Assessment

Controlling persistent organic pollutants—what next?1

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Abstract

Within the context of current international initiatives on the control of persistent organic pollutants (POPs), an overview is given of the scientific knowledge relating to POP sources, emissions, transport, fate and effects. At the regional scale, improvements in mass balance models for well-characterised POPs are resulting in an ability to estimate their environmental concentrations with sufficient accuracy to be of help for some regulatory purposes. The relevance of the parameters used to define POPs within these international initiatives is considered with an emphasis on mechanisms for adding new substances to the initial lists. A tiered approach is proposed for screening the large number of untested chemical substances according to their long-range transport potential, persistence and bioaccumulative potential prior to more detailed risk assessments. The importance of testing candidate POPs for chronic toxicity (i.e. for immunotoxicity, endocrine disruption and carcinogenicity) is emphasised as is a need for the further development of relevant SAR (structure activity relationship) models and in vitro and in vivo tests for these effects. Where there is a high level of uncertainty at the risk assessment stage, decision-makers may have to rely on expert judgement and weight-of-evidence, taking into account the precautionary principle and the views of relevant stake-holders. Close co-operation between the various international initiatives on POPs will be required to ensure that assessment criteria and procedures are as compatible as possible. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Persistent organic pollutants; Bioaccumulation; Biomagnification; Persistence; Global distillation; Risk assessment; Monitoring; Chronic toxicity; Endocrine disruption; Immunotoxicity; Carcinogenicity

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Table 1
Priority substances in the CLRTAP POPs protocol (substances also specified in UNEP Governing Council Decision 19/13c for initial inclusion in the global POPs convention are shown in bold type)

<table>
<thead>
<tr>
<th>Pesticides</th>
<th>Industrial products</th>
<th>Unintentional by-products of combustion and industrial processes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldrin</td>
<td>Hexabromobiphenyl†</td>
<td>Polycyclic aromatic hydrocarbons (PAHs)†</td>
</tr>
<tr>
<td>Chlordane</td>
<td>Polychlorinated biphenyls (PCBs)‡</td>
<td>Polychlorinated dibenzo-p-dioxins (PCDDs)‡</td>
</tr>
<tr>
<td>Chlordecone</td>
<td></td>
<td>Polychlorinated dibenzofurans (PCDFs)‡</td>
</tr>
<tr>
<td>DDT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dieldrin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Endrin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heptachlor</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hexachlorobenzene (HCB)†</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hexachlorocyclohexane (HCH)‡</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mirex</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toxaphene</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Listed under Annex I of the protocol (substances scheduled for elimination).
† Listed under Annex II of the protocol (substances scheduled for restrictions on use).
‡ Listed under Annex III of the protocol (substances scheduled for emission reductions by the use of BAT (best available technology) etc.).

1. Introduction

1.1. Definition

Organic substances that are persistent, bioaccumulative and possess toxic characteristics likely to cause adverse human health or environmental effects are called PBTs (Persistent, Bioaccumulative, Toxic substances). In this context, ‘substance’ means a single chemical species, or a number of chemical species which form a specific group by virtue of (a) having similar properties and being emitted together into the environment or (b) forming a mixture normally marketed as a single product. Depending on their mobility in the environment, PBTs could be of local, regional or global concern. Under the auspices of the United Nations Economic Commission for Europe (UN-ECE) Convention on Long-Range Transboundary Air Pollution (CLRTAP), a protocol on persistent organic pollutants (POPs) has been drawn up in which POPs are defined as ‘a set of organic compounds that: (i) possess toxic characteristics; (ii) are persistent; (iii) are liable to bioaccumulate; (iv) are prone to long-range atmospheric transport and deposition; and (v) can result in adverse environmental and human health effects at locations near and far from their sources’ (UN-ECE, 1998a). In other words, POPs are a subclass of PBTs that are prone to long-range atmospheric transport and deposition. The global extent of POP pollution became apparent with their detection in areas such as the Arctic, where they have never been used or produced, at levels posing risks to both wildlife (Barrie et al., 1992) and humans (Mulvad et al., 1996). Growing concern over recent decades about the potential effects of some man-made chemical substances on human health and the environment has prompted action at many levels from local to global. Some of the international initiatives that address these problems are described below in order to identify the main policy issues and management tools that might contribute to more effective regulation and management of these chemicals.

1.2. Regional initiatives

1.2.1. The CLRTAP POPs protocol

An initiative on POPs was started within the UN-ECE region (comprising eastern and western Europe, Canada and the United States) in 1992 with the establishment of a Task Force on POPs within the framework of the 1979 Convention on Long Range Transport of Air Pollution (CLRTAP); the Convention currently having 43 parties. In 1996, the Executive Body of the Convention established a Preparatory Working Group that drafted a comprehensive negotiating text for a protocol and established a procedure for identifying priority substances to be addressed by it. Starting from an initial list of 107 substances, 16 priority substances were identified for initial inclusion in the protocol comprising 11 pesticides, 2 industrial products and 3 unintentional by-products (Table 1). Excluded from this list are compounds for which insufficient data existed and compounds for which there was no evidence of long-range atmospheric transport.

In 1997, parties to the Convention, meeting in its negotiating body, the Working Group of Strategies, started negotiations and in June 1998, the final draft protocol was presented to the Executive Body for adoption. The protocol is structured in 20 articles and eight annexes. The objective of it is ‘to control, reduce or eliminate discharges, emissions and losses of persistent organic pollutants’. The obligations for the parties to it include:
1. to eliminate the production and use of the substances listed in annex I in accordance with the implementation requirements specified in it;
2. to ensure that the destruction or disposal of the substances listed in annex I is undertaken in an environmentally sound manner;
3. to restrict the substances listed in annex II to the uses described in it;
4. to reduce total annual emissions of the substances listed in annex III; and
5. to develop and maintain emission inventories for the substances listed in annex III.

The designations of the 16 substances in terms of these annexes are included in Table 1.

Some exemptions are allowed because legitimate uses exist for which there are no available alternatives at present (e.g. DDT for encephalitis and malaria control). These exemptions will be regularly reviewed in the light of future technical developments.

Other articles of interest in this context are: article 5—exchange of information and technology; article 6—public awareness; article 8—research, development and monitoring and article 9 in which parties accept obligations that will provide useful components for future development of knowledge about the risk of POPs and alternatives to their uses. Finally, article 14 deals with amendments to the present protocol and includes a reference to the detailed procedure, given in a separate document (EB decision 1998/2), developed to change the list of priority substances (see Section 8, Fig. 3).

1.2.2. Other regional programmes and initiatives address the issue of POPs within the broader context of hazardous substances

1.2.2.1. The Esbjerg declaration. In the Esbjerg Declaration of the 4th International Conference on the Protection of the North Sea in June 1995, ministers agreed to the objective of ‘continuously reducing discharges, emissions and losses of hazardous substances, thereby moving towards the target of their cessation within one generation (25 years) with the ultimate aim of concentrations in the environment near background values for naturally occurring substances and close to zero concentrations for man-made synthetic substances’. As an interim objective it confirmed the goal of ‘reducing by the year 2000, discharges and emissions of substances which are toxic, persistent and liable to bioaccumulate (especially organohalogen substances) and which could reach the environment, to levels that are not harmful to man or nature with the aim of their elimination’.

Subsequently, the targets in this declaration have been adopted by both OSPAR (Oslo–Paris Convention for the Protection of the Marine Environment of the North-East Atlantic) and HELCOM (Helsinki Convention for the Protection of the Baltic) in their respective strategies on hazardous substances agreed in their 1998 ministerial meetings. Similar targets have been adopted by the Arctic Environment Protection Strategy of the Circumpolar Nations and the Barcelona Resolution, adopted by BARCOM (Barcelona Convention for the Protection of the Mediterranean Sea against Pollution).

1.2.2.2. The North American Commission for environmental co-operation (NACEC). Within the framework of the North American Free Trade Area (NAFTA) several North American Regional Action Plans (NARAPs) have been established for DDT, chlordane and PCBs. The main objectives of the PCBs NARAP are to: (a) work toward the virtual elimination of PCBs in the environment, which the task force is interpreting as no measurable release to the environment, and the phase-out of uses for which release cannot be contained; and (b) propose environmentally sound management and control of existing PCBs, throughout their life cycles, with special emphasis given to transboundary shipment of PCBs for disposal/destruction purposes.

The main objective of the DDT NARAP is to reduce the exposure of humans and the environment to DDT and its metabolites through the phased reduction, and eventual elimination of DDT use for malaria control and the elimination of illegal uses of DDT. DDT is currently permitted for limited governmental use for malaria control in Mexico. The DDT NARAP will build on Mexico’s very successful malaria control program, and through an integrated pest-management approach, continue to bring about reductions in the use of DDT.

The objective of the Chlordane NARAP is to reduce the exposure of humans and the environment to chlordane through the phase-out of existing registered uses of chlordane. The chemical currently has limited use in the control of termites. The NARAP will reflect an integrated pest management approach, including the management of existing stocks and the phase-out of chlordane use in North America.

1.2.3. Conclusion

It can be concluded that many parallel actions on POPs are being initiated which provide a very strong drive for action but they will also require urgent efforts to avoid duplication and enhance co-ordination across countries, regions, institutions and social actors.

1.3. Global initiatives on POPs

In the May 1995 United Nations Environment Program (UNEP) Governing Council (GC) decision 18/32, the Inter-organisation Programme for the Sound Management of Chemicals (IOMC) was requested to initiate
an assessment process on POPs, starting with the 12 substances shown (in bold) in Table 1. As a result of this, the International Forum for Chemical Safety (IFCS) concluded, at its meeting in Manila in June 1996, that there was sufficient information to demonstrate that international action, including a global legally binding instrument, will be required to reduce the risks to human health and the environment arising from the release of the 12 POPs. The IFCS recommended to the UNEP GC and the World Health Assembly (WHA), that immediate international action should be initiated to protect human health and the environment from these 12 POPs. Their recommendations were endorsed by the UNEP GC and the WHA in 1997. At the request of the UNEP GC, an Intergovernmental Negotiating Committee (INC) was established with a mandate to prepare, preferably by the year 2000, an international legally binding instrument for implementing international action to reduce and/or eliminate the emissions and discharges of these 12 POPs. Its first session was held in Montreal, Canada, 29 June–3 July 1998.

The INC was requested to establish an expert group for the development of science-based criteria and a procedure for identifying additional POPs as candidates for future international action. UNEP has also initiated a number of immediate actions involving development of alternatives to POPs; identification and inventories of PCBs; available destruction capacity; identification of sources of PCDD/Fs and aspects of their management. Furthermore, UNEP has convened jointly with the IFCS a series of awareness-raising workshops in different regions to help governments prepare for these negotiations and identify POPs-related issues at national and regional levels.

In May 1997, the WHA also endorsed the recommendations of the IFCS and adopted a resolution on POPs, which interalia calls on member states:

- to involve appropriate health officials in national efforts to follow up and implement decisions of the UNEP and WHO governing bodies relating to POPs;
- to take steps to reduce reliance on insecticides for control of vector borne diseases through promotion of integrated pest management approaches in accordance with WHO guidelines and through support for the development and adoption of viable alternative methods of disease vector control; and
- to ensure that DDT is authorised by governments for public health purposes only and limited to government-authorised programmes.

The UNEP Governing Council decision 18/31 from 1995 concerned the Protection of the Marine Environment from land-based activities through a global programme of action (GPA). The decision specifically addressed POPs and called on States to consider how, within the GPA, appropriate attention could be given to support action at a national and regional level on POPs. The GPA was adopted in November 1995 and includes commitments to develop a global, legally binding instrument for the reduction and/or elimination of emissions, discharges and, where appropriate, the elimination of the manufacture and use of the POPs identified in decision 18/32.

1.4. Challenges in effectively implementing provisions in the CLRTAP protocol and the planned UNEP global initiative

The UN-ECE CLRTAP protocol is currently the only international instrument for the control of risks from POPs as a distinct class of chemicals. It represents a comprehensive set of provisions for the elimination or restriction in use of a number of POPs that can provide a good basis for negotiations on the global agreement under UNEP. In this section, challenges in effectively implementing the provisions of the CLRTAP POPs protocol are explored with reference to both the UN-ECE region and the global scale.

The CLRTAP protocol focuses on the atmospheric pathway as a transport route for POPs. Although this pathway is clearly one of the main routes by which POPs reach remote regions, other (in particular aquatic) pathways are likely to be considered for the global instrument. Many of the substances identified in the protocol have already been restricted or phased out within UN-ECE countries. Consequently, implementation of the obligations under the protocol will be less problematic for parties to the CLRTAP than for many countries outside this region where these substances tend to be more widely used.

The CLRTAP POPs protocol identifies a number of substances for elimination (annex I to the protocol). Some exemptions to these obligations are identified which allow production or use in limited circumstances. These are included to accommodate some countries where significant current usage of some POPs precludes immediate phase out. The challenge will be to ensure that actual usage is limited to those authorised activities only. Within the UN-ECE region there will be a need for support and advice for countries in eastern Europe to help them to develop practical implementation plans and monitor compliance. Monitoring compliance for restricted use will be much more difficult than for elimination. The success of monitoring efforts will depend upon access to trained personnel and institutional development.

At the global scale, many countries use more of the POPs listed in the CLRTAP protocol than do UN-ECE countries and may have more difficulties with the elimination of these substances. Also, considerable challenges may present themselves in the implementation of
restricted use of POPs in developing countries. One key
question is whether viable alternatives exist for all the
different situations in which POPs are current used in
developing countries. Any phasing out of POPs will
have to go hand-in-hand with capacity building with
respect to infrastructure, legislative methods of control
and monitoring. Particular problems can result from
old stockpiles of POPs, in particular DDT. The elimi-
nation of the existing stocks in an environmentally
sound manner will be a challenge in some parts of the
world. Illegal (non-essential) uses and illegal trade may
also present major difficulties. There will be a need for
advice, information and training on implementing re-
placements for current POPs usage. These may com-
prise the use of alternative chemicals, the adoption of
environmental, other technical, or medical management
options for controlling pests and vector-borne diseases
as well as changes in methods of use, such as more
efficient application of DDT for malaria control. Dif-
ferent control options for managing pests and vectors
are usually most effective when combined with, and
integrated into, strategies which are ‘customised’ to
address specific situations. On-going activities in this
regard include the newly established Global Integrated
Pest Management facility of the Food and Agriculture
Organisation (FAO)/UNEP/UN Development Pro-
gram/World Bank and the WHO/FAO/UNEP Panel of
Experts on Environmental Management for Vector
Control.

The UN-ECE CLRTAP obligations for PAHs,
PCDD/Fs and HCB are phrased in terms of limit
values for the potential sources, application of BAT to
stationary and mobile sources and reductions in total
national emissions. The challenge will be to encourage
the implementation of BAT where factors such as costs
and effective transfer of technologies will be important.
Structural changes in certain practices and lifestyles
may also lead to significant emission reductions. How-
ever, there are risks that when old technology is re-
placed it may be passed on to countries outside the
UN-ECE area.

The need for emission inventories for POPs is iden-
tified in the CLRTAP protocol. At present, few emis-
sion inventories are available even for the UN-ECE
region and these are uncertain with some sources miss-
ing. The choice of the base year identified under the
protocol (it can be between 1985–1995) may allow for
emission increases from current levels for some coun-
tries. In countries outside the UN-ECE region, emission
sources might be very different. For example, waste
incineration may not represent a major source in some
countries whereas in others, where open incineration is
common, it would be much more significant. In general,
facilities for the disposal of hazardous waste may not
be readily available in many of these countries. This
situation will not change without the introduction of
new technologies and trained personnel. The capacity
to develop emission inventories will have to be en-
hanced both within the UN-ECE region and, even
more so, on a global scale for the UNEP process.
Information on relevant pathways, natural sources and
sinks, is also missing.

Articles described in the CLRTAP protocol referring
to exchange of information, public awareness and re-
search and development, can contribute very signifi-
cantly to the achievement of its objectives and the
future development of fair and effective control options
for POPs. Consequently, it would be extremely cost-ef-
fective in the medium and long term to promote these
activities at both national and international levels. The
challenge will be to put the ideas and issues identified in
these articles into practice. How exactly will the activi-
ties be organised and implemented? Articles referring to
public awareness represent new ground for the CLR-
TAP and it will be important to determine how these
initiatives are to be organised and co-ordinated. The
implementation of article 14 on amendments and the
executive body decision on criteria and procedures to
add new substances to the protocol will be difficult.
POPs are being considered under a number of interna-
tional initiatives and there is a risk that scarce resources
could be inefficiently used in parallel processes. There is
therefore, a need for close co-operation between the
different international initiatives to ensure for example,
that assessment criteria and procedures are as compat-
able as possible.

A major objective of this paper is to provide scientific
guidance in the definition and use of assessment criteria
and procedures in order to ensure consistency through-
out the various international and regional initiatives on
POPs.

2. Sources of POP emissions

2.1. Introduction

Emission inventories for POPs are restricted to rela-
tively few compounds, are generally uncertain and lack
spatial and temporal resolution (UN-ECE, 1994). The
source of entry into the environment for manufactured
POPs is determined by where and how they are used.
Pesticides are intentionally released at their point of
application. Industrial chemical POPs are unintention-
ally released by volatilization, leakage or leaching either
during a product’s lifetime or after ultimate disposal.
Unintentionally produced POPs are by-products of in-
dustrial or combustion processes emitted from both
stationary and mobile sources.
2.2. Pesticides

In many countries, there has been a gradual move towards the use of less persistent and less bioaccumulative pesticides. However, in some developing countries, especially in tropical regions, organochlorine pesticides (such as DDT, HCH, chlordane and heptachlor) are still used in agriculture and to control arthropods of medical or veterinary importance. This is reflected in declining levels of HCH and DDT in human tissues from developed countries whilst in many developing countries these levels remain stable (Loganathan and Kannan, 1994). The use of several organochlorine pesticides (particularly DDT) is still recommended by national and international health organisations to control mosquitoes, flies and lice which spread malaria, typhus and typhoid. However, the WHO predict that with reduced world-wide production, the rapid development of insect resistance and the possible appearance of suitable alternatives, DDT use may cease without significant legal intervention (WHO, 1996). Chlordane and heptachlor are still used to control termites although their use is steadily being phased out in one country after another.

Plants can either absorb these chemicals directly through their leaves or indirectly from the soil. The plants may then be eaten by herbivores and accumulate to relatively high levels in meat and animal dairy products. Pesticide residues in food create an important, though under-reported, exposure route (Repetto and Baliga, 1996).

Pesticides that are not bound in soils or taken up into plants and animals can drain into rivers and lakes and move into the aquatic food chain. Several chlorinated pesticides have been detected in rivers in Tanzania, Colombia, Indonesia, Malaysia, China and Thailand at levels suggesting potentially severe damage (Repetto and Baliga, 1996). The semi-volatile nature of these pesticides also allows them to be dispersed rapidly through air. Iwata et al. (1994) showed that persistent and semi-volatile compounds (including HCHs and DDTs) discharged in the tropics tend to be redistributed on a global scale. In a study of the global distribution of persistent organochlorine pesticides, Simonich and Hites (1995) reported high concentrations not only in some developing countries but also in industrialised countries where the use of many of these compounds have been restricted for many years. For example, the presence of DDT, chlordane, dieldrin, HCHs and toxaphene in southern Ontario has been linked with their use in southern USA, Mexico and the Caribbean (Hoff et al., 1992). The latitudinal distribution of atmospheric HCHs and DDTs suggests that their major contamination source in global terms has shifted from mid to low latitudes during the 1980s (Iwata et al., 1993). Weber and Goerke (1996) also found there had been a significant increase in p,p'-DDE (a metabolite of DDT) in various Antarctic fish species between 1987 and 1991. This is consistent with the fact that usage of many organochlorine pesticides is continuing, and in some cases increasing, in developing countries near the tropics.

In addition to emissions from localised sources represented by treated crops etc., revolatilization from larger contaminated areas, including oceans, soils and forests, also occurs. The cycling of these semi-volatile compounds between environmental compartments makes it difficult to distinguish source from sink. Evaporation during the warmth of the day can change to net deposition with the cold of the night and seasonal temperature changes can have a similar effect, albeit on an annual cycle (Hornbuckle and Eisenreich, 1996). Also, on a longer time scale, the decline in atmospheric HCH over the Arctic Ocean during recent years has reversed the net direction of air–sea gas exchange to the point where some northern waters are now sources of the pesticide to the atmosphere instead of sinks (Bidleman et al., 1995).

2.3. Industrial products

2.3.1. Polychlorinated biphenyls

The polychlorinated biphenyls (PCBs) are a group of chlorinated hydrocarbons consisting of 209 possible congeners ranging from three monochlorinated isomers to the fully chlorinated decachlorobiphenyl isomer. Their physico–chemical properties vary with respect to their degree of chlorination. Generally, water solubility, vapour pressure and biodegradability decrease with an increasing degree of chlorine substitution while hydrophobicity and sorption tendency increase. Their combination of high persistence and mobility means that PCBs have been identified in almost every environmental compartment or matrix (Fiedler, 1997). PCBs were formerly used as dielectric fluids in transformers and large capacitors, as pesticide extenders, plasticisers in sealants, as heat exchange fluids, hydraulic lubricants, cutting oils, flame retardants, dedusting agents, and in plastics, paints, adhesives and carbonless copy paper. Some of their applications resulted in direct or indirect releases into the environment and large amounts were released due to inappropriate disposal, accidents (e.g. transformer fires) and leaks from industrial facilities. Although PCB production in most countries was banned in the 1970s and 1980s, the current world inventory of PCBs is estimated at 1.2 million tonnes with about one third of this quantity circulating in the environment (Duursma and Carroll, 1996). Leakage from old equipment, building materials, stockpiles and landfill sites constitutes a continued threat of PCB emission and some production is reported for certain countries with economies in transition (UN-ECE,
Table 2
Annual emissions of PAH, PCB, HCH and PCDD/Fs in Europe per source category in 1990 (adapted from Berdowski et al., 1997)

<table>
<thead>
<tr>
<th>Source category</th>
<th>PAH (t/y)</th>
<th>PCB (t/y)</th>
<th>HCB (t/y)</th>
<th>PCDDs/PCDFs (g I-TEQ*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel combustion (excluding transport)</td>
<td>6777</td>
<td>5.69</td>
<td>0.46</td>
<td>4304</td>
</tr>
<tr>
<td>Production processes:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iron and steel industry</td>
<td>612</td>
<td>1.46</td>
<td>0.24</td>
<td>1964</td>
</tr>
<tr>
<td>Non-ferrous metal industry</td>
<td>1010</td>
<td>—</td>
<td>0.05</td>
<td>1611</td>
</tr>
<tr>
<td>Organic chemical industry</td>
<td>—</td>
<td>—</td>
<td>0.56</td>
<td>0.2</td>
</tr>
<tr>
<td>Paper and pulp industry</td>
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<td>—</td>
<td>—</td>
<td>4.5</td>
</tr>
<tr>
<td>Road paving with asphalt</td>
<td>112</td>
<td>—</td>
<td>—</td>
<td>1.0</td>
</tr>
<tr>
<td>Cement industry</td>
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<td>—</td>
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<td>19.1</td>
</tr>
<tr>
<td>Glass industry</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.4</td>
</tr>
<tr>
<td>Paint use</td>
<td>593</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Wood preservation</td>
<td>4817</td>
<td>—</td>
<td>—</td>
<td>0.4</td>
</tr>
<tr>
<td>Other solvent use</td>
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<td>0.21</td>
<td>—</td>
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<tr>
<td>Road transport combustion</td>
<td>1488</td>
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<td>—</td>
<td>73.1</td>
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<tr>
<td>Other transport combustion</td>
<td>195</td>
<td>—</td>
<td>—</td>
<td>63</td>
</tr>
<tr>
<td>Waste treatment and disposal:</td>
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<td></td>
</tr>
<tr>
<td>Waste incineration</td>
<td>6</td>
<td>0.05</td>
<td>0.07</td>
<td>2657</td>
</tr>
<tr>
<td>Landfill</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>19.9</td>
</tr>
<tr>
<td>Cremation</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>23.1</td>
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<tr>
<td>Pesticide use</td>
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<td>—</td>
<td>5.76</td>
<td>—</td>
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<tr>
<td>Electrical equipment</td>
<td>—</td>
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<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Natural sources</td>
<td>53</td>
<td>—</td>
<td>—</td>
<td>2.1</td>
</tr>
</tbody>
</table>

* International toxic equivalents

1998a). Some time-trend surveys of PCB concentrations in human adipose tissues show no significant decline thus implying continued exposure of humans, even in developed nations (Loganathan and Kannan, 1994). Conversely, decreasing trends have been observed in tissues of various biota (e.g. fish, seals, birds) of the Baltic Sea (Olsson et al., 1997).

2.3.2. Hexachlorobenzene
Hexachlorobenzene (HCB), in addition to its use as a fungicide, has been used in the manufacture of military pyrotechnics, as a fluxing agent in aluminium smelting, as a porosity control in the manufacture of graphite electrodes, as a peptising agent in the rubber industry and as an intermediate in dye manufacture. It is also a by-product of the manufacture of various chlorine-containing chemicals and is a known impurity in several pesticide formulations. HCB as a pesticide, is banned in many countries and is severely restricted or voluntarily withdrawn in several others. Estimates of the current scale of international production are contradictory. HCB is ubiquitous in the environment and has been measured in foods of all types and has been detected in Arctic air, water and organisms (Ritter et al., 1995).

2.4. By-products
Emission data for developing countries and countries in transition are scarce because of the costly analysis of these contaminants. However, it can be expected that in developing countries, sources will be similar to those in developed countries although their relative importance may be different (UNEP, 1996). A European emission inventory is given for the by-product POPs in Table 2. This is adapted from an inventory for eight heavy metals and 15 POPs for 38 European countries carried out by Berdowski et al. (1997). The base year is 1990 and the results are a mixture of official data (submitted by 14 countries) and default emission estimates. In addition to their emission sources as by-products, the table also includes sources resulting from their intentional use (i.e. in paints, wood preservation, other solvent use and road paving with asphalt for PAH and in electrical equipment for PCBs). Emission estimates are required to serve as reference points in protocols (to assess the effectiveness over time of any actions taken) and as inputs for modelling purposes. However, it should be borne in mind that, for the European POP emission estimates given in Table 2, the uncertainty factors are estimated at between 2 and 5 for PAHs: PCBs and 5–20 for PCDD/Fs (Berdowski et al., 1997).

2.4.1. Dioxins and furans
Polychlorinated dibenzo-para-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), also referred to as dioxins and furans, respectively, are two chemically similar groups of chlorinated aromatic compounds. The PCDD group comprises 75 and the PCDFs 135 possible congeners, 17 of which are reported to have potential health effects. PCDDs and PCDFs are not commercially produced but are formed unintentionally as by-products of various industrial and
Polycyclic aromatic hydrocarbons (PAHs) are compounds containing only C and H, and are the product of any combustion process involving material containing C and H (e.g., coal, oil, petrol, wood). Emissions from anthropogenic activities predominate (see Table 2), but some PAHs in the environment arise from natural combustion such as forest fires and volcanoes (Baek et al., 1991; Howsham and Jones, 1998). There are also some minor biogenic sources (from plants, algae/phytoplankton and microorganisms) (UN-ECE, 1994) and small amounts are formed by diagenesis (i.e., by slow transformation of organic materials in lake sediments). PAHs occur naturally in crude oil and form a significant component of petroleum products such as some paints, creosote (used in wood preservation) and asphalt (used for road paving) and in this sense could be regarded as an intentionally used class of substances as well as being unintentionally produced by-products. PAHs are relatively reactive in the atmosphere but they can persist long enough to become transported over long distances to remote areas. For example, transport of PAHs to the Arctic via atmospheric suspended particulate matter, clearly from coal or oil-burning sources, has been reported by Daisey et al. (1981). Various PAHs have also been measured in remote marine atmospheres over the tropical north Pacific (Gagosian et al., 1981) and the Mediterranean (Siére et al., 1987) confirming their long-range transport potential.

2.5. Parameters determining emission and transfer to the atmosphere

Emissions to the atmosphere depend on a POP’s intrinsic properties, the ambient environmental conditions and the types of process by which it is produced, formed, applied or disposed of. Emissions can both take place in gaseous form and in particle-bound form, the latter being especially important during combustion. The intrinsic properties of a POP that largely determine its primary emissions in gaseous form to the atmosphere and its volatilisation from water, soil and vegetation are its vapour pressure, Henry’s-law constant (i.e., air–water partition coefficient) and octanol–air partition coefficient. Vapour pressure is a measure of the POP’s tendency to migrate in gaseous form from its pure liquid or solid state but does not take into account its tendency to dissolve in water or absorb to other surfaces. Henry’s law constant, being the vapour pressure divided by water solubility, does express the POP’s tendency to migrate into air from solution in water but it does not quantify sorption to organic carbon or lipids. The octanol–air partition coefficient, (being the octanol–water partition coefficient divided by Henry’s law constant) expresses the POP’s tendency to move from air to organic media such as soils and vegetation. Experiments in which emissions of soil-applied pesticides to the atmosphere were measured showed good correlations between the octanol–air partition coefficient and the percentage emission (Finizio et al., 1997a). As the values of all three parameters depend on temperature, it is important to consider this when these parameters are used for screening or for risk assessment purposes.
3. Transport and deposition processes

3.1. Evidence for long-range transport

Many POPs possess a combination of volatility and resistance to photolytic, biological and chemical degradation such that they are capable of long-range atmospheric transport. POPs have been measured on every continent and even in remote regions such as the open oceans (Hargrave et al., 1988; Iwata et al., 1993), deserts, the Arctic (Barrie et al., 1992) and the Antarctic (Tanabe et al., 1982; Bidleman et al., 1993) where no significant local sources exist. PCBs have also been reported in human populations throughout the world (Mes, 1987). The ubiquitous distribution of these chemicals has been known for some time. The presence of DDTs and PCBs in the Antarctic was first reported in the 1960s and 70s (George and Frear, 1966; Sladen et al., 1966; Risebrough and Carmignani, 1972) and contamination of the Arctic by several organochlorines was evident by the 1970s (Bowes and Jonkel, 1975; Clausen and Berg, 1975; Goldberg, 1975; Barrie, 1986).

More recently it has been realized that the concentrations found in Polar regions are surprisingly high given the remoteness from sources (Wania and Mackay, 1993). In the Arctic, unexpectedly high levels of certain organochlorines were observed in seawater (Hargrave et al., 1988), precipitation (Gregor and Gummer, 1989), plankton (Bidleman et al., 1989) and wild animals (Muir et al., 1988; Norstrom et al., 1988). Weber and Goerke (1996) found concentrations of HCB in Antarctic fish to be as high as in North Sea fish. Levels of POPs found in Arctic marine ecosystems (Barrie et al., 1992) are such that there are concerns that biota, especially top predators and aboriginal peoples utilizing marine mammals and fish in their traditional diet (Kinloch et al., 1992), may be adversely affected by chronic exposure to these pollutants (Dewailly et al., 1989).

3.2. The global distillation/fractionation effect

One explanation for the tendency for POPs to migrate and deposit in Polar regions, is the ‘global distillation/fractionation effect’ expounded by Wania and Mackay (1993). It was suggested as long ago as 1974 (Rappe, 1974) that ‘the rule of the cold wall’ might explain the high concentrations of some organochlorines in circumpolar wildlife and that pesticides used in warm climates ‘become evaporated and transported to cool areas where they will be condensed’. The term ‘global distillation’ was first coined by Goldberg (1975) in relation to the atmospheric transfer of DDT from continents to oceans. This phenomenon has also been referred to as the ‘cold condensation’ (Otter, 1981), the ‘cold finger’ (Weschler, 1981) or the ‘cold trap’ (Rahn and Heidam, 1981) effect. More recently, Wania and Mackay (1993) hypothesized that ‘the physico-chemical properties of these chemicals, and certain factors characterizing cold environments, contribute to the long-term spatial distribution patterns of organochlorine chemicals as much as, or even more than, the relative location of emission areas and transport pathways. In particular the volatility of a compound and the ambient temperature level strongly influence the observed distribution pattern.’ In other words, their moderate volatility means that POPs tend to volatilize from tropical and temperate regions of the globe, and condense, and then tend to remain, in colder regions. Wania and Mackay (1996) also suggest that POPs migrate to higher latitudes in a series of relatively short jumps, sometimes termed the ‘grasshopper effect’, whereby they migrate, rest and migrate again in tune with seasonal temperature changes at mid-latitudes (Fig. 1). Each POP may have its own distinctive environmental condensation temperature or temperature range. It has been suggested that the more highly volatile POPs will tend to remain airborne and migrate faster and further towards the polar regions than the less volatile POPs. This should lead to individual POPs separating out in the atmosphere along a temperature or latitudinal gradient, according to their degree of volatility, in a process termed ‘global fractionation’. This also implies that regions of past emission can continue to act as contaminant sources even after releases have declined or ended because of slow release from accumulated chemical reservoirs.

Other evidence from both modelling (Mackay and Wania, 1995) and monitoring (Muir et al., 1990; Calamari et al., 1991; Iwata et al., 1993; Simonich and Hites, 1995) supports the above hypothesis. Also, in a study of spatial trends and historical profiles of organochlorine pesticides in Arctic lake sediments, Muir et al. (1995) found that their results supported two of the main predictions of the cold condensation hypothesis: (i) that the more volatile organochlorines would preferentially accumulate in polar regions and (ii) that temporal trends in their deposition would differ from trends in temperate regions. It appears that there is a growing scientific consensus in favour of the global distillation/fractionation hypothesis.

Several factors are involved in POPs’ tendency to condense, deposit and accumulate in cooler ecosystems. Temperature-dependant physico-chemical properties such as vapour pressure and solubility in water play a strong role in determining the environmental fate of all chemicals. Because of their semi-volatility, POPs can exist in the atmosphere both in the vapour phase and, in a condensed form, adsorbed onto small aerosol-sized particles. Knowing the physical state of a compound is critical to the understanding of its transport and deposition. Atlas (1990), Bidleman et al. (1986) and others have extensively studied the distribution of POPs be-
tween gas and particle phases. Finizio et al. (1997b) have shown that the octanol–air partition coefficient is an excellent descriptor of this distribution. In general terms, cooler conditions favour greater adsorption onto atmospheric particulate matter which is then deposited more rapidly either by dry deposition or by precipitation scavenging (which is more effective for particles than for vapours). Cooler conditions also promote enhanced adsorption from the vapour phase onto vegetation, soil, water, snow and ice at the Earth’s surface. Subsequently, accumulation will be enhanced under cooler conditions due to reduced rates of POP degradation (i.e. increased persistence) and a reduced tendency to revolatilize. POPs encompass a wide range of vapour pressures, the more volatile compounds being transported further towards higher latitudes before encountering temperatures sufficiently low to cause them to become predominantly associated with the particle phase and so subject to more rapid deposition. Thus the global distillation/fractionation hypothesis predicts that these chemicals will become latitudinally (and altitudinally) fractionated according to their volatility. Very volatile compounds may never encounter environmental temperatures sufficiently low to condense appreciably, even if they are persistent.

3.3. Uncertainties in modelling the transport and deposition of POPs

The multi-hop nature of the environmental transport of POPs complicates the estimation of source-receptor links (Wania, 1997). Attempts to relate deposition rates to emission rates are frustrated by the lack of emission data, uncertainties about partitioning between gaseous and aerosol phases and a lack of data on physico-chemical properties, especially as a function of temperature (Vozhzennikov et al., 1997; Atlas, 1990). There are also few data on the effect of different surfaces on deposition rates (Lukoyanov et al., 1992; Horstmann et al., 1997; Vozhzennikov et al., 1997) and considerable uncertainties about reaction or degradation rates of these substances in the atmosphere and in the media of deposition, including soils and water bodies (Vozhzennikov et al., 1997).

Despite these difficulties there is optimism that, at a regional scale and for well characterised POPs, improvements in mass balance models are resulting in an ability to estimate their concentrations in various environmental compartments, with sufficient accuracy to be of help for some regulatory purposes. Larger-scale models are beginning to provide valuable insights and data which can guide and inform regulators. A review of these models showed that accuracy’s within factors of 3–5 could be achieved for relatively well characterized compounds (Cowan et al., 1995). A recent modelling exercise for lindane in Europe achieved a factor of 3 accuracy (Van Jaarsveld et al., 1997). Similar efforts on the series of chlorobenzenes in Canada have been successful in reconciling emission rates with re-

Fig. 1. POP global migration processes. (Reprinted with permission from Wania and Mackay (1996). Copyright (1996) American Chemical Society.)
ported concentrations (MacLeod, M, and D. Mackay, An assessment of the environmental fate and exposure of benzene and the chlorobenzenes in Canada, (submitted for publication)). At a global scale, there has been success in compiling a model of the global distribution of alpha HCH for emissions from 1947 to the present and obtaining concentration data in the atmosphere and oceans which are consistent with monitoring data (Wania, F., D. Mackay, Y.-F. Li, T.F. Bidleman, and A. Strand, Global chemical fate of α-hexachlorocyclohexane. 1. Modification and evaluation of a global distribution model (submitted for publication); Wania, F. and D. Mackay, Global chemical fate of α-hexachlorocyclohexane. 2. Use of a global distribution model for mass balancing, source apportionment, and trend predictions (submitted for publication)). There is a clear need for continuing efforts to obtain monitoring data, physico–chemical properties and emissions for more POPs, and use them to further develop and test models at local, regional, national, continental and global scales.

3.4. Criteria for gauging long-range transport potential

The relevant parameters are:
- Volatility—measured by vapour pressure;
- Persistence in air or water—measured by half-lives;
- Documented evidence (i.e. monitoring data) that the substance undergoes long-range transport and is found in remote regions at relevant concentrations.

3.4.1. Volatility

In the CLRTAP POPs protocol a vapour pressure criterion of < 1000 Pa is suggested. The rationale for this is partly that it excludes volatile chemicals, such as CFCs, which are the subject of other protocols. It also reflects the view that volatile substances are unlikely to partition into terrestrial or aquatic systems. This criterion excludes relatively few chemicals and probably, it could be eliminated with few adverse consequences. It can be argued that, for a substance to be transported in the atmosphere, it should have a vapour pressure exceeding some minimum value. However, it would be difficult to specify such a criterion because of the possibility of the transport of involatile compounds in an aerosol phase and the complication of selection between solid and liquid vapour pressures. It is also difficult to measure very low vapour pressures. In the future, it may be preferable to specify minimum and maximum limits to the octanol–air partition coefficient. This coefficient can be calculated as the ratio of octanol–water and air–water partition coefficient and is believed to give an excellent characterization of partitioning from air to aerosols, soils and vegetation. It is still a fairly recently developed concept and few measurements are available, but is could prove valuable in future assessments of the relative potential for atmospheric transport.

3.4.2. Persistence in air or water

A chemical must have a sufficiently long atmospheric residence time in order to be subject to long-range atmospheric transport. The two major processes controlling atmospheric residence time are degradation rate and rates of deposition/recycling. Important parameters determining the degradation rate of POPs in the atmosphere are temperature and the reaction rate constant for reaction with the OH-radical. The overall degradation rate is generally estimated by a half-life value. An atmospheric half-life greater than 2 days is considered necessary for long-range atmospheric transport in the CLRTAP POPs protocol.

The partitioning of a POP between the gas and particle phases affects its residence time with higher volatility tending to confer longer residence times. The vapour pressure of the POP and the ambient air temperature are therefore important parameters determining its atmospheric residence time. Deposition will take place either as wet or dry deposition. Wet deposition includes both POPs dissolved in the precipitation and POPs bound to particles. Henry’s law constant ($H$) is an important parameter for the partition of POP between gas and water phases. The gas/surface (water, soil, vegetation) exchange process has also been shown to be significant for POPs, important parameters being vapour pressure, $H$, and the octanol–water and octanol–air partition coefficients.

Under the proposed UNEP global POPs initiative, long-range transboundary transport by other means, such as in ocean currents and rivers, will also have to be considered. However, it should be noted that a particular half-life in water appropriate for assessing oceanic transport potential would be inadequate for more rapid, riverine transport.

4. Bioaccumulation

4.1. Definitions

Bioconcentration and the bioconcentration factor (BCF) refer to the uptake of a chemical by an aquatic organism from water. Bioaccumulation refers to uptake from both water and food and the bioaccumulation factor (BAF) is the ratio of organism and water concentrations. Biomagnification factors are usually the ratio of the concentration in the predator to that in the prey, possibly on a lipid-adjusted basis. Not all of the chemical present in the water is necessarily available because of sorption to suspended and dissolved matter, usually organic in nature. This phenomenon is referred to as bioavailability. The most frequently employed descrip-
tor of bioconcentration and bioaccumulation for non-polar organic compounds is the octanol–water partition coefficient, which quantifies hydrophobicity as a determinant of partitioning from water to lipid phases.

4.2. Mechanisms of bioaccumulation

Because of their low solubility in water and their resistance to chemical and metabolic degradation, most POPs are eliminated from organisms very slowly (UN-ECE, 1994). As a consequence of this persistence, POPs can accumulate to relatively high levels in biota even at low environmental exposures. Phytoplankton can sorb dissolved DDT, HCB and PCB directly from the water and it has been suggested that DDT may be accumulated directly through gill membranes in Arctic char (Swain et al., 1992). However, in the aquatic environment the primary route of initial entry into the food chain is through active uptake of POP-contaminated particulate matter by filter-feeders and plankton (Thomann et al., 1992) and at higher trophic levels dietary uptake is more important than direct absorption (UN-ECE, 1994). Deposition and degradation processes and the bioavailability of POPs in terrestrial ecosystems are less well understood. However, it is known that POPs can be absorbed through plant surfaces; pine needles have been found to be useful indicators of atmospheric contamination by organochlorines (Eriksson et al., 1989). For HCB, HCH and toxaphene, the indications are that the air/plant/animal contaminant pathway is the major route taken by these compounds into the arctic terrestrial food chain (Thomas et al., 1992).

The resistance of POPs to chemical and metabolic degradation means that they can become more concentrated the further they move up through food chains (i.e. they are subject to biomagnification). Biomagnification can lead to concentrations in top predators many orders of magnitude higher than in the environment. This is especially true of aquatic food chains which tend to be more complex and longer than terrestrial food chains. Table 3 shows that, for Arctic marine food chains, bioaccumulation factors (BAFs) from water to higher trophic level predators (seal, beluga, seabirds and bears) can be in the order of $10^7$ for toxaphene and HCB and as high as $10^9$ for PCBs.

4.3. Predicting the bioaccumulation potential of a POP

The level of bioaccumulation in a target species depends on the food chain structure of the particular ecosystem in which it lives. For example, Baleen whales which skim the water for plankton are less contaminated than predatory species living in the same region (Ballschmitter, 1996). Even different populations of the same species, living in areas of equivalent ambient contamination, can contain very different levels of POPs simply because of different feeding patterns. For example, it was discovered that in one Canadian walrus population, where levels of contamination with PCB, DDT, toxaphene and chlor dane were particularly high, the animals were feeding on seals as well as molluscs (Segstro et al., 1993). They were, therefore, feeding at a higher trophic level than other less contaminated walrus populations which largely subsisted on molluscs.

Biomagnification in a particular ecosystem can be studied using stable isotope analysis with the ratio of $^{15}$N abundance relative to $^{14}$N in an organism increasing on average 3–5 parts per thousand (‰) compared with its source of dietary nitrogen (Peterson and Fry, 1987) due to the preferential excretion of the lighter isotope during metabolic processes (Gaebler et al., 1966). Using this technique, Kidd et al. (1995) showed that biomagnification through an unusually long food chain in Lake Laberge, Canada was the reason that lake trout and burbot contained amounts of toxaphene and other lipophilic contaminants several times greater than levels found in the same species inhabiting some other subarctic Canadian lakes. The bioaccumulation potential of a substance depends on the different metabolic characteristics of different species. This can result in large differences in biotic persistence for a particular POP. For example, a particular dioxin can
have a half-life of a few weeks in rats whilst in humans it is 7–9 years (Ballschmitter, 1996). Also, differences in the ability of a single animal species to metabolise different POPs, or even the different congeners of the same group of POPs, often hinder attempts to predict biomagnification (Muir et al., 1988). For risk assessment purposes it can be concluded that it is difficult to predict the actual level of exposure of a receptor organism, for a given concentration of POP in its ambient environment, without having detailed knowledge of the species’ position in the ecosystem food web and of the POP’s biotic persistence throughout the relevant food chain. Despite these difficulties there have been successes in applying bioaccumulation models to single organisms and even food chains when there is adequate understanding of the properties of the POP, its bioavailability and the characteristics of the organisms and their diets.

4.4. Bioaccumulation criteria

The primary criterion for bioaccumulation for all chemicals is the bioaccumulation factor (BAF) or in fish, the bioconcentration factor (BCF). A secondary criterion for non-polar, hydrophobic organic chemicals is the octanol–water partition coefficient, if the molecular weight of the substance is less than some critical value, variously estimated to lie between 600 and 1200, and if the substance is not metabolized.

5. Persistence

The simplest approach is to set criteria for half-lives in the four primary media of air, water, soil and sediment. For example, the following criteria have been suggested for the CLRTAP POPs protocol:

- Half-life in air > 2 days;
- Half-life in water > 2 months;
- Half-life in soil or sediments > 6 months.

Although these criteria appear simple and straightforward there are likely to be severe difficulties when applying them:

- Unlike a radionuclide, the half-life of a POP depends on its environment, e.g. the temperature, redox status, incidence of sunlight, the presence of reactive chemical species and the nature of microbial communities. A specific POP thus experiences a spectrum of half lives with variations in time and space. Applying a sharp cut off or a ‘bright line’ is thus likely to be difficult and controversial.

- Although there are established test procedures for biodegradability and for assessing pesticide fate in soils, no standard test protocols exist for measuring half-lives, in the laboratory or the environment, in which all relevant processes in these media are included. There are also difficulties in translating laboratory results to the environment.

- The overall persistence of a chemical in the environment depends on how it is emitted to the environment (i.e. to air, water, or soil) and on how it subsequently migrates between media. The implication is that a substance may be quite short-lived if discharged to air, but long lived if it is discharged to water. Furthermore, a long half-life in a medium may be relatively inconsequential if the substance is not emitted to that medium or is unlikely to transfer to it. For example, an accurate half-life for reaction in air may not be needed for a relatively involatile chemical which is unlikely to evaporate into the atmosphere.

- It should be appreciated that if a criterion of say 6 months is used as a half-life, it will be necessary to observe the chemical concentration decrease for at least two half lives or 1 year. Under environmental conditions, it is inevitable that conditions such as temperature will change substantially during that period and it will be difficult to obtain reproducible results.

- In determining the half-life for a medium, all reaction mechanisms, including biodegradation, hydrolysis, photolysis etc., should be considered but not losses by transport to other media (e.g. by sedimentation or evaporation). If significant migration between media occurs, the residence time in each medium should also be considered in order to estimate the overall persistence in the environment. Despite these difficulties, there remains a need to characterise persistence in order that the highest priority can be applied to the most persistent substances. The general magnitudes of the suggested half-lives are judged correct, at least for initial screening purposes. More effort is needed to develop experimental protocols and predictive methods, and to gather data on observed environmental degradation rates. Where data is not available, expert judgement should be used. If the weight-of-evidence is not convincing then a substance should be initially assumed to meet the criteria based on the precautionary principle.

6. Metabolism and mechanisms of action in biota

The concept of biotic persistence implies that compounds undergoing biomagnification are unlikely to be biotransformed at a high rate in living cells. It might be expected that POPs would not tend to exert toxicity following metabolic transformation and indeed, high toxicity is generally associated with metabolically stable compounds such as PCDD/Fs and co-planar PCBs. Research during recent years has demonstrated a number of important exceptions to this general rule with
methylsulphonyl-containing POP metabolites (e.g. of PCBs and DDT) having being found in mothers milk, as well as in the tissues of marine and terrestrial mammals and birds. Recently, a large number of hydroxylated metabolites derived from chlorinated and brominated aromatic compounds have been demonstrated in human blood plasma as well as in the blood of wild mammals (seals), birds (albatrosses) and fish (salmon). These metabolites exhibit a number of specific effects that add to the profile of activities of their parent compounds (Brouwer et al., 1998). In this section, the receptor-based mechanisms of action of some POPs, and the formation and effects of their metabolites, are discussed.

The rate of formation of metabolites is highly dependent on the degree and position of chlorination. In general, metabolite formation decreases with increasing chlorination, e.g. the half-life of 3,3',4,4'-tetrachlorobiphenyl (3,3',4,4'-TeCB) is 2 days in rats, while 2,2',4,4',5,5'-hexachlorobiphenyl shows a lifetime elimination of only 20% of the dose given in the same species. In addition, the position of the chlorine-substituents is an important factor. Hydroxylation tends to take place on meta and para-positions of aromatic rings. Therefore, POP congeners with chlorine substitution on meta and para positions show much lower rates of metabolism, e.g. the stable congeners of PCDDs and PCBs are all 2,3,7,8-substituted congeners. Moreover, the rate of metabolism is highly species dependent. In general, lower organisms like crustacea and fish have a lower metabolizing capacity than mammals. These species and congener-dependent differences in rates of metabolism will result in considerable differences in the congener patterns of parent compounds and the presence and amount of metabolites formed in different species. This may have important implications for the toxic potency as well as the profile of effects of POPs. In fact, there is a wide species difference in sensitivity and toxic profile for PCBs, PCDDs and PCDFs.

One important molecular mechanism of action of PCDDs, PCDFs and PCBs appears to be receptor-based, involving the so-called Aryl hydrocarbon receptor (AhR). When entering cells, compounds like dioxins bind with high affinity to the cytosolic AhR protein, which then undergoes a process of activation and moves to the nucleus where the liganded-AhR is bound to specific elements (dioxin response elements (DRE)) on the DNA. This results in an increased transcription of the genes that possess a DRE-element in their upstream control units for expression, such as the CYP1A1/2 genes. Consequently, there is a highly increased de novo synthesis of CYP1A1/2 enzymes and other proteins that may be involved in other aspects of the toxic profile. Since AhR-binding affinity, enzyme induction and toxic potency correlate well over a wide range of different congeners it is nowadays widely accepted that the AhR plays a major role in the onset of the toxic profile of many POPs. In fact, CYP1A1/2 induction is widely used nowadays as a biomarker for exposure to dioxin-like POPs. Furthermore, the AhR-theory is used as the basis for the toxic equivalency factor (TEF) concept (Safe, 1994) which uses the relative potencies of individual congeners multiplied by their concentration, summed up over all congeners in a mixture to give rise to a sum-toxic potency, the toxic equivalent (TEQ).

6.1. Effects of hydroxylated POP metabolites

Hydroxylated metabolites of PCBs, PCDDs and PCDFs, as well as of chlorinated benzenes have been found in blood plasma and in several tissues (liver, brain) in experimental animals, as well as in plasma from free-ranging marine mammals and in human subjects (Bergman et al., 1994). In laboratory animals, it has been observed that several of the hydroxy metabolites of PCBs have a high tendency to cross the placental barrier, so entering the foetal compartment, and to cross the blood-brain barrier. (Darnerud et al., 1996; Morse et al., 1996; Brouwer et al., 1998).

Hydroxy–PCBs exhibit their own specific profile of effects, distinct from the effects caused by the parent PCBs. These effects include, direct interference in endocrine systems, including the thyroid system, the estrogen system as well as the retinoid system (Brouwer and Van den Berg, 1986; Jansen et al., 1993; Brouwer et al., 1998). For example, hydroxy–PCBs resemble the structure of the thyroid hormone, thyroxine (T4), resulting in competitive displacement of the natural thyroid hormone, T4 from its major binding proteins, such as plasma transthyretin, the T4-converting enzymes, 5'-deiodinase, and T4-sulfotransferases. Some hydroxy–PCBs show a weak estrogenic potential acting via the estrogen receptor; other hydroxy–PCBs however, were found to be mainly anti-estrogenic. Hydroxy–PCBs are potent uncouplers of mitochondrial oxidative phosphorylation. Furthermore, they inhibit intercellular communication which may result in uncontrolled cellular differentiation and proliferation, tumour promotion and alterations in developmental processes.

6.2. Formation and effects of methylsulphone metabolites

The methylsulphone metabolites are formed in the complex pathway involving entero-hepatic circulation and intestinal microbial metabolism of glutathione (GSH) conjugated xenobiotics. A number of methylsulphones derived from PCB, DDT and chlorinated benzenes are selectively accumulated and retained in specific cell types and tissues in mammals and birds (Brandt and Bergman, 1987). A number of PCB-derived methylsul-
7. Effects

7.1. Introduction

The acute effects of intoxication on animals (from laboratory studies, and accidental spills) and on humans (from accidental consumption of contaminated food, e.g. the HCB poisoning in Turkey, or accidental release of dioxin as happened at Seveso, Italy in 1976) have been fairly well documented for certain POPs. The long-term effects of high-level accidental releases are still not very well known. Recently, Mocarelli et al. (1996) described a female-skewed sex ratio in births about eight years after the Seveso accident which can be directly related to dioxin exposure. Acute and chronic occupational exposure to POPs is of concern in some developing countries where they continue to be used in tropical agriculture.

The often complex and subtle effects of chronic, low-level environmental exposure to POPs are less well understood. In the environment, the universal exposure of organisms to low levels of a wide range of chemical contaminants (and possibly, to stresses of a non-chemical nature) makes it extremely difficult to ascribe an observed effect to any particular one of them. There is also the possibility that, in the environment, toxic substances in combination may act additively, antagonistically or synergistically. There are experimental animal data indicating the existence of interactive effects for complex mixtures of POPs. For example, the PCB mixture Aroclor 1254 antagonises the toxicity of 2,3,7,8 TCDD with respect to hepato, immuno and reprotoxicity (Davis and Safe, 1989). On the other hand, Van Birgelen et al. (1996) found that, while PCB-153 alone did not result in porphyrin accumulation in rats, co-administration of PCB-153 with dioxin revealed a strong synergistic effect. In addition, when comparing the Seveso (2,3,7,8 TCDD) and Yusho/Yucheng (PCBs + dibenzofurans) accidents, a much wider range of effects is observed in the PCB poisoning than in the TCDD intoxication. This suggests that interactive effects of PCBs and PCDD/Fs can also occur in humans.

Attempts to link cause with effect are further complicated because the effects of POP exposure vary considerably depending on species, age, gender and the level, duration and timing (relative to the organism’s life-cycle) of exposure (Swain et al., 1992) and because there may be a considerable delay (up to two or three generations) between POPs exposure and the onset of effects (Murrey et al., 1979). A POP may also degrade to form a more (or less) toxic product requiring knowledge of the various possible transformations that could occur.

There is, however, experimental evidence for some POPs that cumulative low level exposures in animals may be associated with chronic sub-lethal effects such as immunotoxicity, dermal effects, impairment of reproductive performance and carcinogenesis (Ritter et al., 1995). Brouwer et al. (1995) have described the wide range of neurobehavioural, reproductive and endocrine alterations observed in experimental animals following in utero and lactational exposure to PCBs and PCDD/Fs. There are also subtle changes observable in neurodevelopmental and thyroid hormone parameters in human infants at background human body burdens. Consequently, in assessing the effects linked to the presence of POPs in the environment, the full range of toxic endpoints should be considered including the more subtle and complex chronic endpoints described below.
7.2. Chronic effects on experimental animals and wildlife

7.2.1. Immune system effects

Immunosuppression may be one of the most sensitive and relevant environmental threats posed by POPs (Han and Stone, 1997). In numerous experiments with animals, it has been shown that various POPs can suppress immune system function. Subchronic levels of DDT impaired the immune response of mice (Banerjee et al., 1986; Banerjee, 1987), aldrin and dieldrin reduced mouse resistance to viral infection, chlordane and heptachlor were found to affect animals’ developing immune systems and lindane affected macrophage activity in vitro as well as reducing experimental animals’ resistance to infection (Barnett and Rodgers, 1994). Laboratory studies have also shown that immune system function can be impaired by PCDDs (Holsapple et al., 1991), PCBs (Tryphonas et al., 1991) and HCB (Barnett et al., 1987).

Wildlife studies also reveal evidence for the immunotoxic effects of POPs. Herring gull and Caspian tern chicks in the Great Lakes region were found to have smaller thymuses and less T-cell activity the greater their exposure to certain organochlorines (Grasman, 1995). Autopsies on dead beluga whales from the St. Lawrence Seaway, Canada (Martineau et al., 1987, 1988) found high tissue concentrations of organochlorine pesticides and PCBs and severe bacterial infections suggesting immunosuppression. De Guise et al. (1994, 1995) also found more frequent and severe tumours in the St Lawrence beluga whales compared with whale populations elsewhere and concluded that exposure to carcinogenic compounds and decreased resistance to the development of tumours could both have contributed to this. Researchers who assayed blood taken from live bottlenose dolphins off the Florida coast found that decreased T-cell lymphocyte proliferative response was highly correlated with increased levels of bioaccumulative organochlorines, the dolphins also exhibiting infections suggestive of immune dysfunction (Lahvis et al., 1993). In the early 1990s, a massive die-off of striped dolphins in the Mediterranean Sea was attributed to infection by a morbillivirus similar to that causing distemper in carnivores (Aguilar and Raga, 1993). Diseased dolphins were found to carry concentrations of several organochlorines (in particular PCBs) between two and three times the levels commonly found in the healthy population and it has been suggested that the immunodepressive capacity of the PCBs may have been a contributory factor (Borrell and Aguilar, 1991). The morbillivirus was also reported to be responsible for the unusual die-offs of Northern European harbour seals in the Baltic and the North Sea in 1987 and 1988 (Kennedy et al., 1988; Osterhaus and Vedder, 1988; Dietz, et al., 1989) and of Baikal seals in 1988 (Grachev et al., 1989). Brouwer et al. (1989) found that consumption of PCB-contaminated fish from the Dutch Waddensea led to vitamin A and thyroid hormone deficiency in the common seal, both of which could result in increased susceptibility to microbial infections. Further evidence that certain organochlorines may have compromised the seals’ immune systems and so contributed to the die-offs came from a prospective immunologic study on harbour seals (De Swart et al., 1993, 1994, 1995; Ross et al., 1995). Seal pups were fed uncontaminated fish for a 1 year acclimatization period and then split into two groups. One group was fed with herring caught in the polluted Baltic Sea whilst the other group was fed herring from the relatively unpolluted waters around Iceland. The dietary intake of organochlorine pesticides and PCBs of seals fed Baltic fish was several-fold higher than that of the controls and led to a 10-fold higher concentration in their blubber. The group of seals eating Baltic herring showed significantly reduced natural killer cell activity and reduced T-cell proliferative response, antibody response and neutrophil levels. This group ended up with immune responses estimated to be three times weaker than those of the control group and increases in opportunistic infections indicative of immunosuppression. This was the first demonstration of immunosuppression in mammals as a result of exposure to contaminants at ambient levels found in the environment (Osterhaus et al., 1995).

7.2.2. Effects on the endocrine system

The potential effects of so-called endocrine disrupting compounds (EDCs) on the endocrine system have recently gained much attention. It has been suggested that many different adverse health endpoints in wildlife, animals and in humans are or may be, associated with exposure to a variety of EDCs, both anthropogenic and natural in origin. Several agencies have proposed definitions to describe what is actually meant by an endocrine disrupting chemical. The definition proposed by a workshop held at Weybridge, UK in 1996 (European Commission, 1996) was as follows: ‘An endocrine disrupter is defined as an exogenous substance that causes adverse health effects in an intact organism, or its progeny, consequent to changes in endocrine function.’

Several substances classified as POPs have been indicated as being potential endocrine disrupters (Toppari et al., 1996). The evidence is partially based on in vitro studies, investigating the potential of a chemical to bind with for example, the estrogen receptor and to activate the receptor pathway in terms of altered gene expression. For example, several hydroxy-PCBs were tested in in vitro assays for comparative binding to the estrogen receptor. The hydroxy-PCBs all showed some estrogen receptor binding potency, the most potent one, 4-OH-2’,4’,5’-triCB was about 80-times less potent
than the synthetic estrogen, estradiol (Golden et al., 1998). In functional in vitro assays, like proliferation of estrogen-sensitive MCF-7 cells, most of the hydroxy–PCBs tested were found to be anti-estrogenic (Moore, et al., 1997). For DDT, both o,p’-DDT, o,p’-DDD and o,p’-DDE were very weakly estrogenic in in vitro human estrogen receptor assays.

There are also experimental animal data on hormonal changes and alteration in physiological parameters. For example, the PCB mixtures Aroclor 1221,1232, 1242 and 1248 exhibited some degree of estrogenic activity in an in vivo uterotrophic assay, roughly six orders of magnitude lower than estradiol. There were also some changes in the LH (Luteinising Hormone) and FSH (Follicle Stimulating Hormone) secretion by the pituitary. For hydroxy–PCBs, a correlation was found between in vitro estrogen receptor binding and in vivo uterotrophic activity. Also, o,p’-DDT and o,p’-DDE were found to be estrogenic in in vivo uterotrophic assays; about 2500 and 40000 times less potent than estradiol. For hydroxy–PCBs as well as parent PCBs it is well known that thyroid hormone levels are affected in experimental animals (Brouwer et al., 1998). The interaction of the PCBs takes place at multiple levels of the thyroid hormone system, including the thyroid gland, the pituitary-thyroid feedback system, transport of thyroid hormones and enzymatic conversion of thyroid hormones. This also occurs in fetuses born from dams exposed to PCBs. Although both hormonal changes and physiological/developmental effects can be induced following exposure to certain POPs, and it is tempting to suggest that these are linked, there is actually little or no conclusive evidence that this link exists.

There are also a number of wildlife cases where a link between a chemical exposure, its endocrine disrupting effect and observed adverse health outcomes is suggested. For example, associations between elevated residues of PCBs and DDTs and reduced nesting success, increased chick and embryo mortality or reductions in population have been reported for European fish-eating birds (Colborn, 1991). Delayed or abnormal sexual differentiation and/or development have been suggested to be associated with population declines of alligators and the presence of organochlorine pesticides in lakes in Central Florida (Guillette et al., 1994). Environmental exposure to DDE and PCBs has been implicated in various reproductive problems (e.g. low sperm counts, high levels of sperm abnormalities and extremely high incidence of undescended testicles) in the endangered Florida Panther population (Facemire et al., 1995). Concentrations of certain organochlorine pesticides, PCBs, and PCDD/Fs were negatively correlated with testis size and weight, and with the length of the baculum (the penile bone), in young male otters from the Columbia River, USA (Henny and Grove, 1996). The recent Weybridge workshop on endocrine disrupters concluded that ‘some cases exist within the EU area where adverse endocrine effects, or reproductive toxicity, in birds and mammals coincide with high levels of anthropogenic chemicals which have been shown to have endocrine disrupting properties in some test systems’ (European Commission, 1996).

7.2.3. Reproductive and developmental effects

In a literature review by Wren (1991) many laboratory experiments with mice and ferrets are described which demonstrate a direct cause and effect relationship between PCB exposure and immune dysfunction, reproductive failure, enzyme induction, increased kit mortality, deformities, organ enlargements and adult mortality. Declines in European otter populations have also been attributed to environmental exposure to PCBs and other organochlorines (Mason, 1989; Olsson and Sandegren, 1991). There are also many well-known examples of bird populations that have been affected by POPs exposure with decreased or retarded egg production, increased embryo mortality, eggshell-thinning, embryonic deformities, growth retardation and reduced egg hatchability among the effects reported (Han and Stone, 1997). For example, Gilbertson et al. (1991) related embryo deformities and egg mortality in Great Lakes fish-eating birds to organochlorine contaminants. Fox (1992) described abnormalities in Western and Herring gulls in the Great Lakes including increased female–female pairings, and altered nest defence and incubation behaviour resulting from sex ratios being skewed towards females. More recently, pesticides and other synthetic chemicals have been linked with bizarre deformities (e.g. extra legs growing from the abdomen or neck) in frogs across Minnesota and Wisconsin and in the St. Lawrence River Valley in Quebec (Ouellet et al., 1997) although other possible causes are also being considered.

Moreover, reproductive failure in the common seal population inhabiting the western part of the Dutch Wadden Sea was attributed to PCBs after feeding experiments demonstrated that a diet of naturally PCB-contaminated fish from this sea had a detrimental effect on the seals’ reproduction (Reijnders, 1986). Mac and Edsall (1991) demonstrated reduced hatching success and diminished fry survival in lake trout eggs experimentally exposed to PCBs and DDTs and found there was a gradual increase in hatchability and fry survival of Lake Michigan trout since 1984 following a reduction in organochlorine levels in the Great Lakes. In the Baltic in recent years, researchers have seen extreme disturbances of reproduction in several places and among several fish species including perch, burbot, cod and salmon. Although the mechanisms for these disturbances are unproven, it is probable that one or more POPs are involved (Alsberg et al., 1993).
A clear cause and effect relationship with POPs and reproductive failure has been established for mink. Ranch mink exhibit reproductive failure when fed Great Lakes fish containing between 0.3 and 0.5 μg/g PCBs (Aulerich and Ringer, 1977) and tissue levels of PCBs in mink above 50 μg/g produced reproductive failure in captivity (Jensen et al., 1977). López-Martín et al. (1994), in a study of the threatened European mink in Northern Spain, found PCB body burdens to be well over 50 μg/g (with means of 118 μg/g in muscle and 123 μg/g in liver) and suggested that these pollutants could be partly responsible for their decline. The reproductive effects and abnormalities observed in wildlife are consistent with similar effects induced by various POPs in laboratory experiments on animals. Fry and Toone (1981) induced feminization in male California gulls by injecting eggs with DDT in amounts comparable to those found in seabird eggs in southern California in the late 1960s. Chlordane disturbed spermatogenesis and damaged the testes of mice (Balash et al., 1987). HCH fed to male weanling rats decreased testis weights at doses > 50 mg/kg with testicular atrophy resulting from a dose of 250 mg/kg (Velsen et al., 1986). Peterson et al. (1992) describe experiments in which in utero and lactational exposure to a dioxin (2,3,7,8-TCDD) delayed testis descent, reduced the weight of sex organs, inhibited spermatogenesis and demasculinized male rat sexual behaviour. Gray (1992) also describes the adverse impacts on rodent neuroendocrine and hypothalamic sex differentiation and the production of anatomical malformations resulting from perinatal exposure to estrogenic pesticides, PCDDs and PCBs.

7.2.4. Carcinogenesis

There is convincing evidence from laboratory experiments that several POPs can have genotoxic effects or act as tumour promoters (Perera, 1981; Nagayama et al., 1992; Wolfe and Marquardt, 1993). Stranded carcasses of St. Lawrence beluga whales were found to have a high incidence of tumours and contained elevated levels of PCBs, mirex, chlordane and toxaphene (UN-ECE, 1994). Only in the case of PAHs (some of which, particularly benzo(a)pyrene, are highly carcinogenic) have direct links been established between exposure and increased cancer rates in wildlife. For example, the incidence of dermal lesions, tumours and papillomas in the brown bullhead (a bottom-feeding fish from the Great Lakes) was significantly elevated in areas with high PAH levels in the sediments (Government of Canada, 1991).

7.2.5. Neurotoxicity

Developmental toxicology is a rapidly evolving area of environmental toxicology. Much of this progress stems from the observation that there are periods of enhanced sensitivity to chemical toxicity during the early life-stages of organisms, when both structural malformations and persistent functional changes can be induced. With regard to neurotoxicity, a period of extreme sensitivity seems to occur when the developing brain enters a phase of rapid growth, i.e. the so-called ‘brain growth spurt’. Depending on the species examined, this period occurs either during mid-late gestation, around term or in the early post-natal period. In mice and rats, this sensitive period occurs around day 10 post partum, while in guinea pigs the period occurs in mid-late gestation. In humans, the period begins during the third trimester of pregnancy and continues throughout the first 2 years of life.

Studying a number of POPs and non-persistent neurotoxicants, Eriksson et al. have shown that a single low-dose exposure at day 10 post partum may result in persistent changes in spontaneous behaviour (hyperactivity) and learning ability at adult age (Eriksson, 1992; Eriksson and Fredriksson, 1996; Eriksson, 1997). These behavioural changes were correlated with persistent changes in the expression of cholinergic receptor subtypes. However, following dosing at day 3 or 20 post partum, no corresponding effects were observed at comparative doses. As mentioned above, these developmental changes are not restricted to POPs, but can also be induced by certain non-persistent organic chemicals such as pyrethroid, paraquat and nicotine. Interestingly, several persistent environmental pollutants such as DDT (a neurotoxicant by design) and several PCBs induce this type of neurotoxicity, while other PCBs seem to lack activity at corresponding doses. For instance, when PCB 52 was applied as a single dose (1.4 μmol/kg; 0.4 mg/kg) on day 10 post partum, hyperactivity was observed at adult age. Preliminary results also show that a polybrominated diphenyl ether (PBDE 99) induces behavioural toxicity at equimolar doses (1.4 μmol/kg; 0.8 mg/kg).

7.3. Chronic effects on humans

The weight of scientific evidence suggests that some POPs have the potential to cause significant adverse effects on human health both at a local level and, through long-range transport, at regional and global levels (Ritter et al., 1995). For some POPs, especially the pesticides, occupational and accidental high-level exposure is of concern for both acute and chronic exposure. This is particularly true in the developing world where inadequate safety and hygiene practices are the norm in applying, formulating, storing, transporting and manufacturing pesticides (Repetto and Baliga, 1996). Pesticide warning labels are often printed incorrectly or in the wrong language and many users are illiterate. In tropical climates, sprayers rarely wear the uncomfortable and costly protective clothing. For
example, in the Northern Philippines farmers spraying pesticides wore masks in only one quarter of spraying operations and never wore gloves or boots (Alba, 1988). Agricultural field workers rarely observe the re-entry period, the time required between spraying and other fieldwork. Weepers as well as children and other household members in or near newly sprayed fields are also directly exposed to pesticides (Rola and Pingali, 1993).

In any discussion of substitutes for POP pesticides, the greater acute toxicity of many non-POP pesticides should be borne in mind. For example, in the early 1970s the introduction of the neurotoxic organophosphates and carbamates for disease vector control, as alternatives to DDT, resulted in a considerable increase in acute poisoning cases, both accidental and occupational (WHO, 1996).

As noted for wildlife, it is extremely difficult to establish cause and effect relationships between human exposure to low levels of a POP in the environment and particular adverse health effects, not least because of the broad range of chemicals to which humans are exposed at any one time. The contamination of food, including breast milk, by POPs is a worldwide phenomenon (WHO, 1996) and measurable residues of several organochlorine pesticides, PCBs, PCDDs and PCDFs are present in human tissues worldwide (Thomas and Colborn, 1992). Evidence for low-level effects of POPs on humans is more limited than that for wildlife but is consistent with effects reported both in exposed wildlife populations and in laboratory experiments on animals (UN-ECE, 1994).

### Table 4

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<td>10</td>
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#### 7.3.1. Effects on the immune system

The chronic effects of occupational, bystander and near-field exposure to POP pesticides are difficult to assess. For example, few epidemiological studies have been carried out to assess changes in the human immune system from pesticide exposure. Moreover, although pesticide-induced immunosuppression may increase people's susceptibility to infectious and parasitic diseases, these diseases are so prevalent among low-income populations, and malnutrition and unsanitary conditions are so widespread, that distinguishing any greater susceptibility due to immune deficiencies is difficult (Repetto and Baliga, 1996). However, it has been demonstrated that patients chronically exposed to chlordane demonstrated clinical and immunological symptoms highly suggestive of immune pathology and probably a chlordane/heptachlor-induced autoimmune disorder (Broughton et al., 1990). Nearby identical immunological results were found in patients exposed to the fungicide pentachlorophenol (McConnachie and Zahalsky, 1991).

Immune modulating effects have also been detected in people exposed to low-level, environmental concentrations of POPs. Weisglas-Kuperus et al. (1995) found certain immunological aberrations were associated with pre and post-natal exposure of Dutch infants to PCBs and PCDDs. Although their data did not indicate that these aberrations caused any more illness among the infants, they could persist and presage later difficulties such as immune suppression, allergy and autoimmune disease. Swedish investigations have reported that dietary intake of PCBs and PCDD/Fs may be linked to reductions in the population of natural killer cells (Svensson et al. (1993). These cells are believed to play a role in the body's defence against viruses and tumours. However, none of the subjects in this study displayed any signs of health impairment attributable to lowered number of natural killer cells.

As mentioned earlier, POPs tend to migrate to higher latitudes and to bioaccumulate and biomagnify, particularly in marine ecosystems. Because fish, whale, seal, walrus and bear meat are mainstays of their diet, some Canadian Inuit consume relatively large amounts of organochlorine pesticides, PCBs and PCDDs and bioaccumulate them in fatty tissues over years of exposure (Kinloch et al., 1992). The intake of PCBs and toxaphene exceeds the ‘tolerable daily intake’ (TDI) for many Inuit consumers (Kinloch et al., 1992). In the early 1990s the discovery of high levels of PCBs, DDT and HCB in Greenlanders’ adipose tissue (Table 4) and very high levels of PCBs, DDE and mirex in Inuit breast milk prompted concerns about their possible adverse effects on human (particularly infant) health, including increased susceptibility to infections (DeWailly et al., 1993a; Mulvad et al., 1996). Canadian Inuit babies who accumulated high doses of organochlorines were significantly more likely to experience acute otitis (infection of the middle ear) and were harder to vaccinate since many failed to produce a primary antibody response to the usual vaccines. In comparison with bottle-fed babies, these breast milk-fed
babies demonstrated decreased ratios of helper-T cells to effector-T cells that were correlated with duration of breast feeding and organochlorine levels in breast milk (Dewailly et al., 1993b). Infectious disease incidence among the Inuit children appeared to be associated with immune dysfunction (Birnbaum, 1995). Despite this, Kinloch et al. (1992), in their study of the benefits and risks of the Inuit diet, concluded that the known benefits of traditional foods and of breast feeding outweigh the known adverse consequences of contaminant intake associated with the traditional diet. The WHO also maintain that ‘where levels of some POPs in breast milk approach or slightly exceed tolerable levels, breast feeding should not be discouraged since the demonstrated significant benefits of this practice greatly outweigh the small hypothetical risk that POPs may pose’ (WHO, 1996). Although these recommendations are supported in a recent AMAP (Arctic Monitoring and Assessment Programme) report, the authors also suggest that consideration should be given to developing dietary advice to promote the use of less-contaminated traditional food items which will also maintain nutritional benefits (AMAP, 1997).

7.3.2. Endocrine effects

Some researchers have suggested that falling human sperm counts, the increasing incidence of certain reproductive abnormalities in the human male such as spermatogenetic dysfunction, maldescent of testes (García-Rodríguez et al., 1996), malformations of the penis and testicular cancer, as well as breast cancer in women, may be linked to chronic exposure to low levels of hormone-mimicking chemicals (including some POPs). Toppari et al. (1996) have provided an extensive review of the current knowledge about male reproductive health and environmental xenoestrogens. However, at present there is an almost complete lack of exposure data in humans to support such an association.

The incidence of breast cancer in women appears to be rising in many countries and the pathogenesis of breast cancer has been linked with exposure to hormone disrupting chemicals (Davis et al., 1993). Falck et al. (1992) found higher levels of PCBs and DDE in mammary adipose tissue from women with malignant breast cancer compared with women having benign breast cancer. Wolff et al. (1993) demonstrated a positive association between serum DDE (but not serum PCB) and incidence of breast cancer and Dewailly et al. (1994) observed higher levels of plasma PCB and DDE in women with estrogen receptor-positive breast cancer. On the other hand Krieger et al. (1994), in a much larger study, found neither DDE nor PCBs were associated with breast cancer and Safe (1997) reported that occupational exposure to relatively high levels of PCBs and DDT/DDE was not associated with an increased incidence of breast cancer. Key and Reeves (1994), after producing a statistical summary of results from six such studies (including those mentioned above), concluded that it was unlikely that DDT in the environment increased the risk of breast cancer and that there was no evidence of such an association for PCBs.

7.3.3. Developmental, neural and behavioural effects

Signs of impaired neurological development in children, through exposure to PCBs in utero and in their mother’s milk, were demonstrated in a study of 866 infants in North Carolina, USA (Rogan et al., 1986; Gladen et al., 1988). Further evidence that early exposure to some organochlorine pollutants can cause long-term intellectual impairment comes from a series of studies on a group of over 200 children, three-quarters of whom had mothers who had eaten significant amounts of fish known to be contaminated with PCBs and other pollutants from Lake Michigan. Differences were evident at birth with lower birth weight and a smaller head circumference the greater the mother's consumption of Lake Michigan fish (Jacobson et al., 1984). At 7 months of age there were signs of impaired cognitive function in those children exposed to higher PCB levels and at 4 years of age they achieved lower scores in verbal and memory tests (Jacobson et al., 1990). At the age of 11 years these children were again assessed, this time using a range of tests for intelligence quotient (IQ), arithmetic, spelling, reading and comprehension, and the results compared with their prenatal exposure to PCBs as measured in the placenta and mother’s blood and milk (Jacobson and Jacobson, 1996). Their results show evidence of persistent intellectual impairment which has not been overcome by environment or education. They found that children from the group with highest PCB exposure had average IQ levels 6.2 points lower than children from the less exposed groups as well as having poorer verbal comprehension and being more easily distracted. Although much larger quantities of PCBs are transferred postnataally through lactation than in utero, intellectual impairment occurred only in relation to transplacental exposure. The authors concluded that these adverse effects were due to PCB exposure in utero, one possible mechanism being PCB-induced reduction in serum concentrations of thyroid hormones which are needed to stimulate neuronal and glial proliferation and differentiation. They point out that the levels of PCBs carried by the mothers were similar to or slightly above the general population in the United States and that women who do not eat fish may accumulate these compounds from a variety of other food sources.

In a longitudinal, prospective PCB/dioxin breast milk study, started in the Netherlands in 1990 and comprising 418 healthy mother/infant pairs, infants were examined for endocrine, immune and neuro-behavioural development. Higher PCDD, PCDF and PCB levels in
human milk (expressed as TEQs) correlated significantly with lower plasma levels of maternal total triiodothyronine and total thyroxine and higher plasma levels of thyroid stimulating hormone (TSH) levels in infants in the second week and third month after birth (Koopman-Esseboom et al., 1994). Infants exposed to higher than average human milk TEQ levels also had significantly lower plasma-free thyroxine and total thyroxine levels, in the second week after birth, than those exposed to lower than average human milk TEQs. It was concluded that elevated levels of PCBs, PCDDs and PCDFs can alter the human thyroid status. Infant neuro-developmental testing showed a small negative effect of prenatal PCB exposure on the psychomotor score at 3 months (Koopman-Esseboom et al., 1996). At 7 months of age both mental development and psychomotor scores were positively correlated with duration of breast-feeding although for breast-fed infants receiving higher cumulative TEQs the positive effect of breast-feeding on psychomotor outcome was diminished. Transplacental exposure to PCBs had a small negative effect on the neurological condition of 18-month old toddlers (Huisman et al., 1995).

8. Identifying additional POPs as candidates for future international action

8.1. Introduction

Most man-made chemicals have been neither tested nor evaluated for their hazard potential. There are 100106 chemicals in the European inventory of existing chemical substances (EINECS) commonly referred to as ‘existing substances’. These are chemical substances and entities which, by 1981, had been reported to and listed by the EU-Commission as having been marketed during the preceding 10 years. Of these, perhaps 20000–30000 are currently marketed in significant quantities. ‘New substances’ (i.e. those substances not already on the EINECS list) are being notified, but not necessarily marketed, at a rate of about 200 a year and by the end of 1996 amounted to about another 2000 substances (Bro-Rasmussen, 1996). The data and documentation needed to evaluate many of their potential effects on human health and/or the environment exist for about 5000 chemicals. Only for a few hundred is there sufficient knowledge for performing the full hazard/risk assessment described in the Commission of the European Communities (1994) technical guidance document. Priority setting as a prelude to more refined or in-depth risk assessments is recognised as being of critical importance and the process used by the EU is described by Van Leeuwen et al. (1996). The EU toxicological programme for ‘new substances’ involves different levels of testing according to production volume and use. Of the ‘existing chemical substances’ a start has been made on providing data on the ≈ 2500 HPVCs (High Production Volume Chemicals). Although data on most of the toxicity endpoints are available, only a very limited set of data is available for the chronic endpoints described in the previous section. Effects on the endocrine system, for example, have only been studied for a few of the man-made chemicals currently being used and it is likely that other estrogenic chemicals remain unidentified (Toppari et al., 1996). A much more focussed procedure, based on prioritisation using criteria specific to POPs, will be required.

8.2. Prioritisation and assessment schemes

8.2.1. Proposed general risk assessment scheme

Considering the large number of untested chemical substances that exist, of which POPs comprise a specific subset requiring international joint action, it would be appropriate to establish a tiered selection and assessment procedure. A possible scheme for group prioritization of existing chemicals is shown in Fig. 2. Under such a scheme, candidate POPs or PBTs could be placed on a fast track for initial screening prior to a more costly and lengthy, full-scale risk assessment. Initial selection criteria for POPs would comprise long-range transport potential followed by persistence and bioaccumulation potential.

The risk assessment stage will then quantify the actual or predicted levels of environmental exposure to the substance (exposure assessment) and the nature and likely severity of any resulting adverse effects (effects assessment). It is of the utmost importance that the type of effects assessment used is appropriate for the group of chemicals in question. In the case of suspected POPs, this should include testing for the chronic effects considered in Section 7, i.e. immunotoxicity, endocrine disruption and carcinogenicity. When the levels of uncertainty involved in predicting exposure and the consequent possible effects on ecosystems, wildlife or humans are high, expert judgement and weight-of-evidence, based on the precautionary principle, may have to be used to decide whether or not the risks are acceptable. This would be especially so in the case of new substances yet to be released into the environment for which future production, use and emission volumes are only predictions and exposure assessments much more uncertain.

8.2.2. Criteria proposed for the CLRTAP POPs protocol

It is unlikely that the POPs chosen for initial inclusion in the CLRTAP protocol and the proposed UNEP global convention are the only persistent organic substances released into the environment that have the
potential to cause adverse effects in humans and/or the environment at considerable distances from their point of release. Crucial to the long-term success of the CLRTAP POPs protocol and the proposed UNEP global convention on POPs will be the criteria and procedures chosen for adding new substances to their respective initial lists. Science-based criteria have been developed for use within the CLRTAP POPs protocol to achieve this (Fig. 3).

If the risk profile is deemed acceptable by the executive body, and further consideration of the substance is determined to be warranted, one or more technical reviews of the proposal will be conducted. These will be based on the submission and any other relevant information submitted to the executive body. Expert judgement will have to be used to determine, qualitatively, the strength of the case for or against classifying the proposed substance as a protocol POP (IFCS, 1996b).

8.2.3. Criteria to be used for the global UNEP POPs convention

Although the above criteria are likely to influence the procedure to be used within the UNEP global convention on POPs, the CLRTAP process is clearly only concerned with long-range transboundary air pollution. The process used in the global convention is likely to incorporate a broader range of criteria including dispersion in the hydrosphere and via migratory species of animals and the need to reflect possible influences of marine transport and tropical climates (Buccini, 1997). For example, triphenyl tin compounds were identified as high priority compounds after the first two stages of the CLRTAP selection process for the initial list of protocol POPs. However, after assessment in the third stage, these compounds were not included because they are strongly associated with the aquatic phase and there was no evidence of long-range atmospheric transport. Such compounds could be included under the global
POPs convention if the process set up by UNEP takes long-range water transport into account. Clearly, the definition of a POP agreed for the CLRTAP protocol could be modified to suit the purposes of a global convention.

8.2.4. Tests for chronic-toxicity endpoints

Given that a range of man-made chemicals (including several POPs) have the capacity to disrupt the immune and endocrine systems of both wildlife and humans, as well as being potentially carcinogenic, any candidate POP being considered within the proposed general risk assessment scheme (Fig. 2) or the CLRTAP procedure (Fig. 3) should be tested for these effects. Test procedures for several of the relevant endpoints for these effects are still being developed but are expected to become available within the next few years.

8.2.4.1. Immunotoxicity testing. Various tests exist for determining chemical immunotoxicity including in vitro (using tissue, cells or cell components outside the body) and in vivo (performed in living organisms) techniques. A two-tiered battery of tests has been recommended by the US National Institute of Environmental Health Services to gauge the potential for a chemical’s immunotoxic effects on human health (Luster et al., 1988, 1995; Repetto and Baliga, 1996). Tier 1 tests assess changes in sensitive immune parameters. If these are found, or if there is other evidence for immunotoxicity, Tier 2 tests are then performed in order to measure functional changes more fully (Table 5).

8.2.4.2. Testing for endocrine disruption. Although several existing regulatory tests are capable of detecting reproductive and developmental toxicants (ECETOC,
Table 5
A two-tiered testing protocol for chemical immunotoxicity

<table>
<thead>
<tr>
<th>Immune parameter</th>
<th>Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tier 1</td>
<td></td>
</tr>
<tr>
<td>Immuno-pathology</td>
<td>Pathology of immune organs (e.g. thymus, spleen)</td>
</tr>
<tr>
<td>Complete blood counts</td>
<td></td>
</tr>
<tr>
<td>Humoral immunity</td>
<td>B lymphoproliferative response</td>
</tr>
<tr>
<td>Antibody levels</td>
<td></td>
</tr>
<tr>
<td>Cell-mediated immunity</td>
<td>T lymphoproliferative response</td>
</tr>
<tr>
<td>Non-specific immunity</td>
<td>Macrophage/neutrophil/natural killer cell activity</td>
</tr>
<tr>
<td>Tier 2</td>
<td></td>
</tr>
<tr>
<td>Immuno-pathology</td>
<td>Differential blood counts (numbers and proportions of white blood cells and lymphocytes)</td>
</tr>
<tr>
<td>Humoral immunity</td>
<td>Secondary antibody responses (analogous to testing for effectiveness of vaccination against diseases)</td>
</tr>
<tr>
<td>Cell-mediated immunity</td>
<td>Delayed hypersensitivity (i.e. delayed onset of heightened responsiveness to an antigen following an initial challenge)</td>
</tr>
<tr>
<td>Non-specific immunity</td>
<td>Phagocytosis (by macrophages)</td>
</tr>
<tr>
<td>Host resistance models</td>
<td>Bacterial challenge</td>
</tr>
<tr>
<td></td>
<td>Parasite challenge</td>
</tr>
<tr>
<td></td>
<td>Viral challenge</td>
</tr>
<tr>
<td></td>
<td>Tumour challenge</td>
</tr>
</tbody>
</table>

1996) they do not fully cover effects caused by endocrine disrupters. The need to develop a hazard identification strategy for endocrine disrupters was addressed at a recent workshop on 'Endocrine Modulators and Wildlife: Assessment and Testing (EMWAT)' (Tattersfield et al., 1997). The hazard identification strategy they proposed involves three stages and utilises a combination of structure activity relationship (SAR) mathematical models, in vitro tests and in vivo tests (Fig. 4).

In the future, SARs may become available for screening and prioritizing possible endocrine-disrupting, immunotoxic or carcinogenic chemicals for further, more costly testing. SARs are based on the principle that structurally similar chemicals should have similar biological activity and relate specifically-defined toxicological activity of chemicals to their molecular structure and physico-chemical properties. This requires a detailed in vitro toxicological knowledge base for the particular mode of action in question. Given adequate research support, it is envisaged that SARs to predict the binding affinities of the AhR, estrogen receptor (ER), androgen receptor (AR) and, possibly, thyroid receptor should be available within three years (Tattersfield et al., 1997). However, models appropriate for other mechanisms that may have estrogenic effects in vivo (e.g. changes in ligand synthesis) may take longer. The development of SARs for modes of action involving the metabolism and transport of hormones are also likely in the future (Tattersfield et al., 1997). At the EMWAT workshop, it was concluded that high quality SARs should be used as soon as they are available rather than delay their use until all the mechanisms can be modelled.

Several in vitro tests for endocrine disrupting potential are available although they could be further refined to enhance their reliability and selectivity. They are quick, relatively cheap to carry out, and can be used for elucidating mechanisms of action. In certain situations, they can also replace in vivo tests thus reducing the need for animal testing. However, they are limited in possessing only a portion of the metabolic system present in entire animals. Therefore, in the above scheme, in vitro tests are seen as complimentary to, not substitutes for, in vivo tests. Before in vitro tests can be used routinely, suitable tests will have to be selected, optimised and validated using internationally agreed approaches (Tattersfield et al., 1997).

In vivo tests have the advantage of being highly integrative and the capacity to evaluate mixed mechanisms of action and numerous endpoints. Short-term in vivo tests can be rapid and inexpensive and are recommended for use in the screening/prioritizing stage above, given that SARs and/or in vitro tests would be inadequate on their own. More lengthy, and hence more costly, sub-chronic or chronic (multi-generational) studies are recommended for use in the confirmation stage. Although no currently available and validated in vivo tests are appropriate as they stand, several could be readily adapted, and others might form the basis of useful tests after further development (Tattersfield et al., 1997). The possibility of unusual dose-response curves (e.g. inverted ‘U’) for endocrine disrupters would have to be taken into account and doses would, therefore, have to represent a full range from high (possibly just sub-lethal) to low and include typically five doses. Interspecies extrapolation would also be problematic and any practical in vivo testing scheme, involving a very limited number of surrogate species, will inevitably produce false negative and false positive conclusions.
Because many of the test methods are still being developed, it is likely to be a few years yet before a scheme such as that described above becomes a useful and reliable tool. The OECD (Organisation for Economic Co-operation and Development) Environmental Health and Safety Programme is co-ordinating activities in this area in order to develop a common approach to the identification and assessment of endocrine disrupters. The newly established OECD Working Group on Endocrine Disrupters Testing and Assessment (EDTA) met, in Paris in March 1998, to agree on objectives and priorities for international work on the development of methods for the testing and assessment of endocrine disrupters. A consensus on a conceptual framework for investigating chemicals for these effects was reached, based on approaches recommended at international workshops (such as that described above) and the US EDSTAC (Endocrine Disrupters Screening and Testing Advisory Committee). Relevant endpoints to be included in the three tiers of the framework were agreed and the necessary technical work on test methods referred to the expert groups of the OECD Test Guidelines Programme. A validation project was also launched, in which member countries and international industry associations will co-operate, to be co-ordinated by OECD Management Teams consisting of balanced representation from member countries’ governments, academia, industry and public interest groups.

8.2.4.3. Testing for carcinogenicity. This should comprise in vitro tests on mutagenicity (microbial and mammalian mutagenicity tests, chromosome aberration etc.) as well as intercellular communication and cell proliferation assays. When positive in either of the test systems after repeated measurements, in vivo tumour promotion and full carcinogenicity bioassays should be applied.

9. Issues in assessing risk and selecting risk management options for POPs

In schemes for identifying new POPs, such as those described in Figs. 2 and 3, it is necessary to draw a distinction between a scientific risk assessment and policy options relating to the subsequent management of any risks so identified. Agreement on measures to reduce or eliminate these risks will only be achievable if account is taken of the broader societal impact of various measures. Considering that the benefits and risks of substances, and the costs and benefits of measures to manage or reduce those risks, are asymmetrically distributed, some form of comparison of costs and benefits of various options will be needed. As is the case with risk assessment, the level of this analysis must be adequate enough for informing the decision takers but not so detailed as to delay the decisions indefinitely. Deciding which management options are appropriate is only feasible if there is a good understanding of the efficacy and practicability of the measures (i.e. to what extent will the measure actually reduce the risk), and on the socio-economic impact of the proposed measure. Clearly, effective measures with minimal socio-economic impacts would be easy to agree upon whereas it might be difficult to achieve agreement on measures with insignificant effects and considerable socio-economic impacts.

While it would not be necessary to prescribe analytical techniques, it would be useful to consider the range of possible measures and the different implementing
tools and the appropriate combination of tools and measures. Although these have been fairly well provided for in the CLRTAP protocol, recommended product restrictions on substances with considerable industrial, agricultural or consumer application should be supported by initiatives to make users aware of, and able to use, alternative, less hazardous substances or non-chemical approaches. In any case, the suggested alternative should also be compared with the original using a risk-benefit analysis to avoid the substitution of a product we do not like by a product we do not understand.

10. Engaging the public and industry

It is clear from practical experience, as well as from more theoretical considerations, that, to achieve fair and effective results in environmental policy it is crucially important to ensure effective involvement of different stakeholders. This has been recognised within the UNEP POPs process and several NGOs, representing both industry and public interest groups, have been included in the initial IFCS ad hoc working group and subsequent workshops.

The management and assessment of risks can be enhanced by broadening the knowledge base and dialogue through the involvement of stakeholder communities (including the public). The value of extending the peer review community in this way has been documented by several authors (Funtowcz and Ravetz, 1991; Renn, 1995; Wynne, 1996) and a range of methods for facilitating participation have been established (Renn et al., 1995). For example, integrated environmental assessment (IEA) is an approach that allows a broader participation in environmental assessment and decision-making. IEA offers a method of constructing and using scientific knowledge in environmental policy that can not only be peer reviewed scientifically but can also be scrutinised by the stakeholders (e.g. public administrators, community and non-governmental representatives, business people and the media) during the assessment process, not just afterwards (Bailey, 1997).

In the area of POPs control, some form of IEA might prove to be a useful aid for decision-makers, in conjunction with more conventional risk assessments.

Perception of environmental and ecological risks has not been extensively studied outside the human health context (Sjöberg, 1995). The differences between expert and public perceptions of the scale of the POPs risks could be manifested in different ways (as described by Sjöberg). A lack of trust in experts regarding POPs control, coupled with a fear of chemicals in trace amounts that one cannot see, smell or taste, might be expected to result in a situation whereby risks judged to be very small by experts are believed by lay people to be quite large. On the other hand, the lack of overt damage to human health (in most populations) coupled with a general lack of public knowledge about POPs, may result in the opposite situation with the greater risk being perceived by experts. In the case of POPs, differences between other interest groups, such as environmental pressure groups versus industry representatives, may be of greater relevance. Alternatively, there may be significant differences in perception between populations in different regions depending on the extent to which they believe they benefit from, or are harmed by, POPs (e.g. people living in areas where DDT is used successfully against malaria versus certain Inuit groups in Canada exposed to PCB originating from remote sources).

Improvements in the availability of information relating to products would support this process. Many companies have joined ‘Responsible Care’; a voluntary chemical industry organization devoted to environmentally sound production methods and life-cycle product stewardship. However, there maybe scope for further voluntary activity by the chemical and related industries including support for health research programmes and sharing results of laboratory toxicity tests. Many companies (mostly outside the chemical industry), have adopted the principles of ‘The Natural Step’, an international movement dedicated to helping society reduce its impact on the environment and move towards a sustainable future. It began in Sweden in 1989, where over 25 of the largest corporations have now used The Natural Step training to modify operations in accordance with four ‘system conditions for sustainability’. Companies in other European countries, including The Netherlands and the UK, are increasingly adopting the principles of this approach as are many in the USA. The system conditions of The Natural Step are:

1. Materials from the earth’s crust must not systematically increase in nature.
2. Persistent substances produced by society must not systematically increase in nature.
3. The physical basis for the earth’s productive natural cycles and biological diversity must not be systematically deteriorated.
4. There must be fair and efficient use of resources with respect to meeting human needs.

Conditions 2 and 3 are of particular relevance for the control of POPs and are in line with the objectives of the Esbjerg Declaration. Voluntary initiatives such as ‘Responsible Care’ and ‘The Natural Step’ should be seen as complementary to the regulatory approaches for controlling POPs and other hazardous substances. They also offer a means of broadening participation to include enlightened companies and, ultimately, an informed public which can, through their purchasing choices, encourage the wider adoption of these principles.
11. Recommendations

Data
(1) For both model validation and risk assessment purposes, reliable source and emissions data are required, not only for existing POPs, but also for PBTs and hazardous substances in general.
(2) Procedures for gaining such data need to be harmonised and co-ordinated at an international level.
(3) Reliable monitoring data are needed for risk assessment and model calibrations. Such data from different regions should be comparable.

Models
(4) There is a need to improve and validate models of chemical fate in the environment at the local, regional, continental and global scale so that exposures can be estimated with more reliability, especially for ‘new’ chemicals and those for which inadequate monitoring data exist.

Processes and effects
(5) Further research is required on deposition/emission processes, transformation processes and bioavailability of POPs and PBTs in terrestrial ecosystems.
(6) Further research is required on the phytotoxic effects of POPs and PBTs and their effects on soil microbial populations and soil fauna.
(7) Further research is needed on transport processes, persistence, fate and effects of POPs and PBTs in aquatic media.

Effects (general)
(8) Research is required into the effects of mixtures of chemicals similar to those actually encountered in the environment.
(9) Efforts should be increased to develop mechanism-based biomarkers of effect, as well as biologically based sum-parameters to aid the development of relevant human exposure and effects monitoring data.
(10) Further studies are recommended on effect monitoring for POPs making use of existing accidentally high exposed populations (e.g. victims of the Seveso accident) in comparison with those exposed to the highest background levels (e.g. the Inuit).
(11) Reliable, internationally agreed testing methodologies for endocrine disrupters identification and for immunotoxicity should be developed.

Chemical properties
(12) International activities aimed at determining and correlating the key physical, chemical and biological properties of chemicals used for assessment purposes need to be improved and better co-ordinated.
(13) There is a need for accepted test methods for long-term persistence as applied to POPs and PBTs.

Monitoring
(14) A systematic international search of environmental media for the presence of ‘new’ and ‘unexpected’ organic contaminants is required. (To date, there has been undue reliance on fortuitous detection of these substances.)

Risk management
(15) When it is judged that a chemical warrants risk management, the actions required should be clearly defined and a schedule of actions, and the corresponding expected beneficial reductions in concentrations and exposure, should be documented. Progress towards these goals should be reported regularly.

Alternatives to POPs
(16) As a priority, the availability of safer alternative chemicals or alternative practices, as well as training in their use, will have to be facilitated, especially in developing countries. A comprehensive risk-benefit analysis should be the basis for the development of such alternatives.

Co-operation
(17) There is a need for close co-operation between the various international initiatives on POPs to ensure efficient use of scarce resources by, for example, ensuring that assessment criteria and procedures are as compatible as possible.

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