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PERSISTENT ORGANIC POLLUTANTS IN THE FRESHWATER ENVIRONMENT: EFFECTS OF LONG-RANGE TRANSBOUNDARY AIR POLLUTION

Report prepared by the Programme Centre of the International Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes

Introduction

1. This report is an assessment of persistent organic pollutants (POPs) in the aquatic environment caused by long-range transboundary atmospheric transport (LRTAP). The major goal was to look into data relevant for ICP Waters, quantify that which exists data and identify challenges and needs for mapping POPs pollution attributed to LRTAP in surface waters.

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2. The goal would be achieved by:

(a) Identifying relevant substances:

(i) Review the substances addressed by international conventions or protocols;
(ii) Examine their physical, chemical and ecotoxicological characteristics;
(iii) Discuss their atmospheric transport mechanisms and their potential for long-range transport;

(b) Reviewing case studies and central data sets with emphasis on:

(i) The documentation of POP levels in biota, sediments and water;
(ii) The time trends;
(iii) The spatial gradients (lowland–alpine, south–north);

(c) Giving recommendations on future monitoring:

(i) Define high-priority substances;
(ii) Identify susceptible areas or ecosystems.

I. INTERNATIONAL AGREEMENTS ON POPS

3. Several international agreements or treaties have addressed the problem of dispersal of POPs in the environment. Among the most important are the Aarhus Protocol of the Convention on Long-range Transboundary Air Pollution and the Stockholm Convention.

A. The Protocol on POPs

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

5. 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). It severely restricts the use of DDT, hexachlorocyclohexane (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, polycyclic aromatic hydrocarbons (PAHs) and HCB below the levels in 1990 (or an alternative year between 1985 and 1995). Specific limit values are given for the incineration of municipal, hazardous and medical waste.

B. The Stockholm Convention

6. The 2001 Stockholm Convention was organized under United Nations Environmental Programme (UNEP) as a global treaty to protect human health and the environment from POPs. In implementing the Convention, governments would take measures to eliminate or reduce the release of POPs into the environment. The Stockholm Convention entered into force on 17 May 2004. It deals with the so-called “Dirty Dozen” (table 1). 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 products that contain POPs.

II. SELECTED SUBSTANCES AND THEIR CHARACTERISTICS

7. According to the Stockholm Convention the following criteria should be fulfilled in order to classify a substance as a long-range transported POP:

(a) Environmental persistence (half life in water > 2 months, half life in water sediments > 6 months);
(b) Subject to long-range atmospheric transport (half life in air > 2 days);
(c) Potential for biomagnification (bio-accumulation factor for aquatic species > 5000, or logarithm of the octanol-water partition coefficient log Kow > 5);
(d) Environmental adverse effects.

8. As there are many different groups of POPs that have a long-range transport potential, a selection had to be made on their relevance to ICP Waters and on practical considerations. Therefore, this report primarily considers the substances or group of chemicals given in Table 1. Among these, the first twelve are the “Dirty Dozen” addressed by the Stockholm Convention; the other substances were chosen based on their persistence, toxicity and long-range transport potential.

Substance	Pesticide	Industrial compound	Unintended by-product
aldrin	X		
endrin	X		
dieldrin	X		
chlordane	X		
DDT	X		
heptachlor	X		
mirex	X		
toxaphene	X		
hexachlorobenzene	X	X	X
PCB		X	
dioxins and furans			X
polybrominated dephenyl ethers, PBDE		X	
short chained paraffins, SCCP		X	
polychlorinated naphtalenes, PCN		X	
polycyclic aromatic hydrocarbons, PAH			X

Table 1. Selected persistent organic pollutants with potential for long-range atmospheric transport. The first twelve are the “Dirty Dozen” currently addressed by the Stockholm Convention

III. ENVIRONMENTAL PATHWAYS AND MULTIMEDIA MODELS

9. The long-distance pathways of POPs are in general:

(a) Atmospheric transport (gas phase, particles and cloud water);
(b) Oceanic transport (dissolved phase and particles);
(c) Riverine transport (dissolved phase and particles);
(d) Transport with migratory animals;
(e) Anthropogenic transport (products and waste).

10. The transport behavior of POPs and their partitioning between different environmental compartments can be modelled by multimedia models. 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. Therefore, they could become useful in the framework of international agreements.

11. Multimedia models are tools that could 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 have suggested that their results are robust and give reliable information on persistence, potential for long-range transport and partitioning between compartments.

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

13. Screening can be done considering persistence, long-range transport potential and substance partitioning between compartments. In the example given in the report, only two transport-orientated models were used. It might be interesting to complement the approach by running a target-orientated model. Thus, substances that are likely to deposit to cold environments (arctic but also mountains) can also be identified.

14. Discussions to suggest methodologies to use these modelled criteria are on-going in different expert groups (e.g. Organisation for Economic Co-operation and Development (OECD), EMEP Meteorological Synthesizing Centre-East (MSC-East)). Eventually, multimedia models are likely to become useful and efficient tools that could speed up the process of organic compound assessment.

IV. ENVIRONMENTAL LEVELS AND TRENDS

15. In 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) produced two definite assessment reports (AMAP 1998 and 2004). Within the United Nations Environment Programme (UNEP) Chemicals, one global report and twelve regional assessment reports were produced, addressing persistent toxic substances (see: UNEP Chemicals/GEF 2003 and references therein). A concise review of health risks of POPs from LRTAP was made by the Joint WHO/Convention Task Force on the Health Aspects of Air Pollution (2003).

16. In this report, localities with major local sources were avoided due to difficulties of separating local contributions from LRTAP. Except for the Arctic, there were rather few broad assessments of the occurrence and effects of POPs attributed to LRTAP in surface waters. The main effort was on waters receiving direct discharges from industrialized and urban areas. We

therefore focused on some case studies and central data sets from pristine areas and upland waters, such as:

(a) Arctic. Environmental levels documented by AMAP;

(b) Europe. (i) European Union (EU) projects ALPE, MOLAR and EMERGE, data on sediments and biota in alpine lakes; (ii) miscellaneous national data on geographical distribution and trends, such as Nordic data from the environmental monitoring programmes of Sweden, Finland and Norway and Scottish sediment data from Lochnagar (Rose et al. 2001);

(c) North America. A comprehensive study was recently performed in Canada (Muir et al. 2002a and b). Levels of POPs in fish, food webs and sediments were studied in 34 lakes from a large area of Canada. Dated sediment samples revealed the historical deposition trends. Other data sources from North America were also available, such as the United States Geological Survey.

17. Most surveys focused on concentrations in sediments and fish. In general, there were few data on concentrations and trends in the water phase. Analyses of water concentrations were complicated due to low levels and analytical problems (detection limits). The levels in fish were dependent on both the concentrations of the specific POPs in the surface waters and the degree of biomagnification (length of food webs). Sediments were often regarded as excellent tracers for trends in pollution. Dated sediment samples could document historical trends in the flux of POPs to sediments (pollution history) and regional surveys of surface sediments could document the geographical deposition pattern.

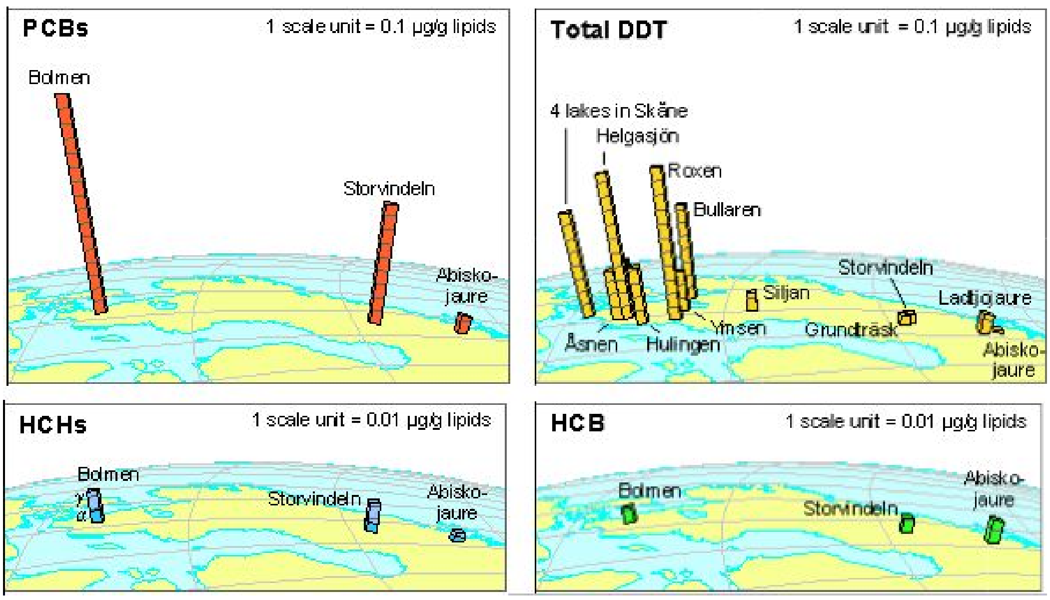

Figure I. POPs in freshwater fish from Sweden, a south-north gradient (Bernes 1998); figures http://www.internat.naturvardsverket.se/documents/pollutants/orggift/orgdok/infiske.gif)

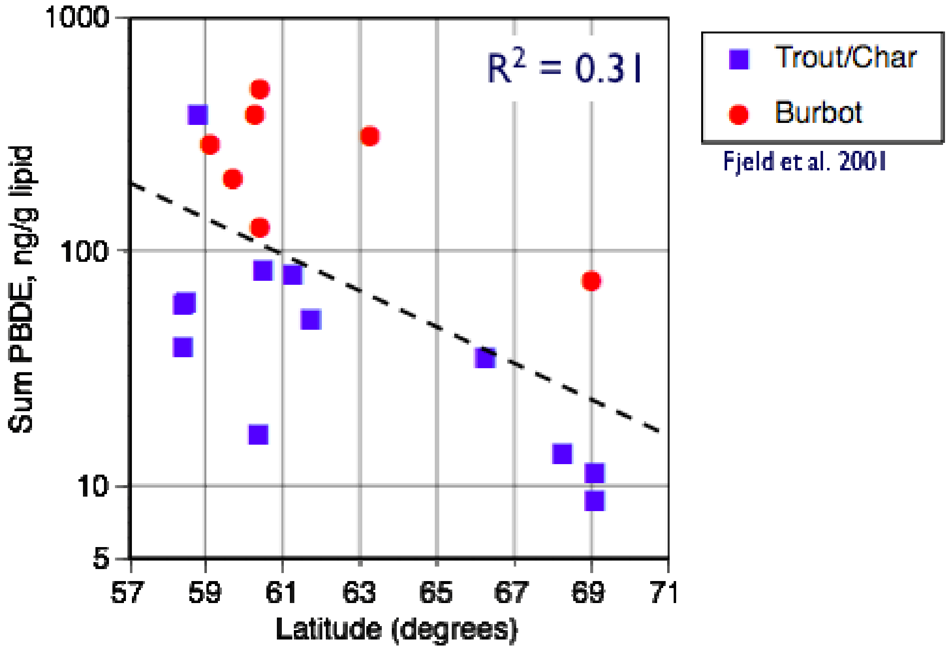

Figure II. Polybrominated dephenyl ethers (PBDE) in freshwater fish from Norway. Muscle fillets of trout and char, liver of burbot. Data from Fjeld et al. 2001

V. CONCLUSIONS AND RECOMMENDATIONS

18. Although great efforts have been put into the reduction of emissions of long-range transported POPs and in monitoring and modelling their atmospheric dispersal, there remains a lack of coordinated surveys on their fate in the freshwater environment. Such surveys are required to provide comprehensive scientific documentation of the effects of the Protocol on POPs and the Convention on POPs. We suggest that a common framework for such surveys be considered.

19. There were few sites with historical trend data. These sites generally showed decreasing levels of the classical POPs (pentachlorophenols (PCB), dichlorodiphenyltrichloroethane (DDT), dioxins etc.).

20. The levels of some new POPs, such as brominated flame retardants (PBDE) and perflourinated alkylated substances (PFAS), were probably rising.

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