters report 75/2004.**

ICP Waters report 76/2004. Proceedings of the 19th meeting of the ICP Waters Programme Task Force in Lugano, Switzerland, October 18-20, 2003. NIVA-report SNO 4858-2004, **ICP Waters report 76/2004.**

Raddum, G.G. 2004. Intercalibration: Invertebrate fauna 09/04. NIVA-report SNO 4863-2004, **ICP Waters report 77/2004.**

Hovind, 2004. Intercomparison 0418. pH, K25, HCO3, NO3 + NO2, Cl, SO4, Ca, Mg, Na, K, Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA-report SNO 4875-2004, **ICP Waters report 78/2004.**

Skjelkvåle et al 2005. Regional scale evidence for improvements in surface water chemistry 1990-2001. *Environmental Pollution.* **137:165-176.**

Fjeld, E. LeGall, A.C, Skjelkvåle, B.L. 2005. An assessment of POPs related to long-range air pollution in the aquatic environment. NIVA-report SNO 5107-2005,, **ICP Waters report 79/2005.**

De Wit, H. and Skjelkvåle, B.L. (eds.) 2005. Proceedings of the 20th meeting of the ICP Waters Programme Task Force in Falun, Sweden, October 18-20, 2004. NIVA-report SNO 5018-2005, **ICP Waters report 80/2005.**

Raddum. G.G. Biological intercalibration: Invertebrates 0905. NIVA-report SNO 5067-2005, **ICP Waters report 81/2005.**

Hovind, H. Intercomparison 0519: pH, Cond, HCO_3, NO_3+NO_2, Cl, SO_4, Ca, Mg, Na, K, Fe, Mn, Cd, Pb, Cu, Ni, and Zn. NIVA-report 5068-2005, **ICP Waters report 82/2005**.