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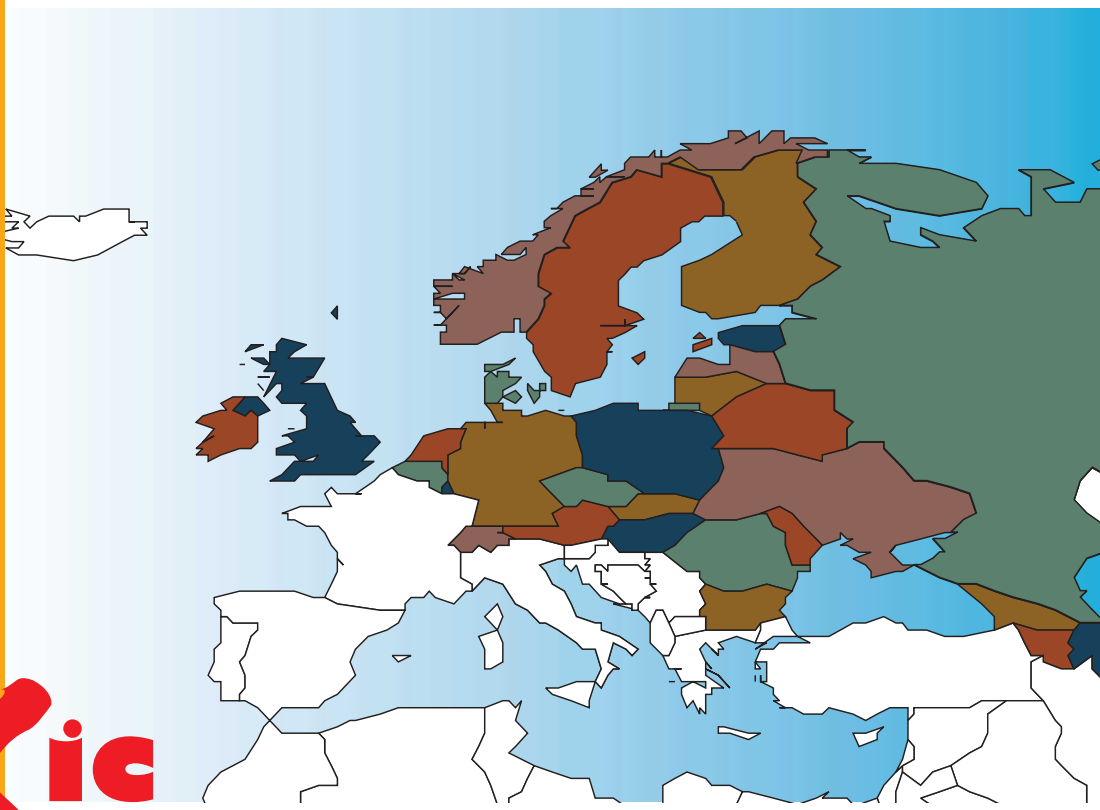

Regionally Based Assessment of Persistent Toxic Substances

December 2002

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CHEMICALS

Regionally Based Assessment of Persistent Toxic Substances

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EUROPE REGIONAL REPORT

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PREFACE

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In 2000, The United Nations Environmental Program asked this Regional Team to participate in a global assessment of PTS, in particular to produce a report on PTS in the European region. This document is intended to meet that request. The report is one of twelve, which make up the global assessment.

The authors are grateful to the all reviewers for their critiques and advice.

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EXECUTIVE SUMMMARY

1. INTRODUCTION

There is a need for a scientifically-based assessment of the nature and scale of the threats to the environment and its resources posed by persistent toxic substances that will provide guidance to the international community concerning the priorities for future remedial and preventive action. The assessment will lead to the identification of priorities for intervention, and through application of a root cause analysis will attempt to identify appropriate measures to control, reduce or eliminate releases of PTS, at national, regional or global levels.

The objective of the project is to deliver a measure of the nature and comparative severity of damage and threats posed at national, regional and ultimately at global levels by PTS. This will provide the GEF with a science-based rationale for assigning priorities for action among and between chemical related environmental issues, and to determine the extent to which differences in priority exist among regions.

The project relies upon the collection and interpretation of existing data and information as the basis for the assessment. No research will be undertaken to generate primary data, but projections will be made to fill data/information gaps, and to predict threats to the environment. The proposed activities are designed to obtain the following expected results:

1. Identification of major sources of PTS at the regional level;
2. Impact of PTS on the environment and human health;
3. Assessment of trans-boundary transport of PTS;
4. Assessment of the root causes of PTS related problems, and regional capacity to manage these problems;
5. Identification of regional priority PTS related environmental issues; and
6. Identification of PTS related priority environmental issues at the global level.

The outcome of this project will be a scientific assessment of the threats posed by persistent toxic substances to the environment and human health. The activities to be undertaken in this project comprise an evaluation of the sources of persistent toxic substances, their levels in the environment and consequent impact on biota and humans, their modes of transport over a range of distances, the existing alternatives to their use and remediation options, as well as the barriers that prevent their good management.

2. SOURCES OF PTS

Persistent Toxic Substances (PTS) can be introduced into the environment via numerous sources and activities. Point and diffuse sources include releases from industrial and domestic sites, traffic, waste disposal operations such as incinerators and landfills. Secondary sources include the spreading of sludge on land and remobilisation of previously deposited compounds from soils and water bodies. Some sources are capable of regulation (such as industrial point sources) while other diffuse emissions represent unregulated and/or difficult to regulate inputs (fugitive releases from landfills, domestic open burning of waste).

During the last decade a large amount of progress has been made in the production of atmospheric emission inventories of several PTS compounds within Europe. However there is still a lack of comparability in inventories produced by various organisations for the same compound group and this reduces transparency when comparing or compiling inventories. Improved emission inventories for PTS have become increasingly important as emission or source driven fate models for regional and global scales are developed. Inventories serve as useful information for decision makers in order to reduce the impact of these pollutants on the environment.

Source inventories represent a crucial step in developing appropriate risk control strategies for PTS – using an inventory of releases to air, water or land it is possible to rank sources in order of importance and so target source reduction measures effectively and incorporate effective risk reduction measures.

During the last two decades there has been a growing interest within environmental research community to understand the fluxes, behaviour, fate, and effects of PTS compounds. Various studies and assessments of PTS

in the environment have been carried out by several international organisations, such as United Nations Environmental Programme (UNEP), the United Nations Economic Commission for Europe (UN ECE), the World Health Organisation (WHO), the Nordic Council of Ministers, the Paris and Oslo Commissions, the Helsinki Commission, and the Great Lakes Commission, as well as the Arctic Monitoring and Assessment Programme (AMAP).

Conlusions

- Within the Region as a whole there is a large amount of data relating to industrial point source emissions to the atmosphere. Sources to air of well studied compounds such as PAHs, PCBs, and PCDDs/Fs are generally well characterised and inventories have been calculated and updated regularly via EMEP. Due to restrictions on the manufacturing and more stringent control of releases, emissions from primary sources have been declining during the last 20 years. Understanding of secondary source inputs and the potential for environmental recycling of individual compounds continues to be limited and few measurements are available.
- Obsolete stocks of pesticides represent a potential source of PTS material particularly within the Central European Countries and Newly Independent States. Exact quantities and components of the stockpiled wastes are unknown at present but quantities are thought to be in excess of 80 000 t.
- For the compounds of emerging concern (e.g. PBDEs, chlorinated parrafins) emission sources to all environmental compartments are very poorly characterised, few formal inventories have been established and there is limited understanding of the principal contemporary source categories. For PBDEs, evidence of increasing concentrations in human tissues from Sweden would suggest that emissions into the Region have been rising during the last 20 years.
- Unlike sources to air, sources to land and water are very poorly quantified for all the PTS compounds.
- Prioritization of sources inputs within the Region as a whole highlight that the following compounds represent ongoing releases in the Region which are of most concern with respect the environment and health:
    - Hexachlorobenzene (HCB)
    - PCBs
    - PCDD/Fs
    - PCP
    - PBDEs
    - Short chain chlorinated paraffins

3. ENVIRONMENTAL LEVELS, TOXICOLOGICAL AND ECOTOXICOLOGICAL CHARACTERISATION

3.1 Levels and trends

The first part of this chapter deals with the environmental levels and trends. The relative spatial and temporal variations in environmental concentrations of PTSs are briefly described. The following sections describe ecotoxicology, toxicology and human exposure to PTS in Region III.

Conclusions

- Region III has a lot of information concerning to environmental levels of PTS, but geographic distribution of the available data is not equal for all parts of Region, better situation is in some countries of EU and Central Europe.
- Very good and traditional monitoring system concerning also PTS exists (EN ECE EMEP, OSPAR, HELCOM) which are oriented to air and deposition (EMEP), seas (OSPAR, HELCOM); some new are ongoing (Caspic Sea, Black Sea). As far as rivers, the monitoring is realised mainly based on the national level, but a lot of multinational or regional activities already exist (Rhine, Danube).
- The measurements of PTS levels in some other compartments such as lakes, soils or vegetation is partly performed based on the international programmes (IM EMEP), national monitoring programmes (soils) or pilot or research projects (biota, lakes). Human exposure is measured and studied on the European levels (activities WHO Europe) and very frequently on the national levels.

- Although monitoring indicates that the loads of some hazardous substances have been reduced considerably over the past ten years especially in the Baltic Sea region, problems still persist. Comprehensive knowledge about the impact of most available chemicals, and their combinations, on human health and the environment is still lacking.
- The increasing number of these man-made substances is a matter of concern and calls for the application of the precautionary principle. On the other hand other seas, such as Black or Caspic still have a lot of heavily contaminated sites, where petroleum hydrocarbons and phtalates are the dominant organic contaminants of the Caspian Sea. Only traces of persistent organochlorines were detected in the Caspian seals (highest section of the food web). But also the level of contamination of the Caspian Sea decreased significantly during the last 10 years.
- The loads of many substances have been reduced by at least 50 % since the late 1980s - mainly due to the effective implementation of environmental legislation, the substitution of hazardous substances with harmless or less hazardous substances, and technological improvements.
- In former communistic countries reductions have been mainly due to fundamental socio-economic changes.
- The organochlorinated pesticides (OCPs) are no longer in use, have never been used, or have even been banned within the Region III. But one serious problem that remains is that in some countries various obsolete pesticides still remain in temporary storage awaiting suitable disposal.
- Polychlorinated biphenyls (PCBs) are no longer produced or used in new ways. Inventories are still being carried out in CEECs. Following an analysis of the legislative situation throughout the CEE part of Region, and the current uses, stockpiles and releases of PCBs measures have been proposed to ensure their safe handling and to reduce releases of PCBs from existing equipment.
- As a results of former production, long time and widespread use and also long-range transport from other part of Globe, OCPs, PCBs, PCDDs/Fs and PAHs and also some newer PTS are found in all environmental compartments including remote high mountain European sites, but principially the decreasing trends are observed.
- In this context, it is important to remember that a lot of countries of Region, such as the UK, Germany and others have a long industrial history, involving combustion activity in the form of wood and coal burning. For example in the UK, over 65 million ton of coal was being burned each year nationally in the 1850s. The smelting of metals and the production of iron and steel also have a long history in the UK and Europe, processes known to have significant PCDDs/Fs emissions. It is important to remember that the history of PCDDs/Fs environmental inputs/burdens in the UK and Europe may therefore not be mirrored in other regions of the world.
- Several studies reported that air PCDDs/Fs levels are declining in urban/industrialized centres. These trends are observed in Western Europe and are believed to be largely due to emission abatement actions taken in the early nineties. The decline of PCDDs/Fs levels in the atmosphere resulted in a decrease of these compounds in “atmospherically impacted” media such as vegetation, cow´s milk and meat products. Moreover, the human dietary intake of dioxins and furans dropped by almost a factor of 2 within the past 7 years.
- Analyses showed a decrease in the concentrations of the PAH compounds in the particle-phase in the ambient air during the second part of 80´s. This is a result of that the cars equipped with catalyst engines became a mandatory 1991. Also improvement of the fuel and the increased use of district heating, contribute to this trend. As far as the last 10 years, and the annual average concentrations of PAHs seem to stagnate due to a permanent increase of motorized traffic on the one hand and a better combustion technology and an increase in the use of natural gas for domestic heating on the other hand.
- Relatively worse situation can be observed in the towns in the former communistic countries, where the number of cars dramatically increased after the political changes. The same problems have all larger cities in CEE countries after the political changes – extremely high increase of town traffic and decreasing contribution from former industrial sources as the result of falling-off of production.

3.2 Ecotoxicology of PTS of regional concern

This chapter describes the effects in organisms other than humans, which have been proved for region Europe III by means of special research. The term “ecotoxicology” will be used to discuss the effects of persistent toxic substances (PTS) on both the aquatic and terrestrial biota.

Conclusions

- Analysis of the observed ecotoxicological effects of PTS on birds, mammals and fish in Europe has shown, that although a wide number of laboratory and manipulated in situ studies with various organisms and effects were conducted and are documented in the literature, one has to carefully and critically evaluate these data.
- On one hand, the controlled laboratory toxicological studies with individual compounds or carefully prepared mixtures usually allow clear dose-response causality between chemical exposure and observed effects to be defined.
- On the other hand, laboratory tests alone seldom adequately describe what is likely to occur in the environment. The often complex and subtle effects of chronic, low-level environmental exposure to PTS are less well understood.
- In the environment, the universal exposure of organisms to low levels of a wide range of chemical contaminants 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.
- PTS can act via different mechanisms and cause various adverse effects in wildlife. Mechanisms causing ecotoxicological effects include non-specific toxicity (narcosis) and more specific mechanisms, such as aryl-hydrocarbon receptor (AHR) mediated toxicity, steroid receptor dependent effects, metabolic activations, immune suppression and neurotoxicity.
- The assessment of priority of PTS, included in the list of the Stockholm Convention, has been performed by scoring them on the basis of data, available in the Region Europe-III.
- The second group of ecotoxicants, which were mentioned in the Stockholm Convention, was also scored.

3.3 Human effects of PTS of regional concern

Many environmental epidemiological studies indicate that correlations do exist between chemical contamination and observed human health effects. To evaluate critically the adverse effects of individual PTS, it is necessary to compare data derived from experiments with the laboratory animals, the results of epidemiological studies due to accidental or occupational exposure, as well as the effects observed for „average“ population.

It is very difficult to elucidate cause and effect relationships between human exposure to low levels of a PTS in the environment and the particular adverse health effects, not least because of the broad range of chemicals to which humans are exposed at any one time. The measurable residues of PCBs, dioxins and various organochlorine pesticides present in human tissues around the world and contamination of food, including breast milk, is also the worldwide phenomenon.

Evidence for low-level effects of PTS on humans are more limited than those for wildlife but are consistent with effects reported both in exposed wildlife populations and in laboratory experiments on animals. This is why the data from „hot-spot“ accidental events or occupational exposures can help to formulate the safety values for PTS. Trying to elucidate the toxicological effects of PTS, one has always to remember about many confounding factors affecting human health (life style, dietary habits), which are often very poorly evaluated.

Concluding the general introduction, it is worthwhile to mention, that WHO came to the conclusion, that „where levels of some PTS 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“. This conclusion has been supported by the report of AMAP, the authors of which 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.

Conclusions

- Analysis of the results of environmental epidemiological studies shows, that correlations do exist between the chemical contamination of air, water and soil and human health. To elucidate the particular effects of individual toxicants (genotoxicity, estrogenic effects, carcinogenicity, neurotoxicity, immunotoxicity, etc.) it is important to compare the above mentioned results with the data, obtained from experiments with the laboratory animals.

- The assessment of priority PTS, included in the list of the Stockholm Convention, has been performed by scoring them on the basis of data, available in the Region Europe-III.
- The second group of toxicants, which were mentioned in the Stockholm Convention, was also scored.

3.4 Human exposure to PTS compounds in Region III – Europe

The persistent bioaccumulative properties of PTS substances means, that they have the capacity to transfer through terrestrial and aquatic foodchains and accumulate in human lipids. As omnivores we occupy a top position in terrestrial and aquatic foodchains and as a result consume a high proportion of food in which persistent lipophilic compounds will have effectively biomagnified. Once ingested, PTSs sequester in body lipids, where they equilibrate at roughly similar levels on a fat-weight basis between adipose tissue, serum, and breast milk.

It is possible to document three distinct types of human exposure to PTS compounds:

- ✓ **High-dose acute** exposure: typically results from accidental fires or explosions involving electrical capacitors or other PCB-containing equipment, or high dose food contamination.
- ✓ **Mid-level chronic** exposure is predominantly due to the occupational exposure, and, in some cases, also due to the proximity of environmental storage sites or high consumption of a PTS-contaminated dietary source, such as fish or other marine animals.
- ✓ **Chronic, low-dose** exposure is characteristic for the general population as a consequence of the existing global background levels of PTSs with variations due to diet, geography, and level of industrial pollution. Low level and population-wide effects are more difficult to study. People are exposed to multiple PTSs during their lifetime and all individuals today carry detectable levels of a range of PTSs in their body lipids.

Over the last 10-15 years as interest in exposure to these compounds has increased there have been numerous surveys of both typical 'background' levels in the population and also small surveys of occupationally exposed individuals whose body lipids contain elevated concentrations.

Compounds are most often monitored in human milk, serum and adipose although milk monitoring is far more widely practiced due to the relative ease of sample collection. Milk not only provides evidence of maternal exposure to contaminants, it also provides information to assess risk to breast-fed infants. Contaminants in breast milk for example increase with maternal age and decrease with the number and duration of lactation periods (e.g. TCDD levels in breast milk decrease roughly 25% after each successive breast-fed child). The most popular compounds for analysis include the OC pesticides and PCBs.

Numerous analyses have now been made of PCBs in samples of human milk from the general population within the region. Countries with a long history of human tissue sampling - from the early 1980s - include the Netherlands, Sweden and Germany. Within the Central European Countries, Slovakia, the Czech Republic and Poland also have a sizeable database of information spanning the last 10-15 years. Standardized collection and analytical protocols now exist for analysing many PTS compounds in breast milk in these countries in addition to tissue banking facilities. For example, between 1986 and 1997 over 3 500 milk samples were analysed in Germany for a range of organochlorine compounds. Far fewer analyses of human samples have been made for PCDD/Fs, principally due to the high cost. As a general rule, travelling eastwards within the Region, the number and size of data sets for all compounds reduces significantly.

Evidence from market basket surveys of principal foods and food groups suggest that exposure to many of the classical PTS compounds via food is very similar throughout the Region. This is also supported by the extensive movement of food products throughout Europe providing many consumers with a 'European' average food basket of produce. To a large extent personal choices in food preferences will ultimately control our intake of persistent compounds throughout life. Since aquatic foodchains are subject to a greater loading of many pollutants than terrestrial ones, individuals who consume fish and seafood obtain an appreciable proportion of their annual intake via this route. For example, fishermen on the east coast of Sweden who have eaten fatty Baltic fish (herring and salmon) almost daily were found to have roughly twice the blood levels of DDT, PCBs and dioxins than people with a more average fish intake.

European exposure to dioxins via food has declined considerably during the last decades. This is due to successful efforts that have led to the reduction of many known dioxin sources. Today the estimated intake by the European population of PCDDs/Fs and non-ortho PCBs, expressed as WHO-TEQs, is 1.2-3.0 $pg.kg^{-1}$

bw.day^{-1}. Since the 80´s various tolerable daily intake „recommendations“ have been used, and for many population groups, such as new-borns and high fish consumers, these recommendations have been exceeded, and still are. Recently a tolerable weekly intake (TWI) of dioxins, furans and non-ortho PCBs, corresponding to 14 pg WHO-TEQ.kg^{-1} bw, was set by the EU Scientific Committee on Food (SCF).

The SCF has, as of 2002, established maximum limit values for dioxins and furans in consumer food on the European market in order to reduce the overall dioxin contamination of the food-chain, and the exposure of the European population. The goal is to have a 25 % decline in the exposure by year 2006. The $WHO_{PDDDs/Fs}$-TEQ maximum limits, based so far on the concentrations of PCDDs/Fs only, are set for foods such as meat, fish, poultry, dairy products and oil and fats and range from 0.75-6 pg.g^{-1} lipid. With one exception the $WHO_{PDDDs/Fs}$-TEQ maximum limit is set on lipid basis, namely for fish. For fish the EU limit is 4 $WHO_{PDDDs/Fs}$-TEQ.g^{-1} fresh weight.

The absolute and relative contributions of PCDDs/Fs and non-ortho and mono-ortho PCBs to the total WHO-TEQs of six foods – chicken, beef, butter, human milk, salmon and cod liver from Northern Europe, were determined and compared to the current EU limit values. For all foods studied, PCBs contribute to more than 50 % to the total WHO-TEQ. For cod liver the contribution of PCBs to the total WHO-TEQ is high at more than 80 %. Sum TEQ levels in the salmon and cod liver reflects the relatively highly contaminated aquatic food-chain.

Conclusions

- In summary, human exposure to PTS compounds in dominated by intake via terrestrial and aquatic food products which have high lipid content and have been subject to bioaccumulation within agricultural foodchains e.g. milk, meat, eggs and fish, (particularly oily and/or long-lived species). Exposure is generally well characterized and quantified for PCBs and PCDD/Fs and a range of organchlorine pesticides. The vast majority of adult exposure will be below current WHO guideline values. Individuals exceeding the guideline value will be dominated by subsistence fishermen and their families, individuals who consume several meals of oily fish each week in addition to those consuming locally produced foods in the vicinity of an on-going source of contamination.
- Human lipid concentrations of well characterized compounds such as PCBs and PCDD/Fs have been declining significantly in recent years throughout the Region at a rate of approximately 5% per year since the early 1990s. This decline coincides with European restrictions on the manufacture and release of these compounds into the environment and in particular, into the atmosphere. For some PTS compounds of emerging concern such as PBDEs, there is some evidence of increasing trends in human breast milk during the last 20 years.
- Breast-fed infants represent a distinct sub-group of the population whose exposure to PCDD/Fs and Dioxin-like PCBs will exceed current guideline values based on bodyweight for the first few months of life. In view of the significant declining trends in TEQ concentrations in breast milk over the last 20 years, WHO strongly recommend that breast feeding is encouraged and promoted for the child benefit.

4. ASSESSMENT OF MAJOR PATHWAYS OF CONTAMINANTS TRANSPORT

As many persistent toxic substances are semivolatile, their atmospheric transport can occur either in the gas phase or in the particle phase of the atmosphere. Due to their low vapour pressure, PTSs tend to partition mainly into organic carbon containing media, such as soil, sediment, biota or aerosols. However, their volatility is often high enough to allow for long-range transport in a way that has been described as the ”grasshopper effect”. This means that the chemical is trapped in an organic phase without being degraded, and is then released back into the atmosphere, allowing for a short transport, after which it is trapped again and the procedure continues until the chemical is ultimately degraded. This “grasshopper effect” allows persistent chemicals of low vapour pressure to be transported long distances to areas where they have never been used, which is of concern both for ethical and environmental reasons. Transboundary movement may also be possible via large water bodies, where chemicals of low water solubility can be transported a long way via water particles and suspended sediment material or chemicals with high water solubility can be very effectively transported in the dissolved state. Migrating fish could also contribute to this phenomenon.

Regardless of in which medium a chemical is being transported, what ultimately determines a chemical’s potential of long-range transport and thus transboundary movement are its partitioning properties in combination with the nature of the environmental media in or between which the transport occurs. Therefore,

crucial in order to achieve an adequate description of a chemical's movement, is to create a picture, which accurately describes the possible transport pathways that a chemical substance can undergo. This is a complicated task, since the complexity of the environment cannot be underestimated. As a first approach, the environment can however be divided into basic units, or compartments, which might include air with aerosols, water with water particles, soil, sediment and vegetation, or other significant media. The aim is then to achieve a description of transport processes and to derive a full picture of the movement of chemicals within the region being assessed.

Today, most PTS are banned and not "primarily" emitted in the European region. Transboundary air transport has been shown to be important for the occurrence of these chemicals in northern Europe. Atmospheric deposition is an important pathway for PTS to both aquatic and terrestrial ecosystems. The cold climate in the northern part of the region may favour the deposition of the PTSs. Environmental compartments, such as vegetation, soil and sediments, will act as reservoirs for PTSs. In this region, contaminated sites, so-called "hot spots", will also constitute as significant reservoirs for PTSs. PTSs may be re-emitted back from the ecosystem to the atmosphere and be transported both within and from the region into the Arctic areas (grasshopper effect).

Conclusions

- Transboundary transport is important for the occurrence of PTS in the European region. Atmospheric transport processes are important pathways for PTS to both aquatic and terrestrial ecosystems.
- The evidence of LTR in the region has been investigated both with measurements and modelling.
- An integrated monitoring/modelling approach is applied for assessment of PTS contamination in the European region. This approach includes arrangement of superstation network, model assessment of contamination levels and national measurement campaigns. In modelling activities accumulation in the compartments other than atmosphere is important.
- At present there exist a lot of multicompartment PTS transport models both steady-state and dynamic describing PTS fate in the environment. In the framework of LRTAP Convention the EMEP/MSCE-POP model is used for assessment of PTS contamination in the region.
- Modelling activities are useful for evaluation of PTS redistribution between various environmental compartments, long-term trends of environmental contamination, spatial distribution of concentrations in different media (atmosphere, soil, seawater, vegetation) and transboundary transport.
- Some PTS possess very high long-range transport potential and hemispheric/global scale is reasonable for them to assess European contamination. The hemispheric version of EMEP/MSCE-POP model indicates the ability of some PTS to transport to and from the European region.
- PTS often possess very high long-range transport potential and hemispheric/global scale is reasonable to assess European contamination. The results of EMEP/MSCE-POP model indicate the ability of some PTS such as PCBs, PCDDs/Fs, γ-HCH.

5. PRELIMINARY ASSESSMENT OF THE REGIONAL CAPACITY AND NEED TO MANAGE PTS

Region III has 29 countries, 22 from them signed and 8 already ratified SC. Many countries of the Region also signed (24 from 36 which signed this Protocol in that time) and ratified (11 from 12) the Aarhus Protocol to the Convention on Long-Range Transboundary Air Pollution on POPs.

The production and use of PCBs and OCPs are restricted or banned with very few exceptions. Air, water, soils, plants and foods are legally protected against hazardous substances in the Region. The PTS inventories of releases to air, water, land and products are ongoing process. Few countries has complex emission inventory based on the measurement of real emission factors, all countries based on EMEP and CORINAIR activities are using the European Atmospheric Emission Guidebook for annual inventory, but lack of actual inventories exist as far as water and land releases and the products contents of PTS. The most "open" problem is PTS by-products such as PCDDs/Fs, PAHs, HCB. Also the inventory of obsolete pests is on the acceptable level. The evidence of PTS hot spots is still problem in CEECs.

Conclusions

- The production and use of PCBs and OCPs are restricted or banned with very few exceptions. Region has legal, economical and political capacity for solution of PTS environmental problems mainly based on the EU strategy and co-operation between EU and accession countries.

1. INTRODUCTION

1.1. BACKGROUND

The introduction of xenobiotic chemicals that are generally referred to as "persistent toxic substances" (PTS) into the environment and their resulting effects is a major issue that gives rise to concerns at local, national, regional and global scales. Many of the substances of greatest concern are organic compounds characterised by persistence in the environment, resistance to degradation, and acute and chronic toxicity. In addition, many are subject to atmospheric, aquatic or biological transport over long distances and are thus globally distributed, detectable even in areas where they have never been used. The lipophilic character of these substances causes them to be incorporated and accumulated in the tissues of living organisms leading to body burdens that pose potential risks of adverse health effects. Toxic chemicals, which are less persistent but for which there are continuous releases resulting in essentially persistent exposure of biota, raise similar concerns. The persistence and bioaccumulation of PTS may also result in an increase over time of concentrations in consumers at higher trophic levels, including humans.

A sub-group of the persistent toxic substances are the "persistent organic pollutants" (POPs) identified by the international community for immediate international action[1]. These chemicals have serious health and environmental effects, which may include carcinogenicity, reproductive impairment, developmental and immune system changes, and endocrine disruption, thus posing a threat of lowered reproductive success and in extreme cases possible loss of biological diversity.

1.2. OVERVIEW OF THE RBA PTS PROJECT

Following the recommendations of the Intergovernmental Forum on Chemical Safety[2], the UNEP Governing Council decided in February 1997 (Decision 19/13 C) that immediate international action should be initiated to protect human health and the environment through measures which will reduce and/or eliminate the emissions and discharges of an initial set of twelve persistent organic pollutants (POPs). Accordingly an Intergovernmental Negotiating Committee (INC) was established with a mandate to prepare an international legally binding instrument for implementing international action on certain persistent organic pollutants. To date three[3] sessions of the INC have been held. These series of negotiations have resulted in the adoption of the Stockholm Convention in 2001. The initial 12 substances fitting these categories that have been selected under the Stockholm Convention include: aldrin, endrin, dieldrin, chlordane, DDT, toxaphene, mirex, heptachlor, hexachlorobenzene, PCBs, dioxins and furans. Besides these 12, there are many other substances that satisfy the criteria listed above for which their sources, environmental concentrations and effects are to be assessed.

Persistent toxic substances can be manufactured substances for use in various sectors of industry, pesticides, or by-products of industrial processes and combustion. To date, their scientific assessment has largely concentrated on specific local and/or regional environmental and health effects, in particular "hot spots" such as the Great Lakes region of North America or the Baltic Sea. In response to the long-range atmospheric transport of PTS, instruments such as the Convention on Long-Range Trans-boundary Air Pollution (LRTAP) under the auspices of the UN Economic Commission for Europe (UNECE) have been developed. The Basel Convention regulates the trans-boundary movement of hazardous waste, which may include PTS. Some PTS are covered under the recently adopted Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade. FAO has initiated a process to identify and manage the disposal of obsolete stocks of pesticides, including PTS, particularly in developing countries and countries with economies in transition.

1.2.1. Objectives

There is a need for a scientifically-based assessment of the nature and scale of the threats to the environment and its resources posed by persistent toxic substances that will provide guidance to the international community

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1 The initial twelve POPs are: aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, toxaphene, polychlorinated biphenyls, dioxins and furans.

2 Conclusions of the IFCS sponsored Experts Meeting on POPs and final Report of the *ad hoc* working group on POPs, Manila, 17-22 June 1996, "Persistent Organic Pollutants: Considerations for Global Action".

3 At the time of the submission of the project proposal, October 1999.

concerning the priorities for future remedial and preventive action. The assessment will lead to the identification of priorities for intervention, and through application of a root cause analysis will attempt to identify appropriate measures to control, reduce or eliminate releases of PTS, at national, regional or global levels (Annex D).

The objective of the project is to deliver a measure of the nature and comparative severity of damage and threats posed at national, regional and ultimately at global levels by PTS. This will provide the GEF with a science-based rationale for assigning priorities for action among and between chemical related environmental issues, and to determine the extent to which differences in priority exist among regions.

1.2.2. Results

The project relies upon the collection and interpretation of existing data and information as the basis for the assessment. No research will be undertaken to generate primary data, but projections will be made to fill data/information gaps, and to predict threats to the environment. The proposed activities are designed to obtain the following expected results:

1) Identification of major sources of PTS at the regional level;
2) Impact of PTS on the environment and human health;
3) Assessment of trans-boundary transport of PTS;
4) Assessment of the root causes of PTS related problems, and regional capacity to manage these problems;
5) Identification of regional priority PTS related environmental issues; and
6) Identification of PTS related priority environmental issues at the global level.

The outcome of this project will be a scientific assessment of the threats posed by persistent toxic substances to the environment and human health. The activities to be undertaken comprise an evaluation of the sources of persistent toxic substances, their levels in the environment and consequent impact on biota and humans, their modes of transport over a range of distances, the existing alternatives to their use and remediation options, as well as the barriers that prevent their good management.

1.3. METHODOLOGY

1.3.1. Regional divisions

To achieve these results, the globe is divided into 12 regions namely: Arctic, North America, Europe, Mediterranean, Sub-Saharan Africa, Indian Ocean, Central and North East Asia (Western North Pacific), South East Asia and South Pacific, Pacific Islands, Central America and the Caribbean, Eastern and Western south America, Antarctica. The twelve regions were selected based on obtaining geographical consistency while trying to reside within financial constraints.

1.3.2. Management structure

The project is managed by the project manager situated at UNEP Chemicals in Geneva, Switzerland. Each region is controlled by a regional coordinator assisted by a team of approximately 4 persons. The co-ordinator and the regional team are responsible for promoting the project, the collection of data at the national level and to carry out a series of technical and priority setting workshops for analysing the data on PTS on a regional basis. Besides the 12 POPs from the Stockholm Convention, the regional team selects the chemicals to be assessed for its region with selection open for review during the various workshops undertaken throughout the assessment process. Each team writes the regional report for the respective region.

1.3.3. Data processing

Data is collected on sources, environmental concentrations, human and ecological effects through questionnaires that are filled at the national level. The results from this data collection along with presentations from regional experts at the technical workshops, are used to develop regional reports on the PTS selected for analysis. A priority setting workshop with participation from representatives from each country results in priorities being established regarding the threats and damages of these substances to each region. The

information and conclusions derived from the 12 regional reports will be used to develop a global report on the state of these PTS in the environment.

The project is not intended to generate new information but to rely on existing data and its assessment to arrive at priorities for these substances. The establishment of a broad and wide- ranging network of participants involving all sectors of society was used for data collection and subsequent evaluation. Close cooperation with other intergovernmental organizations such as UNECE, WHO, FAO, UNPD, World Bank and others was obtained. Most have representatives on the Steering Group Committee that monitors the progress of the project and critically reviews its implementation. Contributions were garnered from UNEP focal points, UNEP POPs focal points, national focal points selected by the regional teams, industry, government agencies, research scientists and NGOs.

1.3.4. Project funding

The project costs approximately US$4.2 million funded mainly by the Global Environment Facility (GEF) with sponsorship from countries including Australia, France, Germany, Sweden, Switzerland and the USA. The project runs between September, 2000 to April, 2003 with the intention that the reports be presented to the first meeting of the Conference of the Parties of the Stockholm Convention projected for 2003/4.

Results from the project will be used by the GEF and other funding agencies to provide priorities for future remedial action to reduce or eliminate these substances from the environment. In addition, the project will provide support to international conventions such as the Rotterdam Convention, the UNECE LRTAP Convention, the Regional Seas Agreement and the Stockholm Convention. It will present opportunities for bilateral or multilateral action, network building and co-operation within and between regions and stimulate research through the identification of data gaps.

1.4. SCOPE OF THE EUROPEAN REGIONAL ASSESSMENT

1.4.1. Introduction

Europe is the largest chemical-producing region in the world, accounting for 38 % of the total; Western Europe alone accounts for 33 % (UN ECE, 1997; EEA 1998). Chemical production and use provide 2 % of Europe´s GDP and 7 % of its employment.

The number of existing chemicals on the market is large, but the exact number is unknown. Over 100 000 were registered in the European Inventory of Existing Commercial Chemical Substances (EINECS) in 1981, but current estimates of marketed chemicals varies widely, from 20 000 to as many as 70 000. Little is known about the toxicity of about 75 % of these chemicals. Of the existing chemicals, some have been selected for risk assessment by various international conventions or bodies. The increasing interest is focused on the chemical properties of persistent and bioaccumulative chemicals and most of the activities involve the development of substance risk profiles.

1.4.2. Omissions/weaknesses

The numerous data that have been used to estimate PTS emissions and human exposure levels are only of limited comparability (Liem and van Zorge, 1995).

Over the last 40 years of continuous determination of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in environmental samples, the analytical procedures have been changing according to the developments in the analysis of trace substances. Unfortunately, comparisons between contemporary analytical results and older data can be questionable because of differences in the analytical procedures. The authors of various reports and papers have used different formats for the presentation of their material and often such important data as the number of samples, date of sampling and limit of detection, have been ommitted(Kočan et al., 1994a, b; Schutz et al. 1998).

Consequently, some of the data presented in this study should be treated as indicating general levels and trends in environmental contamination and human exposure to PCBs and certain OCPs. Where possible, trends and other evaluations given in this report will include qualifying information to allow a better insight into the validity and comparability of the data.

Analytical uncertainty will largely influence the comparisons between the estimated dioxin emissions for the several countries. However, reported values should be regarded as best available estimates so far (Liem and van Zorge, 1995).

Based on the published data, no clear indication of substantial differences in dioxin levels of common sources can be noted. Some differences exist in food consumption patterns between the selected countries and some differences occur in the selection of foods likely to contribute to the total dioxin intake. Obviously, these differences are not reflected in the intakes that have been estimated for the different background exposures in the selected countries.

1.4.3. Other European Assessment projects

A number of regional organisations have already conducted assessments of persistent toxic substances. Where they exist, the present project will rely on these assessments which include the Quality Status of the North East Atlantic completed by the Oslo and Paris Commission, the State of the Arctic Environment completed by the Arctic Monitoring and Assessment Programme, the State of the Marine Environment of the Baltic of the Helsinki Commission, and the work accomplished in the European Union through the Dangerous Substances Directive.

1.4.3.1. The Convention on Long-Range Trans-boundary Air Pollution (LRTAP)

In the European region, in addition to EU Directives and regional initiatives, countries, which are members of EU and newly associated states, are guided by a number of regional and international treaties (EEA, 1998; HELCOM, 2000; OSPAR, 2000).

Regionally the most important one is The Convention on Long-Range Trans-boundary Air Pollution (LRTAP), adopted in 1979 under the auspices of the United Nations Economic Commission for Europe (UNECE) covers Europe and North America. This Convention includes measures for eliminating or restricting use, reducing consumption and unintentional emissions or contamination, eliminating waste and improving the management of chemicals. The POPs Protocol of this Convention includes 16 pollutants – 12, which are on the list of SC plus chlordecone, hexabromobiphenyl, hexachlorocyclohexanes and polycyclic aromatic hydrocarbons.

Based on the decisions of Steering Body of CLRTAP and WHO Europe, the new evaluation of some POPs from the list of POPs Protocol and some new candidate substances is developed.

1.4.3.2. OSPAR Convention

The 1992 OSPAR Convention for the Protection of the Marine Environment of the North-East Atlantic requires that Contracting Parties shall 'take all possible steps to prevent and eliminate pollution and shall take the necessary measures to protect the maritime area against the adverse effects of human activities so as to safeguard health and to conserve marine ecosystems and, when practicable, restore marine areas which have been adversely affected'.

To provide a basis for such measures, Contracting Parties are required to undertake and publish at regular intervals joint assessments of the quality status of the marine environment and of its development, for the maritime area covered by the Convention. These assessments should also evaluate the effectiveness of measures taken or planned for the protection of the marine environment, and identify priorities for action (Article 6 of and Annex IV to the OSPAR Convention).

1.4.3.3. HELCOM activities with regard to hazardous substances including POPs

The first Helsinki Convention was signed in 1974 by the then seven Baltic coastal states and entered into force on 3 May 1980. In the light of political changes, and developments in international environmental and maritime law, a new convention was signed in 1992 by all the states bordering on the Baltic Sea and the European Community. After ratification the Convention entered into force on 17 January 2000. The Convention covers the whole of the Baltic Sea area including inland waters as well as the water of the sea itself and the seabed. Measures are also taken in the whole catchment area of the Baltic Sea to reduce land-based pollution.

The Helsinki Commission adopted in its 19th Meeting (26 March 1998) the HELCOM Recommendation 19/5 concerning the HELCOM Objective with regard to Hazardous Substances. The HELCOM Objective with regard to hazardous substances is to prevent pollution of the Convention Area by continuously reducing discharges, emissions and losses of hazardous substances towards the target of their cessation by the year 2020,

with the ultimate aim of achieving concentrations in the environment near background values for naturally occurring substances and close to zero for man-made synthetic substances. Hazardous substances are substances that are toxic, persistent and liable to bioaccumulate, or otherwise give reason for concern - by influencing the hormone or immune systems (HELCOM).

1.5. GENERAL DEFINITIONS OF CHEMICALS

1.5.1. Persistent Toxic Substances

The twelve persistent organic pollutants (POPs) from the Stockholm Convention are separated into three groups, pesticides, industrial compounds and unintended by-products. One compound belongs to more than one group, hexachlorobenzene. It belongs to all three groups, pesticides (fungicide), industrial compounds (by-product) and unintended by-products. The regional specific PTS are also defined. Besides the twelve substances selected under the Stockholm Convention (aldrin, endrin, dieldrin, chlordane, DDT, heptachlor, mirex, toxaphene, hexachlorobenzene, PCBs, dioxins and furans), the following substances have also been included in this assessment: atrazine, polybrominated diphenyl ethers, lindane, organic mercury, organic tin, pentachlorophenol, polyaromatic hydrocarbons, short chain chlorinated paraffins, hexabromobiphenyl, phthalates, nonylphenols and tert-octylphenol.

1.5.2. Pesticides

1.5.2.1. Aldrin

Chemical Name: 1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-endo,exo-5,8-dimethano-naphthalene ($C_{12}H_8Cl_6$).

CAS Number: 309-00-2

Properties: Solubility in water: 27 $\mu g.l^{-1}$ at 25°C; vapour pressure: 2.3 x 10^{-5} mm Hg at 20°C; log K_{OW}: 5.17-7.4.

Discovery/Uses: It has been manufactured commercially since 1950, and used throughout the world up to the early 1970s to control soil pests such as corn rootworm, wireworms, rice water weevil, and grasshoppers. It has also been used to protect wooden structures from termites.

Persistence/Fate: Readily metabolized to dieldrin by both plants and animals. Biodegradation is expected to be slow and it binds strongly to soil particles, and is resistant to leaching into groundwater. Aldrin was classified as moderately persistent with half-life in soil and surface waters ranging from 20 days to 1.6 years.

Toxicity: Aldrin is toxic to humans; the lethal dose for an adult has been estimated to be about 80 $mg.kg^{-1}$ body weight. The acute oral LD_{50} in laboratory animals is in the range of 33 $\mu g.g^{-1}$ body weight for guinea pigs to 320 $mg.kg^{-1}$ body weight for hamsters. The toxicity of aldrin to aquatic organisms is quite variable, with aquatic insects being the most sensitive group of invertebrates. The 96-h LC_{50} values range from 1-200 $\mu g.l^{-1}$ for insects, and from 2.2-53 $\mu g.l^{-1}$ for fish. The maximum residue limits in food recommended by FAO/WHO varies from 0.006 $mg.kg^{-1}$ milk fat to 0.2 $mg.kg^{-1}$ meat fat. Water quality criteria between 0.1 to 180 $\mu g.l^{-1}$ have been published.

1.5.2.2. Chlordane

Chemical Name: 1,2,4,5,6,7,8,8-Octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene ($C_{10}H_6Cl_8$).

CAS Number: 57-74-9

Properties: Solubility in water: 56 $\mu g.l^{-1}$ at 25°C; vapour pressure: 0.98 x 10^{-5} mm Hg at 25 °C; log K_{OW}: 4.58-5.57.

Discovery/Uses: Chlordane appeared in 1945 and was used primarily as an insecticide for control of cockroaches, ants, termites, and other household pests. Technical chlordane is a mixture of at least 120 compounds. Of these, 60-75% are chlordane isomers, the remainder being related to endo-compounds including heptachlor, nonachlor, diels-alder adduct of cyclopentadiene and penta/hexa/ octachlorocyclopentadienes.

Persistence/Fate: Chlordane is highly persistent in soils with a half-life of about 4 years. Its persistence and high partition coefficient promotes binding to aquatic sediments and bioconcentration in organisms.

Toxicity: LC_{50} from 0.4 $mg.l^{-1}$ (pink shrimp) to 90 $mg.l^{-1}$ (rainbow trout) have been reported for aquatic organisms. The acute toxicity for mammals is moderate with an LD_{50} in rat of 200-590 $mg.kg^{-1}$ body weight (19.1 $mg.kg^{-1}$ body weight for oxychlordane). The maximum residue limits for chlordane in food are, according to FAO/WHO between 0.002 $mg.kg^{-1}$ milk fat and 0.5 $mg.kg^{-1}$ poultry fat. Water quality criteria of 1.5 to 6 $\mu g.l^{-1}$ have been published. Chlordane has been classified as a substance for which there is evidence of endocrine disruption in an intact organism and possible carcinogenicity to humans.

1.5.2.3. DDTs (Dichlorodiphenyltrichloroethane)

Chemical Name: 1,1,1-Trichloro-2,2-bis-(4-chlorophenyl)-ethane ($C_{14}H_9Cl_5$).

CAS Number: 50-29-3.

Properties: Solubility in water: 1.2-5.5 $\mu g.l^{-1}$ at 25°C; vapour pressure: 0.2 x 10^{-6} mm Hg at 20°C; log K_{OW}: 6.19 for *pp'*-DDT, 5.5 for *pp'*-DDD and 5.7 for *pp'*-DDE.

Discovery/Use: DDT appeared for use during World War II to control insects that spread diseases like malaria, dengue fever and typhus. Following this, it was widely used on a variety of agricultural crops. The technical product is a mixture of about 85% *pp'*-DDT and 15% *op'*-DDT isomers.

Persistence/Fate: DDT is highly persistent in soils with a half-life of up to 15 years and of 7 days in air. It also exhibits high bioconcentration factors (in the order of 50 000 for fish and 500 000 for bivalves). In the environment, the product is metabolized mainly to DDD and DDE.

Toxicity: The lowest dietary concentration of DDT reported to cause egg shell thinning was 0.6 $mg.kg^{-1}$ for the black duck. LC_{50} of 1.5 $mg.l^{-1}$ for large mouth bass and 56 $mg.l^{-1}$ for guppy have been reported. The acute toxicity of DDT for mammals is moderate with an LD_{50} in rat of 113-118 $mg.kg^{-1}$ body weight. DDT has been shown to have an estrogen-like activity, and possible carcinogenic activity in humans. The maximum residue level in food recommended by WHO/FAO range from 0.02 $mg.kg^{-1}$ milk fat to 5 $mg.kg^{-1}$ meat fat. Maximum permissible DDT residue levels in drinking water (WHO) is 1.0 $\mu g.l^{-1}$.

1.5.2.4. Dieldrin

Chemical Name: 1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydroexo-1,4-endo-5,8-dimethano-naphthalene ($C_{12}H_8Cl_6O$).

CAS Number: 60-57-1

Properties: Solubility in water: 140 $\mu g.l^{-1}$ at 20°C; vapour pressure: 1.78 x 10^{-7} mm Hg at 20°C; log K_{OW}: 3.69-6.2.

Discovery/Uses: It appeared in 1948 after World War II and used mainly for the control of soil insects such as corn rootworms, wireworms and catworms.

Persistence/Fate: It is highly persistent in soils, with a half-life of 3-4 years in temperate climates, and bioconcentrates in organisms. The persistence in air has been estimated in 4-40 hrs.

Toxicity: The acute toxicity for fish is high (LC_{50} between 1.1 and 41 $mg.l^{-1}$) and moderate for mammals (LD_{50} in mouse and rat ranging from 40 to 70 $mg.kg^{-1}$ body weight). However, a daily administration of 0.6 $mg.kg^{-1}$ to rabbits adversely affected the survival rate. Aldrin and dieldrin mainly affect the central nervous system but there is no direct evidence that they cause cancer in humans. The maximum residue limits in food recommended by FAO/WHO varies from 0.006 $mg.kg^{-1}$ milk fat and 0.2 $mg.kg^{-1}$ poultry fat. Water quality criteria between 0.1 to 18 $\mu g.l^{-1}$ have been published.

1.5.2.5. Endrin

Chemical Name: 3,4,5,6,9,9-Hexachloro-1a,2,2a,3,6,6a,7,7a-octahydro-2,7:3,6-dimethanonaphth[2,3-b]oxirene ($C_{12}H_8Cl_6O$).

CAS Number: 72-20-8

Properties: Solubility in water: 220-260 $\mu g.l^{-1}$ at 25 °C; vapour pressure: 2.7 x 10^{-7} mm Hg at 25°C; log K_{OW}: 3.21-5.34.

Discovery/Uses: It has been used since the 50s against a wide range of agricultural pests, mostly on cotton but also on rice, sugar cane, maize and other crops. It has also been used as a rodenticide.

Persistence/Fate: Is highly persistent in soils (half-lives of up to 12 years have been reported in some cases). Bioconcentration factors of 14 to 18 000 have been recorded in fish, after continuous exposure.

Toxicity: Endrin is very toxic to fish, aquatic invertebrates and phytoplankton; the LC_{50} values are mostly less than 1 $\mu g.l^{-1}$. The acute toxicity is high in laboratory animals, with LD_{50} values of 3-43 $mg.kg^{-1}$, and a dermal LD_{50} of 5-20 $mg.kg^{-1}$ in rats. Long term toxicity in the rat has been studied over two years and a NOEL of 0.05 $mg.kg^{-1}$ $bw.day^{-1}$ was found.

1.5.2.6. Heptachlor

Chemical Name: 1,4,5,6,7,8,8-Heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene ($C_{10}H_5Cl_7$).

CAS Number: 76-44-8

Properties: Solubility in water: 180 $\mu g.l^{-1}$ at 25°C; vapour pressure: 0.3 x 10^{-5} mm Hg at 20°C; log K_{OW}: 4.4-5.5.

Production/Uses: Heptachlor is used primarily against soil insects and termites, but also against cotton insects, grasshoppers, and malaria mosquitoes. Heptachlor epoxide is a more stable breakdown product of heptachlor.

Persistence/Fate: Heptachlor is metabolised in soils, plants and animals to heptachlor epoxide, which is more stable in biological systems and is carcinogenic. The half-life of heptachlor in soil is in temperate regions 0.75 – 2 years. Its high partition coefficient provides the necessary conditions for bioconcentrating in organisms.

Toxicity: The acute toxicity of heptachlor to mammals is moderate (LD_{50} values between 40 and 119 $mg.kg^{-1}$ have been published). The toxicity to aquatic organisms is higher and LC_{50} values down to 0.11 $\mu g.l^{-1}$ have been found for pink shrimp. Limited information is available on the effects in humans and studies are inconclusive regarding heptachlor and cancer. The maximum residue levels recommended by FAO/WHO are between 0.006 $mg.kg^{-1}$ milk fat and 0.2 $mg.kg^{-1}$ meat or poultry fat.

1.5.2.7. Hexachlorobenzene

Chemical Name: Hexaclorobenzene (C_6Cl_6).

CAS Number: 118-74-1

Properties: Solubility in water: 50 $\mu g.l^{-1}$ at 20°C; vapour pressure: 1.09 x 10^{-5} mm Hg at 20°C; log K_{OW}: 3.93-6.42.

Discovery/Uses: It was first introduced in 1945 as fungicide for seed treatments of grain crops, and used to make fireworks, ammunition, and synthetic rubber. Today it is mainly a by-product in the production of a large number of chlorinated compounds, particularly lower chlorinated benzenes, solvents and several pesticides, but this problem does not already exist in Europe. HCB is emitted to the atmosphere in flue gases generated by waste incineration facilities and metallurgical industries.

Persistence/Fate: HCB has an estimated half-life in soils of 2.7-5.7 years and of 0.5-4.2 years in air. HCB has a relatively high bioaccumulation potential and long half-life in biota.

Toxicity: Many of the available acute and chronic aquatic toxicity studies failed to demonstrate effects at or below the solubility limit, but based on validated long-term studies for fish, crustaceans and algae, a 90 days study on the freshwater fish O. Mykiss revealed the lowest NOEC of 3.7 $\mu g.l^{-1}$. The acute toxicity of HCB is low with LD_{50} values of 3.5 $mg.kg^{-1}$ for rats. Mild effects of the [rat] liver have been observed at a daily dose of 0.25 $mg.kg^{-1}$ bw. HCB is known to cause liver disease in humans (porphyria cutanea tarda) and has been classified as a possible carcinogen to humans by IARC.

1.5.2.8. Mirex

Chemical Name: 1,1a,2,2,3,3a,4,5,5a,5b,6-Dodecachloroacta-hydro-1,3,4-metheno-1H-cyclobuta-[cd]pentalene ($C_{10}Cl_{12}$).

CAS Number: 2385-85-5

Properties: Solubility in water: 0.07 $\mu g.l^{-1}$ at 25°C; vapour pressure: 3 x 10^{-7} mm Hg at 25°C; log K_{OW}: 5.28.

Discovery/Uses: The use in pesticide formulations started in the mid 1950s largely focused on the control of ants. It is also a fire retardant for plastics, rubber, paint, paper and electrical goods. Technical grade

preparations of mirex contain 95.19% mirex and 2.58% chlordecone, the rest being unspecified. Mirex is also used to refer to bait comprising corncob grits, soya bean oil, and mirex.

Persistence/Fate: Mirex is considered to be one of the most stable and persistent pesticides with a half-life in soils of up to 10 years. Bioconcentration factors of 2 600 and 51 400 have been observed in pink shrimp and fathead minnows, respectively. It is capable of undergoing long-range transport due to its relative volatility (VPL = 4.76 Pa; H = 52 $Pa.m^{-3}.mol^{-1}$).

Toxicity: The acute toxicity of Mirex for mammals is moderate with an LD_{50} in rat of 235 $mg.kg^{-1}$ and dermal toxicity in rabbits of 80 $mg.kg^{-1}$. Mirex is also toxic to fish and can affect their behaviour (LC_{50} (96 hr) from 0.2 to 30 $mg.l^{-1}$ for rainbow trout and bluegill, respectively). Delayed mortality of crustaceans occurred at 1 $\mu g.l^{-1}$ exposure levels. There is evidence of its potential for endocrine disruption and possibly carcinogenic risk to humans.

1.5.2.9. Toxaphene

Chemical Name: Polychlorinated bornanes and camphenes ($C_{10}H_{10}Cl_8$).

CAS Number: 8001-35-2

Properties: Solubility in water: 550 $\mu g.l^{-1}$ at 20°C; vapour pressure: 3.3 x 10^{-5} mm Hg at 25°C; log K_{OW}: 3.23-5.50.

Discovery/Uses: Toxaphene has been in use since 1949 as a nonsystemic insecticide with some acaricidal activity, primarily on cotton, cereal grains fruits, nuts and vegetables. It was also used to control livestock ectoparasites such as lice, flies, ticks, mange, and scab mites. The technical product is a complex mixture of over 300 congeners, containing 67-69% chlorine by weight.

Persistence/Fate: Toxaphene has a half life in soil from 100 days up to 12 years. It has been shown to bioconcentrate in aquatic organisms (BCF of 4 247 in mosquito fish and 76 000 in brook trout).

Toxicity: Toxaphene is highly toxic in fish, with 96-hour LC_{50} values in the range of 1.8 $\mu g.^{-1}$ in rainbow trout to 22 $\mu g.l^{-1}$ in bluegill. Long term exposure to 0.5 $\mu g.l^{-1}$ reduced egg viability to zero. The acute oral toxicity is in the range of 49 $mg.kg^{-1}$ body weight in dogs to 365 $mg.kg^{-1}$ in guinea pigs. In long term studies NOEL in rats was 0.35 $mg.kg^{-1}$ $bw.day^{-1}$, LD_{50} ranging from 60 to 293 $mg.kg^{-1}$ bw. For toxaphene exists a strong evidence of the potential for endocrine disruption. Toxaphene is carcinogenic in mice and rats and is of carcinogenic risk to humans, with a cancer potency factor of 1.1 $mg.kg^{-1}.day^{-1}$ for oral exposure.

1.5.3. Industrial Chemicals

1.5.3.1. Polychlorinated biphenyls

Chemical Name: Polychlorinated biphenyls ($C_{12}H_{(10-n)}Cl_n$, where n is within the range of 1-10).

CAS Number: Various (e.g. for Aroclor 1242, CAS No.: 53469-21-9; for Aroclor 1254, CAS No.: 11097-69-1);

Properties: Water solubility decreases with increasing chlorination: 0.01 to 0.0001 $\mu g.l^{-1}$ at 25°C; vapour pressure: 1.6-0.003 x 10^{-6} mm Hg at 20°C; log K_{OW}: 4.3-8.26.

Discovery/Uses: PCBs were introduced in 1929 and were manufactured in different countries under various trade names (e.g., Aroclor, Clophen, Phenoclor). They are chemically stable and heat resistant, and were used worldwide as transformer and capacitor oils, hydraulic and heat exchange fluids, and lubricating and cutting oils. Theoretically, a total of 209 possible chlorinated biphenyl congeners exist, but only about 130 of these are likely to occur in commercial products.

Persistence/Fate: Most PCB congeners, particularly those lacking adjacent unsubstituted positions on the biphenyl rings (e.g., 2,4,5-, 2,3,5- or 2,3,6-substituted on both rings) are extremely persistent in the environment. They are estimated to have half-lives ranging from three weeks to two years in air and, with the exception of mono- and di-chlorobiphenyls, more than six years in aerobic soils and sediments. PCBs also have extremely long half-lives in adult fish, for example, an eight-year study of eels found that the half-life of CB153 was more than ten years.

Toxicity: LC_{50} for the larval stages of rainbow trout is 0.32 $\mu g.l^{-1}$ with a NOEL of 0.01 $\mu g.l^{-1}$. The acute toxicity of PCB in mammals is generally low and LD_{50} values in rat of 1 $g.kg^{-1}$ bw. IARC has concluded that PCBs are

carcinogenic to laboratory animals and probably also for humans. They have also been classified as substances for which there is evidence of endocrine disruption in an intact organism.

1.5.4. Unintended by-products

1.5.4.1. Dioxins and furans

Chemical Name: PCDDs ($C_{12}H_{(8-n)}Cl_nO_2$) and PCDFs ($C_{12}H_{(8-n)}Cl_nO$) may contain between 1 and 8 chlorine atoms. Dioxins and furans have 75 and 135 possible positional isomers, respectively.

CAS Number: Various (2,3,7,8-TetraCDD: 1746-01-6; 2,3,7,8-TetraCDF: 51207-31-9).

Properties: Solubility in water: in the range 0.43 – 0.0002 $ng.l^{-1}$ at 25°C; vapour pressure: 2 – 0.007 x 10^{-6} mm Hg at 20°C; log K_{OW}: in the range 6.60 – 8.20 for tetra- to octa-substituted congeners.

Discovery/Uses: They are by-products resulting from the production of other chemicals and from the low-temperature combustion and incineration processes. They have no known use.

Persistence/Fate: PCDDs/Fs are characterized by their lipophilicity, semi-volatility and resistance to degradation (half life of TCDD in soil of 10-12 years) and to long-range transport. They are also known for their ability to bio-concentrate and biomagnify under typical environmental conditions.

Toxicity: The toxicological effects reported refers to the 2,3,7,8-substituted compounds (17 congeners) that are agonist for the AhR. All the 2,3,7,8-substituted PCDDs and PCDFs plus coplanar PCBs (with no chlorine substitution at the ortho positions) show the same type of biological and toxic response. Possible effects include dermal toxicity, immunotoxicity, reproductive effects and teratogenicity, endocrine disruption and carcinogenicity. At the present time, the only persistent effect associated with dioxin exposure in humans is chloracne. The most sensitive groups are fetus and neonatal infants.

Effects on the immune systems in the mouse have been found at doses of 10 $ng.kg^{-1}$ $bw.day^{-1}$, while reproductive effects were seen in rhesus monkeys at 1-2 $ng.kg^{-1}$ $bw.day^{-1}$. Biochemical effects have been seen in rats down to 0.1 $ng.kg^{-1}$ $bw.day^{-1}$. In a re-evaluation of the TDI for dioxins, furans (and planar PCB), the WHO decided to recommend a range of 1-4 TEQ $pg.kg^{-1}$ bw, although more recently the acceptable intake value has been set monthly at 1-70 TEQ $pg.kg^{-1}$ bw.

1.5.5. Other PTS of emerging concern in Europe

1.5.5.1. Atrazine

Chemical Name: 2-Chloro-4-(ethlamino)-6-(isopropylamino)-s-triazine ($C_{10}H_6Cl_8$).

CAS Number: 19-12-24-9

Properties: Solubility in water: 28 mg/L at 20°C; vapour pressure: 3.0 x 10^{-7} mm Hg at 20°C; log K_{ow}**:** 2.34.

Discovery/Uses: Atrazine is a selective triazine herbicide used to control broadleaf and grassy weeds in corn, sorghum, sugarcane, pineapple, christmas trees, and other crops, and in conifer reforestation plantings. It was discovered and introduced in the late 50's. Atrazine is still widely used today because it is economical and effectively reduces crop losses due to weed interference.

Persistence/Fate: The chemical does not adsorb strongly to soil particles and has a lengthy half-life (60 to >100 days). Atrazine has a high potential for groundwater contamination despite its moderate solubility in water.

Toxicity: The oral LD50 for atrazine is 3090 mg/kg in rats, 1750 mg/kg in mice, 750 mg/kg in rabbits, and 1000 mg/kg in hamsters. The dermal LD50 in rabbits is 7500 mg/kg and greater than 3000 mg/kg in rats. Atrazine is practically nontoxic to birds. The LD50 is greater than 2000 mg/kg in mallard ducks. Atrazine is slightly toxic to fish and other aquatic life. Atrazine has a low level of bioaccumulation in fish. Available data regarding atrazine's carcinogenic potential are inconclusive.

1.5.5.2. Polybrominated diphenyl ethers (PBDEs)

Chemical Name: Polybrominated diphenyl ethers ($C_{12}H_{(10-n)}Br_nO$, where n = 1-10). As in the case of PCBs the total number of congeners is 209, with a predominance in commercial mixtures of the tetra-, penta- and octa-substituted isomers.

CAS Number: Various (PeBDE: 32534-81-9; OBDE: 32536-52-0; DeBDE: 1163-19-5)

Properties: Solubility in water: 0.9 $ng.l^{-1}$ at 25°C (PeBDE); vapour pressure: 3.85 x 10^{-3} to <10^{-7} mm Hg at 20-25 °C; log K_{OW}: 4.28 - 9.9.

Discovery/Uses: Since the 1960s, three commercial PBDE formulations are in production. The pentabrominated product is used principally to flame retard polyurethane foams in furniture, carpet underlay and bedding. Commercial octa is a mixture of hexa- (10-12%), hepta- (44-46%), octa- (33-35%) and nonabromodiphenyl (10-11%) ethers. It is used to flame retard a wide variety of thermoplastics and is recommended for injection moulding applications such as high impact polystyrene (HIPS). The deca product (a single congener) is used predominantly for textiles and denser plastics such as housings for a variety of electrical products in particular TVs and computers.

Persistence/Fate: Data on environmental fate, although limited, suggest that biodegradation is not an important degradation pathway, but that photodegradation may play a significant role. They have already been found in high concentrations in marine birds and mammals from remote areas. The half-lives of PBDE components in rat adipose tissue vary between 19 and 119 days, the higher values being for the higher brominated congeners.

Toxicity: The available data suggest that the lower (tetra- to hexa-) PBDE congeners are likely to be carcinogens, potential endocrine disruptors, and/or neurodevelopmental toxicants. Studies in rats with commercial PeBDE indicate a low acute toxicity via oral and dermal routes of exposure, with LD_{50} values > 2 000 $mg.kg^{-1}$ bw. In a 30-day study with rats, effects on the liver could be seen at a dose of 2 $mg.kg^{-1}$ $bw.day^{-1}$, with a NOEL at 1 $mg.kg^{-1}$ $bw.day^{-1}$. The toxicity to *Daphnia magna* has also been investigated and LC_{50} was found to be 14 $\mu g.l^{-1}$ with a NOEC of 4.9 $\mu g.l^{-1}$. DecaBDPO was not toxic to the sediment organism *Lumbriculus varigatus* at the highest dose tested, 5 000 $mg.kg^{-1}$ dry sediment (Krueger et al., 2001a,b,c) in ether 2 or 5% total organic carbon. DBDPO was not toxic to earthworm reproduction at the highest dose tested, 4 910 $mg.kg^{-1}$ dry soil (Aufderheide et al., 2001). The 28 Day EC50 for survival and the 56 Day EC50 for reproduction were both > 4 910 $mg.kg^{-1}$ dry soil. The NOEC for survival and reproduction was 4 910 $mg.kg^{-1}$ dry soil. Further, earthworms did not absorb DBDPO. DBDPO was also not toxic when tested in six terrestrial plant species (soybean, ryegrass, onion, corn, cucumber and tomato) at the highest dose tested, 6 250 $mg.kg^{-1}$ dry soil (Porch and Krueger, 2001). No effects were observed on emergence, survival, or growth on any of the six plant species tested, and the NOEC was 6 250 $mg.kg^{-1}$, the highest dose tested. They are intensively tested, but in general data on toxicology is still limited, they potential endocrine disrupting properties were not confirn in both *in vivo* and *in vitro.* There are concerns over the health effects of exposure.

1.5.5.3. Lindane (γ-HCH)

Chemical Name: 1,2,3,4,5,6-Hexachlorocyclohexane (mixed isomers) ($C_6H_6Cl_6$).

CAS Number: 608-73-1 (γ-HCH, lindane: 58-89-9).

Properties: γ-HCH: solubility in water: 7 $mg.l^{-1}$ at 20°C; vapour pressure: 3.3 x 10^{-5} mm Hg at 20°C; log K_{OW}: 3.8.

Discovery/Uses: There are two principle formulations: "technical HCH", which is a mixture of various isomers, including α-HCH (55-80%), β-HCH (5-14%) and γ-HCH (8-15%), and "lindane", which is essentially pure γ-HCH. Historically, lindane was one of the most widely used insecticides in the world. Its insecticidal properties were discovered in the early 1940s. It controls a wide range of sucking and chewing insects and has been used for seed treatment and soil application, in household biocidal products, and as textile and wood preservatives.

Persistence/Fate: Lindane and other HCH isomers are relatively persistent in soils and water, with half lives generally greater than 1 and 2 years, respectively. HCH are much less bioaccumulative than other organochlorines because of their relatively low liphophilicity. On the contrary, their relatively high vapour pressures, particularly of the α-HCH isomer, determine their long-range transport in the atmosphere.

Toxicity: Lindane is moderately toxic for invertebrates and fish, with LC_{50} values of 20-90 $\mu g.l^{-1}$. The acute toxicity for mice and rats is moderate with LD_{50} values in the range of 60-250 $mg.kg^{-1}$. Lindane resulted to have no mutagenic potential in a number of studies but an endocrine disrupting activity.

1.5.5.4. Organic mercury

Chemical Name: The main compound of concern is methyl mercury ($HgCH_3$).

CAS Number: 22967-92-6

Properties: Solubility in water: 0.1 $g.l^{-1}$ at 21°C ($HgCH_3Cl$) and 1.0 $g.l^{-1}$ at 25ºC ($Hg(CH_3)_2$); vapour pressure: 8.5 x 10^{-3} mm Hg at 25°C ($HgCH_3Cl$); log K_{OW}: 1.6 ($HgCH_3Cl$) and 2.28 ($Hg(CH_3)_2$).

Production/Uses: There are many sources of mercury release to the environment, both natural (volcanoes, mercury deposits, and volatilization from the ocean) and human-related (coal combustion, chlorine alkali processing, waste incineration, and metal processing). It is also used in thermometers, batteries, lamps, industrial processes, refining, lubrication oils, and dental amalgams. Methyl mercury has no industrial uses; it is formed in the environment by methylation of the inorganic mercurial ion mainly by microorganisms in the water and soil.

Persistence/Fate: Mercury released into the environment can either stay close to its source for long periods, or be widely dispersed on a regional or even world-wide basis. Not only are methylated mercury compounds toxic, but highly bioaccumulative as well. The increase in mercury as it rises in the aquatic food chain results in relatively high levels of mercury in fish consumed by humans. Ingested elemental mercury is only 0.01% absorbed, but methyl mercury is nearly 100% absorbed from the gastrointestinal tract. The biological half-life of mercury is 60 days.

Toxicity: Long-term exposure to either inorganic or organic mercury can permanently damage the brain, kidneys, and developing fetus. The most sensitive target of low level exposure to metallic and organic mercury following short or long term exposures appears to be the nervous system.

1.5.5.5. Organic tin

Chemical Name: Organotin compounds comprise mono-, di-, tri- and tetrabutyl and triphenyl tin compounds. They conform to the following general formula $(n\text{-}C_4H_9)_nSn\text{-}X$ and $(C_6H_5)_3Sn\text{-}X$, where X is an anion or a group linked covalently through a hetero-atom.

CAS Number: 56-35-9 (TBTO); 76-87-9 (TPTOH)

Properties: Solubility in water: 4 $mg.l^{-1}$ (TBTO) and 1 $mg.l^{-1}$ (TPTOH) at 25°C and pH 7; vapour pressure: 7.5 x 10^{-7} mm Hg at 20°C (TBTO) 3.5 x 10^{-8} mmHg at 50ºC (TPTOH); log K_{OW}: 3.19 - 3.84. In sea water and under normal conditions, TBT exists as three species in seawater (hydroxide, chloride, and carbonate).

Discovery/Uses: They are mainly used as antifouling paints (tributyl and triphenyl tin) for underwater structures and ships. Minor identified applications are as antiseptic or disinfecting agents in textiles and industrial water systems, such as cooling tower and refrigeration water systems, wood pulp and paper mill systems, and breweries. They are also used as stabilizers in plastics and as catalytic agents in soft foam production. It is also used to control the shistosomiasis in various parts of the world.

Persistence/Fate: Under aerobic conditions, TBT takes 1 to 3 months to degrade, but in anaerobic soils may persist for more than 2 years. Because of the low water solubility it binds strongly to suspended material and sediments. TBT is lipophilic and tends to accumulate in aquatic organisms. Oysters exposed to very low concentrations exhibit BCF values from 1 000 to 6 000.

Toxicity: TBT is moderately toxic and all breakdown products are even less toxic. Its impact on the environment was discovered in the early 1980s in France with harmful effects in aquatic organisms, such as shell malformations of oysters, imposex in marine snails and reduced resistance to infection (e.g. in flounder). Molluscs react adversely to very low levels of TBT (0.06-2.3 $ug.l^{-1}$). Lobster larvae show a nearly complete cessation of growth at just 1.0 $ug.l^{-1}$ TBT. In laboratory tests, reproduction was inhibited when female snails exposed to 0.05-0.003 $ug.l^{-1}$ of TBT developed male characteristics. Large doses of TBT have been shown to damage the reproductive and central nervous systems, bone structure, and the liver bile duct of mammals.

1.5.5.6. Pentachlorophenol (PCP)

Chemical Name: Pentachlorophenol (C_6Cl_5OH).

CAS Number: 87-86-5.

Properties: Solubility in water: 14 $mg.l^{-1}$ at 20°C; vapour pressure: 16 x 10^{-5} mm Hg at 20°C; log K_{OW}: 3.32 – 5.86.

Discovery/Uses: It is used as insecticide (termiticide), fungicide, non-selective contact herbicide (defoliant) and, particularly as wood preservative. It is also used in anti-fouling paints and other materials (e.g. textiles,

inks, paints, disinfectants and cleaners) as inhibitor of fermentation. Technical PCP contains trace amounts of PCDDs and PCDFs

Persistence/Fate: The rate of photodecomposition increases with pH ($t_{1/2}$ 100 hr at pH 3.3 and 3.5 hr at pH 7.3). Complete decomposition in soil suspensions takes >72 days, other authors reports half-life in soils of 23-178 days. Although enriched through the food chain, it is rapidly eliminated after discontinuing the exposure ($t_{1/2}$ = 10-24 h for fish).

Toxicity: It has been proved to be acutely toxic to aquatic organisms and have certain effects on human health, at the time that exhibits off-flavour effects at very low concentrations. The 24-h LC_{50} values for trout were reported as 0.2 $mg.l^{-1}$, and chronic toxicity effects were observed at concentrations down to 3.2 $\mu g.l^{-1}$. Mammalian acute toxicity of PCP is moderate-high. LD_{50} oral in rat ranging from 50 to 210 $mg.kg^{-1}$ bw have been reported. LC_{50} ranged from 0.093 $mg.l^{-1}$ in rainbow trout (48 h) to 0.77-0.97 $mg.l^{-1}$ for guppy (96 h) and 0.47 $mg.^{-1}$ for fathead minnow (48 h).

1.5.5.7. Polyaromatic hydrocarbons (PAHs)

Chemical Name: PAHs is a group of compounds consisting of two or more fused aromatic rings.

CAS Number:

Properties: Solubility in water: 0.00014 -2.1 $mg.l^{-1}$ at 25ºC; vapour pressure: from 0.0015 x 10^{-9} to 0.0051 mm Hg at 25°C; log K_{OW}: 4.79-8.20

Discovery/Use: Most of these are formed during incomplete combustion of organic material and the composition of PAHs mixture varies with the source(s) and also due to selective weathering effects in the environment.

Persistence/Fate: Persistence of the PAHs varies with their molecular weight. The low molecular weight PAHs are most easily degraded. The reported half-lives of naphthalene, anthracene and benzo(e)pyrene in sediment are 9, 43 and 83 hours, respectively, whereas for higher molecular weight PAHs, their half-lives are up to several years in soils/sediments. The BCFs in aquatic organisms frequently range between 100-2 000 and it increases with increasing molecular size. Due to their wide distribution, environmental pollution by PAHs has aroused global concern.

Toxicity: The acute toxicity of low PAHs is moderate with an LD_{50} of naphthalene and anthracene in rat of 490 and 18 000 $mg.kg^{-1}$ body weight respectively, whereas the higher PAHs exhibit higher toxicity and LD_{50} of benzo(a)anthracene in mice is 10$mg.kg^{-1}$ body weight. In *Daphnia pulex*, LC_{50} for naphthalene is 1.0 $mg.l^{-1}$, for phenanthrene 0.1 $mg.l^{-1}$ and for benzo(a)pyrene is 0.005 $mg.l^{-1}$. The critical effect of many PAHs in mammals is their carcinogenic potential. The metabolic action of these substances produces intermediates that bind covalently with cellular DNA. IARC has classified benz[a]anthracene, benzo[a]pyrene, and dibenzo[a,h]-anthracene as probable carcinogenic to humans. Benzo[b]fluoranthene and indeno[1,2,3-c,d]pyrene were classified as possible carcinogens to humans.

1.5.5.8. Short chain chlorinated paraffins (SCCPs)

Chemical Name: Polychlorinated alkanes ($C_xH_{(2x-y+2)}Cl_y$), in the case of SCCPs alkanes with C_{10-13}. They are manufactured by chlorination of liquid n-alkanes or paraffin wax and contain from 30 to 70% chlorine. The products are often divided in three groups depending on chain length: short chain (C_{10} – C_{13}), medium (C_{14} – C_{17}) and long (C_{18} – C_{30}) chain lengths. Only the SCCPs are usually considered as priority substances.
CAS Number: 85535-84-8

Properties: They are largely depending on the chlorine content. Based on the EU risk assessment, these are the values for SCCPs: water solubility: 150 to 470 $\mu g.l^{-1}$ at 20°C; vapour pressure: 1.6 x 10^{-4} mm Hg (0.021 Pa) at 40°C (with predicted range for C_{10}-30% chlorine to C_{13}-70% chlorine of 3.3 x 10^{-4} to 6.0 x 10^{-8} mm Hg at 20°C); log K_{OW}: in the range from 4.39 to 8.69.

Discovery/Uses: The largest application of CPs is as a plasticizer, where only MCCPs are used generally in conjunction with primary plasticizers such as certain phthalates in flexible PVC. The chlorinated paraffins also impart a number of technical benefits, of which the most significant is the enhancement of flame retardant properties and extreme pressure lubrication.

Persistence/Fate: CPs may be released into the environment from improperly disposed metal-working fluids or polymers containing chlorinated paraffins. Loss of chlorinated paraffins by leaching from paints and coatings

may also contribute to environmental contamination. Short chain CPs with less than 50 % chlorine content seem to be degraded under aerobic conditions. The medium and long chain products are degraded more slowly. CPs are bioaccumulated and both uptake and elimination are faster for the substances with low chlorine content.

Toxicity: The acute toxicity of CPs in mammals is low with reported oral LD_{50} values ranging from 4 - 50 $g.kg^{-1}$ bw, although in repeated dose experiments, effects on the liver have been seen at doses of 10 – 100 $mg.kg^{-1}$ $bw.day^{-1}$. Short-chain and mid-chain grades have been shown, in laboratory tests, to show toxic effects on fish and other forms of aquatic life after long-term exposure. The NOEC identified in the EU risk assessment for the most sensitive aquatic species tested was 5 $\mu g\ l^{-1}$.

1.5.5.9. Hexabromobiphenyl (HxBB)

Chemical Name: Hexabromobiphenyl ($C_{12}H_4Br_6$).

CAS Number: 59536-65-1

Properties: Solubility in water: 0.6 $\mu g.l^{-1}$ at 25°C; vapour pressure: 10^{-7} mm Hg at 20°C; log K_{OW}: 6.39.

Discovery/Uses: The production of polybrominated biphebyls (PBBs) began in 1970. HxBB was used as a fire retardant mainly in thermoplastics for constructing business machine housing and industrial (e.g. motor housing) and electrical (e.g. radio and TV parts) products. Smaller amounts were used as a fire retardant in coating and lacquers and in polyurethane foam for auto upholstery.

Persistence/Fate: HxBB is strongly adsorbed to soil and sediments and usually persist in the environment. HxBB resists both chemical and biological degradation. HxBB has been found in several sediment samples from the estuaries of large rivers and has been identified in edible fish.

Toxicity: Few toxicity data are available from short-term tests on aquatic organisms. The LD_{50} values of commercial mixtures show a relatively low order of acute toxicity (LD_{50} range from > 1 to 21.5 $g.kg^{-1}$ body weight in laboratory rodents). Oral exposure of laboratory animals to PBBs produced body weight loss, skin disorders, and nervous system effects, and birth defects. Humans exposed through contaminated food developed skin disorders, such as acne and hair loss. PBBs exhibit endocrine disrupting activity and possible carcinogenicity to humans.

1.5.5.10. Phthalates

Chemical Name: They encompass a wide family of compounds. Dimethylphthalate (DMP), diethylphthalate (DEP), dibutylphthalate (DBP), benzylbutylphthalate (BBP), di(2-ethylhexyl)phthalate (DEHP)($C_{24}H_{38}O_4$) and dioctylphthalate (DOP) are some of the most common.

CAS Nos.: 84-74-2 (DBP), 85-68-7 (BBP), 117-81-7 (DEHP).

Properties: The physico-chemical properties of phthalic acid esters vary greatly depending on the alcohol moieties. Solubility in water: 9.9 $mg.l^{-1}$ (DBP) and 0.3 $mg.l^{-1}$ (DEHP) at 25°C; vapour pressure: 3.5 x 10^{-5} (DBP) and 6.4 x 10^{-6} (DEHP) mm Hg at 25°C; log K_{OW}: 1.5 to 7.1.

Discovery/Uses: They are widely used as plasticizers, insect repellents, solvents for cellulose acetate in the manufacture of varnishes and dopes. Vinyl plastic may contain up to 40% DEHP.

Persistence/fate: They have become ubiquitous pollutants, in marine, estuarine and freshwater sediments, sewage sludges, soils and food. Degradation ($t_{1/2}$) values generally range from 1-30 days in soils and freshwaters.

Toxicity: The acute toxicity of phthalates is usually low: the oral LD_{50} for DEHP is about 25-34 $g.kg^{-1}$, depending on the species; for DBP reported LD_{50} values following oral administration to rats range from 8 to 20 $g.kg^{-1}$ body weight; in mice, values are approximately 5 to 16 $g.kg^{-1}$ body weight. In general, DEHP is not toxic for aquatic communities at the low levels usually present. In animals, high levels of DEHP damaged the liver and kidney and affected the ability to reproduce. There is no evidence that DEHP causes cancer in humans but they have been reported as endocrine disrupting chemicals. The EPA proposed a Maximum Admissible Concentration (MAC) of 6 $\mu g.l^{-1}$ of DEHP in drinking water.

1.5.5.11. Nonylphenols (NPs) and tert-octylphenol (t-OP)

Chemical Name: NP: $C_{15}H_{24}O$; OP: $C_{14}H_{22}O$.

CAS Number: 25154-52-3 (NP).

Properties: Solubility in water: 6.3 $\mu g.l^{-1}$ (NP) at 25°C; vapour pressure: 7.5 x 10^{-4} mm Hg at 20°C (NP); log K_{OW}: 4.5 (NP) and 5.92 (OP).

Discovery/Uses: NP and OP are the starting material in the synthesis of alkylphenol ethoxylates (APEs), first used in the 60s. These compounds are highly effective cleaning agents or surfactants that have been widely used in a number of industrial sectors including textiles, pulp and paper, paints, adhesives, resins and protective coatings. Alkylphenols can also be used as plasticisers, stabilizers for rubbers, lube oil additives, and the alkylphenol phosphite derivatives can be used as UV stabilisers in plastics.

Persistence/Fate: NP and OP are the end degradation products of APEs under both aerobic and anaerobic conditions. Therefore, the major part is released to water and concentrated in sewage sludges. NPs and t-OP are persistent in the environment with half-lives of 30-60 years in marine sediments, 1-3 weeks in estuarine waters and 10-48 hours in the atmosphere. Due to their persistence they can bioaccumulate to a significant extent in aquatic species. However, excretion and metabolism is rapid.

Toxicity: NP and OP have acute toxicity values for fish, invertebrates and algae ranging from 17 to 3 000 $\mu g.l^{-1}$. In chronic toxicity tests the lowest NOEC are 6 $\mu g.l^{-1}$ in fish and 3.7 $\mu g.l^{-1}$ in invertebrates. The threshold for vitellogenin induction in fish is 10 $\mu g.l^{-1}$ for NP and 3 $\mu g.l^{-1}$ for OP (similar to the lowest NOEC). Alkylphenols are endocrine disrupting chemicals also in mammals.

1.5.5.12. Organolead compounds

Chemical Name: Alkyllead compounds may be confined to tetramethyllead (TML, $Pb(CH_3)_4$) and tetraethyllead (TEL, $Pb(C_2H_5)_4$).

CAS Number: 75-74-1 (TML) and 78-00-2 (TEL).

Properties: Solubility in water: 17.9 $mg.l^{-1}$ (TML) and 0.29 $mg.l^{-1}$ (TEL) at 25°C; vapour pressure: 22.5 and 0.15 mm Hg at 20°C for TML and TEL, respectively; log K_{OW}.

Discovery/Uses: Tetramethyl and tetraethyllead are widely used as "anti-knocking" additives in gasoline. The release of TML and TEL are drastically reduced with the introduction of unleaded gasoline in late 70's in USA and followed by other parts of the world. However, leaded gasoline is still available which contribute to the emission of TEL and to a less extent TML to the environment.

Persistence/Fate: Under environmental conditions such as in air or in aqueous solution, dealkylation occurs to produce the less alkylated forms and finally to inorganic lead. However, there is limited evidence that under some circumstances, natural methylation of lead salts may occur. Minimal bioaccumulations were observed for TEL in shrimps (650x), mussels (120x) and plaice (130x) and for TML in shrimps (20x), mussels (170x), and plaice (60x).

Toxicity: Lead and lead compounds has been found to cause cancer in the respiratory and digestive systems of workers in lead battery and smelter plants. However, tetra-alkyllead compounds have not been sufficiently tested for the evidence of carcinogenicity. Acute toxicity of TEL and TML are moderate in mammals and high for aquatic biota. LD_{50} (rat, oral) for TEL is 35 mg $Pb.kg^{-1}$ and 108 mg $Pb.kg^{-1}$ for TML. LC_{50} (fish, 96hrs) for TEL is 0.02 $mg.kg^{-1}$ and for TML is 0.11 $mg.kg^{-1}$.

1.5.5.13. Chlordecone

Chemical Name: Decachlorooctahydro-1,3,4-methene-2H-cyclobuta(cd)pentalen-2-one ($C_{10}Cl_{10}O$). Also known as Kepone.

CAS Number: 143-50-0

Properties: Solubility in water: 7.6 $mg.l^{-1}$ at 25°C; vapour pressure: < 3 x 10^{-5} mm Hg at 20°C; log K_{OW}: 4.50.

Discovery/Uses: Chlordecone is released to the atmosphere as a result of its manufacture and use as an insecticide. Chlordecone also occurs as a degradation product of the insecticide Mirex. As a fungicide against apple scab and powdery mildew former use and to control the colorado potato beetle, rust mite on non-bearing citrus, and potato and tobacco were worm on gladioli and other plants. Chlordecone was formerly registered for the control of rootborers on bananas. Non-food uses included wireworm control in tobacco fields and bait to control ants and other insects in indoor and outdoor areas.

Persistence/Fate: The estimated half-life in soils is between 1-2 years, whereas in air is much higher, up to 50 years. It will not be expected to hydrolyse, biodegrade in the environment. Also direct photodegradation is not significant similarly as evaporation from water. General population exposure to chlordecone occurs mainly through the consumption of contaminated fish and seafood.

Toxicity: Workers who were exposed to high levels of chlordecone over a long period (more than one year) showed harmful effects on the nervous system, skin, liver, and male reproductive system. These workers were probably exposed mainly through touching chlordecone, although they may have inhaled or ingested some as well. Animal studies with chlordecone have shown effects similar to those seen in people, as well as harmful kidney effects, developmental effects, and effects on the ability of females to reproduce. There are no studies available on whether chlordecone is carcinogenic in people. However, studies in mice and rats have shown that ingesting chlordecone can cause liver, adrenal gland, and kidney tumors. Very highly toxic for some species such as Atlantic menhaden, sheepshead minnow or donaldson trout with LC50 between 21.4 – 56.9 $\mu g.l^{-1}$.

1.5.5.14. Endosulfan

Chemical Name: 6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzo-dioxathiepin-3-oxide ($C_9H_6Cl_6O_3S$).

CAS Number: 115-29-7.

Properties: Solubility in water: 320 $\mu g.l^{-1}$ at 25°C; vapour pressure: 0.17 x 10^{-4} mm Hg at 25°C; log K_{OW}: 2.23-3.62.

Discovery/Uses: Endosulfan was first introduced in 1954. It is used as a contact and stomach insecticide and acaricide in a great number of food and nonfood crops (e.g. tea, vegetables, fruits, tobacco, cotton) and it controls over 100 different insect pests. Endosulfan formulations are used in commercial agriculture and home gardening and for wood preservation. The technical product contains at least 94% of two pure isomers, α- and β-endosulfan.

Persistence/Fate: It is moderately persistent in the soil environment with a reported average field half-life of 50 days. The two isomers have different degradation times in soil (half-lives of 35 and 150 days for α- and β-isomers, respectively, in neutral conditions). It has a moderate capacity to adsorb to soils and it is not likely to leach to groundwater. In plants, endosulfan is rapidly broken down to the corresponding sulphate, on most fruits and vegetables, 50% of the parent residue is lost within 3 to 7 days.

Toxicity: Endosulfan is highly to moderately toxic to bird species (Mallards: oral LD_{50} 31 - 243 $mg.kg^{-1}$) and it is very toxic to aquatic organisms (96-hour LC_{50} rainbow trout 1.5 $\mu g.l^{-1}$). It has also shown high toxicity in rats (oral LD_{50}: 18 - 160 $mg.kg^{-1}$, and dermal: 78 - 359 $mg.kg^{-1}$). Female rats appear to be 4–5 times more sensitive to the lethal effects of technical-grade endosulfan than male rats. The α-isomer is considered to be more toxic than the β-isomer. There is a strong evidence of its potential for endocrine disruption.

1.6. PHYSICAL SETTING

1.6.1. Physical/geographical description of the terrestrial Europe

Europe forms little more than 7 per cent of the land surface of the Earth. It is the second smallest continent, being nearly 30 per cent larger than Oceania, but less than a quarter of the size of Asia. Region III covers round the three quarters of this area.

A characteristic feature of Europe is the Alpine ridge, a permanent divide in the continent for climate, history and trade. The plains are home to most economic and social activities; the so-called “cradle” of European welfare and power.

This complex and fragmented geography and geology has to a large extent driven Europe’s history and its political and territorial complexity. Geography and geology have contributed significantly to the political subdivisions found in Europe today, as well as to the conflicts and changes which have occurred and continue to influence the configuration of European countries and regions.

Europe has a rich and varied nature and wildlife, despite the extent of modification to which the natural environment has been subjected. The trends however, give cause for concern: valued ecosystems everywhere

are facing stress and decline, the list of endangered species continues to lengthen and for many species there is a lack of information. Due to the high level of public awareness and concern in Europe, there is a realisation of the need to complement an essentially defensive approach, based on the protection, with new policies designated to create or restore nature and wildlife in Europe (for example Natura 2002).

1.6.2. Climate and meteorology

The complex and fragmented structure of Europe contributes to the variable meteorological and climatological conditions: from the Mediterranean in the south, through temperate oceanic in the west and temperate continental in the east to boreal in the north. These principal types contain many subdivisions linked to altitude (eg, Alpine climate), position and aspect in plains or valleys and the distance from the sea. Temporal variations of climate have also influenced historical and economic development.

Region III lies across three climatic zones:

1) the circumpolar zone - the northern tip of Scandinavia, the Svalbard archipelago and northern Iceland;
2) the subtropical zone - the area south of the Alps, Dinaric Alps and Balkans;
3) the temperate zone - warm in the central south and west, and cool further north especially in eastern Scandinavia and Finland.

The climatic features of Europe also change in an easterly direction: the greater the distance from the Atlantic, the more the climate becomes continental (ie, drier, with greater seasonality and diurnal temperature regimes).

The influence of the Atlantic is strongly felt owing to the warm North Atlantic Current or Drift originating from the Gulf Stream which reaches the shores of Western Europe beyond 45°N (mainly on the coast of Ireland, Britain and Norway, as well as all the way to the Russian island of Novaya Zemlya). Thanks to this current, the whole area experiences a positive temperature anomaly in winter which gradually decreases south and eastwards across the continent.

1.6.3. European freshwater environments

1.6.3.1. Rivers

In comparison to its land area, Europe has the longest coastline of all the continents. European rivers discharge a total of 3,100 km^3 of fresh water to the sea each year, this is about 8 per cent of total world discharge. About 70 European rivers have a catchment area exceeding 10 000 km^2. The three largest rivers in Europe, the Volga, the Danube and the Dnepr, drain one quarter of the continent, but are only small by world standards, their catchments ranking 14th, 29th and 48th, respectively. The 31 largest European rivers, all of which have catchments exceeding 50,000 km^2, drain approximately two thirds of the continent.

The Volga and the Ural which flow south and the Kura, which flows east drain into the Caspian Sea while the Dnepr and the Don drain south into the Black Sea (Table 1.1). The largest river to discharge into the Black Sea is the Danube, which has its catchments in 16 countries of central Europe and the Balkans. The main rivers to discharge into the Baltic Sea are the Neva, the Wisla, the Oder, and the Neman. Ten rivers with catchments larger than 50 000 km^2, drain into the Atlantic and the North Sea with the Rhine and the Elbe being the largest.

Table 1.1: European main rivers

River	Mean discharge [km^3.yr]	Length [km]
Volga	230	3 530
Danube	205	2 850
Dnepr	52	2 270
Don	38	1 870
Severnaja Dvina	148	740
Pechora	129	1 810
Neva	79	75
Ural	-	2 540
Wisla	31	1 050
Kura	18	1 360

1.6.3.2. Lakes

There are more than 500,000 natural lakes larger than 0.001 km^2 (1 ha) in Europe; of these about 80-90 per cent are small with a surface area between 0.01 and 0.1 km^2; only about 16 000 have a surface area exceeding 1 km^2. Three quarters of the lakes are located in Norway, Sweden, Finland, and the Karelo-Kola part of the Russian Federation.

Nineteen natural lakes larger than 400 km^2 are found in Sweden, Finland, Estonia and the north-western part of the Russian Federation, and three in Central Europe – Lake Balaton, Lac Leman, and Bodensee (Table 1.2).

Table 1.2: Large European lakes

1.1.1.1.1.1 Natural lake	Country	Area [km^2]	Mean depth [m]	Maximum depth [m]
Ladoga	Russia	17.670	51	258
Onega	Russia	9.670	30	120
Vänern	Sweden	5.670	27	106
Peipus	Estonia, Russia	3.570	23	47
Vättern	Sweden	1.912	39	128
Vygozero	Russia	1.285	7	24
Saimaa	Finland	1.147	12	82
Mälaren	Sweden	1.140	13	61
Ilmen	Russia	1.124	3	10
Beloye	Russia	1.120	4	20

1.6.4. European marine environment

1.6.4.1. The Baltic Sea

The Baltic Sea covers 415 266 square kilometres, while its catchment extends over an area about four times as the sea itself. Thirteen countries lie within the catchment area of the Baltic Sea. Maritime transport of goods between the Baltic States plays an essential role and over 500 million tonnes of cargo are transported across the Baltic Sea each year (HELCOM, 2001).

The Baltic Sea is almost totally enclosed by land, and only connected to the North Sea by a narrow and shallow straits around Denmark and Sweden. This limits the exchange of water with the open sea. It typically takes about 25-30 years for all the water in the Baltic Sea to be replaced. The inflow of water from the North Sea is the main source of oxygen for the deep waters of the Baltic Proper, and is very significant for nutrient cycles..

Nearly 85 million people inhabit the Baltic Sea catchment area (15 million people live within 10 kilometres of the coast). Population density varies from over 500 inhabitants per square kilometre in the urban areas of Poland, Germany and Denmark to less than 10 inhabitant per square kilometre in the northern areas of Finland and Sweden. A remarkably large part (60-70%) of the territory is agricultural land in Germany, Denmark and Poland. Forests Wetlands and lakes constitute from 65 to 90% of the catchment area in Estonia, Finland, Russia and Sweden.

The environmental quality of the Baltic Sea is largely influenced by the input of pollutants – particularly excessive nutrients and hazardous substances.

1.6.4.2. North and Norwegian Seas - OSPAR region

The North Sea is a biologically rich and productive region. The densely populated, highly industrialized countries bordering it conduct major fishing activities, carry out oil and gas offshore activities, extract sand and gravel, use it for dumping dredged material and for pipelines and cables. The North Sea is one of the most frequently traversed sea areas of the world and two of the world's largest ports are situated on the North Sea coast. In addition, the coastal zone is used intensively for recreation.

Healthy ecosystems provide both goods and services to humanity. The intensive and sometimes conflicting uses of the North Sea cause a number of problems in relation to a healthy ecosystem and to securing its sustainable use. The effects of hazardous substances, eutrophication, and ecological effects of fisheries comprise the most important issues.

The North Sea is very productive, due in part to large inputs of nutrients leading to high primary production, the basis for all food chains. The intricate webbing of the food chains in the North Sea makes the ecosystem durable, yet vulnerable to major alternations such as overexploitation of single species, which can be deleterious.

1.6.4.3. The Black Sea

The Black Sea is the world´s largest land-locked inland sea (Bakan and Büyükgüngör, 2000). It has a surface area of $4.2*10^5$ km^2 and an average depth of 1 240 m (Fillman et al., 2002).. The hydrographic regime is characterized by low salinity surface water of river origin overlying high salinity deepwater of Mediterranean origin. The north-western area is subject to the discharge of large rivers (the Danube, Dnieper and Dniestr). The sea´s only link to other seas is with the Mediterranean through the Bosphorus (which is the world´s narrowest strait, with an average width of 1.6 km, depth of 36 m and a total length of 31 km), the Sea of Marmara and the Dardanells. To the north, the Black Sea is connected with Sea of Azov through the shallow Kerch Strait, which has a depth of less than 20 m. The Black Sea is surrounded by six countries located in Europe and Asia. Although only these six countries surround it, the total catchment area draining into the Black Sea covers a vast area of the European continent, being over five times the size of the sea itself and includes parts of 21 countries (EEA, 1995). At least 171 milion people live in the Black Sea basin and about 81 milion of these live in the Danube basin alone. Almost one third of continental Europe drains into it and, during the last 30 years, the Black Sea environment has surffered a catastrophic degradation from the waterborne waste from 17 countries.

1.6.4.4. The Caspian Sea

The Caspian Sea is the largest land-locked sea in the world, which is surrounded by the five countries of Azerbaijan, Kazakhstan, Turkmenistan, Iran and Russia. The area of the Sea is 371 000 km^2. Another peculiarity deals with the fact that this watershed lies 28 m below the sea level. It has five main inlet rivers but no outlets and acts as a reservoir for watersheds in the region (Kajiwara et al., 2002).

1.7. PATTERNS OF DEVELOPMENT/SETTLEMENT

Population is a key element in the human impact on the environment. Population growth is often held to be the root cause of environmental problems, but the interaction between population, economic development and environmental change are too complex to support this conclusion. Other important factors, such as distributional patterns, migration and living standards, have a major role affecting the impact of population on natural resources and the environment.

The European population reached about 680 million people in 1990, which represented 12.8 per cent of the world`s population. Historical trends can be examined by using UN statistics (Table 1.3), which provide historical data for Europe (excluding the European part of the former USSR) and for all the former USSR`s share of world population declined from 7 to 5 per cent and is expected to decline further to 4 per cent by 2025. The total population for Europe and the former USSR is projected to reach 966.8 million in 2025 (Europe`s Environment, EEA, 1995).

Table 1.3: Population (1960-1990) and population projection (2020) (Europe`s Environment, EEA, 1995)

Country	1960	1990	2020
Austria	7 048	7 712	8 248
Belarus	8 056	10 259	
Belgium	9 119	9 967	10 535
Bulgaria	7 867	8 991	8 842
CSFR (former)	13 654	15 662	16 549
Denmark	4 581	5 140	5 279
Estonia	1 216	1 583	1 656
Finland	4 430	4 982	5 228
Germany	72 674	79 365	74 964
Hungary	9 984	10 553	10 459
Ireland	2 832	3 503	3 309
Latvia	2 129	2 687	2 743
Lithuania	2 779	3 731	4 101
Luxemborg	315	382	410
Moldova	2 885	4 362	

Country	1960	1990	2020
Netherlands	11 487	14 952	17 410
Norway	3 581	4 246	4 862
Poland	29 561	38 180	43 322
Romania	18 407	23 207	25 901
Russian Federation	117 534	148 041	
Soviet Union (former)	214 335	281 344	307 635
Sweden	7 480	8 566	9 467
Switzerland	5 362	6 712	7 538
Ukraine	41 869	51 839	
United Kingdom	52 373	57 411	62 080

Migration inside Europe has historically been characterised by long-term movements from less developed to more prosperous regions. Eastern Europe has experienced considerable migration in the post-war period. Until 1989, Latvia had the highest population growth in all of Europe, due to movements from Russia, Belarus and Ukraine.

The complex links between population, the environment and economic development are still not fully understood. The trends in three important indicators – fertility, life expectancy and living standards – across the various regions of the world may provide important insights for assessing future trends.

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2. SOURCES OF PTS

2.1. BACKGROUND INFORMATION TO PTS SOURCES

Persistent Toxic Substances (PTS) can be introduced into the environment via numerous sources and activities. Point and diffuse sources include releases from industrial and domestic sites, traffic, waste disposal operations such as incinerators and landfills. Secondary sources include the spreading of sludge on land and remobilisation of previously deposited compounds from soils and water bodies. Some sources are capable of regulation (such as industrial point sources) while other diffuse emissions represent unregulated and/or difficult to regulate inputs (fugitive releases from landfills, domestic open burning of waste).

During the last decade a large amount of progress has been made in the production of atmospheric emission inventories of several PTS compounds within Europe. However there is still a lack of comparability in inventories produced by various organisations for the same compound group and this reduces transparency when comparing or compiling inventories. Improved emission inventories for PTS have become increasingly important as emission or source driven fate models for regional and global scales are developed. Inventories serve as useful information for decision makers in order to reduce the impact of these pollutants on the environment.

Source inventories represent a crucial step in developing appropriate risk control strategies for PTS – using an inventory of releases to air, water or land it is possible to rank sources in order of importance and so target source reduction measures effectively and incorporate effective risk reduction measures.

2.2. DATA COLLECTION AND QUALITY CONTROL ISSUES

2.2.1. Introduction

During the last two decades there has been a growing interest within environmental research community to understand the fluxes, behaviour, fate, and effects of PTS compounds (Holoubek et al., 1993). Various studies and assessments of PTSs in the environment have been carried out by several international organisations, such as United Nations Environmental Programme (UNEP), the United Nations Economic Commission for Europe (UN ECE), the World Health Organisation (WHO), the Nordic Council of Ministers, the Paris and Oslo Commissions, the Helsinki Commission, and the Great Lakes Commission, as well as the Arctic Monitoring and Assessment Programme (AMAP).

2.2.2. Emission inventories

The approach on how emission inventories are being established varies dependent on the compound of interest. A critical element in compiling useful baseline series of information on PTS sources is the quality of the data used. The uncertainties, whether due to a general lack of proper data or methodological errors, result in varying emission data quality.

A further source of uncertainly is the tendency to use emission factors measured under steady state operating conditions and to treat measurements outside this 'ideal' window as outliers. Improving and updating emissions monitoring databases is clearly key to improving inventory estimates.

Obviously, the extrapolations involved with emission estimates are high and at a national level the risk of over- or under-estimating use for a given year is high. Uncertainties in usage are further amplified when this data is used as the basis for annual emissions to different media.

EMEP represents an important focal point for an integrated programme of monitoring and evaluating the long-range transport of substances in Europe. This is particularly important for establishing compliance of the Parties to the Convention on Long Range Transboundary Air Pollution (LRTAP) with their Protocol obligations.

In 1991 the UN ECE Task Force on Emission Inventories was established to help developed the procedures and methodologies for emission estimation and reporting for various persistent air pollutants. An Atmospheric Emission Inventory Guidebook is currently being prepared within this Task Force. The Guidebook is organised in the form of chapters, each representing various categories, subcategories, or even activities that generate emission of atmospheric pollutants. The guidebook also includes information on main groups of PTSs (POPs) (Holoubek et al., 1993; Parma et al.,1995).

2.2.3. Conceptual approach

For some well-studied PTS, notably PCDD/Fs and PCBs it has been noted that the flux to air, calculated from a knowledge of known anthropogenic source, fails to account for the corresponding deposition flux. This highlights the potential that inventories are incomplete and significant sources are missing. The recycling of compounds between the air/soil and air/water offers an alternative possibility and highlights the significance of secondary re-suspension and emissions.

Despite the improvements in inventory estimates a number of issues remain unresolved.

- Inadequate characterisation of known emission sources
- Greater understanding of the potential for recycling from environmental sinks –
- Incorporate trans-boundary processes into national emission estimates to highlight the potential impact of these inputs
- Potential for releases of PTS from stockpiled compounds

2.2.3.1. Obsolete stocks

Obsolete pesticides are old, out-dated, pesticides, unused for various reasons and stockpiled as a kind of waste or waiting to be waste and include large quantities of banned organochlorine compounds that are highly persistent in the environment, such as Dieldrin, Endrin, HCH, DDT and others. Dealing with obsolete stocks is a global problem. The world total is estimated to be over 500 000 tons. (Poznan, 2001). While exact quantities are unknown, large stockpiles also exist in Central Eastern European Countries (CEEC) and the Newly Independent States (NIS).

To combat the problem of obsolete pesticides a further accumulation of obsolete pesticide stocks has to be prevented. Inventories of obsolete pesticide stocks have to be carried out, followed by a safe and environmentally sound disposal of bulk quantities of obsolete pesticides. Historical changes in the NIS and CEEC caused that together with the advent of market economy the further accumulation of expired or obsolete pesticides has come to a halt. But these countries still have not solved the problem of safe storage for these pesticides, they have only poor information concerning the quantity and they are lacking the technical and/or financial resources for the safe disposal.

Inventories on obsolete pesticides are nearly finished in the Baltic States and Poland. Many International Organisations are working on the issue of unwanted and expired pesticide stocks. These include FAO, UNEP Chemicals, WHO, IUNIDO, industry and NGOs. The problem in Central and Eastern Europe is particularly severe as highlighted in the Table 2.1 below. Within CEE countries there are few special sites for dangerous materials or incinerators in which these types of hazardous mixed wastes could be safety burnt. The risks associated with large-scale storage of compounds poses a particular environmental risk. The principal uncertainly in terms of these obsolete stocks is characterisation in terms of PTS content. Little is known of the composition of the waste material and is must be recognised that within the 'cocktail' of possible chemicals, PTS substances will be present in unknown amounts.

Table 2.1: Obsolete pesticides in the CEE countries

Country	Waste in Tons	Others: soil, water	Remarks
Azerbaijan	20 000		
Armenia	Incomplete information considerable stocks of obsolete pesticides		Toxicological studies and proof of serious health effects
Belarussia	6 000 -7 000		
Bulgaria	4 391 Overstocking, forbidding and restricting the usage		Measurements of OCPs in water and soil are/were performed
Czech Republic	The main part of obsolete pests was destroyed in early 90` s.		The levels of HCHs, DDTs, HCB and many others in the air, water, sediments, soils, biota and human are regularly monitored
Estonia	DDT – 5 654 kg HCB – 140 kg HCH 2 055 kg		The levels of OCPs are measured mainly in marine ecosystem
Eastern Germany (former)	Several 100 000s	Large scale soil pollution	Leaching from big dump sites into groundwater

Country	Waste in Tons	Others: soil, water	Remarks
Georgia	400 2 000 (report 1999)		High groundwater concentrations in wells and in rivers
Hungary	Ideas for inventory presented and start up of pilot project	49.000 tons soil?	The levels of OCPs are measured in various matrices including ecotoxicological testing
Latvia	1 480	Includes DDT 170t HCH 155 t	
Lithuania	2 000-4 500	Includes DDT 80t HCH 24 t	
Moldavia	6 600		
Poland	50-60 000 in bunkers 160 000 – stored in the former producers area	Direct spread from bunkers to surrounding soil and threat to groundwater	Measurements of OCPs in water, sediments, soils, biota and human were/are performed
Romania	In 1995 the amount of obsolete pesticides were 1166.59 tonnes (512.19 t - forbidden, 568.2 t - expired, 86.2 t - non-identified)	Big chemical plants from Bacau, Râmnicu Vâlcea, Craiova, Pitesti, Turda	The pesticides are stored in 709 different storage points all over the country The POPs identified in these stockpiles are Toxaphene, Heptachlor, DDT and Lindan Measurements of OCPs in water and soil are/were performed
Russian Federation	17-20 000 former production at 23 factories		
Slovenia	350-400		Measurements of OCPs and other pests in water, sediments, soils and human were/are performed
Slovak Republic	Ideas for inventory presented and start up of pilot project		The levels of OCPs and other pests were/are measured in water, sediments, soils, biota including man
Ukraine	15 000	Large regional diffuse soil pollution	

The EU Directive on the disposal of PCBs/PCTs, 96/59/EC, requires that measured are taken to ensure safe disposal of used PCB, to avoid release of the compounds and breakdown products into the environment. This specific compound group will be summarised later in section 2.5.

2.3. PESTICIDES

2.3.1. Aldrin

Aldrin is an organochlorine pesticides and has been manufactured commercially since 1950, and used throughout the world up to the early 1970s. A major use of aldrin was as a soil insecticide. Hence, aldrin-treated soil was an important source of aldrin and its reaction product dieldrin in the environment.

Within the Region, no emission measurements have been reported for air and soil. Emissions to water have been estimated in Germany.

2.3.2. Chlordane

Chlordane is not produced in Europe (IARC, 1979). Both the amounts of chlordane produced and used have decreased considerably in recent years. It is a versatile, broad spectrum, contact insecticide and is used mainly for non-agricultural purposes (primarily for the protection of structures, but also on lawn and turf, ornamental trees, and drainage ditches)

Entry into the atmosphere occurs mainly through aerial applications of dusts and sprays, soil erosion by the wind, and volatilisation from soil and water. In spite of its very low mobility in soil, chlordane may be a low-level source of contamination in groundwater when applied by subsurface injection. Chlordane can be dissipated from surface water by volatilisation, sorption to bottom and suspended sediments and particulates, and uptake by aquatic organisms. Chlordane is not produced in Europe.

Within the Region, no emission measurements have been reported.

2.3.3. DDTs

DDT was widely used during the Second World War to protect the troops and civilians from the spread of malaria, typhus and other vector borne diseases. Following this, DDT was widely used on a variety of agricultural crops and for the control of disease vectors as well. It is still being produced and used for vector control. Growing concern about adverse environmental effects, especially on wild birds, led to severe restrictions and bans in many developed countries in the early 1970s. DDT is still used to control mosquito vectors of malaria in numerous countries. Many pesticide companies have been involved with DDT production. By 1991, only Enichem Synthesis (Italy), Hindustan Insecticides (India) and P.T Montrose Pesticido Nusantara (Indonesia) were listed by UN Environment Programme (UNEP) as basic producers. There is no continuous record of world production of DDT, and estimates of usage vary widely. UNEP suggested that world consumption between 1971 and 1981 was 68,800 tonnes per year. From 1950 to 1970, more than 20,000 tonnes of DDT were used annually in the Soviet Union (former USSR).

DDT has also been detected in virtually all organochlorine monitoring programs and is generally believed to be ubiquitous throughout the global environment (IPCS 1989).

Within the Region, emission data is limited to a single estimate of releases to water (150 kg) in Poland (HELCOM 1998).

2.3.4. Dieldrin

Dieldrin is the principal reaction product of aldrin, an important soil insecticide. As a product it is used mainly for the protection of wood and structures against attack by insects and termites and in industry against termites, wood borers, and textile pests (moth-proofing). It acts as a contact and stomach poison. Dieldrin is no longer used in agriculture. It has been used as a residual spray and as a larvacide for the control of several insect vectors of disease. Such uses are no longer permitted in a number of countries (IPCS 1989). Dieldrin is no longer used in agriculture in Europe.

Within the Region, emission data is limited to a single estimate (2.3 kg) of point source industrial discharges to surface water in the UK (Environment Agency 2001).

2.3.5. Endrin

Endrin is an organochlorine insecticide, which has been used since the 1950s against a wide range of agricultural pests, mostly on cotton but also on rice, sugar-cane, maize, and other crops. It is also used as a rodenticide. Since the early 1950s, endrin was made in the USA by Shell and Velsicol and in the Netherlands by Shell. Its use has been banned in many countries and severely restricted in others. Shell discontinued manufacture of endrin in 1982; it is still manufactured in Mexico (IPCS 1984). Its use has been banned throughout Europe.
Within the Region, emission data is limited to a single estimate (0.078 kg) of point source industrial discharges to surface water in the UK (Environment Agency 2001).

2.3.6. Heptachlor

Heptachlor is a non-systemic stomach and contact insecticide, used primarily against soil insects and termites. It has also been used against cotton insects, grasshoppers, some crop pests and to combat malaria. Heptachlor is metabolised in animals to heptachlor epoxide, whose toxicity is similar to that of heptachlor, and which may also be stored in animal fat. The use of heptachlor has been banned in Cyprus, Ecuador, the EU, Portugal, Singapore, Sweden, Switzerland and Turkey. Its use is severely restricted in Argentina, Israel, Austria, Canada, Czechoslovakia, Denmark, Finland, Japan, New Zealand, Philippines, USA and USSR. The chemical properties of heptachlor (low water solubility, high stability, and semi-volatility) favour its long-range transport, and heptachlor and its epoxide have been detected in arctic air, water and organisms.

Within the Region, no emission measurements have been reported.

2.3.7. Hexachlorobenzene

Hexachlorobenzene (HCB) is a fungicide that was first introduced in 1945 for seed treatments of grain crops. HCB is also a by-product of the manufacture of industrial chemicals including carbon tetrachloride, perchlorethylene, trichloroethylene and pentachlorbenzene. It is a known impurity in several pesticide formulations, including pentachlorophenol and dicloram and may be present as an impurity in others. HCB may

still be found in the food chain from its former use as a pesticide, however, the main source of release into the environment is now probably as a by-product of certain industrial processes such as aluminium smelting and some older technologies of production of perchloroethylene and vinyl chloride monomer. Some aluminium smelters use hexachloroethane (HCE) gas to remove hydrogen gas from the molten aluminium before it solidifies. However, HCE gas can form HCB in the smelter. Manufacture of vinyl chloride monomer and volatile halocarbons is known to produce HCB as a by-product. Another potential source of HCB is the usage of pentachlorophenol (PCP), which can be contaminated with HCB during manufacture, and the electrolytic production of magnesium and aluminium.

The use of HCB in such applications was discontinued in many countries in the 1970s owing to concerns about adverse effects on the environment and human health. HCB was also a by-product of the manufacture of industrial chemicals including carbon tetrachloride, perchlorethylene, trichloroethylene and pentachlorbenzene, this problem aready does not exist in main countries of the Region. It is a known impurity in several pesticide formulations, including pentachlorophenol and dicloram and may be present as an impurity in others.

Currently, the principal sources of HCB in the environment are estimated to be the manufacture of chlorinated solvents (probably only in some older technologies in CEECs), the manufacture and application of HCB-contaminated pesticides, and inadequate incineration of chlorine-containing wastes (Bailey 2001). A substantial portion of HCB measured in the atmosphere is thought to come from volatilisation of "old" HCB on the soil from past contamination. It should be noted that only a small fraction of the HCB generated as a by-product may be released, depending on the process technology and waste- disposal practices employed. For example, according to the US Toxic Chemical Release Inventory (TRI), releases of HCB from the ten largest processing facilities were 460 kg, most of this to air, compared with almost 542 000 kg transferred offsite as waste.

Within the Region, emission estimates for releases to air have been estimated for each country via EMEP (1995). Total emissions to air within the region have been estimated to be over 8 200 t.

2.3.8. Mirex

Mirex began to be used in pesticide formulations in the mid 1950s. The insecticidal use of mirex has been largely focused on the control of the imported fire ant *Solenopsis saevissima richteri,* in southeastern USA. Mirex, under the name Dechlorane, is also used as a fire retardant in plastics, rubber, paint, paper, and electrical goods, and as a smoke-generating compound, when combined with zinc oxide and powered aluminium. Little information is also available on worldwide production and use, but patents for the use of mirex exist in several countries including Belgium, the Federal Republic of Germany, the Netherlands, and the United Kingdom in the mid-1970s.

Within the Region, no emission measurements have been reported.

2.3.9. Toxaphene

Toxaphene (or camphechlor) is a mixture of over 670 chemicals, including chlorinated camphene (ATSDR 1990). The principal use of toxaphene in the past was for pest control on cotton crops in North America and its use increased as the use of DDT was phased out. It was also used to control pests in livestock and poultry, and on other field crops. All uses were banned in 1990. Toxaphene has been measured in many environmental media around the world. Because of the large variability in total toxaphene data, few reliable conclusions can be drawn about trends or geographic differences in toxaphene concentrations. Toxaphene was used in Estonia until 1984 and prohibited in Latvia in March 2000.

Limited use of Toxaphene has been carried out within the region. Within the Region, no emission measurements have been reported.

2.4. INDUSTRIAL CHEMICALS

2.4.1. Polychlorinated biphenyls

Polychlorinated biphenyls (PCBs) are complex mixtures of chlorinated hydrocarbons that have been used extensively since the 1930s. They are industrial products or by-products formed via industrial processes.

PCBs enter water mainly from discharge points of industrial and urban wastes into rivers, lakes, and coastal waters. On account of their low water solubility, it is expected that most of the PCBs discharged will be

adsorbed by sediment at the bottom of rivers or lakes and transport will be mainly via waterborne particles. PCBs in soil, derive from particulate deposition (often concentrated in urban areas), wet deposition, the use of sewage sludge as a fertilizer, and leaching from landfill sites. The EU Directive on the disposal of PCBs/PCTs, 96/59/EC, requires that measures are taken to ensure safe disposal of used PCB, to avoid release of the compounds and breakdown products into the environment.

Within the Region, releases to air have been estimated for each country via EMEP (1995; 1998). Total emissions to air within the region have been estimated to be over 74 t. Emissions to water are predicted to be large, although there is a paucity of estimates within the Region as a whole. No data has been reported on emissions to land.

New PCBs inventory in Poland suggests that roughly 35-50 % of capacitors and 1 % of transformers contain PCBs still in use in Poland (Falandysz and Szymczyk, 2001). An estimated total amount of PCB contaminated oil in stock or service is up to 17 500 t, i. e. 3 500-5 000 t in capacitors, 3 000 t in transformers, and 8 000-9 500 t on other electromagnetic equipment such as breaker switches, choking coils, measuring transformers, starters, voltage regulators or other machinery.

The up-to-date facilities for safe disposal of PCBs wastes are non- existent in Poland similarly as in other CEE countries.

2.5. UNINTENDED BY-PRODUCTS

2.5.1. Dioxins and furans

Polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) constitute a complex group of persistent environmental chemicals. They are ubiquitous in the environment and are formed as trace amounts of undesired impurities in the manufacture of other chemicals such as chlorinated phenols, PCBs and others. They are also unwanted by-products of a wide range of manufacturing processes including smelting, bleaching of paper pulp and the manufacturing of some herbicides and pesticides. In terms of dioxin release into the environment, solid waste incinerators with inadequate clean-up technologies have been targeted as important contributors to total emissions to air.

Considerable effort has been expended in the UK and Western Europe to try and quantify and rank PCDD/F primary sources and emissions to the environment, principally the atmosphere, so that cost-effective source reduction measures can be taken (e.g. UNEP 1999; Eduljee and Dyke, 1996; Duarte-Davidson *et al*., 1997; Alcock *et al*., 1998 EU, 2000) The majority of the are based on ∑TEQ with the most recent on a congener-specific basis (Alcock et al., 2001). Within CEC countries, limited information exists in Czech Republic, Slovakia, Poland and Slovenia and there is a lack of information in others (Holoubek et al., 2000; Falandysz et al., 1997). Unlike air, very limited information is available on the sources of dioxins entering surface waters. Dioxins enter water mainly from discharge points of industrial and urban wastes into rivers, lakes, and coastal waters. A European assessment of releases to water concluded that release estimates were so uncertain that further research and data collection are essential to quantify releases. The UK has attempted to estimate emissions to water but was not able to quantify releases due to the limited amount of emission factors available (Environment Agency 1997). While not quantified, total releases to water are likely to be significantly less than releases to land and air.

Unlike air, there has been limited attempts to define inputs of dioxins to land. Dioxins in soil, derive from particulate deposition (often concentrated in urban areas), wet deposition, the use of sewage sludge as a fertilizer, and leaching from landfill sites. Soils, landfills and contaminated sediments have been identified as an important reservoir source of dioxins i.e. containing material which is not newly generated but concentrated from other sources. Total releases to land in the UK was estimated to be between 1 500 and 12 000 I-TEQ g per year. (Environment Agency 1997), a value significantly higher than emission to air. The majority of TEQ was contained within material for landfill. A European assessment of releases to land concluded that release estimates were so uncertain that further research and data collection were essential to verify the scale of releases from different source sectors. Sectors, which have a high potential for release include, chemical and pesticide production and use, accidental fires, disposal of MSW to landfill and the non-ferrous metal industry.

There have been an increasing number of observations, which appear to indicate that dioxins may have been present in the environment for considerably longer than the onset of the chlorine industry (*eg*. Kjeller *et al*.,

1991; Alcock *et al*., 1998; Silk *et al.*, 1997), and that they may be formed through non-anthropogenic activities. For example, studies at Lancaster University have detected the presence of PCDD/Fs in environmental samples collected and stored from the late-1800s (Alcock *et al*., 1998) and believe this is consistent with the emission of trace quantities of PCDD/Fs from combustion of coal/wood and/or metal smelting activities prior to the development of the 'Chlorine Industry' during this century. Results are highly consistent with reports of PCDD/Fs in Mississippi clay, German kaolinite and Australian sediments. Taken together, these studies provide a strong indication that PCDD/Fs are formed by natural processes. There is little doubt that the vast majority of PCDD/Fs are formed through anthropogenic activity, however an unquantified amount may be formed via natural processes and this could have consequences for dioxin inventory estimates

Within the Region, releases to air have been estimated for each country via EMEP (1995; 1998). Total emissions to air have been estimated to be over 7 t. Estimates of emissions to water have not been made due to the lack of emission factor information. Emissions of PCDD/Fs to soils have been reported for the following countries Austria, Ireland, Luxembourg, Norway, Netherlands, Sweden, Switzerland and the UK (EU-DGXI 1994; Environment Agency 1997). Estimates to soil are between 4 and 30 times greater than emissions to air in countries where both estimates are reported.

The use of highly contaminated Brazilian citrus pulp as a component of cow´s feed resulted in an increase of the dioxin body burden in humans in 2 Länders of Germany (1998), which is not tolerable under the aspect of preventive health care and exposure of breast-fed babies (Vieth et al., 2002). An effective control of samples of human origin, food and also of feed is a necessary precondition for an early detection of an avoidable additional body burden and a successful strategy to prevent additional dioxin input.

2.6. OTHER PTS OF EMERGING CONCERN IN EUROPE

2.6.1. Brominated flame retardants

Polybrominated diphenyl ethers (PBDEs) represent important additive flame retardants with numerous uses within industrial and domestic electronic equipment and textiles. PBDEs are similar in behaviour (hydrophobic, lipophilic, thermally stable) to the well studied contaminants PCBs. Growing evidence suggests that PBDEs are widespread global environmental pollutants and that they are capable of bioaccumulation in foodchains.

Three commercial PBDE formulations are in production. The penta- product is used principally to flame retard polyurethane foams in furniture, carpet underlay and bedding. Demand has decreased significantly in Europe in the last 10 years although global demand is continuing to climb with the vast majority 97% (8290 tonnes) used in North America in 1999. Production in Europe was estimated to be 210 tonnes in 1999. The deca- product consists predominantly of a single congener, BDE 209. Global demand was 54800 tonnes in 1999 (Renner 2000) with the majority (44%) consumed in North America, compared to only 14% throughout the whole of Europe. Deca- is used predominantly for textiles and denser plastics such as housings for a variety of electrical products in particular TVs and computers. Commercial octa- is a mixture of hexa- (10-12%), hepta- (44-46%), octa- (33-35%) and nonabromodiphenyl (10-11%) ethers. It is used to flame retard a wide variety of thermoplastics and is recommended for injection moulding applications such as high impact polystyrene (HIPS).

Despite several years of increasing interest in these compounds, our understanding of the principal environmental sources remains limited. Reservoirs of commercial mixtures associated with products have not been broadly quantified on a national scale and possible release to different environmental compartments remains uncertain. A preliminary emission inventory for PBCE-47 releases to air has been estimated for the UK (Alcock et al., 2002). Total estimated annual emissions of 13.8 kg are dominated by releases form furniture, carpets, vehicles, incineration of waste and secondary steel production.

No data is available for other countries.

2.6.2. Lindane (γ-HCH)

The importance of technical HCH as insecticide in general and Lindane in specific is declining in Europe. While in a period from 1970 to 1979 HCH made up around 13% of the insecticides used in Europe, it was reduced to fewer than 5% in the period of 1991 to 1996 (BREIVIK ET AL. 1999). However, there is a large regional variance in the use of insecticides depending on the latitude (less in the north and more in southern

parts of Europe) and the crops grown (cereals and soya requiring relatively less insecticides than, for example, maize, rape and further rice and cotton).

Estimates of γ-HCH use and emissions in European countries for every year from 1970 to 1996 were made by J. Pacyna et al. (1999). According to these estimates total γ-HCH emission in Europe decreased by 3.5 between 1970 and 1996. Its physicochemical properties suggest that it is predominantly gaseous at moderate temperatures and volatilisation will be an important route of dissipation to the atmosphere, particularly in high temperature conditions. Lindane enters water from direct application from use in agriculture and forestry, from precipitation and, to a lesser extent, from occasional contamination of wastewater from manufacturing plants.

Within the Region, releases to air have been estimated for each country via EMEP (1996; 1998) and via NAEI (1999) in the UK. Total emissions to air within the region have been estimated to be over 85 t. Estimates of emissions to water and soil, have not been reported.

2.6.3. Organic mercury

Mercury is a naturally occurring metal, which has several forms. It combines with carbon to form organic mercury compounds. The most common of these, methylmercury, is produced mainly by anaerobic microorganisms in water and soil. More mercury in the environment can increase the amounts of methylmercury that these microorganisms produce. Importantly, in terms of exposure, methylmercury builds up in the tissues of fish with larger and older fish tending to have the highest levels. Methyl mercury may be volatised or emitted into the air from combustion sources such as incinerators and power plants. Municipal solid-waste incinerators and coal-burning power plants are both substantial sources of methyl mercury, the latter because mercury is a contaminant in coal. When mercury is emitted to air it occurs in one of several different forms, and the emissions of each of these species can be estimated individually. Three species of mercury are identified 1) Hg^0 un-reactive gaseous elemental Hg, 2) Hg-p attached to particulate material and RGM reactive gaseous mercury (includes both inorganic and organic forms normally in the Hg^{2+} oxidised form). Although inventories have estimated inputs of these constituents estimates of associated methylmercury formation have not been made.

On the basis of the limited data available, it appears that the most significant mercury emissions are those to air from combustion activities (particularly coal-fired power stations), primary metals production and the chlor-alkali industry (OSPAR 2000).

Within the Region, no data has been reported for emissions to air, water and soil.

2.6.4. Organic tin

Organic tin compounds comprise mono-, di-, tri- and tetrabutyl and triphenyl tin compounds and their impact on the environment is well known. Tributyl tin compounds are considered to be the most hazardous of all tin compounds and several studies in various parts of the world oceans have been demonstrated including shell malformations of oysters, imposex in marine snails, reduced resistance to infection in flat fish and effects on the human immune system. The main primary source of tributyl tin is leaching from sea ship hulls. Related activities that cause emissions of tributyl tin compounds are sea ship traffic, docking activities and dumping of dredged material. In addition sources include industrial discharges from production/formulation of all organic tin compounds, atmospheric deposition of organic tin compounds, tributyl tin compounds used for wood conservation: application, leaching, dumping of conserved wood as waste, antiseptic or disinfecting use of tributyl tin compounds and disposal of harbour sediments contaminated with organic tin compounds (OSPAR 2000). The issue of tributyl tin compounds has been widely discussed by the OSPAR Working Group on Inputs into the Marine Environment (INPUT). Organic tin compounds are on the OSPAR List of Chemicals for Priority Action.

Within the Region, no data has been reported for emissions to air and soil. Estimated inputs of tributyl tin to water have been reported for Belgium, Denmark, Germany, The Netherlands, Norway, Sweden and the UK (OSPAR 2000) totalling 68 t.

2.6.5. Pentachlorophenol

Because of their broad pesticidal efficiency spectrum and low cost, PCP and its salts have been widely used as algicides, bactericides, fungicides, herbicides, insecticides, and molluscicides with a variety of applications in the industrial, agricultural, and domestic fields. Its salt, sodium pentachlorophenate (C_6Cl_5NaO – NaPCP), is

used for similar purposes and readily degrades to PCP. World production of PCP is estimated to be of the order of 30 000 tonnes per year. Since 1991, EU legislation has limited the use and application of PCP-based products in order to minimise human exposure (EC 91/179/EEC). The relatively high volatility of PCP and the water solubility of its ionised form and release into the environment from a number of diffuse sources have led to widespread contamination of the environment with this compound.
The identified main sources of PCP, NaPCP and PCPL into the environment are:

- Production of PCPL from PCP;
- Treatment of wood (sapstain control agent);
- Impregnation of heavy-duty textiles and fibres (fungicide);
- Use and disposal of PCP, NaPCP and PCPL treated wood and textiles (including imported goods);
- Contaminated sites (former PCP production and wood preservation plants) and treatment of contaminated soil and groundwater;
- Natural sources or burning processes.

Because of its high vapour pressure, PCP easily evaporates from treated wood surfaces, and the loss may be as high as 30–80% a year (WHO, 1987). Volatilisation from water to air is pH dependent, and only the non-ionised form seems to be volatile (WHO, 1987). Although PCP is ubiquitous, there is little information on its concentrations in ambient air (WHO, 1987) Emissions, discharges and losses of PCP and NaPCP are likely from wood in use – most of which will have been treated with PCP in the past. Volatilisation can be an important source of loss of PCP from water and soil surfaces as well as from PCP-treated materials. In particular higher temperatures can increase this process significantly.

Within the Region, limited data has been reported for emissions to air and soil. Emissions of PCP to air in the UK have been estimated to be 482 t, the vast majority of which (89%) is associated with volatilisation of treated wood (NETCEN 1999). Estimated inputs of pentachlorophenol to water have been reported for Germany 14 kg (HELCOM 1998) and the UK of 10 kg (Environment Agency 2001).

2.6.6. Polycyclic aromatic hydrocarbons

The polycyclic aromatic hydrocarbons (PAHs) are a group of compounds consisting of molecules containing 3 or more fused benzene rings, although bicyclic compounds are often included in the term (e.g. USEPA 16 PAHs). PAH compounds are toxic and bioconcentrate in invertebrates in the aquatic environment. Vertebrates are able to metabolise PAHs, however the resultant metabolites are reactive compounds and some of these are carcinogenic.
Combustion sources are thought to account for over 90% of the environmental burden of PAHs. In particular stationary point sources account for around 90% of these inputs (Howsam and Jones 1998). Inputs to the atmosphere are dominated by emissions associated with residential heating (coal, wood, oil and gas burning) and industrial processes such as coke manufacture Non-combustion processes such as the production and use of creosote and coal-tar (and the remediation of sites contaminated with these substances), though poorly quantified, are potentially very significant primary and secondary sources. The significance of these inputs may be set to increase within Europe as legislative restrictions on emissions from combustion processes continue to be enacted.

Few comprehensive, large scale inventories of PAH sources of estimates of their emissions have been compiled, Howsam and Jones (1998) having compiled a representative cross section of these. An indicative overview of sources and sub-sources of PAHs is shown in table 2.2.

Table 2.2: Indicative overview of sources and sub-sources of PAHs (from OSPAR 2001)

NOSE Codes[4]	Sources	Discharges to water	Emissions to air
	Agricultural Activities		
110.03	On field burning of stubble/straw	X	XX
	Transport and infra structure		
201	Road transport	XX	XX
202.03	Inland waterways	X	X
202.04	Maritime Activities	X	X
202.05	Air traffic		XX
	Building materials		
105.16	Construction and demolition (use of creosote treated timber)	XX	X
	Households		
101.07	Other equipments (domestic combustion of wood, oil, coal and peat)	X	XX
	Small and medium industrial activities (SME)		
	Industrial activities (IPPC)		
101	Combustion processes (Power generation)	X	XX
104.07/ 105.07	Manufacture of pulp, paper and paper products, publishing and printing (combustion of wood)		XX
104.09/ 105.09	Manufacture of chemicals, chemical products and man-made fibres		XX
104.12	Manufacture of basic metals and metal products (Carbide production)	(X)	XX
105.01.21/ 107.04.06	Wood preservation without solvents/ Preservation of wood with solvents (creosote and carbolineum treated timber)	X	XX
105.12.01	Coke oven furnaces (door leakage and extinction)	X	X
105.12.03	Pig iron tapping	(X)	(X)
105.12.08	Smelters of Iron and Steel	X	XX
105.12.11	Rolling mills	(X)	(X)
105.12.21/ 15.12.22	Aluminium production	XX	XX
105.12.41/ 105.12.42	Ferro alloy Industry	X	XX
105.12.91	Building and repairing of ships	X	X
105.13.05	Anode production	X	XX
106	Extraction and distribution of fossil fuels and geothermal energy (prod. water and cutting)	XX[5]	(X)
	Waste disposal		
109.02	Waste water treatment	X	XX
109.03	Waste incineration and pyrolysis (incl. cable burning)	X	XX
109.04	Open burning of Agricultural wastes (except stubble burning	(X)	(X)
109.05	Cremation		(X)
109.06	Solid waste disposal on land (Land fill activities)	(X)	
	Contaminated land/sediments		
	Sediments in lakes and rivers	(X)	
	Contaminated sites and soils	(X)	

XX major, X medium, (X) minor - Importance is indicated based on 'Background document concerning the identification of anthropogenic sources of PAH emissions as a basis for making decisions on measures'. Norwegian Pollution Control Authorities, 1997.

[4] The NOSE codes refers to EUROSTAT 'Proposal for NOSE amendments', January 1999.

Time trend analysis using a variety of depositional media (sediment cores, polar ice and peat) has shown that developed countries have succeeded in reducing PAH emissions from a wide range of sources through technological applications and legislation in addition to a marked shift away from the use of coal and coal products. Nations undergoing rapid industrialisation may well prove to be an increasingly significant source of PAH in global terms as their populations continue to grow as the number of mobile and industrial sources increase.

A growing body of work on PAHs is addressing questions on the emissions of derivatives of the parent PAH – the alkyl PAHs - which have been known for some time to constitute a large proportion of emissions form combustion sources.

Within the Region, releases to air have been estimated for each country (EMEP 1995; EMEP 1998; OSPAR 2001). Total emissions to air within the region have been estimated to be over 385 t. Estimates of emissions to water have been made by OSPAR (2001) for Belgium, Denmark, Finland, Germany, the Netherlands, Norway, Sweden and the UK. No data is reported for inputs to soils.

2.6.7. Short chain chlorinated paraffins

Chlorinated paraffins, complex mixtures of straight chain chlorinated hydrocarbon molecules with a range of chain lengths (short C_{10-13}, intermediate C_{14-17} and long C_{18-30}) and degrees of chlorination (between 40 - 70 % weight basis) were first produced as extreme pressure additives around 1930. Over 200 commercial formulations with a range of physical and chemical properties exist which make them useful in a wide range of applications, such as secondary plasticizers in PVC and other plastics (C_{14-17}), extreme pressure additives (all chain lenghts), flame retardants (all chain lenghts), sealants (all chain lenghts) and paints (all chain lenghts).

In 1985, the estimated world production of chlorinated paraffins was ~300 000 tonnes (WHO 1996). The widespread uses of chlorinated paraffins probably provide the major source of environmental contamination. Chlorinated paraffins may be released into the environment from improperly disposed metal-working fluids containing chlorinated paraffins or from polymers containing chlorinated paraffins. Loss of chlorinated paraffins by leaching from paints and coatings may also contribute to environmental contamination. The potential for loss during production and transport is expected to be less than that during product use and disposal.

About 4 % of the European consumption of chlorinated paraffins is estimated to be C_{10-13}, 84% C_{14-17} and 12% C_{20-30} (Euro Chlor, 1996).

The 1999 EU Risk Assessment Report on C_{10-13} chloroalkanes reported that as of 1996 SCCPs were being manufactured, under a variety of trade names, by two companies in the EU (In 1992/93 there were five producers). Total annual production, based on 1994 Euro-Chlor figures, was estimated at less than or equal to 15 000 tonnes per year. This figure dropped to less than 3 000 tonnes in 2001. The EU Assessment identified and described the following applications for SCCPs: metal working, rubber, paints, sealants, leather, textiles and other unspecified uses. Table 2.3 is excerpted from the EU Assessment (Euro-Chlor, 1995 *in* European Commission, 2000).

Table 2.3: Applications for SCCPs in 1994

Application	Quantity used [tonnes.year^{-1}]	Percentage of total use
Metal working	9,380	71.02%
Rubber	1,310	9.91%
Paints	1,150	8.71%
Sealants	695	5.26%
Leather	390	2.95%
Textiles	183	1.40%
Others	100	0.75%
Total	13 208	100%

The total annual sales (by two companies) dropped to 2 700 tonnes per year in 2001. Table 2.3a is provided by Euro-Chlor, 2002.

Table 2.3a: Applications for SCCPs in 2001

Application	Quantity used [tonnes.year^{-1}]	Percentage of total use
Metal working	457	16.87%
Textiles & Rubber	975	35.97%
Paints	358	13.22%
Sealants	324	11.95%
Leather	0	0.00%
Others	594	21.91%
Total	2 709	100.00%

As indicated in Table 2.3, the largest uses of SCCPs were in the metal working industry, generally in lubricating or cutting oils used in both ferrous and non-ferrous applications. Common applications for SCCP-based cutting oils include grinding, polishing, honing, cutting, drilling, stamping, drawing and broaching. This emissive use has been drastically reduced in 2001, as shown in Table 2.3a.

Risk assessment and risk management showed a need for regulating the Short Chained Chlorinated Paraffins (SCCPs) and restrict their use in main fields of current applications. OSPAR and the EU–Programme on Existing Chemicals suggested these measures and legislation has been issued by the EU-Commission (Directive 2002/45/EC, banning the use of SCCPs in metalworking fluids and fat-liquoring of leather).

The widespread, numerous contemporary uses of chlorinated paraffins result in the major source of environmental contamination, particularly to the aquatic environment. They may be released into the environment from improperly disposed metal-working fluids containing chlorinated paraffins or from polymers containing chlorinated paraffins. Loss of chlorinated paraffins by leaching from paints and coatings may also contribute to environmental contamination. The potential for loss during production and transport is expected to be less than that during product use and disposal. It is believed that 50% of the chlorinated paraffins produced in the world have carbon chain lengths of between 14 and 17 and a chlorine content of between 45 and 52%.

The EU Assessment identifies sources having potential for releases of SCCPs to water, air and soil. These sources include production sites for SCCP, production sites for the formulation of metal working fluids and leather finishing agents, metal working, rubber working and leather finishing plants.It also presents estimates of releases to air and water from the production and use of SCCPs. The estimates are made mostly using emissions factors. Uses are metal working (formulation and use), rubber formulations, paints and sealants, and leather and textile applications. Summary data estimate total release from both production and use to air in the EU is 393.9 kg.year^{-1}; and to water 1,784 tons.year^{-1}. The largest estimated releases are associated with metal working applications (formulation and use). The EU Assessment cautions, that these estimates are uncertain due to the many assumptions made in their calculation. The figures should be largely lower in 2001 with the drastic reduction of sales, especially in emissive applications.

In the EU risk assessment, emissions from articles are also discussed and products that may contain and emit SCCPs are described as including:

- Flame retardants in rubber (proportion 1-10%), with applications mostly in high density conveyor belts. Belts may also be recycled into other products at the end of their life.
- Plasticisers in paints and other coatings; also to improve water resistance, chemical resistance and nonflammability. Mostly industrial/specialist applications; used in proportions of 1-10% in paints.
- Additives in sealing compounds in building, automotive and industrial applications. The leachability and volatility of short chain length chlorinated paraffins over the lifetime of the sealant (typically 20 years) was reported to be low.
- Leather - as a fat liquoring agent, usually applied to moist dressed leather in the form of an emulsion – this application has ceased in 2001.

- Textiles - SCCPs used mostly in backcoating operations for sail cloths, industrial protective clothing, lorry tarpaulins,etc.

The EU Assessment concludes that product scenarios posing greater than negligible risk to consumers include use of metal working fluids and exaggerated wearing of leather garments that have been treated with SCCPs.

The OSPAR Report considered different products containing SCCP to be potential sources of emissions, and that this could be the case not only during production and use, but also when the articles become waste and are sent to landfill. SCCPs were also identified as a possible source of polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs) formation via incineration of wastes (CSTEE 1998; *in* OSPAR, 2001). An estimate was given of annual emissions of 9 tons a year in Europe from surfaces with paint containing SCCP (ibid). Other products that are potential sources of SCCP emissions include: rubber, textiles, sealants and polymers.

Within the Region, no data has been reported for emissions to air and soil. Estimated inputs of short chain paraffins to water have been reported for Germany at 74 t (OSPAR 2000).

2.6.8. Hexabromobiphenyl

Within Europe, a mixture of highly brominated PBBs (mainly hexabromobiphenyl) called Bromkal 80-9 D was produced in Germany until mid- 1985. Technical grade decabromobiphenyl (Adine 0102) was known to be produced in France up to the late 1980s. As far as is known, there is no current production of PBBs within Northern Europe and no emission data has been reported.

2.7. CONLUSIONS

- Within the Region as a whole there is a large amount of data relating to industrial point source emissions to the atmosphere. Sources to air of well studied compounds such as PAHs, PCBs, and PCDDs/Fs are generally well characterised and inventories have been calculated and updated regularly via EMEP. Due to restrictions on the manufacturing and more stringent control of releases, emissions from primary sources have been declining during the last 20 years. Understanding of secondary source inputs and the potential for environmental recycling of individual compounds continues to be limited and few measurements are available.
- Obsolete stocks of pesticides represent a potential source of PTS material particularly within the Central Euopean Countries and Newly Independent States. Exact quantities and components of the stockpiled wastes are unknown at present but quantities are thought to be in excess of 80 000 t.
- For the compounds of emerging concern (e.g. PBDEs, short chain chlorinated paraffins) emission sources to all environmental compartments are very poorly characterised, few formal inventories have been established and there is limited understanding of the principal contemporary source catagories. For PBDEs, evidence of increasing concentrations in human tissues from Sweden would suggest that emissions into the Region have been rising during the last 20 years.
- Unlike sources to air, sources to land and water are very poorly quantified for all the PTS compounds.
- Prioritization of sources inputs within the Region as a whole highlight that the following compounds represent ongoing releases in the Region which are of most concern with respect the environment and health:
    - Hexachlorobenzene
    - PCBs
    - PCDD/Fs
    - PCP
    - PBDEs
    - Short chain chlorinated paraffins

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3. ENVIRONMENTAL LEVELS, TOXICOLOGICAL AND ECOTOXICOLOGICAL CHARACTERISATION

3.1. LEVELS AND TRENDS

3.1.1. Introduction

The first part of this chapter deals with the environmental levels and trends. The relative spatial and temporal variations in environmental concentrations of PTSs are briefly described. The following sections describe ecotoxicology, toxicology and human exposure to PTS in Region III.

3.1.2. Air

3.1.2.1. Regional programmes

Air is an important transport medium for PTS in general. Reporting ambient air concentrations reflects the concentration during the sampling period but, due to rapid transport and fast mixing of pollutants in air, PTS concentrations will change quite rapidly

Heavy metals and persistent organic pollutants (POPs) were included in EMEP's monitoring programme in 1999. However, by 1995, co-operation concerning heavy metals and POPs between EMEP and other international programs was extended. This co-operation included the establishment of a database and collection of already available data on POPs among the participants. A number of countries have been reporting POPs within the EMEP area in connection with different national and international programmes such as HELCOM, AMAP, OSPARCOM, MEDPOP.

Few of the sites have reported data for POPs to date (see Table 3.1-3.2). The stations are generally located distant from local emission sources in order to be representative for a larger region (Figure 3.1).

Table 3.1: List of monitoring stations included in the POP data base.

Country	Station codes	Station name	Location		Height above sea
			Lat.	Long.	(m)
Belgium	BE0004R	Knokke	51°21'N	3°20'E	0
Czech Republic	CZ0003R	Kosetice	49°35'N	15°05'E	534
Iceland	IS0091R	Stórhöfdi	63°24'N	20°17'W	118
Ireland	IE0002R	Turlough Hill	53°02'N	6°24'W	420
Netherlands	NL0009R	Kollumerwaard	53°20'N	6°17'E	0
Norway	NO0042G	Spitsbergen, Zeppelinfjell	78°54'N	11°53'E	474
	NO0099R	Lista	58°06'N	6°34'E	13

Table 3.2: General information about sampling and analysis of POPs in air in 1999

Country	Sites	POPs	Sampling period	Sampler	Analytical methods
Czech. Rep	CZ0003R	PAHs, PCBs, DDTs, HCHs, HCB	24 hrs every week	High volume	GC-MS
Iceland	IS0091R	PCBs, pesticides	15d	High volume	
Norway	NO0042G	PAH, pesticides, HCHs, HCB, PCBs	48h	High volume	GC-MS
	NO0099R	α-HCH, γ-HCH, HCB	48h	High volume	GC-MS
GC-MS: Gas chromatography with mass spectrometry					

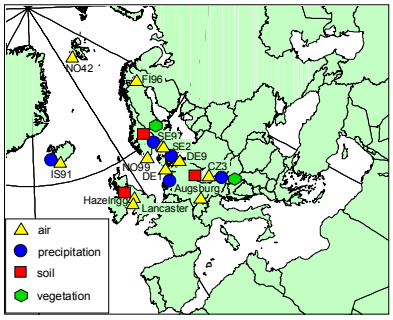


Figure 3.1: Location of monitoring stations, which have reported data to the EMEP heavy metal and POP database

Table 3.3: General information about sampling and analysis of POPs in air in 1999

Country	Sites	POPs	Sampling period	Sampler	Analytical methods
Czech. Rep	CZ0003R	PAHs, PCBs, DDTs, HCHs, HCB	24 hrs every week	High volume	GC-MS
Iceland	IS0091R	PCBs, pesticides	15d	High volume	
Norway	NO0042G	PAH, pesticides, HCHs, HCB, PCBs	48h	High volume	GC-MS
		α-HCH, γ-HCH, HCB			
	NO0099R		48h	High volume	GC-MS
GC-MS: Gas chromatography with mass spectrometry					

Figures 3.2 and 3.3 show temporal trends for α-HCH and γ-HCH in air at 6 stations. The concentration level of α-HCH at the Norwegian stations is relatively high compared to the other stations, but decreasing. This is probably due to higher input of technical HCH at high latitudes (EMEP, 2000; Breivik et al., 1999).

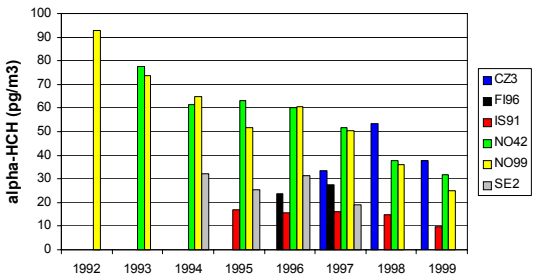


Figure 3.2: Annual weighted means for α-HCH during 1992-1999

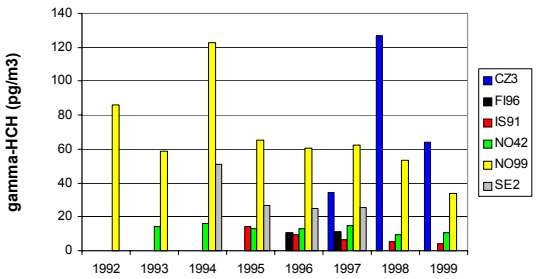
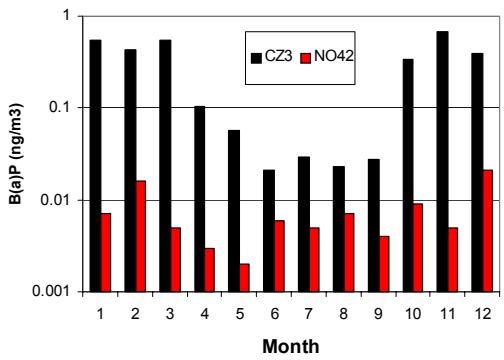


Figure 3.3: Annual weighted means for γ-HCH during 1992-1999

Benzo(a)pyrene (also other PAHs) is rapidly destroyed by UV. In the absence of local sources, therefore, a pronounced seasonal trend is to be expected, which is seen especially for CZ03 (Figure3.4). Data for PTS have been reported only from countries around the North and Baltic Seas, in the Arctic and from the Czech Republic.

Figure 3.4: Concentrations of benzo(a)pyrene in air+aerosol at two EMEP-stations, 1999.



3.1.2.2. Subregional programmes

3.1.2.2.1.EU

Results for dioxins in air are available for only eight Member States (Table 3.4) (Buckley-Golder et al., 1999).

Table 3.4 shows that the concentrations in ambient air range from below 1 fg I-TEQ.m^{-3} to several hundred fg I-TEQ.m^{-3}. The extremely high concentration of 14 800 fg I–TEQ.m^{-3} was measured in the Panteg area of Pontypool in South Wales, which is very close (~150 m) to an industrial waste incinerator.

Table 3.4: Summary of ambient air concentrations (fg TEQ.m^{-3}) and deposition [pg TEQ.m^{-2}.d^{-1}] from EU Member States

	Ambient Air				Deposition	
	Unspecified	Urban	Rural	Contaminated	Urban	Rural
Austria	1.3-587					
Belgium		86-129	70-125		<1-12	<1-3.1
Germany	2-812				<1-464	
Luxembourg		54-77	30-64			
Netherlands		4-99	9-63	6-140		
Sweden	5.4-53.7	<1-29				
UK		0-810	1-24	14,800	<1-312	0-517

In several countries strong seasonal trends have been determined for ambient air concentrations. A typical seasonal trend is displayed in Figure 3.5 for the cities of Augsburg and Burgkirchen in southern Germany.

The cause for these variations is not fully understood: whereas in some regions additional combustion activities, such as heating of private homes, might be responsible for higher emissions, other authors find that meteorological conditions, with more frequent inversion layers and lower mixing heights in the air column, might explain the differences.

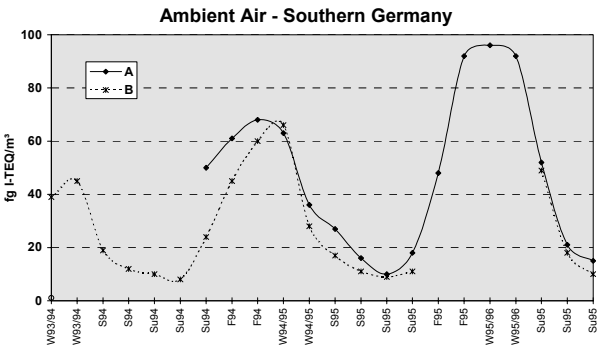


Figure 3.5: Seasonal trend of ambient air concentrations of dioxin in southern Germany. Median concentrations obtained from the networks around the MSWIs at Augsburg and Burgkirchen (n=223)

3.1.2.2.2.Baltic region

Concentrations of HCHs in air from the Baltic Sea drainage basin, specifically Southern Norway, were measured as early as 1981 (Oehme and Manø, 1984). A few years later, Bidleman et al. (1987) reported concentrations of HCHs in air in southern Sweden. A total of 337 measured concentration values for the western atmospheric compartment were aggregated and are shown in Agrell et al. (2001) together with the calculated concentration time trends. The seasonal pattern of measured air concentrations at the coastal stations in Lista, Norway were shown (Haugen et al. 1998) and Rörvik, Sweden (Brorström-Lundén, 1995; 1996).

3.1.2.3. National programmes and measurements

Extensive monitoring of PTS in the Region was/is done as part of each countries commitment to the United Nations Economic Commission for Europe's (UNECE) POPs Protocol to the 1979 Geneva Convention on Long Range Transboundary Air Pollution (Peters et al., 1999).

Retrospective analysis of archived air filters have confirmed declining concentrations of PCBs since the early 1960s - 1970s in rural UK air. (Figure 3.6).

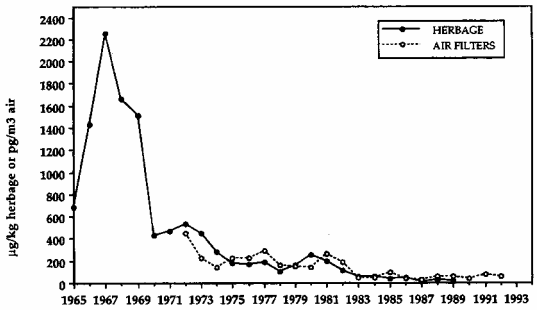


FIGURE 1. PCB concentrations detected in the archived air filters (averaged for both rural sites) aad on herbage collected annually and stored at Rothamsted Experimental Station (data from ref 10).

Figure 3.6: PCB concentrations detected in the archived air filters (two rural sites) and on herbage collected annually and stored at Rothamsted Experimental Station

Within the PHARE Project EU/93/AIR/22 "Local Studies of Air Quality in the Cities of Bratislava and Kosice. National Needs Assessment of Air Pollution" PCBs, HCB, DDTs, PCDDs/Fs concentrations were measured in 24-hr ambient air samples collected around Slovakia in 1996/97 (8-times at 20 sampling sites involving urban, industrial, agricultural, and background areas).

Concentrations of tetrachlorobenzenes, pentachlorobenzene, hexachlorobenzene and α–, β–, γ– and δ–HCH in air and deposition were measured at three different contaminated sites in Greppin, Roitzsch (both near Bitterfeld) and Leipzig (Germany) during five time intervals of 14 days in the summer months of 1998 (Popp et al., 2000).

DDTs, HCHs, CHLs, HCB and PCB concentrations were determined on monthly intervals in ambient air samples collected in city of Gdańsk (Poland) in 1991-92 (Falandysz et al., 1998). Ambient air levels of OCCs were studied in the Gulf of Riga (Estonia) (Roots, 1996).

Atmospheric concentrations of PCBs (indicator congeners) were measured every week from 1992 to 1995 in Lista, a coastal station in Southern Norway (Haugen et al., 1999). No obvious concentration decrease could be observed during the 4 years.

PCBs in the lower atmosphere were studied on the regional and rural levels round the Baltic region (Backe et al., 2000; Agrell et al. (1999); Bremle and Larsson (1998); Brorström-Lundén et al. (1994). Comparison PCB data from various studies is complicated because of the various quantification techniques and reporting conventions used by different laboratories. Comparison of the data suggests that PCB levels in Southern Norway are rather high, namely, in the range of concentrations reported in recent years for urban areas in the UK and Germany.

Air samples were collected along a transect from the city of Stockholm urban area (Sweden) to the open coastal area of the Baltic Sea for determination of PAHs and PCDDs/Fs (Broman et al., 1991). The investigation area is, of course, also affected by long-range transport of PAHs and PCDDs/Fs primarily from European countries.

Some measurements of PCDDs/Fs in ambient air were also done in Poland, in city of Krakow (Grochowalski et al., 1995, 1997) or in Prague and some other towns in the Czech Republic (Holoubek et al., 2000) or Slovakia (Kočan et al., 2000).

Several studies have been made of urban air contamination by various PTS (UK, Germany). The first project was performed in early 90´s withmeasurements focused on PAHs (London, Manchester and Cardiff, Stevenage - Halsall et al., 1993, 1994, 1999; Smith, 1999; west London - Beak et al., 1992). Extensive studies have been undertaken throughout most of the European continent including a variety of differing ambient environments in Germany, Austria, Netherlands, Belgium and Scandinavia.

The latest PAH, nitro-PAH and oxy-PAH study (particle-phase) in ambient air was sampled in the Helsinki area (Finland) by ZTV in the early 1990s (1993 - 1994) (Sandell et al., 1999; Tuominen, 1990), urban, an industrial, rural and residential areas in Flanders (Wauters and Lenelle, 1999). Analyses showed a decrease in the concentrations of the PAH compounds in the particle-phase in the ambient air during the second part of 80´s.

In comparison with OCPs and PCBs, PAH concentrations in the atmosphere show a seasonal fluctuation with higher values in winter and lower in summer, which trend was the same as was observed in Middle European regional background observatory in Kosetice, South part of Czech Republic (See Figure 3.4) (Vana et al., 1997, 2001, Holoubek et al., 2002).

Also ambient air measurements of newer types of POPs have been established. (see Lee at al., 2002a and Lee et al., 2002b for details). The results from are summarized in Table 3.5.

Table 3.5: The median values and range of determined levels of PCNs and PBDEs in UK $pg.m^{-3}$

Site	PCNs		Site	PBDEs	
	Mean	Range		Mean	Range
Hazelrigg	111	30.5-309	Hazelrigg	12	2.8-37
Chilton	85.0	31.2-184	Chilton	11	3.4-33
			Mace Head	3.1	0.2-11

3.1.3. References

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3.1.4. Deposition

3.1.4.1. Regional programmes

Today, the PTS sampling stations for deposition measurements operated in Europe are few and mostly found around the North Sea as well as in the Czech Republic. Data from these stations are routinely reported to EMEP, OSPARCOM and HELCOM. The location of the sampling stations is given in figure 3.1.

Table 3.6: General information about sampling of POPs in precipitation in 1999 reporting to EMEP-database

Country	Sites	POPs	Sampling period	Sampler equipment*
Belgium	BE0004R	Pesticides, HCHs	Monthly	Wet only sampler
Czech. Rep	CZ0003R	PAHs, PCBs, DDTs, HCHs, HCB	Every event	Wet only sampler
Iceland	IS0091R	PCBs, pesticides, HCHs, HCB	15d	Bulk sampler
Ireland	IE0002R	Pesticides, HCHs, PCBs	Monthly	Bulk sampler
Netherland	NL0091R	γ-HCH	Monthly	Bulk sampler
Norway	NO0099R	α-HCH, γ-HCH, HCB	Monthly	Bulk sampler
Sweden	Se 2	PAHs, PCBs, DDTs, HCHs, HCB	Monthly	Bulk sampler
* The two collection principals, bulk or wet-only sampling, are used for deposition measurements				

PCBs, DDTs, HCHs and PAHs in precipitation and their calculated deposition are evaluated with respect to temperature, latitude and sampling-site etc.. No significant decreasing trends in the deposition fluxes of the measured POPs was found at the Swedish West Coast between 1996 - 2000.

3.1.4.2. Baltic region

Sampling of PCBs, DDTs and HCHs was carried out continuously during 1991/92 at 16 sampling stations around the Baltic Sea (Agrell et al., 2001). The deposition fluxes of the POPs were calculated from the concentrations in rain. Overall, the variation in the PCB deposition was small between the stations. The median values varied between 1.2 to 5.6 $ng.m^{-2}.d^{-1}$. Variability between stations was larger for the pesticides, about 10 times for DDTs and 25 times for HCHs, with median values of 0.15 $ng.m^{-2}.d^{-1}$ and 1.30 $ng.m^{-2}.d^{-1}$, respectively.

Brorström-Lundén (1995) found higher deposition fluxes of HCHs and PCBs over the Skagerak during 1990-1994, compared to the Baltic Sea (PCBs 10-15 $ng.m^{-2}.d^{-1}$ and of HCHs 5-15 $ng.m^{-2}.d^{-1}$ (α, β and γ-HCH, Table 3-14). Higher deposition of HCHs was also found by Hilbert and Poulsen (1992) in a study in Denmark in 1990.

A study of spatial and temporal variations of the PCBs concentrations in precipitation was also carried out in a region of southern Sweden (Backe et al., 2002). The PCBs concentration ranged between 1.18 and 81.4 $ng.l^{-1}$. No seasonal trends in PCB concentration in precipitation were found.

3.1.4.3. National programs and measurements

In Lithunia the deposition of benzo(a)pyrene (BaP) to soil and vegetation, with special emphasis on the forest ecosystem have been investigated (Milukaite, 1998). The average annual flux generally increased from year to year, except for 1993. The estimated the total annual flux of BaP to Lithuania, ranged from 624 kg in 1993 to 2574 kg in 1995.

Bulk deposition of PAHs and PCDDs/Fs have been measured in UK (Toxic Organic Micropollutants Survey (TOMPS)), (Halsall et al., 1995). The annual average of ΣPAH deposition in Manchester and Cardiff during 1991/92 was 5.2 and 4.1 $\mu g.m^{-2}.d^{-1}$ respectively. Urban fluxes are generally higher compared to rural locations (EMEP data (Gevao et al., 1998)) reflecting a) importance of the urban centre as a source of PAH and b) the large decline in many atmospheric PAH species moving away from urban areas.

ΣPCDD/F (2,3,7,8-isomers) annual median flux for Manchester and Cardiff was 1.42 and 1.01 $\mu g.m^{-2}.d^{-1}$, respectively (Halsall et al., 1995. Hiester et al. (1993) collected monthly bulk deposition samples from Nov 1991 to Oct 1992 and reported a mean annual ΣPCDD/F flux of 1.52, 0.38 and 0.78 $\mu g.m^{-2}.d^{-1}$ for the German cities Düsseldorf, Cologne and Dortmund respectively. Similar to the UK study, the PCDD profile was dominated by the hepta- and octa-dioxins.

Previous precipitation measurements reported mostly the concentration of the POPs in water. Rain samples were analysed in Germany in the early 1980s (Georgii and Schmitt, 1983). The total concentration of PAHs were 1.8 $\mu g.l^{-1}$ in Frankfurt am Main in February, 1981. Lower values were measured by Levsen et al. (1981) in Hannover (600 $ng.l^{-1}$), Leuenberger et al., (1988), in a rural site in Switzerland (490 $ng.l^{-1}$) and Quaghebeur et al. (1983) in Belgium (140 $ng.l^{-1}$). Recently, a study of the seasonal variation of the concentrations of PAHs in precipitation has been carried out at a rural site by Lake Balaton, Hungary, (Kiss et al., 1997, 2001).

Despite the extensive investigations on the PAH content of atmospheric precipitation and aerosol samples all over the world the availability of data from Eastern Europe is limited for background monitoring programme in South Bohemia (Vana, Holoubek et al., 2001) or some studies (Kiss et al., 1997; Simkova et al., 1996).

3.1.4.4. References

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3.1.5. Snow and ice

Snow and ice influence the deposition and fate of PTS in cold regions. Due to their high porosity, falling snowflakes have been proposed to be more effective at scavenging atmospheric particles than rain. In addition, large specific surface area of ice crystals enhances the adsorption of gaseous hydrophobic contaminants from the atmosphere.

PAHs, PCBs and HCHs are found in all snow samples collected in remote high mountain European sites. Despite the predominance of atmospheric mechanisms for the transport of these compounds to these high-altitude sites, their concentrations in snow do not exhibit parallel geographic distributions. Thus, PAHs are found in higher amounts in the Tatra and Caledonian mountains, PCBs in the Alps and HCHs in the Alps and Pyrenees.

For example, snow cores were collected in the catchment area of five remote mountain lakes in Europe (Carrera et al., 2001) PAHs were found in higher amounts in the Tatra and Caledonian mountains, PCBs are higher in the Alps and HCHs are higher in the Alps and Pyrenees.

3.1.5.1. References

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3.1.6. Aquatic ecosystems

3.1.6.1. Introduction

Inputs of POPs to the hydrological cycle are principially via discharges of sewage and industrial effluents, urban runoff, leachates from solid waste landfill sites, atmsopheric deposition and of increasing concern, agricultural runoff (Scrimshaw and Lester, 1996).

3.1.6.2. Seas

3.1.6.2.1.Introduction

Many organic substances are released to the marine environment. Many of them are degraded rather effectively, while more persistent compounds may be distributed over large areas and accumulate in organisms. Most of the PTS are made up of several hundreds or even thousands of individual compounds. This complicates the presentation of analytical results since these can represent the whole mixture or one or several individual compounds. Furthermore these results can be related to different matrices, for example wet weight, dry weight or lipid weight. Additionally variations in the composition of the matrix can influence the result, for example the number of particles in the air or water, the organic carbon content of the sediment and the lipid content of the tissue. The absence of information on these factors limits the extent to which data from different sources can be compared.

3.1.6.2.2.North Sea, Norwegian Sea – OSPAR region

In sediments DDD is the major component of the DDT derivatives; but data are usually reported as total DDT. Comparison with EACs is difficult because only an EAC for DDE is available. The available data however, have not revealed any locations with significantly elevated concentrations. As HCB is hydrophobic concentrations in the relatively few sea water samples analysed are in the $ng.l^{-1}$ range or below the detection limit.

Dieldrin has no known use today but previous usage may still affect the environment. Data from Regions I and II indicate low and decreasing concentrations in the marine environment. Triazines, such as atrazine and simazine, are still being used in some applications and are still detected in sea water, the highest levels are observed along the coast.

Concentrations of PCBs in ocean water are generally very low and this makes reliable quantification difficult. Concentrations of PCBs in filtered ocean water are usually reported to be in the low $pg.l^{-1}$ range.

Information on dioxin levels in the Convention area is scarce, but a few point source emissions have been well studied, such as in Frierfjorden in Region II. Comparison of measurements for surface sediments shows that dioxin concentrations seem ten to twenty times lower in samples from the Barents Sea than in samples from the northern North Sea.

Lindane is also more watersoluble than most of the other chlorinated hydrocarbons discussed in this report, and a major input is via rivers from the application areas. There are indications of a slight decrease in the riverine input of lindane to the Irish Sea. In water, lindane concentrations are higher in the southern North Sea and the German Bight than in the north-western North Sea. The highest concentrations exceed the EAC (0.5 – 5 $ng.l^{-1}$).

Concentrations of α-HCH ranged from 0.1 to 0.7 $ng.l^{-1}$ (mean value 0.28 $ng.l^{-1}$), and γ-HCH from 0.1 to 4.0 $ng.l^{-1}$ (mean value 1.1 $ng.l^{-1}$).

Both the atmospheric and aquatic pathways of PAHs to the maritime area are important. Information on riverine inputs is very limited. Emissions of PAHs from North Sea riparian states have been estimated at 7 000 t in 1990. Atlantic sea water concentrations range from 0.3 $ng.l^{-1}$ for individual, more water-soluble, lower molecular weight PAHs (two and three ring compounds) to less than 0.001 $ng.l^{-1}$ for the high molecular weight PAHs (five or more ring compounds). Higher concentrations were generally found in coastal and estuarine samples with total PAH concentrations ranging from not detectable to 8 500 $ng.l^{-1}$.

Polybrominated diphenyl ethers (PBDEs), especially those with four to six bromine atoms, are found in biota and sediments in the marine environment far from known sourcesFew data available on chlorinated paraffin concentrations in the Convention area. Sediment from river mouths was found to contain up to 10 $ng.g^{-1}$ dw, fish samples from the North Sea have been shown to contain up to 100 $ng.g^{-1}$ ww. A recent EU risk assessment for short-chained chlorinated paraffins with a high degree of chlorination identified a need to limit the exposure of aquatic organisms to local emissions associated with metalworking applications.

3.1.6.2.3.Baltic Sea

The general concentration trend in the Baltic Proper suggests an increase of PCB concentrations from the early 1970s and onwards (ICES, 2000). This is an apposing trend to the decreasing concentration trends for PCBs in biota from the Baltic Proper (HELCOM, 1996; Roots et al, 1996, 1999).

Gulf of Finland, a sub-basin of the Baltic Sea was found to be severely polluted, with Σ PCDDs/Fs concentrations as high as 101 000 $pg.g^{-1}$ dw and 479 pg $TEQ.g^{-1}$ dw. One of the industrial processes where PCDDs/Fs are formed as by-products, is the synthesis of chlorophenols (Isosaari et al., 2002a,b; Korhonen et al., 2002). In Finland, chlorophenols were manufactured in 1939-1984, and used as a wood preservative Ky 5 (mainly 2,3,4,6-tetrachlorophenol). The chemical plant was situated next to the Kymijoki River, which discharges into the Gulf.

Highest PAHs concentrations, up to 35.2 $ng.g^{-1}$ dw, have been found in the southern most Baltic Sea (Gulf of Gdansk, Lübeck Bay, Mecklenburg Bay, Arkona Basin). Somewhat elevated concentrations were observed from the eastern Gulf of Finland as well as from the northern Gulf of Bothnia (up to 17.0 $ng.g^{-1}$ dw and 20.9 $ng.g^{-1}$ dw, respectively).

The down-core PAH concentrations in general show peak concentrations in the 1970s and early 1980s, thereafter decreasing somewhat. In the sediment cores from Mecklenburg Bight, Southern Baltic Sea, increasing PAH concentrations were detected between 6 and 10 cm (between 1945 and 1965) reflecting a higher anthropogenic influence during that time (Witt and Trost, 1999; Dannenberger, 1996; Dannenberger and Lerz, 1996; 1998).

Organotin compounds, mainly tributyltin (TBT), are still regularly used as antifoulants on large-sea going vessels.. Organotin compounds are found in sediments as tri- (TBT), di- (DBT) and monobutyltin (MBT), of which DBT and MBT are brake down products of TBT.

The highest concentration of organotin is typically found in sediments from harbours, port channels, near shipyards and along ship lanes. In several locations the majority of butyltin compounds were present as TBT, which suggests recent exposure of the localised aquatic environment to TBT.

For polybrominated diphenylethers (PBDE), dioxins and furans information in Baltic Sea sediments is very limited. A few Swedish results reveal that dioxins and furans are present in Baltic sediments in the concentrations level of few $pg.g^{-1}$ (Kjeller and Rappe 1995, de Wit et al., 1990).

The long term monitoring of DDTs, PCBs, HCB and HCHs in biota samples that has been carried out in the Baltic since the 1970s has been used to verify the models. Interestingly, these unique temporal trends do not support the model. Concentrations decrease at a similar rate both in the warmer south as in the colder north. (Bignert *et al.* 1998). Many authors consider the Baltic herring (*Clupea harengus membras L.*) to be a good indicator of the Baltic Sea ecosystem pollution by PBTs (Roots, 1996; Falandysz, 1984; Falandysz et al., 1997d, f). Its role as a bioindicator is currently increasing.

The concentrations of ∑ DDTs and PCBs in herring muscle are highest in southern Baltic Proper and decrease to the north and west and are similar in the Kattegat and the Bothnian Bay. Concentrations vary between 61-710 $ng.g^{-1}$ lw for ∑ DDTs and between 120-2 800 $ng.g^{-1}$ lw for PCBs (Figure 3.7).

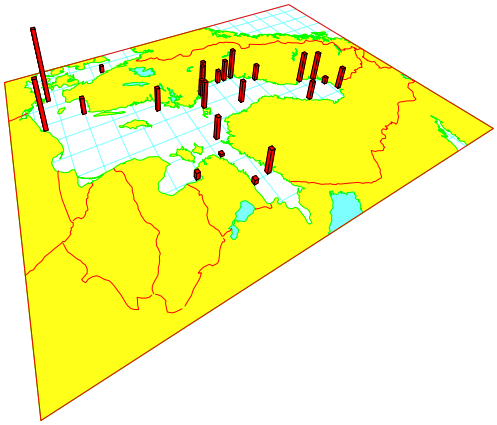
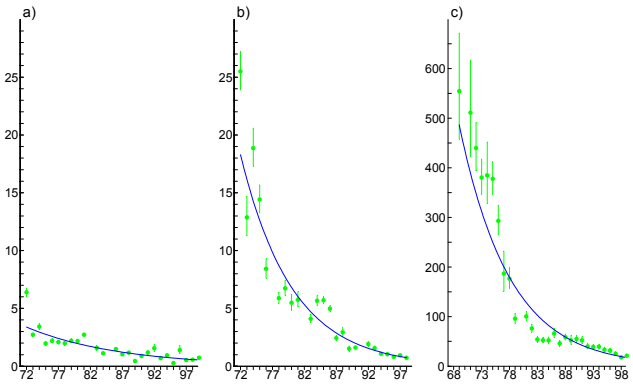


Figure 3.7: Spatial distribution in concentrations of PCBs in herring muscle. Lowest concentration is found outside the Estonian coast [120 $ng.g^{-1}$ l.w.] and highest near the Polish coast [2 800 $ng.g^{-1}$ l.w.]

The temporal trend for ∑ DDTs in herring is decreasing over the entire period. The longest time series, going back to the late 1960s-early 1970s show decreasing concentrations by about 7% per year in herring from southern Bothnian Sea and by 11-12% per year in both herring and guillemot egg from the Baltic Proper (Figures 3.8 and 3.9).

The dioxin concentrations, expressed as the TEQ value, in 7 pools of herring muscle along the Finnish coast vary between 165 and 329 $pg.g^{-1}$ l.w. (Vartiainen *et al.,* 1997). The highest concentrations were found in the inner part of the Gulf of Finland. Corresponding value on a wet weight basis was 2.9-24 $pg.g^{-1}$. The highest wet weight concentrations were found in samples comprising fat specimens of high age from the Bothnian Sea and the Gulf of Finland. found in the Finnish material is probably mainly explained by the higher age classes analysed.

Figure 3.8: Concentrations of ∑ DDTs ($ng.g^{-1}$ l.w.) in muscle tissue of herring (1972-1998); a) southern Bothnian Sea, b) the southern Baltic Proper and c) in guillemot egg (1968-1998) from the central Baltic Proper. The 95% confidence interval for the annual geometric mean is given. The significant log linear regression line for the trend is indicated.



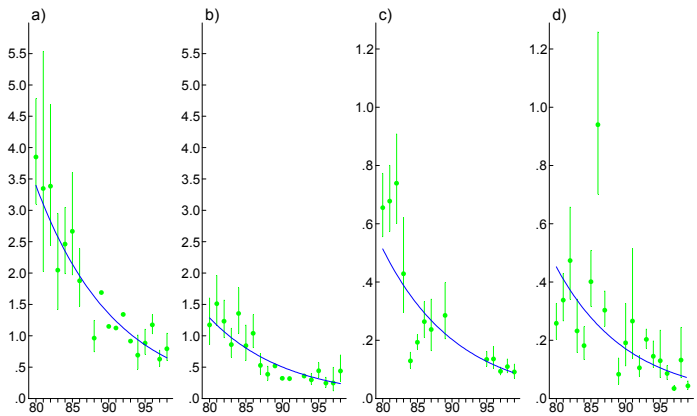


Figure 3.9: Concentrations of ∑DDTs ($ng.g^{-1}$ l.w.) in fish samples (1980-98); cod liver in a) the Baltic Proper, b) the Kattegat; perch muscle in c) Gulf of Bothnia and d) the Baltic Proper. The 95% confidence interval for the annual geometric mean is given. The significant log linear regression line for the trend is indicated.

The European otter (*Lutra lutra*) is a widespread species on the Euroasian continent. Since the 1950s some European otter populations have declined dramatically. Many different explanations for the decline had been presented: e.g habitat destruction and direct or indirect influences of eutrophication, acidification and toxic chemicals. In the beginning of 1980s, PCBs were suggested to be an important reason for the otter population decline. Based on the results of various studies, PCBs seemed to be an important agent for the explanation of the otter decline and the present distribution in Europe (see Table 3.7).

Table 3.7: PCBs and DDTs concentrations in otter (*Lutra lutra*) muscle tissues [$\mu g.g^{-1}$] (Sjőasen et al., 1997)

Area	N	Sampling year	PCBs Mean (range)	DDTs Mean (range)
Norway	23	1970s	17 1.6 - 30	1.7 0.18 - 5.9
Sweden	53	1970s	120 4.7 - 970	4.1 ND - 27
UK	14		53 ND - 300	18.5 ND - 85
Denmark	16		16 7.5 - 60	0.9 0.39 - 1.88
Czech Republic	8		130	

			19 - 260	
Spain	21		100 4.4 - 1 000	
Latvia	8	1991-2	2.3 0.4 - 10	0.22 0.028 - 0.76
Austria/Czech Republic	11	1990-4	38[1] (12.7)[2] (4.2 - 130.0)[1] (1.3 - 130.0)[2]	
[1] (Gutleb and Kranz, 1998), measured value, geometric mean and range [2] (Gutleb and Kranz, 1998), level calculated by described model, geometric mean and range				

3.1.6.2.4.The Black Sea

Concentrations of DDTs, HCHs and PCBs in Black Sea fish and mammals are high by comparison with those reported for other regional seas (Tanabe et al., 1997a,b).

The extent of contamination of the Black Sea by selected organochlorines compounds has been assessed through the analysis of surficial sediments taken from throughout the region (Filman et al., 2002). Concentrations of HCHs at sites influenced by the Danube delta are among the highest recorded on a global basis (up to 40 $ng.g^{-1}$ dw). The ratio between the α– and γ–isomers was relatively low indicating contamination through the use of lindane.

The highest concentrations of hydrocarbons were detected in the Danube, Dnieper, and Dniester River Estuaries and other point sources of pollution located offshore Romania and Bulgaria where oil production and refining is carried out (i.e., Constantza, Varna). The concentrations of PAHs in the SPM of the Danube, Dnieper and Dniester Estuaries (ca. 1 600 $pg.l^{-1}$) are higher than in other estuaries of the western Mediterranean (ca. 560 $pg.l^{-1}$).

The vertical profiles of PAHs and UCMs show maximum in surficial waters and two submaxima at the biomass and redox cline where the composition of PAHs is modified attributable to bacterial processes, there is an enrichment referred to POC. The large portion of anoxic conditions in the water column leads to a better preservation of hydrocarbons through the water column than in well- oxygenated seas allowing a large portion of PAHs to reach the sediments.

3.1.6.2.5.Caspian Sea

PCBs, OCPs and organotin compounds were determined in blubber and liver of Caspian seals (*Phoca caspica*) found stranded on the coast of the Caspian Sea an outbreak of canine distemper virus (CDV) in 2000 (Kajiwara et al., 2002).

Among organochlorines analyzed, DDTs were the most dominant contaminants. Caspian seals collected in 2000 during the epizootic had higher concentrations of organochlorines than healthy individuals sampled in 1998. However, the blubber layer was generally thinner in the seals collected in 2000 than those in the previous surveys. Although compositions of organochlorine pesticides in seals suggested that the contamination status in the Caspian Sea is improving, the levels found in Caspian seals in 2000 were comparable to those in other marine mammals that have suffered from epizootics. This implies that the present status of contamination found in Caspian seals poses a risk of immunosuppression.

3.1.6.2.6.References

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3.1.6.3. Freshwaters – rivers and lakes

3.1.6.3.1.Introduction

On of the most important environmental goals today is to decrease eutrophication (Söderström et al., 2000). However, it has been suggested that reduced eutrophication causes an increased availability and exposure of pollutants to biota in aquatic environments and there is a need for more knowledge about the processes involved. Higher concentration of PCBs on particles in the oligotrophic lake was related to high biomass of diatoms with high lipid content. Eutrophication results in lower volatilization compared to the oligotrophic lake.

Many regional rivers have extensive meadows which are flooded at high water (Elbe, Rhine, Oder, Danube). River sediment is brought into the wetlands by the flooding, causing pollution of these areas with compounds that are transported by the river. POPs and heavy metals are typical types of pollutants that are strongly represented in the wetlands. Due to very high density of industrial and agricultural sources of pollution near to the main regional rivers, most river sediments are highly contaminated with various pollutants. At high flood, sediment is remobilised from the river bed and transported downstream. The mechanism of self-cleaning will remove most of the contaminated material from the river bed in the future. In contrast, material deposited in the meadow will not be removed at high flood, because in summer vegetation stabilises the young sediments. The soil profiles from these rivers floodplains therefore show the history of flood event and past sediment pollution. Additionally, atmospheric inputs might contribute to their contamination.

High mountain lakes are some of the remote areas under potential stress by PTS (Vilanova et al., 2002). These lakes can be defined as those situated above the timberline receiving their waters through atmospheric fallout. Their ecological and environmental value is high because they have often support unique species of plant and animal communities. They are often the headwater catchments of water supplies and excellent sensors of environmental change for entire mountain environments.

Remote mountain lakes are excellent indicators of pollutant deposition and its effects as they are not influenced by direct forms of disturbance such as land-use change and wastewater point. Furthermore, geological and climatic factors combined with shallow soils and high relief results in their being more sensitive and vulnerable to such pollutants. The sediments records of mountain lakes are known to provide reliable archives of atmospherically deposited pollutants (Rose et al., 1999) while the ability to produce sediment core chronologies using radionuclides (e.g., ^{210}Pb,^{137}Cs, ^{241}Am) allows the date of depositional events and the rate of any recorded change to be calculated.

3.1.6.3.2.River Elbe

Monitoring the actual concentrations of chemicals in Germany was a part of activities of German Environmental Speciman Bank (ESB)..This sampling is performed routinely in River Elbe and River Rhine as limnic ecosystems.

Investigations of sediments and fish (bream) along the river Elbe have shown that the eastern sampling sites (Prossen, Dresden) have been heavily contaminated by HCB, DDT metabolites, PCBs and octachlorostyrene (OCS). This observation is probably a result of the considerable pollution of the River Elbe by industrialized areas (e.g. Pardubice, Neratovice, Usti) in the CR. Furthermore, sediments at the station Dresden are highly contaminated because they were strongly subjected to effluents of a pulp mill and chemical industries until 1991. Elevated levels of HCH isomers in bream muscles and livers were observed downstream between Aken and Heinrichsberg due to the influxes of the rivers Mulde and Saale as well as discharges from pesticide plants located in Magdeburg.

PCBs were the major organochlorine contaminants (70 %) in breams of a typical industrialized area (Saarland) in contrast to agricultural areas of East-Germany, where DDT metabolites were the dominant pollutants (80 %).

This is caused by the continued application of DDT in former GDR after DDT has been banned in Western Europe.

Biomonitoring was also used in Germany for determination of others pesticides from the PTS list such as dieldrin which was determined in eels from North Bavarian rivers (LAU Erlangen) or from Hamburg waters in 1995/96 (Götz et al., 1998).

On the other hand, similarly as in other countries of Region III, there are only a few data for toxaphene residues in Germany for monitoring purposes. Toxaphene congeners were determined in eels from river Main in Lower Frankonia 1995 (LUA Erlangen) and in eels from the river Elbe as well as in eels from Schwarze Elster, Mulde und Saale (1998/99) (ARGE ELBE).

The same set of data as for DDT or HCB in Germany are available also for PCBs (measurements of PCB congeners in unfiltrated surface water of the rivers Elbe, Schwarze Elster and Mulde, in sedimented suspended matter from the rivers Elbe, Schwarze Elster, Mulde and Saale, Rhine and Berlin river system; in breams, eels from these sites etc. (Heinisch and Kettrup, 2001; ARGE ELBE and LAU Halle/Saale).

As far as HCHs, especially in the region of production devices as well as landfills the ballast isomers are to be found mostly in greater amounts, whereas in the regions of application the percentage of γ-HCH predominates. These relationships are demonstrated by the distribution in Berlin waters. The water of the Berlin river system is especially suitable for such a demonstration because e.g. the Teltowkanal (TK) is strongly influenced by an enterprise, which produced lindane upto 1989. Other surface waters, e.g. the Tegeler See and the Niederneuendorfer See are completely free of such influences and show exclusively HCH loads due to applications (allotment gardens, agriculture).

A lot of very useful results from German ESB were published during recent years (Marth et al., 1999). Results of ten years of experience in the determination of chlorinated hydrocarbons in herring gull eggs collected in the North and Baltic Seas, were published by Marth et al. (2000). POPs concentrations in bream livers from the River Elbe between 1993 – 1997 were also presented (Marth et al., 2001).

One from the first papers, which summarized the determination of PCBs and organochlorine pesticides in water and sediments in former Czechoslovakia, was published by Nondek and Frolikova (1991). During 1987-90, water and sediment samples taken from more than 200 localities (streams and reservoirs) were analysed. From this time, the determination of water and sediment quality is determined as a part of an international programme "Project Elbe"..The main sources of PCBs were Skoda car factory at Mlada Boleslav and an industrial dump site upstream of Mlada Boleslav. The contamination of Sumava Lakes was described as a result of atmospheric transport to non-industrialised areas. The lakes are located in South-West Bohemia, far from industrial sources, in a natural park at an altitude of 1 028 - 1 096 m a.s.l.

Concentrations of PCBs were described as Delor 103 and Delor 106 and they are summarised together with HCB, lindane and DDE for all three sampling sites in the Table 3.8

Table 3.8: Concentrations of PCBs and other OCCs in bottom sediments from rivers Labe and Jizera and from Sumava Lakes, 1989 [$ng.g^{-1}$]

Sampling site (numbers of site)	HCB	γ-HCH	DDE	PCBs (low as Delor 103)	PCBs (high as Delor 106)
Elbe River (15), 1989	< 1 - 440	ND	< 5 - 205	< 20 - 1 800	50 - 1 900
Jizera River (10), 1990					15 - 450
Sumava Lakes (3), 1986	0.8 - 2.0	0.5 - 1.8	1.0 - 1.6		15 - 40
Hincovo Pleso (High Tatras, Slovakia)	0.9	2.4	1.2		15

3.1.6.3.3.River Rhine

The River Rhine is polluted by many different types of industrial and municipal waste water as well as diffusive inputs from superficial runoff. Some tributaries like Aare, Neckar, Main, Mosel and Ruhr add further quantities of inorganic and organic compounds to the river, so that the highest concentrations were regularly found in the lower Rhine (Brauch, 1993).

A large amount of pesticides were produced in the Rhine basis area, because many chemical plants are located along the river Rhine. In the past there have been a number of isolated incidents of organic chemical pollution.

A vivid example of this was a spill of endosulfan in 1969 and the Sandoz storehouse fire in 1986, which had severe ecological consequences.

Little is known about the pesticide pollution in the river Rhine before 1985. Concentrations were relatively low (regularly below 0.1 $\mu g.l^{-1}$ per individual pesticide) and did not provoke special attention.

Compared to the data of 1986, pesticide concentrations in the river Rhine were much lower in 1987 and 1988. After the Sandoz "shock" (Nov. 1986) the input of highly polluted waste waters effluents from pesticide production sites into the river Rhine was stopped or strongly reduced. It may be concluded that for the period 1986 to 1988 point pollution of individual pesticides from wastewater effluents was the dominant pathway for entering the river. Within that period and afterwards a lot of measures were taken to reduce pesticide discharges by wastewater treatment and/or closing production sites in the Rhine basin area.

Superficial runoff was now the dominant entering pathway for pesticides into the river Rhine. Seasonal fluctuations of atrazine could still be observed each year in June and July. In contrast to earlier results the peak concentrations were quite low.

3.1.6.3.4.River Danube

During the period of 1995 - 1997, the "Danube Pesticide Regional Study", a project supported by PHARE, was completed (Bratanova et al., 1998). The data on the occurrence of pesticides in the water were collected from 10 of the Danube riparian countries: Germany, Austria, Slovakia, Hungary, Slovenia, Croatia, Bulgaria, Romania, Moldova and Ukraine. The data from period of 1990 - 1995 were included in the study.

The most positive findings of pesticides (i.e. those over the detection limits of the respective methods) in the Danube water relate to organochlorine pesticides (HCHs, HCB and DDT) and atrazine and its degradation product desethylatrazine. Remarkably high levels and high proportion of positive samples have been found for some chlorophenols.

DDT and lindane data from Romania exceeded by one to two orders of magnitude those from the other countries. Some findings can be episodically high, for example mean concentration of DDT in Danube water from Slovakia was 0.047 $\mu g.l^{-1}$, but findings up to 0.26 $\mu g.l^{-1}$ were reported (Veningerova et al., 1996). It is also interesting that lindane and other HCH isomers were detected in two of the nine examined Danube tributaries, both of them on the Romanian teritory (lindane - river Olt, 0.15 $\mu g.l^{-1}$ and river Arges 0.25 $\mu g.l^{-1}$ (Bujis et al., 1992). This would indicate occasional unauthorized uses of organochlorine pesticides in some parts of the region and also suggests Romania as one of the 'hottest' spots for environmental contamination with chlorinated pesticides in the Danube River basin.

Residues of HCB were detected quite frequently in the Danube River (35 % positive samples). Most of the positive findings come from the Slovakian and Bulgarian part of the Danube. Data indicate that levels of DDT in Bulgarian section of the Danube dropped considerably between the seventies and the nineties i.e. from 0.098 $\mu g.l^{-1}$ in the seventies to below 0.001 $\mu g.l^{-1}$ in the nineties. Levels of lindane in the Bulgarian part did not show any pronounced decreasing trends. Data from the Slovakian part of the Danube indicate a drop off in DDT, γ- and β-HCH concentrations by about 50 % between early seventies and late eighties.

A flood disaster took place in all Moravian part of the Czech Republic in July 1997. Agricultural areas and plenty of industrial and municipal landfills located along the River Morava and upstream of the Odra catchment area were flooded. As a result many types of toxic substances including PTS could have entered the surrounding environment. Also sediments from both rivers and its tributaries beds were washed out and re-deposited over flooded areas releasing different toxic substances previously accumulated.

Danube Delta is the largest wetland in Europe (580 000 ha), situated in the southeast of Romania and northwest of the Black Sea (Covaci et al., 2002). Data about the current contamination status of the lower Danube River and Danube Delta are very scarce. For organic pollutants, no systematic measurements are done in water and fish and thus, no data are available in the literature. Sediments collected in 1994 from the Danube Delta (Winkels et al., 1998) did not contain measurable concentrations of PCBs (< 5 $ng.g^{-1}$). Unfortunately, no measurements of pesticides, the main organochlorine contaminants in Romania (Covaci et al., 2001), were done at that time.

In 2000, PCBs and OCPs were measured in sediments collected at the mouth of the Danube Delta (Fillmann et al., 2002) and it was found that the high concentrations associated with the Danube indicate that the river is a major source of contamination to the Black Sea. In another study, PCBs and OCPs were measured in bird´s eggs collected in 1997 from the Danube Delta (Aurigi et al., 2000). It was found that DDTs are the main

contaminants in all samples The aim of a recent study (Covaci et al., 2002) was to evaluate the occurrence of important organic contaminants (PCBs, DDTs, HCHs, HCB, PBDEs) in biota (invertebrates, different species of fish and cormorant tissues) collected from the Danube Delta.

In comparing samples colleted in 1982 and 1997, contaminant levels were lower in samples of 1997 than those detected during the earlier survey. Such observation was expected since many chlorinated hydrocarbons have been banned by many European and other countries in the past 10 years.

3.1.6.3.5.River Odra

The River Odra is a one of the biggest rivers flowing to the Baltic Sea with the river basin of 118,861 km^2 (Protasowicki et al., 1999). Being the border river, it contains the contamination from Poland, Czech, and Germany e.g. the municipal and industrial wastes from 20 Polish and German cities may be found there. Because the river basin covers also a lot of the agricultural area, the subterranean waters feed it with noticeable amounts of organic matter, harmful and toxic substances. Therefore the Odra waters on the length of 741.9 km are below the 3rd class of purity, according to Polish standards, due to the amount of chemical, physical, and biological contamination.

No systematic investigations of sediments and waters on the pollution level by regulated organic compounds, i.e., polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides, volatile organic compounds (VOCs), have been conducted in that region. However, the data concerning the content of these compounds in the Baltic Sea, which can be considerably contaminated by the Odra River, have been recently published. A flood disaster took place in south of Poland in July 1997 similarly as other countries of Central Europe (Wolska et al., 1999).

The flood of 1997, as a result of flooding many cites, towns and villages along the Odra and ground water waterlogging of over 500 000 ha of arable land, caused the increase of the contamination of the Odra waters (Protasowicki et al., 1999)..

3.1.6.3.6.Russian rivers

The contribution of gross riverine organochlorine pesticide (OCPs) transport to estuaries of Russian seas and Lake Bajkal was determined to help understand OCPs transboudary transfer and to provide a basis for estimating Russia´s contribution to global pollution by these pesticides (Zhulidov et al., 2000). The official OGNK/GSN data ranks sea/ocean/lake basins in the following order based upon the amounts of total OCPs received from agricultural use: Eastern Arctic > Western Arctic > Pacific > Baltic > Caspian > Azov/Black > Bajkal. A similar ranking was obtained using an independent set of data: Eastern Arctic > Pacific > Caspian > Western Arctic > Baltic > Azov/Black. In terms of riverine flow-associated discharge of HCH isomers estuaries of the Kara, Okhotsk and Beloye (White/Barents seas received more pesticides than other seas. No HCH was discharged to estuaries of the Eastern Siberian and Bering seas. For DDT and its derivative (DDE), estuaries of the Kara, Caspian, Okhotsk and Baltic Seas received the greatest amounts. During our study period (1988 - 1996), HCH transport was more prevalent in the majority of rivers reflecting both the official ban on the use of DDT in the former Soviet Union and the greater popularity of HCH as a pesticide. In general, it appears that Russian rivers play a significant role in OCP contamination of some estuaries of regional seas, especially those of the eastern Arctic basin, such as the Kara Sea.

3.1.6.3.7.Britannia and Ireland

Trends in the concentrations of atrazine, lindane and simazine in the estuary of the River Thames between 1988 and 1997 were examined using linear regression methods to determine whether attempted reductions in pesticide discharges had improved estuarine water quality (Power et al., 1999). Concentrations of all the studied pesticides declined over the period, despite the influences of drought induced reductions in freshwater flow from the Thames catchment. Measured concentrations in the Thames Estuary are now similar to those found in other UK and European estuaries, suggesting that the Thames estuary is no longer of special concern.

PCDDs/Fs were detected in all sediment samples and the results provide a valuable data set for UK freshwaters (Rose et al., 1994).. The general distribution was very wide because of the inclusion of contaminated and background sites, but does reflect the overall frequency distribution of concentrations across England and Wales.

In order places results potentially contaminated sites into context, a number of background sites were also chosen for PCDDs/Fs analysis. If the background sites chosen are representative, the results suggest that in UK rivers the total PCDDs/Fs background concentrations are < 1 000 $pg.g^{-1}$, with a I-TEQ < 6 $pg.g^{-1}$. Whilst the

homelogue group and contribution to I-TEQ profiles from these background sites do vary, most show the predominance of OCDF/D and, to a lesser extent, HpCDD. Values are comparable to those found in UK soils and to surface sediments in other parts of Europe. The results indicate that the background PCDDs/Fs total concentrations in river sediment in England and Wales may originate primarily from direct deposition and indirect catchment runoff of atmospherically derived PCDDs/Fs. In general, levels of PCDDs/Fs in river sediments sampled were higher in industrial and urban areas.

3.1.6.3.8.Lakes

PAH concentrations detected in most central European Lakes are intermediate between contaminated sites near to urban/industrial centres (values of thousand $ng.g^{-1}$) and remote marine or lacustrine areas (a few hundred $ng.g^{-1}$). Lakes from Tatra Mountains have PAH levels similar or exceeding the concentrations reported for sediments near to urban suggesting atmospheric transport of PAHs to these environments is very significant.

PCBs, HCHs, DDTs, HCB and endosulfans were measured in waters from three European remote mountain lakes (Alps and Caledonian mountain from Region III and Pyrenee) (Vilanova et al., 2002). High HCHs concentrations were measured in the Alps (and also in Pyrennes), which was among the highest recorded in continental waters. Levels of other determined pollutants were low in comparison with other continental waters.

From determined HCHs, the most abundant isomer in Alpine lake was γ-HCH. These high levels of HCHs are close to the highest concentrations described for lacustrine waters. These results are surprising for such remote sites that only receive atmospheric input. The dominance of γ–isomer is in agreement with the accepted HCH product in the present European legislation.

These trends were confirmed also by measurements of bulk deposition concentrations of PCBs, HCHs, HCB and endosulfans in these remote European high mountains areas. The compounds of present use in agriculture, namely endosulfans and γ-HCH, exhibit large differences in mean deposition fluxes between the evaluated sites. In contrast, the compounds whose use is now banned exhibit a more uniform geographic distribution of deposition fluxes for α-HCH, PCBs and HCB (Carrera et al., 2002).

PCDDs/Fs were measured in 16 sections of sediment core from a freshwater lake in rural England (Green et al., 2001), Esthwaite Water, Cumbria, U.K. (54°21´N, 3°00´W). Local industries such as mining, quarrying, charcoal burning, and iron smelting appear to have had a minor impact on the PCDDs/Fs deposition in the lake. Since 1900, two major peaks in PCDDs/Fs input to the lake were evident. The first, reaching a maximum in the 1930s, had an unusual homologue pattern dominated by high molecular weight PCDFs, and the source of this input is unknown. The second, with a maximum in the 1970s, is in keeping with previously reported time trends for Europe and North America. Pre-1900, the TCDD/F isomer pattern was dominated by dimerization products of 2,4-dichlorophenol. Despite detailed knowledge of the catchment and of industry in the surrounding area, the identity of some sources and the contribution of other known sources remain unclear for each era.

The historical trends in the concentrations of toxaphene, its component homologue groups, and individual chlorobornane congeners, were determined in a dated sediment core from a mountain lake, Lochbagar, in Scotland, U.K., representing the first such profiles outside of North America (Rose et al., 2001). Toxaphene has been neither used nor produced in the U.K., and while some production was undertaken in France and Germany (1955 - 1990, main production in the early 1980s (Saleh, 1991), much of this was exported to Eastern Europe and Cuba (Heinish et al., 1994). Therefore, Lochnagar and its sediment record are ideally placed to monitor the long-range transport and historical deposition of this pollutant to an area of Europe remote from any direct treatment.

The profile of total toxaphene showed a bimodal distribution with maxima in the mid-1970s and early 1990s unlike the unimodal PCB profile (maximum 1973) in the same core. The earlier toxaphene peak shows agreement with the U.S. source curve and therefore may correspond to modelled global patterns while the later peak may be due to long-range transport from eastern and southern Europe or from still lower latitudes. Sediment toxaphene concentrations (14 $ng.g^{-1}$ dry wt (dw) at surface; 40 $ng.g^{-1}$ dw at maximum) and accumulation rates (surface 0.42 ng cm^{-2} yr^{-1}; maximum 1.6 ng cm^{-2} yr^{-1}) were considerably higher than levels in untreated sites in the Great Lakes region and the Canadian Arctic and are equivalent to those reported for the Great Lakes themselves where there have been additional riverine inputs.

The sediment record of total PCBs was also studies for the same Lochnagar sediment core. PCB concentrations begin to increase in levels dated to the mid-1930s and undergo a large increase during the 1960s. This increase

coincides very well with the known production of PCBs in the U.K. (Harrad et al., 1994; Gevao et al., 1997; Kidd et al., 1995). PCB profiles in dated sediment cores collected in remote lakes in Northern Finland (68 - 69° N) also show post-1950 deposition of PCBs with maximum in the 1970s (Vartianen et al., 1996). A peat core from an ombrotropic bog in northwest England also showed maximum PCBs in slices dated to the late 1960s and an approximately 50% decline in concentrations between 1970 and 1990 (Sanders et al., 1992).

PCDDs/Fs were detected in sediments from the 17th to 19th Century onwards with toxic equivalents (I-TEQ) below 1 $pg.g^{-1}$. Sediments at this time were dominated by OCDD in Herrenwieser See, comparable with results from 8000-year-old marine sediments and 19th Century sediments from Green Lake (New York).

The contamination of various Estonian water bodies with PAHs has been studied since 1972 (Veldre and Karlova, 2002). and demonstrated that Estonian small lakes were not highly polluted with BaP.

3.1.6.3.9.Freshwater biota

The use of bioindicators and bioaccumulators is very common in various POPs monitoring and research programmes and studies.

Example of these types of studies concerning to the determination of indicator and DL PCBs was done by Gregor and Hajslova (1998). Following samples of pooled fish (fillets, skin removed) collected in autumn 1997 were analysed: (i) barbel caught in Elbe river, locality Hrensko - close to the German border; yellow eel, from the same sampling site; roach caught in Skalica river, locality downstream from Rozmital and roach caught in Skalice river upstream from Rozmital.

12 years ago, a serious pollution incident by Delor 103 (Czechoslovakia name of PCBs- containing technical PCBs mixture with 48 %, w/w, chlorine) occurred at the locality Rozmital. Observed values indicate continuing high PCBs input at sampling sites downstream from Rozmital. Ten-fold higher total TEQs were found in fish living here compared to that collected upstream. Concentrations of non-ortho and mono-ortho substituted PCBs determined in barbel from Elbe river even exceeded values reported for some freshwater fish (pike-perch, perch) collected in seriously polluted Rhine, Meuse and their side-rivers. Hence, considering results obtained for barbel from Czech part of Elbe, may be assigned among the strongest PCB-contaminated waters in Europe.

High levels of dioxins and dioxin-like PCBs in eel from Dutch freshwater were reported in a screening of Dutch fishery products (van Leeuwen et al., 2002). To protect the Dutch citizens from the intake of high levels of dioxins by consumption of contaminated eel, a Dutch maximum residue limit (MRL) for eel was set at 8 pg PCDDs/Fs-TEQ.g^{-1} ww. Anticipating the new European MRL for dioxins and furans in fish (4 g PCDDs/Fs-TEQ.g^{-1} ww), an extensive survey was carried out on PCB and dioxin contamination of eel from the Netherlands.

Levels in farmed and imported eel are significantly lower those in the highest wild eel samples and none of farmed and imported eel (mostly farmed) exceed the EU MRL. The current MRL only accounts for the PCDDs/Fs-TEQ whereas for these samples PCBs are the main contributing compounds (61-97 %) to the total dioxin toxicity (total TEQ). In this respect, the EU MRL does not satisfy for protection of consumers.

3.1.6.3.10.References

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3.1.7. Terrestrial ecosystems

3.1.7.1. Introduction

Soils are natural sinks for persistent and lipophilic compounds, which adsorb to the organic carbon of the soil and, once adsorbed, remain relatively immobile (Buckley-Golder et al., 1999). Soils can receive inputs of environmental pollutants *via* different pathways of which the most important are: atmospheric deposition, application of sewage sludge or composts, spills, erosion from nearby contaminated areas. The concentrations in soil tend to reflect the baseline contamination of a region. Thus, urban areas exhibit higher concentrations than rural.

3.1.7.2. Regional and subregional activities

Most data are available for dioxin concentrations in soils, as a number of intensive surveys have been carried out. In almost all countries a broad range of dioxin concentrations was detected, as illustrated in Table 3-60, with the lowest concentrations below 1 pg I-TEQ.g^{-1} d.m. and the highest around 100 pg I-TEQ.g^{-1} d.m. In the Netherlands, most soil samples have been taken in the neighbourhood of municipal solid waste incinerators, where concentrations up to 252 pg I-TEQ.g^{-1} d.m. have been detected.

The highest concentrations reported are shown in the last column of Table 3.9. As the extent of measurement programmes varies considerably from one country to another, it is not possible to identify any individual country with dioxin concentrations in soils, which are significantly higher or lower than any other.

Table 3.9: Summary of dioxin concentrations in soil from EU Member States [pg TEQ.g^{-1} d.m.]

	Other types	Forest	Pasture	Arable	Rural	Contamin.*
Austria		<1-64	1.6-14			332
Belgium	2.7-8.9				2.1-2.3	
Finland						>90,000
Germany		10-30	<1-30	<1-25	1-5	30,000
Ireland	<1-8.6	4.8	<1-13			
Luxembourg	1.8-20	6.0			1.4	
The Netherlands					2.2-16	98,000
Sweden					<1	11,446
United Kingdom	<1-87				<1-20	1,585
* maximum measured concentration at contaminated sites						

Contemporary soil samples from 46 sites across the UK and 12 sites in Norway have been analysed for a range of PCBs congeners (Lead et al., 1997, Meijer et al., 2002). Results show spatial differences, in terms of concentration and congener profile. The difference is partly caused by an increased proportion of the mid-molecular weight congeners in the samples from Norway. The soils from southern Norway and the UK contained similar amounts of PCBs per unit area; those from northern Norway contained lesser amounts.

3.1.7.3. National monitoring programmes

Many monitoring and research projects which focused on soil contamination of PTS were performed during last ten years in CEE countries (Sáňka et al., 2000; Holoubek et al., 1994; Podlešáková et al., 1998).

Background values for heavy metals, PAHs and PCBs in the soils of Bulgaria were determined (Atanasov et al., 2001). Also soil samples from arable and forest areas in South Bulgaria were also collected and analysed for the presence of priority organic pollutants (PAHs, PCBs, OCPs) (Shegunova et al, 2001). The main pesticides found were DDE, DDD and DDT. Similarly, the assessment of the quality of contaminated soils in Romania, was given by Dumitru (2001). PAHs were determined in moldovian soils (Teyrytze et al., 2001).

The levels of HCH in soils of the Slovak Republic were described by Schlosserova (1993). Few, very broad campaigns (1984, 1987-89) were performed (1 711 samples of soils and agricultural products). The value of latter campaign showed that the contents of HCHs had decreased about thirty times in comparison to the samples studied in years 1986-89 (Table 3-65).

3.1.7.4. Soil contamination - research projects and pilot studies

Soil samples were collected in 1994 from various sites in a former Soviet army base localised near the town of Swinoujscie in the north-western corner of Poland and the possible contamination with PCBs was investigated (Falandysz et al, 1997). Elevated concentrations of PCBs in soil in a former military grounds were observed in US base in Veitnam and in the surroundings of many former Soviet army bases in Poland, former Czechoslovakia, former GDR and former Soviet Union.

Surface soil and sediment samples collected from the cities of Krakow, Katowice and Chorzow city in southern part of Poland in 1993 - 1994 were analysed for residue levels of hexachlorobenzene (HCB), isomers of hexachlorocyclohexane (α-, β-, γ-HCH), and DDT and its metabolites (DDD and DDE), chlordane compounds (CHLs) and polychlorinated biphenyls (PCBs) in order to evaluate their concentrations and distribution (Falandysz et al., 2000). Soil from the city of Katowice is relatively more polluted mainly by PCBs, but also by the other organochlorines. Both the soil in the cities of Krakow and Katowice are more polluted by organochlorines than soil from many other places in Poland.

In 1983/4 on the territory of the former GDR 260 000 ha of forests were treated with high amounts of DDT/lindane preparations from aircraft to combat the black-arched moth (*Lymanthria monacha*). Before that, in 1975 a stepwise ban for DDT was passed, which mainly worked well. The levels of Σ DDTs and also the percentage of the parent substance DDT usually decreased after banning. Other border-crossing co-treatments have been registered in the former Czechoslovakia, now the Czech Republic. The Table 3.10 describes higher levels Σ DDTs residues with high percentages of DDT in soil samples from the boundary mountain and decreasing levels if we are coming from the former neighbour, the former GDR towards the inner parts of Czech Republic and south border mountains (Sumava Mountains). Σ DDTs residues and the percentage of the parent substance are particularly low in the south of the Czech Republic, in the Sumava Mountains as well as in the area of CHMI/TOCOEN regional background observatory Kosetice.

Table 3.10: Σ DDTs and percentages of the parent substance DDT in soil samples from the Czech Republic [$ng.g^{-1}$]

Sampling site	DDT	DDE	DDD	Σ DDTs	% DDT in Σ DDTs*	References
Mumlava, Krkonose, 1 190 m, 1995	33	8	na	41	80	Holoubek et al., 1996;
Pudlava, Krkonose, 1 140 m, 1995	179	70	na	249	72	
Paseracky chodnicek, 1 310 m, 1995	99	36	na	135	73	
Jedlova, Luzicke hory, 710 m, 1995	302	84	na	386	78	
Lesna, Krusne hory, 800 m, 1995	2 390	795	na	3 185	75	

Sampling site	DDT	DDE	DDD	Σ DDTs	% DDT in Σ DDTs*	References
Nacetin, Krusne hory, 710 m, 1995	4 013	1 164	na	5 177	78	
Usti nad Labem, M, 1995	1 133	1	1	1 135	100	Podlesakova, 1996
Teplice, M, 1995	1 207	146	256	1 609	75 (89)	
Karlovy Vary, M, 1995	398	122	36	556	72 (77)	
Sokolov, M, 1995	522	209	40	771	68 (71)	
Cheb, M, 1995	264	167	25	456	58 (61)	
Kladno, M, 1995	63	53	7	123	51 (54)	
Praha, M, 1995	1 044	1 054	1	2 099	49 (50)	
Mnisek pod Brdy, M, 1995	651	245	4	900	72 (73)	
Pribram, M, 1995	28	31	1	60	47 (47)	
Boubin, Sumava, 1995	11	7	na	18	61	Holoubek et al., 1996
Cesky Krumlov, M, 1995	1	1	1	3	33 (50)	Podlesakova, 1996
Prachatice, M, 1995	1	1	1	3	33 (50)	
Kosetice, 1995	0.2	9	0.2	1.3	15	Vana et al., 2001

M – maximal value from 5 – 60 samples

* number without parantheses – original number of Heinisch and Kettrup, in parantheses - Σ DDTs DDT + DDE – same values for all samples from various authors

The measurements of PCBs and OCPs content in soil samples from Slovakia were part of very unique study concerning the environmental and human population load in anarea contaminated with PCBs (Kocan et al., 1999). As far as soil contamination – see more details in the Chapter Hot spots. A summary of results from measurements of soil samples is described in the Table 3.11.

Table 3.11: Summary of concentrations of PCBs and OCPs in soils [ng.g^{-1} d.w.]. Study of environmental and human exposure load in the area contaminated with PCBs (Kocan et al., 1999)

Pollutants	Dumps (n=6)	Producers of precoated gravel (n=8)	District Michalovce (n=11)	District Stropkov (n=4)
Σ PCBs	170 - 8 600	43 - 53 000 000	1.5 - 28	3.6 - 9.2
HCB	< 0.2 - 3.9	< 0.2 - 8.9	0.028 - 3.7	0.57 - 5.1
DDT + DDE	< 0.009 - 1 080	1.1 – 20	0.65 - 51	1.5 - 490

Very complex review of contemporary information on the concentrations, burdens and fate of PAHs was published by Maliszewska-Kordybach (1999).

Mean contents of PAHs in urban soils are within the range of about 1 000 - 3 000 ng.g^{-1} but values of 30 000 to 50 000 ng.g^{-1} were found in some locations. The average PAHs level in rural European soils is rather uniform with median values of about 300 - 400 ng.g^{-1}.

The evaluation the content of PAHs in arable soils in Poland with special focus on the agricultural areas exposed to anthropogenic stress was performed as a part of country-wide Agricultural Soils Monitoring Programme in the years 1995 - 1997 (Maliszewska-Kordybach and Terelak, 1998).

Concentrations of selected PTS (PCBs, HCHs, DDTs, HCB) in soil from different Romanian locations (Covaci et., 2001). Soil samples from Iassy were compared with soil samples collected from different locations all over Romania, which includes various types of sites (rural, urban, industrial and near waste incineration facilities, plus one near OLTCHIM factory). A comparison of concentrations of POPs in soils from different types of sites revealed that highest concentrations were found near industrial sites, especially near an organochlorine producing factory (OLTCHIM –Rm. Vilcea). Except for DDTs, all POPs were significantly higher than in other locations,. Even after more than 10 years from the DDT ban, DDTs concentrations in soil were significantly higher at rural sites, sometimes close to the actual tolerance limits for agricultural purposes.

3.1.7.5. High-mountain ecosystems, using of needles as a bioindicator

Many recent studies have used vegetation which bioaccumulates organic pollutants for monitoring studies (Larsen et al., 1985; Reischl et al., 1989; Moser et al., 1991; Kylin 1994; Simonich and Hites, 1995). Vegetation has been used to indicate ubiquitous pollutant contamination levels. In order to determine the general contamination level of cities, countries, and continents, many samples from variety of locations are required in order to minimise the effect of point sources and overcome the inherent variability of samples from the same size. Vegetation integrates contamination over time, and vegetation samples are much easier to collect than air samples, especially in remote locations. Vegetation has been used to identify point sources of organic pollutants, to determine regional contamination within cities, countries, and continents, and to determine the global contamination of organic pollutants (Simonich and Hites, 1995).

As biomonitors are also frequently used the outer waxy surfaces of pine needles, kale or grass, which absorb atmospheric lipophilic pollutants and serve as an excellent monitoring system for many of PTS (Buckley-Golder et al., 1999; Weiss et al., 1998, 2000; Calamari et al., 1991, 1994; Simonich et Hites, 1995; Holoubek et al., 2000). The advantage of biomonitors, such as pine needles, is that they are widely spread over Europe and samples can be easily obtained. As there is a database of measurements taken from a wide range of locations over long periods of time, the analytical results from different locations or years can be compared. However, a linear correlation between PTS concentrations in pine needles, or any other vegetation, and the high volume samplers or deposition samples cannot be established. The concentrations in biomonitors reflect the ambient air concentrations during the time of exposure (growth period) of the plant. With pine needles, accumulating effects over several years can be determined.

Vegetation has been used by many countries to monitor ambient air concentrations. The use of these biomonitors was found useful for both routine programmes on a long-term basis and to identify potential hotspots around point sources of emissions. The use of kale was successfully implemented around a steel producing plant in Luxembourg, where mean concentrations up to 106 pg I-TEQ.g^{-1} d.m. were detected; in Germany 12.6 pg I-TEQ.g^{-1} d.m. were determined close to combustion sources. In Austria, spruce needles were used as biomonitors: the background concentrations were in a very narrow range between 0.3 and 1.9 pg I-TEQ.g^{-1} d.m. Normally, baseline concentrations were around 0.5 pg I-TEQ.g^{-1} d.m. in rural areas and around 1-1.7 pg I-TEQ.g^{-1} d.m. in urban areas. Studies from Bavaria and Hesse in Germany reported that mean dioxin concentrations in pine needle ranged from 0.53 to 1.64 pg I-TEQ.g^{-1} d.m. However, in the neighbourhood of the Brixlegg copper reclamation plant in Austria, between 51 and 86 pg I-TEQ.g^{-1} were determined. In Welsh Rye grass, which is typically exposed for four weeks during the summer, concentrations were between 0.5 and 1 pg I-TEQ.g^{-1} d.m. However, as mentioned above, a linear correlation between dioxin concentrations in vegetation and the high volume air samplers or deposition samples cannot be established.

Selected PTS compounds (PAHs, PCBs, OCPs, PCDDs/Fs) are monitored in the air, soils and needles from sampling sites located in Czech boundary high-mountain ecosystems (Holoubek et al., 1994c, 1998a, b), similarly also in Poland (Migaszewski, 1999).

A series of papers by Kylin and co-workers (Kylin et al., 1994; Strachan et al., 1994; Eriksson et al., 1989; Jensen et al., 1992) has outlined the use of Scots pine (P. Sylvestris L.) needles to determine the regional contamination of organochlorines in Europe. Calamari et al. (1994) used pine needles to determine regional contamination of DDT, HCHs and HCB in Europe. Persistent organochlorine compounds (OCPs, PCBs, PCDDs/Fs) in spruce needles from Western Finland (Sinkkonen et al., 1995). Reischl et al.(1987) have reported on somewhat higher concentrations in spruce needles collected from a rural area in Northern Bavaria. The study of the pathway of benzo(a)pyrene (BaP) migration from bulk deposition to soil and vegetation, with special emphasis on the forest ecosystem, was performed in Lithunia (Milukaite, 1998). 25 remote forest sites from all over Austria and located far away from settlements, factories and public roads were investigated (Weiss et al., 1998, 2000). All sites in the Alps are located several hundred meters above the bottom of the valley. Three exposed alpine mountains sites situated at one slope but at different altitudes (altitude profile) were included to investigate the influence of altitude on the concentrations detected (Weiss et al., 1996; 1998a; Horstmann and McLachlan, 1998). Scots pine (*Pinus sylvestris* L.) bark samples were collected at two field sites (Neuglobsow, Rösa) and in different years between 1987 and 1996 in the east of Germany (Schulz et al., 1999).

3.1.7.6. Terrestrial wildlife

An important part of the programme the German Environmnetal Specimen Bank is focused on the terrestrial ecosystems especially in the areas of the national parks of mud flats in Schelswig-Holstein and Lower Sacony (North Sea) and the areas of Sarland and the Halle/Leipzig/Bitterfeld as urban-industrialized regions (Kettrup et al., 2002). Soil samples, earthworms (*Lumbricus terrestris* and *Allolobophora longa*), and deer livers (*Capreolus capreolus*) as well as in city dove eggs (Columbia livia f. domestica) were analysed for the PTS under list of SC contents in these model regions.

In suburban Warsaw the concentrations of organochlororine insecticides and PCBs were measured in eggs, brains, livers, carcasses and stomac contents (wet weight) and lipids of house sparrow (Passer domesticus) and tree sparrow (Passer montanus) nestlings in 1988 - 1989, and in 1995 only in brains of mature and one-year birds (Niewiadowska et al., 1998). It was widely used in years 1955 - 1975 to fight against the Colorado beetle. It was banned from retail trade in 1971 and withdrawn from use by 1974.

3.1.7.7. Cow´s milk

Cows' milk has been used by several countries as a biomonitor for ambient air contamination around potential dioxin point sources. Based on experiences from The Netherlands and Germany, cows' milk concentrations around 1 to 3 pg I-TEQ.g^{-1} fat should be considered as background for highly industrialised and densely populated countries. Both countries have set upper limits for the marketing of cows' milk, which are at 5 and 6 pg I-TEQ.g^{-1} fat, respectively. The German regulation states that if dioxin concentrations above 3 pg I-TEQ.g^{-1} fat are detected, such concentrations should not be considered as background; a nearby dioxin source should be identified and, if possible, eliminated. In view of these experiences and guidelines, the numbers in Table 3.12 show data from hotspots that have been identified and subsequently monitored in Austria. The case of the Brixlegg copper reclamation plant in Austria revealed a severe problem for the farmers in the neighbourhood. In Austria, it was more than five years before the dioxin concentrations returned to background levels. The surveys performed in Ireland were designed to obtain a general overview on concentrations in cows' milk and did not target any point source. All concentrations were very low, based on general European data for dairy products.

Table 3.12: Summary cows' milk concentrations as biomonitors around potential dioxin point-sources from EU Member States [pg TEQ.g^{-1} fat]

	Austria	Ireland
Source	Copper reclamation plant	General surveys, no point source
Range	5-69.5	0.13-1.5

To assess the presence of PCDDs/Fs in the Irish environment, the Environmental Protection Agency (EPA) of Ireland conducted a study on the levels of PCDD/Fs in cow's milk in 1995 (Hamm et al., 2001). It was found that I-TEQs in Irish cow's milk samples from so-called background stations were lower than other European countries.

When comparing the PCDD/F TEQs of the Irish cow's milk samples from the current study with those of 1995, it can be seen that the low PCDD/F level found in 1995 is confirmed by the year-2000 data. As can be seen from Table 3.13, the range of values is even slightly lower in the background samples from 2000. I-TEQs are used for comparison since the older data were calculated by using I-TEFs. Compared to recent cow's milk data from other European countries (e.g. France, Germany, Spain) dioxin levels of Irish cow's milk are still in the lowest range. The same seems to be true for the total TEQ when including the dioxin-like PCBs.

Table 3.13: Comparison of the 1995 and 2000 PCDD/F data of Irish cow's milk from background locations

Year of sampling	Minimum [pg I-TEQ.g^{-1} fat]	Maximum [pg I-TEQ.g^{-1} fat]	Median [pg I-TEQ.g^{-1} fat]	Mean [pg I-TEQ.g^{-1} fat]
1995 (n=20)	0.14	0.50	0.21	0.23
2000 (n=24)	0.09	0.35	0.20	0.20

3.1.7.8. Sewage sludge

In Austria and Germany, sewage sludge for application in agriculture has to be analysed for dioxins and comply with legal limit values. These countries have established a maximum permissible concentration of 100 pg I-TEQ per g dry matter for sewage sludge applied to agricultural land. Additional data were available from Denmark, and the UK. As can be seen from Table 3.14, in general, the concentrations ranged from below 1 pg I-TEQ.g^{-1} d.m. to around 200 pg I-TEQ.g^{-1} d.m, with levels in Germany reaching over 1 000 pg TEQ.g^{-1} d.m. Average concentrations of dioxin in sewage sludge are quite similar for each country, lying between 15 and 40 pg I-TEQ.g^{-1} d.m. These findings indicate that similar sources are responsible for the contamination in sludge. The results, mainly from Germany and Sweden, revealed that "normal" effluents from households, especially from washing machines, could explain these results. Additional inputs can originate from dishwashers but also run-off from streets and from roofs. Industrial inputs, where untreated effluents enter the municipal sewer systems, can cause very high contamination in sewage sludge. In such cases, more than 1 000 pg I-TEQ.g^{-1} d.m. has been detected.

Table 3.14: Summary of sewage sludge concentrations from EU Member States [pg TEQ.g^{-1} d.m.]

Country	Austria	Denmark	Germany	Sweden	UK
Range	8.1-38	0.7-55	0.7-1,207	0.02-115	9-192
Average	14.5	21	20-40	20	

3.1.7.9. References

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3.1.8. Hot spots

3.1.8.1. Introduction

The sources and environmental levels of the PTSs in the countries of Central and Eastern Europe are broadly described in the State-of-the-Art Report (Holoubek et al., 2000). The first complex descriptions of the state of environmental pollution with PTS types of compounds in Central and Eastern European countries (CEECs), was prepared by Heinisch et al. (1994,1997a,b,c).

Special attention must be given to obsolete PTS pesticides. This problem poses the greatest danger to the environment and people, which is brought about by 'chemization' of agriculture in the CEE countries. Many of the CEE countries have no special sites for the storage of hazardous waste or installations in which these types of chemicals could be safely disposed of by combustion or non-combustion processes. In Poland, the stockpile of obsolete pesticides is estimated to be about 60 000 tonnes – about 10 000 t in tombs, 25 000 t in storehouses and about 25 000 t at farms round the country (Stobiecki, 1998). The 1996 inventory of banned organochlorine pesticides stockpiles in Bulgaria showed about 35 t, which is relative high quantity for the small territory of Bulgaria (Tasheva, 1998). There are 15 000 t or 22 000 000 t stockpiles in Ukraine mostly containing pesticides (Kundiev, 1997). The situation with obsolete organochlorine pesticides might be similar in other CEE countries.

3.1.8.2. Former USSR

Highest levels of atmospheric air pollution with polycyclic aromatic hydrocarbons (PAHs) are found in cities where the world`s largest aluminium and steel plants are located: Shelekhov, Novokyznetsk, Bratsk, Magnitogorsk, Nizny Tagil, Krasnoyarsk, Chelyabinsk and some others, where the PAH content in the air amounts to 5 – 15 $ng.m^{-3}$ (Kurlyansky, 1997). By the data (Milyaev, 1997), total emissions of benzo(a)pyrene in Russia in 1991 and 1992 were 174.863 ($t.y^{-1}$) and 89.408 ($t.y^{-1}$) respectively.

Ten thousands of tonnes of DDT and HCH were used in the USSR in the period of 1950s-80s. DDT was being used even almost 20 years after its ban (Fedorov, 1999; Fedorov and Yablokov, 1999, Kundiev, 1997).

The pollution by dioxins and dioxin-like compounds are especially serious in the cities of (1) former chemical weapons production (Novocheboksarsk, Volgograd, Dzerdzinsk, Chapaevsk, Berezniki, Novomoscowsk, etc.), (2) former PCB production and capacitors filled with PCBs (Dzerdzinsk, Novomoscowsk, Serpukhov, etc.), and (3) the manufcture of organochlorine pesticides (Ufa, Chapaevsk, Volgograd, Novocheboksarsk, Dzerdzinsk, Vulnary, etc.) (Fedorov, 1999; Fedorov and Yablokov, 1999).

In Russia, PCBs were produced from 1939 to 1989-1993 mainly at plants "Orgsteklo" (Dzerdzinsk) and " Orgsynthesis" (Novomoscowsk) under three trademarks: Sovol (a mixture of tetra- and pentachlorinated PCBs used as a plasticiser in paints and varnishes, total 1939-1993 production was 52 500 t; Sovtol (Sovol mixed with 1,2,4-trichlorobenzene mostly in a ratio of 9:1, then called Sovtol-10, used in transformers, total 1939-1990 production – 57 000 t) and TCB (mixed isomers of trichlorobiphenyl used in capacitors, total 1968-1990 production – 70 000 t (AMAP, Report, 2000).

It was shown that the most contaminated are the Central, Ural and North-Western Russian economic regions. Ufa, Shchelkovo, Noginsk, Chapayevsk and Dzerzhinsk (where chemical plants using chlorophenols operate) are characterized by increased dioxin levels in the environment (Danilina, 1997). It was estimated that in 1995 dioxin emissions in the areas of Chapayevsk, Dzersinsk and Ufa were 740 g, 480 g and 900 g respectively (Kurlyanski, 1997). Dioxin air pollution may have other sources. High dioxin concentrations were observed in workmen´s settlement in Chapaevsk and other sites outside of plant. The origins of this dioxin contamination are most likely atmospheric transport and deposition from the plant territory. High PCB levels were found in soil samples taken in 1988 the vicinity of a capacitor plant in Serpuchov: 2 km to the north from the plant concentration was up to 35.7 ppm, and at 0,3 km to the south - up to 11 000 ppm. There is a serious dioxin pollution of water sources in the towns, including Belaya River with tributaries in Ufa, Chapayevka River in Chapayevsk (and the Volga) and others.

The main source of dioxin contamination in Ufa is the plant Khimprom. For 55 years of the plant operation several chloroorganic products containing dioxins as by-products have been manufactured at large scale – 2,4-D, 2,4,5-trichlorphenol (TCP) and other chlorophenols. In 1964-1967, there was the production of butyl ester of 2,4,5- trichlorophenoxyacetic acid (50-60 tons per month). During the production 128 cases of chloracne at workers were observed. Industrial buildings where these chemicals were produced still exist and they remain hazardous in terms of dioxin pollution. ly. Samples of technical 2,4,5-TCP contained up to 0.65 ppm of 2,3,7,8-TCDD. Such a long period of producing dioxin hazardous products resulted in pollution of the Khimprom plant territory. Soil samples from the plant territory contain dioxin from 0.4 to 10 ppb including the soil at the depth of several meters. The highest pollution was found in the samples taken near a chlororganic waste incinerator that had been a source of dioxin emission for a long time. The territory of the industrial waste landfill site is an area of extreme pollution. Thus in bottom sediment of the pond formed by ground waters from the plant and landfill site territory the concentration of 200 ppb was found. Analyses of human milk samples taken in towns villages of the region showed the highest levels in samples from Ufa and from neighbouring (about 100 km) Blagoveshchensk (25.9-27.1 pg $TEQ.g^{-1}$). This is most probably due to transfer of pollution from the chemical plants to the town. Increased PCDDs/Fs level in milk samples from Iglinsky and Sterlitamaksky (21.9 and 26.7 pg $TEQ.g^{-1}$) districts are accounted for by their location in the vicinity of industrial centres.

3.1.8.3. PCBs in Slovakia

PCBs called Delor (Delotherm, Hydelor) were produced in the Chemko chemical plant in Strazske (Michalovce District) in eastern Slovakia from 1959 to 1984. Officially 21 482 tonnes of PCBs were produced: 9 869 tonnes, i.e. 46 percent, was exported mainly to former East Germany and the rest, i.e. 11 613 t was used inside former Czechoslovakia [Kocan et al. 1998]. There was an attempt to manufacture polychlorinated terphenyls in Chemko. About 35 t were produced of which about 30 t were used at glue production for furniture industry.

It has been estimated that in addition to the amount produced about 1 600 t of PCB waste were generated during the production. A part of the Chemko PCB waste entered the environment mainly via the factory effluent canal causing the contamination of the Laborec River and Zemplinska Sirava Lake. Another part could lie at a Chemko landfill site in a form of contaminated soil mixed with miscellaneous production waste. The rest, that is about 1 000 t, is stored in store-houses situated on the territory of the factory including lots of drums that were collected in 1992 in a forest area above the Chemko factory. There is an ongoing project dealing with the non-combustion disposal of the waste PCB formulations are still used in Slovakia in closed systems. According to questionnaires sent in 1997 to PCB users, the PCBs are used only in power capacitors which are located at transformer and switchgear units. Up to 1 000 t of PCBs could be encased in power capacitors that are still in use or disabled and stored at their users.

Analyses showed that highest PCB levels were found in a muddy part of an effluent canal flowing from the Chemko factory (mean 3 000 ppm, dry weight). No doubt that polluted effluent canal emptying into the Laborec River has caused its contamination (3.9 ppm behind vs 0.052 ppm in front of the confluence). The Zemplinska Sirava Lake (33.5 km^2 in surface area) that is partly filled from the Laborec contained several hundred times higher PCB levels if compared with a similar lake in a control area (1.7 to 3.1 ppm vs 0.007 to 0.01 ppm). The control area was the Stropkov district about 60 km upwind and upstream far from Chemko in Strazske. Based on those findings, one can estimate that many tonnes of PCBs are still adsorbed in the sediments of the effluent canal, Zemplinska Sirava and Laborec (Kocan et al. 1999, 2001, Petrik et al. 2001b).

Samples were taken from an upper soil layer near the disposal sites of the PCB manufacturer (Chemko), agricultural fields in the districts of Michalovce (polluted area) and Stropkov (control area), and at several plants around Slovakia preparing gravel coated with asphalt formerly using PCBs in their heat-exchangers. PCB levels in the soil samples taken from the agricultural fields near some towns and villages were considerably lower (on average 0.008 ppm) than those taken from the neighbourhood of the disposal sites and plants mixing asphalt and gravel. Those plants are often situated close to quarries, i.e. in mountains on rocky ground, have been preparing asphalted gravel to be used for road construction. It is known that because of the untightness in heat-exchanging systems filled with PCBs hundreds of tonnes of PCBs leaked from those systems. PCB concentrations peaked at 53 000 ppm in a soil sample taken under one of the heat-exchangers. However, high PCB levels were also observed in agricultural (35 and 38 ppm) or forest soil (3.9 and 7.5 ppm) taken near those plants. As soil from the vicinity of the major Chemko landfill site, which could be contaminated by air transported particles only, contained increased PCB levels (0.4 to 5.8 ppm), it is likely that this dump may contain large quantities of PCBs. Similarly PCB waste might be present in the municipal dump

of Michalovce (district town) since increased PCB concentrations were found in a sample collected close to the dump (0.17 ppm) (Kocan et al. 1999, 2001).

Likewise the sediment, fish from the Michalovce waters contained much higher PCB levels than those from the control area. The maximum lipid adjusted value peaked even at 900 ppm. It was confirmed that predatory fishes are more exposed than fishes feeding on plankton or benthic food. It was observed that the environmental pollution of the Michalovce District with PCBs has reflected in the exposure of forest and field wildlife, as well.

Higher PCB content found in some foods available in the polluted district of Michalovce in particular that come from locally raised animals has evidently caused increased exposure of the human population of that district. Average PCB concentration of 4.2 ppm in blood lipids taken from the human general population living in the Michalovce District was 3.5-times higher than that in the control Stropkov area (1.2 ppm). People eating foods coming from animals kept on small family farms at their houses and fed mainly with local feed contained significantly higher PCB levels in their blood serum lipids. While an average of 8.6 ppm was found in the blood lipids of former Chemko workers, blood lipids of fishermen consuming fish from Laborec and Zemplinska Sirava contained 11.2 ppm on average (the max value was 60 ppm; the highest level found in the blood lipids of a fisherman outside the study was 230 ppm).

Within the 2nd round of the WHO-coordinated exposure study on the levels of PCBs, PCDDs and PCDFs in human milk running in 1993 it was shown that PCB content in samples coming from the area of former PCB production in Slovakia and an area of PCB application (paint industry) in the Czech Republic were 3—25-times higher than levels in samples from other European countries. Dioxin levels were similar to the European average although PCDF contribution was dominating because of high PCB exposure (WHO/ECEH 1996).

3.1.8.4. Spolana Neratovice in the Czech Republic

The chemical factory of Spolana Neratovice is situated approximately 25 km north of Prague at the Elbe River. It produced in the period 1965-68 the chlorine herbicide 2,4,5-T and chlorinated phenols. A part of 2,4,5-T was even exported to the USA and was applied as the component of "Agent Orange" within the Vietnam war. During production due to equipment failures, a huge amount of dioxins (in particular, the most toxic 2,3,7,8-TCDD) was formed and former factory buildings containing products, intermediates, installations, etc. currently belong to the most dioxin-contaminated sites on the globe. Moreover, soil in the factory is highly contaminated with organochlorine pesticides produced there, as well. The 2,4,5-T and chlorophenols production was stopped in 1968 when about 80 cases of occupational diseases developed (55 workers were hospitalized mainly with severe chloracne manifestations and porphyria) (Pazderova-Vejlupkova et al., 1981, Pelclova et al., 2001).

Chemical analysis proved an extremely high degree of contamination of waste products stored in production buildings, building walls and floors, air, soil and ground water. The highest concentration of dioxins (over 24 ppm of 2378-TCDD) was measured in the residues of chemical substances. It is assumed that there are tons of that waste stored in the buildings. The immediate toxic impact of dioxins in the air of the contaminated buildings was proven by a rabbit experiment in the 1970s. Rabbits in cages were located in the buildings to be exposed only to dioxin-contaminated air. The rabbits started to died on the 7th day of the experiment. Autopsy showed a significant damage of the liver, lung and kidney.

The Spolana factory including some of the dioxin-contaminated buildings were flooded in 2002 and one can expect dioxin release into agricultural fields and Elbe River and its sediment. The extent of environmental contamination will be mapped in detail. In addition, a start will be made to produce a definitive long term solution for the dioxin-contaminated buildings and soil in their vicinity in Spolana Neratovice (Zemek and Kocan, 1991, Kocan et al., 1991).

3.1.8.5. Bitterfeld

Besides the Buna-Werke, the chemical enterprise Chemiekombinat Bitterfelf (CKB) was the most important production and processing site of organochlorine substances in the former GDR. In 1980s, not only di-, tri- and tetrachloromethane and trichloroethane were produced in amounts of 10 000-20 000 $t.y^{-1}$, but also 73 000 t technical HCHs were synthesized in 1967-1982 and processed to 5 500 t of lindane. In the same period, estimated 50 000 t DDT were synthesized at the CKB. Especially problemat was the yield of very high amounts of waste products like hexa- and pentachloroethane and the “ballast isomers” α–, β–, δ– and ε–HCH. These persistent and toxic substances were disposed of in former brown coal mines.

This procedure has led to environmental burdens because not only in the immediate vicinity of the CKB, but also in the river Mulde, directly influenced by the CKB, partially up to the present DDT and HCH may be found in the sediments and fishes. Comparisons with two other rivers from the region have been documented in Heinisch et al. (2001).

Time series of the course of DDTs and HCHs contents in monthly sediment samples of the rivers Mulde, Saale and Elbe in Saxony-Anhalt are shown in Table 3.15.

Table 3.15: Sediment contents of DDTs and HCHs in monthly collected sediment samples from the rivers Mulde, Saale and Elbe, Saxony-Anhalt (arithmetic means of all samples per year)

Year	Contents of Σ DDTs [ppb]			Contents of Σ HCHs [ppb]		
	Mulde/ Dessau	Elbe/ Magdeburg	Saale/ Gr. Rosenb.	Mulde/ Dessau	Elbe/ Magdeburg	Saale/ Gr. Rosenb.
1994	4 840	305	100	410	40	20
1995	1 590	290	90	855	230	15
1996	2 170	485	75	1 356	10	< 5
1997	445	225	70	235	20	< 5
1998	835	275	80	965	30	10
1999	1 040	285	65	970	25	10
Σ DDTs = Σ DDT + DDE + DDD (2,4´ isomers); Σ α– + β– + γ– + δ– + ε–HCH						

Especially the aquatic sediment represents a sink and slowly flowing source for the substances. The presence of partially strongly enhanced HCH and DDT concentrations in the vicinity of the CKB could be found in earthworms (*Lumbricus terrestris),* city dove eggs *(Colomba livia),* deer livers *(Capreolus capreolus)* and pine shoots *(Pinus sylvestris)* as late as in the ninetees.

3.1.8.6. References

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3.1.9. Conclusions

Region III has a wealth of information concerning environmental levels of PTS, but geographic distribution of the available data is not equal for all parts of Region, with a better situation is in some countries of the EU and Central Europe.

Very good and traditional monitoring systems concerning PTS exists (EN ECE EMEP, OSPAR, HELCOM) which are oriented to air and deposition (EMEP), seas (OSPAR, HELCOM); some new are ongoing (Caspic Sea, Black Sea). As far as rivers, monitoring is mainly conductedon the national level, but a lot of multinational or regional activities already exist (Rhine, Danube).

The measurements of PTS levels in some other compartments such as lakes, soils or vegetation is partly performed based on the international programmes (IM EMEP), national monitoring programmes (soils) or pilot /research projects (biota, lakes). Human exposure is measured and studied on the European levels (activities WHO Europe) and very frequently on the national levels.

Although monitoring indicates that the loads of some hazardous substances have been reduced considerably over the past ten years especially in the Baltic Sea region, problems still persist. Comprehensive knowledge about the impact of most available chemicals, and their combinations, on human health and the environment is still lacking. The increasing number of these man-made substances is a matter of concern and calls for the application of the precautionary principle. On the other hand seas such as Black or Caspic still have a lot of heavily contaminated sites where petroleum hydrocarbons and phtalates are the dominant organic contaminants of the Caspian Sea. Only traces of persistent organochlorines were detected in the Caspian seals (highest section of the food web). Levels of contamination of the Caspian Sea have decreased significantly during the last 10 years.

The loads of many substances have been reduced by at least 50 % since the late 1980s - mainly due to the effective implementation of environmental legislation, the substitution of hazardous substances with harmless or less hazardous substances, and technological improvements.

In former communist countries reductions have been mainly due to fundamental socio-economic changes.

The OCPs are no longer in use, have never been used, or have even been banned within the Region III. But one serious problem that remains is that in some countries various obsolete pesticides still remain in temporary storage awaiting suitable disposal.

Polychlorinated biphenyls (PCBs) are no longer produced or used in new ways. Inventories are still being carried out in CEECs. Following an analysis of the legislative situation throughout the CEE part of Region, and the current uses, stockpiles and releases of PCBs measures have been proposed to ensure their safe handling and to reduce releases of PCBs from existing equipment.

As a results of former production, long time and widespread use and also long-range transport from other part of the Globe, OCPs, PCBs, PCDDs/Fs and PAHs and also some newer PTS are found in all environmental compartments including remote high mountain European sites, but principially decreasing trends are observed.

In this context, it is important to remember that a lot of countries of Region, such as the UK, Germany and others have a long industrial history, involving combustion activity in the form of wood and coal burning. For example in the UK, over 65 million ton of coal was being burned each year nationally in the 1850s. The

smelting of metals and the production of iron and steel also have a long history in the UK and Europe, processes known to have significant PCDDs/Fs emissions. It is important to remember that the history of PCDDs/Fs environmental inputs/burdens in the UK and Europe may therefore not be mirrored in other regions of the world.

Several studies reported that air PCDDs/Fs levels are declining in urban/industrialized centres. These trends are observed in Western Europe and are believed to be largely due to emission abatement actions taken in the early nineties. The decline of PCDDs/Fs levels in the atmosphere resulted in a decrease of these compounds in "atmospherically impacted" media such as vegetation, cow´s milk and meat products. Moreover, human dietary intake of dioxins and furans dropped by almost a factor of 2 within the past 7 years.

Analyses showed a decrease in concentrations of PAH compounds in the particle-phase in ambient air during the second part of 80´s. This is a result of cars equipped with catalyst engines becoming mandatory after 1991. Also improvements to fuel and the increased use of district heating, contribute to this trend. As far as the last 10 years, the annual average concentrations of PAHs seem to stagnate due to a permanent increase of motorized traffic on the one hand and a better combustion technology and an increase in the use of natural gas for domestic heating on the other.

Relatively worse situations can be observed in the towns in the former communist countries, where the number of cars dramatically increased after the political changes. The same problems are apparent inall larger cities in CEE countries after the political changes – an extremely high increase of town traffic and decreasing contributions from former industrial sources as the result of declining production.

3.2. ECOTOXICOLOGY OF PTS OF REGIONAL CONCERN

3.2.1. Introduction

This chapter describes the effects in organisms other than humans, which have been proved for Region III Europe by means of special research. The term "ecotoxicology" will be used to discuss the effects of persistent toxic substances (PTS) on both the aquatic and terrestrial biota. This approach is well correlated with the definitions given to "ecotoxicology" during the last 25 years. For example, it has been stated by Truhaut (1977), that ecotoxicology is the branch of science concerned with the study of toxic effects, caused by natural and synthetic pollutants, to the constituents of ecosystems in an integrated context. Moriarty (1983) pointed out that ecotoxicology is the natural extension from toxicology, the science of poisons on individual organisms, to the ecological effects of pollutants. Jorgensen (1990) was considering ecotoxicology as the science of toxic substances in the environment and their impact on living organisms. Landis and Yu (1995) have defined ecotoxicology as the branch of science dealing with the study of the impacts of pollutants upon the structure and function of ecological systems (from molecular to ecosystem). Hoffman (1995) was considering ecotoxicology as the science of predicting effects of potentially toxic agents on natural ecosystems and non-target species.

3.2.2. Overview of harmful effects

As a consequence of persistence and high bioaccumulation potential, PTS can accumulate to relatively high levels in biota even at low environmental exposures e.g. for the Great Lakes (Swain et al., 1992) and Lake Baikal (Lebedev et al., 1998; Poliakova et al., 2000). In the aquatic environment the primary root of initial entry into the food chain is through active uptake of PTS-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 PTS are less well understood. However it is known that PTS can be absorbed through plant surfaces. In particular, pine needles have been found to be useful indicators of atmospheric contamination by organochlorine ecotoxicants (Eriksson et al., 1989). For HCB, HCH and toxaphene, 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).

Since the results of manipulated toxicity tests can significantly differ from the ecological reality we will discuss only results based preferentially on reported field studies and observations. Indoing so, we will bear in mind, that in some cases adverse (or non-physiological/irregular) effects are observed in the field, but the links/correlations between these effects and chemical contamination are complicated and are hard to be evaluated as a causal/specific/selective result of contamination (especially with respect to particular single chemicals or group of chemicals). In many situations no particular chemical is often identified as responsible for the observed effect.

3.2.3. Mechanisms of harmful effects

The most important known adverse effects of PTS in biota other than human include:

- Reproductive impairment and other endocrine-dependent effects;
- Neurobehavioral toxicity;
- Genotoxicity and carcinogenicity;
- Immunotoxicity

The majority of adverse effects observed in the field relates to vertebrate animals (fish, birds, mammals). On the other hand, laboratory evidence as well as the target toxicity of pesticides directly implicate significant adverse effects in other biota (invertebrates, algae, plants, bacteria). Suprisingly, there is a significant lack of information concerning the ecological consequencies of PTS toxicity to organisms belonging to the lower levels of trophic chains (primary producers – algae, plants, bacteria).

3.2.3.1. Nonspecific toxicity (narcosis)

Simple, nonspecific toxicity is a characteristic of all organic chemicals that can traverse a biological membrane (Lipnick, 1993). All organisms – bacteria, plants, invertebrates, and vertebrates – can exibit narcotic effects when exposed to organic chemicals, and such responses have been found in laboratory experiments.The actual mechanism of action is not known, the two leading theories being the „membrane swelling“ and the „protein pocket“ (Abernethy et al., 1988). The universality of narcotic effect is reinforced by the fact that specifically acting chemicals, such as pesticides, often exibit narcosis in nontarget species, but in much higher concentrations than those of specific effects. Narcosis is mostly affected by hydrophobicity of the compounds e.g. while the LC50s of can vary by six orders of magnitude being 1-10 mM for small fish and invertebrates (McCarty et al., 1992).

Practically, all priority PTS exibit polar narcosis; additions of halogen (Cl, Br) atoms usually increases hydrophobicity and thus narcotic toxicity. In addition to direct acute mortality, chemicals causing narcosis were shown to decrease long term survival, development and growth, and reproduction. Chronic effects typically occur at levels about an order of magnitude below those of acute effects (McCarty and Mackay, 1993; Zeeman, 1995; Zeeman et al., 1995).

3.2.3.2. Specific (receptor-mediated) toxicity

The actions of chemicals with specific mechanisms of toxicity, as is often the case with pesticides and other PTS, can include interactions with receptors in various parts of biota.

3.2.3.2.1.Receptors in nervous system

DDT is understood to act on the nerve axon by binding to a receptor associated with the sodium or the potassium gate in the membrane of axon (Kapoor et al., 1972; Coats et al., 1977). Several other insecticides (cyclodienes, toxaphene, lindane) interact with the γ-aminobutyric acid (GABA) receptor in the nervous system (Pong et al., 1982; Mellin et al., 1983). It has been also reported that neurotoxicants may interfere with normal behaviour in organisms that may be exposed to greater risks of predation or be unable to hunt for food (Morgan and Kiceniuk, 1991).

3.2.3.2.2.Inhibition of enzymes

Several herbicides act as photosynthetic inhibitors. Atrazine competitively inhibit photosynthesis through binding to the plasto-quinone receptor site in the D-1 protein of the photosyntetic complex (Fuerst and Norman, 1991; Devine et al., 1993). Methyl mercury salts inhibit the activities of NAD-dependent malate dehydrogenase isolated from various plants *(Cucumis sativus L., Triticum aestivum L., Solanum tuberosum)* much more efficient than the other organomercury compounds (Milaeva et al., 1999). They also inhibit the respiratory chain terminal enzyme – cytochrom c oxidase isolated from Russian sturgeon *(Asipenser gueldenstaedti B.)* in Caspian Sea (Milaeva et al., 1999). It has been shown recently that organotin salts may act as noncompetitive inhibitors towards the activity of L-lactate: NAD oxidoreductase (lactate dehydrogenase), isolated from the liver of Russian sturgeon *(Asipenser gueldenstaedti B.)* in Caspian sea (Kolyada et al., 2001).

3.2.3.3. Reproductive and other endocrine/hormone-dependent effects in wildlife

The potential effects of so-called endocrine disrupting compounds (EDCs) on the endocrine system have recently gained much attention and have been reviewed (Vos et al., 2001). 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 ment 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“.

Direct evidence for hormonal modulators has been obtained in mammals (Nelson, 1974), birds (Turner and Eliel, 1978) and fish (Thomas and Smith, 1993). Although invertebrates have some steroid hormones (ecdyson, molting hormone), information is lacking on xenobiotic-steroid receptor interactions.

In vertebrates, reproduction is controlled by several hormones secreted by the hypothalamus-pituitary-gonadal (HPG) axis. Xenobiotics can affect multiple targets within the HPG axis including synthesis of hormones, posttranslational modifications, excretion, transport, competition or block at the receptor precise cites and mechanisms of action of particular chemicals. Embrios are extremely sensitive to estrogens (or xenoestrogens)

with steroidal activity during the critical in the early life-history cycle. Jobling et al. (1996) have shown that like estrogen, the toxic compounds regulate the activity of estrogen-responsive genes by binding to estrogen receptors and cause changes in the sexual characteristics of individuals. They disrupt the hormonal systems, affecting sex organ development, behavior and fertility. The effects are not necesserily apparent immediately, but they may become manifest later when the offspring reaches sexual maturity (Fry, 1995).

For invertebrates the best example of endocrine disruption effect is that of tributyl tin (TBT) compounds used in antifouling paints and causing in areas of heavy boat traffic imposex (the imposition of male characteristics on females, e.g., penis or vas deferens) in many species of marine snails. Studies performed in Europe include the experimental observations of imposex in dogwhelk *(Nucella lappilus*) from British and French coastal waters (Bryan and Gibbs, 1991; Huet et al., 1996) and common whelk (*Buccinum undatum)* from Danish waters (Strand, 1998) and Eastern Scheldt-North Sea (Mensink et al., 1998). This phenomenon is held responsible for global declines in populations of several species. TBT ecotoxicants are considered to inhibit cytochrom P450 dependent aromatase (CYP19) responsible for conversion of testosteron to estradiol. Apart from the imposex in marine snails, effects in other invertebrates are poorly documented.

Several PTS (particularly derivatives of DDT and PCBs with lower chlorine content) interact with estrogen receptor (ER) and the binding remains longer than with estradiol. Some of PTS were shown to bind to other than estrogen receptor. For example, o,p'- DDT was found to interact with progesteron receptor or progestin membrane receptor and atrazine has been shown to bind to the androgen receptor (Korach and MacLachlan, 1995). However, non-estrogen steroid actions of xenobiotic compounds have received relatively little attention.

The antiestrogenic activity of several PTS has been reported. Mechanisms include "hormonal blocking" action (binding to estrogen receptor, but without induction of effects) or enhanced clearance of steroids (due to induction of cytochrom P450 by AHR-active PCBs or PCDDs/PCDFs), or disruption of second messenger systems such as cAMP, calcium and others (Thomas, 1989).

3.2.3.4. AHR-mediated toxic responses

Most of the actions of PTS-like PCDDs, PCDFs and planar PCBs can be ascribed to the consequences of an initial binding to what has become known as the aryl hydrocarbon receptor (AHR), although this binding protein is now more properly termed a ligand activated transcription factor. This binding brings to the multiple changes in gene transcription leading to increases in biotransformation enzymes, modulation of cell cycling proteins and other responses. Inappropriate gene expression resulting from the high affinity binding and long-term occupancy of the receptor may be the basis of the toxicity. However, although the mechanisms of early molecular changes are well understood, the relationship between changes in gene regulation and observed toxicity are still unresolved.

It has become apparent that the sequence of events from dioxins binding to gene transcription involves other transcription factors, chaperons (such as HSP90) and regulatory proteins. The net result is the association of dioxin-AHR with another factor, the AHR nuclear translocator (AHRNT), in the nucleus followed by binding of the complex to dioxin responsive regulatory elements (DREs) in enhancer regions upstream of particular genes. Downstream activation of promoter regions then occurs with production of mRNA from the genes. Most of the molecular events for transcription of the CYP1A1 gene have been elucidated. For other genes the sequence of events is far less clear but probably occurs in a similar manner and the number of known AHR-regulated genes is still increasing (Fisher et al., 1989). While several PAHs also act through AHR, they were not clearly demonstrated to have comparative toxic effects, probably as a result of their greater rates of metabolic clearance.

Specific effects of dioxins and related compounds include the body weight loss, immunosuppression, edema, dermal toxicity, developmental and reproductive toxicity, neurobehavioral toxicity, liver and endocrine toxicity, alterations in lipid metabolism and gluconeogenesis, modulation of responsiveness to hormones and growth factors, alterations of circulating levels of hormones, thymic atrophy, cancer, tumor promotion and induction of various enzyme activities that are associated with induction of cytochrome P4501A1 (Poland and Knutson, 1982).

3.2.3.5. Immunotoxicity

Immunosuppression may be one of the most sensitive and relevant environmental threats posed by PTS. It has been shown in numerous studies, that various ecotoxicants can supress immune system function.

PCB mixtures were shown to alter several morphologic and functional aspects of the immune systems, such as loss of thymic cortical lymphocytes, reduction of germinal center size, reduction of leucocyte and T-limphocyte counts, altered reactivity of immune system, reduced antibody production against patogens, reduced skin reactivity. Defects in the macrophage and natural-killer cell activities resulted in increased susceptibility to normally tolerated bacterial, viral and parasitic infections. These effects have been reproduced in birds, fishes, rodents and non-human primates (Descotes, 1988; Dunier, 1994; Tryphonas et al., 1995).

Dioxins, namely TCDD is probably one of the most widely known immunotoxic xenobiotics. Immunotoxicity is expressed as lymphoid tissue depletion, functional alteration in immune responsiveness, and increased susceptibility to infectious diseases. Prenatal exposure to TCDD is more immunosuppressive than comparable effects in adults, namely due to toxicity to developing T-cells in thymus (Descotes, 1988; Wong et al., 1992; Dunier, 1994). The immunotoxicity of TCDD depends on AHR; generation of primary antibody response appears to be particularly sensitive (Birnbaum, 1994).

Several other PTS of regional concern including organotin ecotoxicants and derivatives of heavy metals have been shown to be immunotoxic in many different species (Zeeman and Brindley, 1981; Anderson and Zeeman, 1995; Bernier et al., 1995).

3.2.4. Ecotoxicological effects on the particular types of biota

3.2.4.1. Birds

The first ecotoxicological effects were observed in the Netherlands in the 1960s incormorants due to aldrin and dieldrin contamination. These were followed by more detailed field studies,performed in seven colonies of cormorants in the Rhine and Meuse estuaries (Van Hattum et al., 1993; Dirksen et al., 1995).

Intensive field studies have been performed in the Rhine, Meuse and Schelde estuaries (Murk et al., 1994; Bosveld et al., 1995 and 1999) with eight colonies of common terns in Belgium and Netherlands. In Study 1 researchers were looking for *in ovo* exposure to PTS (in terms of TEQs) and effects on hatchlings. Study 2 has been devoted to postnatal exposure and effects on development chicks.

The principal conclusions made on the basis of these field studies are:

The Rhine and Meuse sedimentation areas are among the most highly contaminated in the world;

The ecotoxicological effects of PTS on cormorants are substantial, but no significant effects observed on common terns;

Cormorants and common terns are not threatened on the national and international levels;

Effects are most significant in sedimentation areas, where the population of fish is the highest.

Weak estrogenic activities of DDT derivatives and PCB mixtures ("hormonal mimics") were observed *in vivo*, including feminizing effects at male gull embryos, reptiles, as well as laboratory rodents (Bulger and Kupfer, 1985; Nelson, 1974; Fry and Toon, 1981).

It has been observed (Luoma, 1992) that male sea gulls may ignore nesting colonies, and females may pair and nest together as a consequence of modified behavior by estrogenic chemicals such as DDT, DDE, dioxins, PCBs, and alkylphenols. It has been found by Kelce et al. (1995) that some of these toxicants can also block androgen receptor-mediated processes, and in doing so, act as androgen receptor antagonists.

Bergeron et al. (1994) provided a straightforward demonstration of PCBs acting in birds as xenobiotic estrogens. Eggs of the red-eared slider turtle *(Trachemys scripta)* were exposed to either different concentrations of PCBs, or the hormone, estradiol-17β. Because this species displays temperature-dependent sex determination, researchers could manipulate the sexes of hatchlings by controlling incubation temperatures.

There are also many well known examples of bird populations that have been affected by PTS exposure with decreased or retarded egg production, increased embryo mortality, egg-shell thinning, embryonic deformities, growth retardation and reduced hatchling success being among the effects reported (Han and Stone, 1997).

Developmental toxicity of dioxins and related compounds with embryo lethalities was observed in several bird species: chicken, ring-necked pheasant, turkey, eastern bluebird, mallard duck, domestic duck, golden eye, herring gull, black headed gull (Brunstrom, 1988). Besides mortality of embryos, structural malformations were reported in fish-eating water birds (Peterson and Walker, 1992; Ludwig et al., 1993; Peterson et al., 1993, Giesy et al., 1994). In several fish-eating birds, dioxins and related ecotoxicants have interfered with the

turnover of vitamin A and thyroid hormone levels (Hakansson et al., 1992; Lans et al., 1993). However, the toxicological relevance of this mechanism of action should be validated. Exposure of birds to dioxins and PCBs showed incidence of hemorrhagies, indicating interactions with the hepatic vitamine K cycle. Since 2,2‘,4,4‘,5,5‘-HxCB (extremely weak AHR agonist) was more potent than TCDD, a nonAHR mechanism seems to be involved (Bouwman et al, 1992; Ivens et al., 1993).

It has been also shown, that in birds, the LOAEL based on egg dose is 240 $pg.g^{-1}$ for chicken embryo mortality (Spitsbergen et al., 1991), cardiovascular malformations in chicken (Cheung et al., 1981) or embryo mortality in double crested cormorants is less than 100 $pg.g^{-1}$ egg (Ludwig et al., 1993; Giesy et al., 1994).

The clear relation between decreased egg-shell thickness, as determined in bird of pray, and DDE has been obtained in some of the European regions (Bergman, 2002).

3.2.4.2. Mammals

Exposure levels of PCBs, determined as internal doses and range of effects on reproduction among seals, otters and mink including fetotoxicity, teratogenicity and endocrine mediated effects are accepted as effects in these wildlife species living in certain more polluted areas. However, some other lesswell established effects were apparent that could be attributed to PCBs such as immunotoxicological effects and neurobehavioral effects. PCB effects observed in wildlife are due to exposure to ‘weathered PCB’, which means that the composition of the PCB congeners is verydifferent from the composition in the PCB productsas manufactured (Bergman, 2002).

Both DDT and PCBs are transformed to what we may regard as traditional lipophilic and persistent compounds. Hence methylsulfonyl-DDE is one of those compounds, an extremely potent toxicant for the adrenal in which it induces cell necrosis in the cortex *zona fasciculate*. It is reasonable to believe that the hypertrophic growth of the adrenals observed in grey seals from Baltic Sea is due to this DDE metabolite. Depending on their structure, some of the rapidly metabolized PCB-congeners are transformed to more persistent metabolites, PCB methylsulfones ($MeSO_2$-PCBs). These are compounds with only slightly lower lipophilicity than the parent compound but for the majority of all $MeSO_2$-PCBs their reactivity is lowered by the introduction of the methylsulfonyl group in the molecule. Consequenly, we have a new group of persistent compounds potentially causing toxic effects in species with high enough levels of the metabolites. It was shown (Brandt et al., 1992), that 3-methylsulphonyl-DDE and various nonplanar PCBs which form up to 10% of total concentrations of parental compounds within the body, have strong adrenocorticolytic effect causing also the necrosis of *zona fasciculata* in mice at the levels comparable to the concentrations found in seal blubber (3-6 $\mu g.g^{-1}$ – the highest concentrations ever found in wildlife!).

Reproductive failure in various mammals species due to exposure to dioxin-like compounds were characterized by reduced fertility, reduced litter size, effects on the gonads of females, alterations in menstrual and estrus cycles (Morrissey and Schwetz, 1989; Peterson et al., 1993). However, the most sensitive sign is embrio mortality (Peterson and Walker, 1992). Reproductive failure in the common seal population inhabiting the western part of Dutch Wadden Sea was attributed to PCBs after feeding experiments demonstrated that a diet of naturally PCB-contaminated fish had a detrimental effect on the seals‘ reproduction (Reijnders, 1986).

Decreased growth is generally observed in all classes of vertebrates that possess AHR after exposure to dioxin-like compounds, either experimentally or in contaminated food. The response tends to be more apparent in mammals, possibly because presence of edema in birds and fish masks the reduction in body tissue mass. Thymic hypoplasia, subcutaneous edema and decreased fetal growth were reported for mammals in several papers (Couture et al., 1990; Peterson et al., 1993).

It has been shown also, that in-utero and lactational exposure to dioxins causes postnatal alterations in neurobehavioral and male reproductive functions in rhesus monkey and rats, including reduced anogenital distance, delayed time to testis decent, reduction in sex organ weights, decreased daily sperm production, decreased ejaculated sperm numbers, feminization of sexual behavior (Mably et al., 1992a,b,c; Peterson et al., 1993; Gray et al., 1996).

Subchronic levels of DDT impaired the immune response of mice (Banerjee, 1987), aldrin and dieldrin reduced mouse resistance to viral infection, chlordane and heptachlor were found to affect animal‘s developing immune systems and lindane affected macrophage activity *in vitro* as well as reducing experimental animal‘s resistance to infection (Barnett et al., 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).Studies with seals from Baltic Sea fed with PCB-contaminated fish suggest alterations in immune system by contaminants in the fish (Ross et al., 1995).

Several organochlorine pesticides, such as HCB, mirex, lindane, chlordane,dieldrin and DDT with metabolites have been demonstrated to affect resistance to infections in vertebrates (Descotes, 1988; Wong et al., 1992; Dunier, 1994; Thomas, 1995). In rodents PCP interferes with phagotic activity and reduces antibody production (Wong et al., 1992).

In a literature review (Wren, 1991) many laboratory experiments with mink and ferrets are described which demonstrate a direct cause and effect relationshiip between PCB exposure and immune disfunction, 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).

3.2.4.3. Fish

There are several studies in Europe of ecotoxicological effects on fish. In particular, researchers have seen extreme disturbances of reproduction in different regions 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 PTS are involved (Alsberg et al, 1993).

It has been shown also for various fish species, that PCP interferes with phagotic activity and reduces antibody production (Wong et al., 1992). The LOAELs for malformations in trout were in the same range as that for blue-sac syndrome associated mortality 40-55 pg TCDD.g^{-1} egg (Spitsbergen et al.,1991; Walker, 1991).

Developmental toxicity of PCDDs and related compounds was observed in several fish species, characterized by pericardial and yolk-sac edema, subcutaneous hemorrhages, craniofacial malformations and other effects culminated in death (Spitsbergen et al.,1991; Walker, 1991).

It has been shown in Great Britain (Purdom et al., 1994; Harries et al., 1996, 1997; Jobling et al., 1998; Routledge et al., 1998; Mattiesen et al, 1998; Allen et al., 1999), Sweden (Sandstrom et al., 1997; Andersson et al., 1998; Larsson et al., 1999) and Netherlands (Janssen et al., 1997) that various fish species – rainbow trout, roach, flounder and perch have elevated blood vitellogenin and in some cases testicular abnormalities, intersex (up to 100%), ovotestis (up to 20%) and decreased turnover of steroids. The authors have concluded that sewage effluents, containing xenoestrogens, are responsible for the effects.

Inhibition of spawning in female species of sand goby has been observed in UK and the authors (Waring et al., 1996) believe that diluted sewage sludge is the main reason to explain this observation. Andersson et al. (1998) and Sandstrom et al. (1997) have concluded in their studies, that the reduced plasma sex hormone levels, reduced gonad growth and delayed sexual maturity for various fish species in Sweden are due to chlorinated organic chemicals, particularly from the bleached kraft pulp mill effluents.

It is important to mention the results of semi-field Dutch studies (Besselink et al., 1998), showing the reduced vitamin A levels in flounder due to ecotoxicological effects of PAHs, as well as the observation of the decreased fecundity for the Baltic Sea cod, which has been explained by the authors (Petersen et al, 1997) due to the effects of lipophilic xenobiotics.

3.2.4.4. Plants

Most of the data available are dealing with the compounds (polychloroolefines, chloroacetic acids, etc.), which are not considered in this document.

3.2.5. Ecotoxicological databases and laboratory and field studies

3.2.5.1. Important reviews

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3.2.6. Data gaps

To assess the priority of PTS for the particular regions the scoring for various PTS, included in the list of priority ecotoxicants in the Stockholm Convention, has been performed and the results are given in the Table 3.16.

Table 3.16:

Scoring by matrix		
Substances	Ecotoxicological effects	Data gaps
Aldrin	1	It is difficult to point out ecotoxicological effects of these compounds since their effects, as indicated in toxicological experiments or through accidents are hidden behind the effects observed for the PTS present at the highest concentrations and/or the effects of the most toxic compounds
Chlordane	1	
Dieldrin	1	
Endrin	1	
Heptachlor	1	
Hexachlorbenzene	2	
Mirex	0	
Toxaphene	No data	
DDT	1+	There are enough data to describe the fate and effects for these ecotoxicants and to make temporal and geographical comparison for
PCBs	2	
Dioxins	2	
Furans	2	

The second group of ecotoxicants, which has been mentioned in the documents of the Stockholm Convention was scored and the results of this scoring are given in Table 3.17.

Table 3.17:

Scoring by matrix		
Ecotoxicant	Ecotoxicological effect	Data gaps
Atrazine	1	There are enough data to describe the fate and effects for these ecotoxicants and to make temporal and geographical comparison
HCH	1	

Scoring by matrix		
Ecotoxicant	Ecotoxicological effect	Data gaps
PCP	1	for.
Organolead compounds	1	
Organomercury compounds	2	
Organotin compounds	2	
PAHs	2	
Chlordecone	0	The data are controversial and more research is needed for these ecotoxicants to make certain conclusions .
Endosulphan	0	
Nonylphenols	0	
Octylphenols	0	
Phtalates	0	
Chlorinated paraffins	1	The intensive research is still needed to make any conclusions on the effects of these ecotoxicants, but detailed assessment is a possible to find in EU Risk Assessment.
PBDEs	1	

Conclusions

Analysis of the observed ecotoxicological effects of PTS on birds, mammals and fish in Europe has shown, that although a wide number of laboratory and manipulated in situ studies with various organisms and effects were conducted and are documented in the literature, one has to carefully and critically evaluate these data. On one hand, the controlled laboratory toxicological studies with individual compounds or carefully prepared mixtures usually allow clear dose-response causality between chemical exposure and observed effects to be defined. On the other hand, laboratory tests alone seldom adequately describe what is likely to occur in the environment. The often complex and subtle effects of chronic, low-level environmental exposure to PTS are less well understood. In the environment, the universal exposure of organisms to low levels of a wide range of chemical contaminants 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.

PTS can act via different mechanisms and cause various adverse effects in wildlife. Mechanisms causing ecotoxicological effects include non-specific toxicity (narcosis) and more specific mechanisms, such as aryl-hydrocarbon receptor (AHR) mediated toxicity, steroid receptor dependent effects, metabolic activations, immune suppression and neurotoxicity.

The assessment of priority of PTS, included in the list of the Stockholm Convention, has been performed by scoring them on the basis of data, available in the Region Europe-III (Table 3.16). The second group of ecotoxicants, which were mentioned in the Stockholm Convention, was also scored (Table 3.17).

3.2.7. References

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3.3. HUMAN EFFECTS OF PTS OF REGIONAL CONCERN

3.3.1. Introduction

Many environmental epidemiological studies indicate that correlations do exist between chemical contamination and observed human health effects. To evaluate critically the adverse effects of individual PTS, it is necessary to compare data derived from experiments with the laboratory animals, the results of epidemiological studies due to accidental or occupational exposure, as well as the effects observed for „average“ population.

As it was pointed out in Chapter 3.2, it is very difficult to elucidate cause and effect relationships between human exposure to low levels of a PTS in the environment and the particular adverse health effects, not least because of the broad range of chemicals to which humans are exposed at any one time. The measurable residues of PCBs, dioxins and various organochlorine pesticides present in human tissues around the world (Thomas and Colborn, 1992) and contamination of food, including breast milk, is also the worldwide phenomenon (WHO, 1996)

Evidence for low-level effects of PTS on humans are more limited than those for wildlife but are consistent with effects reported both in exposed wildlife populations and in laboratory experiments on animals (UN-ECE, 1994). This is why data from „hot-spot“ accidental events or occupational exposures can help to formulate safety values for PTS. Trying to elucidate toxicological effects of PTS, one has always to remember themany confounding factors affecting human health (life style, dietary habits), which are often very poorly evaluated.

Concluding the general introduction, it is worthwhile to mention that WHO (1996) came to the conclusion, that „where levels of some PTS 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“. This conclusion has been supported by the report of AMAP (1997), the authors of which 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.

3.3.2. Overview of harmful effects

Since 1775, when British physician Persival Pott discovered, that soot is responsible for skin cancer in chimney-sweeps, many examples have been collected showing the toxicological effects of harmful chemicals on human health. These effects will firstly be classified and later some examples of adverse health effects of PTS of regional concern will be considered.

3.3.2.1. Genotoxic effects

Toxic compounds and their products may damage genetic materials such as chromosomes or DNA and because of this can be discussed in terms of "genotoxicity".

Di Gulio et al. (1995) discussed the possibility for toxicants to produce single or double strand breaks. Shugart (1995) has shown that xenobiotics and their metabolites may bind covalently to a base or, less frequently, to another portion of DNA molecule to form the molecular adduct.

Jones and Parry (1992) came to the conclusion that due to chromosome breakage the expected diploid chromosome number (2N) can be disrupted and result in a deviation from the usual number of chromosomes (aneuploidy) or structural aberrations in chromosomes. Toxicants that cause chromosome damage in living cells are classified as clastogenic. All of these genotoxic effects can have mutagenic (causing mutations), carcinogenic (causing cancer), and teratogenic (causing developmental malformations) consequences.

Within the group of various methods available to assess genotoxicity (flow cytometry, combined with fluorescence; ^{32}P-labeling method and others) the estimation of DNA breakage and its correlation with exposure to genotoxic contaminants is widely used. Particularly, an alkaline unwinding assay to estimate the degree of single-strand breakage has been described by Shugart (1988).

3.3.2.2. Estrogenic effects

Current knowledge on the effects of environmental xenoestrogens on the male reproductive health has been reviewed recently (Toppari et al., 1996), and has shown that at present there is an almost complete lack of exposure data in humans to support such an association.

It has been suggested recently (e.g. Garcia-Rodriguez et al, 1996), that falling human sperm counts, the increasing incidence of certain reproductive abnormalities in humans such as spermatogenic dysfunction, maldescent of testes, malformations of the penis and testicular cancer, as well as breast cancer in women, may be linked to the chronic exposure to low levels of the hormone-mimicking chemicals (including various PTS).

In one of the earlier studies Balash et al., (1987) demonstrated that Chlordane disturbed spermatogenesis and damaged the testes of mice. Peterson et al. (1992) described experiments in which *in utero* and lactational exposure to 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 described 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.

Brouwer et al. (1995) demonstrated the wide range of neurobehavioral, reproductive and endocrine alterations observed in experimental animals following *in utero* and lactational exposure to PCBs and PCDDs/Fs. There were also subtle changes observed in neurodevelopmental and thyroid hormone parameters in human infants at background human body burdens. Consequently, in assessing effects linked to the presence of PTS in the environment, the full range of toxic endpoints should be considered including the more subtle and complex chronic effects.

It was found recently (Meerts et al., 1998), that halogenated bisphenol A derivatives, chlorinated and brominated phenols, benzenes and diphenyl ethers also give rise to profound thyroid hormone system modulating effects. This information, which was originally derived from studies on PCBs, PCDDs and PCDFs ("traditional contaminants"), can be applied as tools to discover, or predict the activity of "new contaminants" such as PBDEs/PCDEs and other halogenated compounds.

3.3.2.3. Carcinogenicity

It has been known for more than thirty years that cancer is a result of heritable change in cells, where the toxic compounds (carcinogens) modify a gene or its normal relation to other genes which result in neoplasia - hyperplasia, caused, at least, in part, by an intrinsic heritable abnormality in the involved cells (La Via and Hill,

1971). The recent important publication, edited by Kitchin (1998), summarized information on the effects of various chemicals on cancer, published previously in many important books (first of all, in the regular IARC monographs on the evaluation of the carcinogenic risks to humans).

In one of the recent monographs of IARC (1997) it was concluded that TCDD should be considered as a definite human carcinogen. Committee on Carcinogenicity (Department of Health, 1998) agreed that TCDD is a potent carcinogen in laboratory animals, but suggested, that the information from the most heavily occupationally exposed cohorts was showing, at most, only a weak carcinogenic effect in these individuals. It therefore concluded there were insufficient epidemiological and toxicological data on TCDD to propose a casual link with cancer in humans, but it would be prudent to consider TCDD as a "probable weak human carcinogen".

Breast cancer in women appears to be rising in many countries and pathogenesis of breast cancer has been linked with exposure to hormone disrupting chemicals (Davis et al., 1993). There were several studies (Falck et al., 1992; Wolff et al., 1993; Dewailly et al., 1994) supporting this hypothesis with observations of higher levels of DDE and PCBs both in mammary adipose tissue and plasma. However, the situation became controversial, when Krieger et al. (1994), Key and Reeves (1994), and Safe (1997) have performed much larger studies and, after producing a statistical summary of results from these studies, concluded that itis unlikely that DDT in the environment is increasing the risk of breast cancer, and that for PCBs there is no evidence of such an association.

3.3.2.4. 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 the 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 takes place either during mid-late gestation, around term or in the early post-natal period. In humans, this sensitive period begins during the third trimester of pregnancy and continues throughout the first two years of life..

It has been observed (Eriksson et al., 1992, 1996, 1997) that a single low-dose exposure at 10th day *post partum* may result in persistent changes in spontaneous behaviour (hyperactivity) and learning ability at adult age in mice and rats. These behavioural changes were correlated with persistent changes in the expression of cholinergic receptor subtypes. However, following dosing at 3rd or 20th day *post partum,* no corresponding effects were observed at comparative doses. Various PTS such as DDT (a neurotoxicant by design) and some PCBs induce this type of neurotoxicity, while other PCBs seem to lack activity at corresponding doses.

Organomercury compounds (particularly, methyl and ethyl derivatives), unlike inorganic mercury salts and mercury vapor, have characteristic features of neurointoxication (Sarafian and Verity, 1991). The characteristic features of poisoning with organomercury toxicants are the persistence of neurological symptoms (the so-called "Minamata desease", due to the first observation of the methylmercury adverse effects on human health in the region of Minamata Bay in Japan) (Mottet N.K. et al., 1998).

Organolead compounds (tetramethyl and tetraethyl lead) were traditionally used as antiknock additives to gasoline, but after discovering of their adverse effects on human health, particularly, on the nervous system, they are step by step eliminated from use. The most toxic lead containing species, like organic derivatives of mercury (RHg^+) and tin (R_3Sn^+), are the cations R_3Pb^+ (Gong et al., 1995; Audesirk et al., 1995), which are formed in the environment due to biometylation of inorganic salts of lead and in organisms because of tetraalkyllead metabolism.

3.3.2.5. Immunotoxicity

Several epidemiological studies have been carried out to assess changes in the human immune system from pesticide exposure. Although pesticide-induced immunosuppression may increase people's susceptibility to infectious and parasitic deseases, these deseases 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 shown (Broughton et al., 1990), that patients chronically exposed to Chlordane demonstrated clinical and immunological symptoms

highly suggestive of immune pathology and probably the Chlordane/ Heptachlor-induced autoimmune disorder. Nearly identical immunological results were found in the patients exposed to pentachlorophenol as fungicide (McConnachie and Zahalsky, 1991).

3.3.2.6. Enzyme dysfunction and substrate pool shifts

Toxicants can have significant effects on enzymes and these effects are used routinely as biomarkers. For example, it has been shown by Peakall (1992) that PCBs may interfere with heme synthesis, possibly by inhibiting uroporphyronogen decarboxylase or by P-450 generation of oxyradicals that oxidize porphyrinogens.

3.3.2.7. General cytotoxicity and histopathology

The studies of toxicological effects at the cell, tissue and organ level of organization have been carried out quite intensively and this is why the histopathological biomarkers are used very widely.

3.3.2.8. Necrosis

Pathological alterations of cells, tissues, or organs (lesions) indicate exposure to toxicants and suggest mechanism of action. Cytotoxicity (toxicity causing cell death) may be reflected in a tissue or target organ as necrosis (cell death from disease or injury). Pyknosis, the most obvious evidence of necrosis, involves the cell nucleus.

3.3.2.9. Inflammation

It has been shown, that inflammation is a response to cell injury or necrosis that isolates and destroys the offending agent or damaged cells. For example, hepatic necrosis due to toxicant action can be accompanied by inflammation (Hinton and Lauren, 1990).

3.3.3. National and regional human health effects reports

The incidence of mass intoxication of 80 workers at one of the plants producing 2,4,5-T in Czechoslovakia happened in 1965-68. A ten year study has been performed for this incidence (Pazderova-Vejlupkova J. et al., 1981; Holoubek et al., 2000). Firstly, it was shown that 2,3,7,8-TCDD was the cause of intoxication (dioxin has been found in the final product and on the walls of the plant, but the results have never been published). Secondly, it has been observed that most of the 55 exposed workers developed chloracne and 11 manifested porhyria *cutanea tarda.* Half of the patients suffered from metabolic disturbances, i.e. pathologically elevated lipids with abnormalities in the lipoprotein spectrum. 40% of the patients had pathological changes in the glucose tolerance test. More than 30% had biochemical deviations indicative of a mild liver lesion. Histological examination revealed light steatosis, or periportal fibrosis, or activation of Kupffer cells. In 17 persons symptoms of nervous system focal damage existed, with predominance of peripheral neuron lesion of the lower extremities. The majority of patients suffered from various psychological disorders. By 1981, when these results were published, two patients died of bronchogenic lung carcinoma; one - of liver cirrhosis; one - of rapidly developed, extremely unusual type of atherosclerosis *precipu cerebri.*

Another example of the long-term effects of high-level accidental releases of dioxins has been described recently by Mocarelli et al. (1996). The sadly famous accident in Seveso (Italy) had as one of the endpoints the female-skewed sex ratio in births about eight years after, which can be directly related to the dioxin exposure.

Swedish investigations have reported that dietary intake of PCDDs/PCDFs and PCBs may be linked to reductions in the population of natural killer cells (Svensson et al, 1993). These sells are believed to play a role in the body's defense against viruses and tumors. However, none of the subjects in this study displayed any signs of health impairment attributable to lowered number of natural killer cells.

Immune modulating effects have been detected in the Netherlands in people exposed to low-level environmental concentrations of PTS. In particular, it has been shown (Weisglas-Kupertus ET al., 1995), that certain immunologic aberrations were associated with pre- and post-natal exposure of Dutch infants to PCDDs and PCBs. Although their data did not indicate that these aberrations caused any more illness among the infants, they could persist and predict later difficulties such as immune suppression, allergy and autoimmune disease.

In the Russian Federation there were at least, two „hot-spots“, Chapayevsk (Samarskaya oblast‘) and Ufa (Bashkortostan Republic), in which big plants producing organochlorine products (primarily, PCBs and pesticides) released large amounts of dioxin into the environment.

Epidemiological studies performed in Chapaevsk since 1969 untill 1998 (Korrick et al., 1998; Kluev et al, 2001; Revich, 2001) have shown that the workers of the plant were having chloracne, endocrine deseases, hepatitis, suppressed quantities of spermatazoids, reduction of immunological tolerance, 17.5% death rate due to malignant neoplasms. The typical cancers are of lung and larynx for men, and - of breast for women. Within the population of the city – the increased frequency of spontaneous aborting, late histozes, increased concentrations of dioxins in human milk, high frequency of birth light in weight children, delay of boy‘s genital development, children‘s congenital malformations and high content of hormons in boy‘s blood.

The epidemiological studies performed in Ufa in 1966-67 (Goncharov et al., 1999; Kluev et al., 2001; Revich, 2001) have shown that the workers of the plant were having chloracne and many other deseases, including increased frequency spontaneous abortion and genital disproportion of newborns with excess of girls over boys.

In Slovakia the effects of organic xenobiotics in human placentas on allergic sensitization of newborns were studied (Reichrtova et al., 1998). The statistically significantly higher concentrations of 17 out of 21 PTS under the investigation have been shown in the placental samples collected from the industrialized region if compared to the rural one. Parallel, the increase in the total immunoglobulin E level in the ambilical blood samples gothered from industrial region was found, evoked possibly by organic xenobiotics. External placental parameters differed as well.

The exposure of infants to PCBs and OCPs (HCB, HCH, DDT) from human milk has been studied in Poland (Czaja et al., 1997). 462 human milk samples from Warsaw and various regions of the country were analyzed. The EDI values for PCBs averaged 2.8 $\mu g.kg^{-1}$ $bw.d^{-1}$, which exceed the reference values of 1 $\mu g.kg^{-1}$ $bw.d^{-1}$ (FDA US) or 0.6 $\mu g.kg^{-1}$ $bw.d^{-1}$ (National Food Agency of Denmark). As to the OCPs levels, it was shown that higher concentrations of HCB and DDT were observed from the more industrialized regions of the country.

The study in Russia of the dynamics (over 1.5 years and 3 years) of latent pathological effects to the nervous system, caused by small doses of organomercury compounds (25 persons were fed meat and diary foodstuffs containing 1-10 $ng.g^{-1}$ of EtHgX for 2-3 months), showed an increase in complaints indicating pathology of hypothalamic structures in brain, and a reduction in complaints concerned with the pathology of peripheral nervous system (Mukhtarova, 1977).

Data gaps

To assess the priority of PTS for the particular regions the scoring for various PTS, included in the list of priority toxicants in the Stockholm Convention, has been performed and the results are given in Table 3.18.

Table 3.18:

Scoring by matrix		
Toxicant	Toxicological effects	Data gaps
Hexachlorbenzene	1	There are enough data to describe the fate and effects for these substances and to make temporal and geographical comparison for
PCBs	1	
Dioxins/furans	1	
Aldrin/endrin	0	It is difficult to point out toxicological effects of the compounds since their effects, as indicated in toxicological experiments are hidden behind the effects observed for the PTS present at the highest concentrations and/or the effects of the most toxic compounds
Chlordane	0	
DDT	0	
Dieldrin	0	
Heptachlor	0	
Mirex	0	
Toxaphene	No data	Intensive research is needed

The second group of toxicants, which has been mentioned in the documents of the Stockholm Convention, was scored and the results of this scoring are given in Table 3.19.

Table 3.19:

Scoring by matrix		
Toxicant	Toxicological effect	Data gaps
Atrazine	1	There are enough data to describe the fate and effects for these substances and to make temporal and geographical comparison for.
Organolead compounds	2	
Organomercury compounds	1	
PAHs	2	
PCP	1	
HCH	0	The data are controversial and more research is needed for these pollutants to make certain conclusions.
Chlordecone	0	
Endosulphan	0	
Nonylphenols	0	
Octylphenols	0	
Phtalates	0	
Organotin compounds	No data	The intensive research is needed to make any conclusions on the effects of these substances.
Chlorinated paraffins	1	The intensive research is still needed to make any conclusions on the effects of these ecotoxicants, but detailed assessment is a possible to find in EU Risk Assessment.
PBDEs	1	

3.3.4. Conclusions

Analysis of the results of environmental epidemiological studies shows that correlations do exist between the chemical contamination of air, water, soil and human health. To elucidate the particular effects of individual toxicants (genotoxicity, estrogenic effects, carcinogenicity, neurotoxicity, immunotoxicity, etc.) it is important to compare the above mentioned results with the data obtained from experiments with laboratory animals. The assessment of priority PTS, included in the list of the Stockholm Convention, has been performed by scoring them on the basis of data, available in the Region Europe-III (Table 3.18). The second group of toxicants, which were mentioned in the Stockholm Convention, was also scored (Table 3.19).

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3.4. HUMAN EXPOSURE TO PTS COMPOUNDS IN REGION III – EUROPE

3.4.1. Introduction

The persistent bioaccumulative properties of PTS substances means, that they have the capacity to transfer through terrestrial and aquatic foodchains and accumulate in human lipids. As omnivores we occupy a top position in terrestrial and aquatic foodchains and as a result consume a high proportion of food in which persistent lipophilic compounds will have effectively biomagnified. Once ingested, PTSs sequester in body lipids, where they equilibrate at roughly similar levels on a fat-weight basis between adipose tissue, serum, and breast milk.

It is possible to document three distinct types of human exposure to PTS compounds:

High-dose acute exposure: typically results from accidental fires or explosions involving electrical capacitors or other PCB-containing equipment, or high dose food contamination.

Mid-level chronic exposure is predominantly due to the occupational exposure, and, in some cases, also due to the proximity of environmental storage sites or high consumption of a PTS-contaminated dietary source, such as fish or other marine animals.

Chronic, low-dose exposure is characteristic for the general population as a consequence of the existing global background levels of PTSs with variations due to diet, geography, and level of industrial pollution. Low level and population-wide effects are more difficult to study. People are exposed to multiple PTSs during their lifetime and all individuals today carry detectable levels of a range of PTSs in their body lipids.

Over the last 10-15 years as interest in exposure to these compounds has increased there have been numerous surveys of both typical 'background' levels in the population and also small surveys of occupationally exposed individuals whose body lipids contain elevated concentrations.

Compounds are most often monitored in human milk, serum and adipose although milk monitoring is far more widely practiced due to the relative ease of sample collection. Milk not only provides evidence of maternal exposure to contaminants, it also provides information to assess risk to breast-fed infants. Contaminants in breast milk for example increase with maternal age and decrease with the number and duration of lactation periods (e.g. TCDD levels in breast milk decrease roughly 25% after each successive breast-fed child). The most popular compounds for analysis include the OC pesticides and PCBs.

Numerous analyses have now been made of PCBs in samples of human milk from the general population within the region. Countries with a long history of human tissue sampling - from the early 1980s - include the Netherlands, Sweden and Germany. Within the Central European Countries, Slovakia, the Czech Republic and Poland also have a sizeable database of information spanning the last 10-15 years. Standardized collection and analytical protocols now exist for analysing many PTS compounds in breast milk in these countries in addition to tissue banking facilities. For example, between 1986 and 1997 over 3500 milk samples were analysed in Germany for a range of organochlorine compounds. Far fewer analyses of human samples have been made for

PCDD/Fs, principally due to the high cost. As a general rule, travelling eastwards within the Region, the number and size of data sets for all compounds reduces significantly.

Evidence from market basket surveys of principal foods and food groups suggest that exposure to many of the classical PTS compounds via food is very similar throughout the Region. This is also supported by the extensive movement of food products throughout Europe providing many consumers with a 'European' average food basket of produce. To a large extent personal choices in food preferences will ultimately control our intake of persistent compounds throughout life. Since aquatic foodchains are subject to a greater loading of many pollutants than terrestrial ones, individuals who consume fish and seafood obtain an appreciable proportion of their annual intake via this route. For example, fishermen on the east coast of Sweden who have eaten fatty Baltic fish (herring and salmon) almost daily were found to have roughly twice the blood levels of DDT, PCBs and dioxins than people with a more average fish intake.

European exposure to dioxins via food has declined considerably during the last decades (Lindström et al., 2002). This is due to successful efforts that have led to the reduction of many known dioxin sources. Today the estimated intake by the European population of PCDDs/Fs and non-ortho PCBs, expressed as WHO-TEQs, is 1.2-3.0 $pg.kg^{-1}$ $bw.day^{-1}$. Since the 80´s various tolerable daily intake „recommendations" have been used, and for many population groups, such as new-borns and high fish consumers, these recommendations have been exceeded, and still are. Recently a tolerable weekly intake (TWI) of dioxins, furans and non-ortho PCBs, corresponding to 14 pg WHO-TEQ.kg^{-1} bw, was set by the EU Scientific Committee on Food (SCF).

The SCF has, as of 2002, established maximum limit values for dioxins and furans in consumer food on the European market in order to reduce the overall dioxin contamination of the food-chain, and the exposure of the European population. The goal is to have a 25 % decline in the exposure by year 2006. The $WHO_{PDDDs/Fs}$-TEQ maximum limits, based so far on the concentrations of PCDDs/Fs only, are set for foods such as meat, fish, poultry, dairy products and oil and fats and range from 0.75-6 $pg.g^{-1}$ lipid. With one exception the $WHO_{PDDDs/Fs}$-TEQ maximum limit is set on lipid basis, namely for fish. For fish the EU limit is 4 $WHO_{PDDDs/Fs}$-TEQ.g^{-1} fresh weight.

The absolute and relative contributions of PCDDs/Fs and non-ortho and mono-ortho PCBs to the total WHO-TEQs of six foods – chicken, beef, butter, human milk, salmon and cod liver from Northern Europe, were determined and compared to the current EU limit values. For all foods studied, PCBs contribute to more than 50 % to the total WHO-TEQ. For cod liver the contribution of PCBs to the total WHO-TEQ is high at more than 80 %. Sum TEQ levels in the salmon and cod liver reflects the relatively highly contaminated aquatic food-chain.

The yearly average dioxin levels in Belgian cow´s milk show a clear decreasing trend from 3.1 pg TEQ.g^{-1} fat (range 1.3-5.1, n=8) in 1994 to 1.1 pg TEQ.g^{-1} fat (range 0.5-1.9, n=29) in 2001. In 2000 the background dioxin level in cow´s milk had reached 48 % of the 1995 level (Table 3.20).

Table 3.20: Recent background levels [pg WHO-TEQ.g^{-1} fat] for European dairy products

Country	Product	PCDDs/Fs	Non-ortho PCBs	References
Belgium	Raw milk, 2001, n=29	1.15	1.65	Van Cleuvenbergen et al., 2002
	Pasteurized milk, 2001, n=35	1.11*	1.14*	Focant et al., 2001
	Cheese, 2000-2001, n=15	0.93*	1.16*	FIS, 2002
The Netherlands	Milk-butter-cheese, 1999, n=6**	0.64*	0.69*	Freijer et al., 2001
	Raw milk, 1998-1999, n=12	0.64*	0.87*	
Germany	Milk-dairy products, 1998, n=26	0.77*	1.55*	First, 2001
Various European countries	Butter, 1998, n=8	0.72*	0.94*	Santillo et al., 2001
	Cheese, 2000-2001, n=15	0.65*	0.85*	FIS, 2002
* lower bound value (< LOQ=0); ** composite samples				

3.4.2. PCBs

The main source of PCB exposure to the general population is through food, particularly animal fats and fish. During the past 20 years, many thousands of samples of different foodstuffs have been analysed for PCB

contamination throughout the Region, in particular fish, meat, and milk. Typical contemporary levels for the most important PCB-containing food items are animal fat, 20-240 $ng.g^{-1}$; cow's milk, 5-200 $ng.g^{-1}$; butter, 0-80 $ng.g^{-1}$; fish, 10-500 $ng.g^{-1}$, on a fat basis. Certain fish species (eel) or fish products (fish liver and fish oils) contain much higher levels, up to 10 $\mu g.g^{-1}$. Vegetables, cereals and fruits typically contain low concentrations of <10 $ng.g^{-1}$. PCBs in human adipose tissue and breast milk contain relatively high concentrations of mainly the higher chlorinated PCBs, such as PCB 118, PCB 153, PCB 138 and PCB 180.

PCB residues in the adipose tissue of the general population in industrialized countries range from less than 1 up to 5 $\mu g.g^{-1}$, on a fat basis. Average concentrations of total PCBs in human milk fat are in the range of 0.5-1.5 $\mu g.g^{-1}$ fat, depending on the donor's residence, life-style, and the analytical methods used. For example, women who live in heavily industrialized, urban areas, or who consume a lot of fish, especially from heavily contaminated waters, may have higher PCB concentrations in their breast milk. An overview of tissue concentrations of PCBs within the Region is given in the Table 3.21 below.

Table 3.21: PCBs in human tissues [$ng.g^{-1}$]

Country	N	Media	Year of collection	Mean	Range	Comments	References
Armenia							
Austria	13	M	1992-93	381		Urban (Sum 6 PCBs)	Liem and Theelen 1997
	21	M	1992-93	303		Rural (Sum 6 PCBs)	
	13	M	1992-93	449		Industrial (Sum 6 PCBs)	
Azerbaijan							
Belarus							
Belgium	8	M	1992-93	275		Brabant (Sum 6 PCBs)	Liem and Theelen 1997
	20	M	1992-93	306		Liege (Sum 6 PCBs)	
	6	M	1992-93	260		Brussels (Sum 6 PCBs)	
	9	M	1992-93	-		Flanders (Sum 6 PCBs)	
	200	B	1999	550	460-664	Flanders women	Covaci et al
Bulgaria							
Czech Republic	63	M	1985	2 830		standard commercial mixture Delor 106	Holoubek et al.,
	11	M	1992-3	532		Kladno (Sum 6 PCBs)	Liem and Theelen 1997
	11	M	1992-3	1 068		Uherske(Sum 6 PCBs)	
	17	M	1993-94	940			Holoubek et al., 2000
	292	M	1994	1 600			
	385	M	1995	1 400			
	295	M	1996	900			
	61	A	1996-9		21-309 pg g TEQ		
	84	A	1993-4	3 570		Ng/g (138+153+180 x 1.7)	
	20	A	1995	5 785		Ng/g (138+153+180 x 1.7)	
	31	A	1996-7	3 803		Ng/g (138+153+180 x 1.7)	
Denmark	48	M	1992-3	209 ng g		7 cities (Sum 6 PCBs)	Liem and Theelen 1997
Estonia		M	1984	0.12	0.006-0.017	mg kg wet wt	Roots,
Finland	10	M	1992-3	189		Helsinki (Sum 6 PCBs)	Liem and Theelen 1997
	24	M	1992-3	133		Kuopio (Sum 6 PCBs)	
Georgia							
Germany	69	M	1984/85	750			Holoubek et al., 2000

Country	N	Media	Year of collection	Mean	Range	Comments	References
	68	M	1990/91	630			
	10	M	1992-3	380		Berlin (Sum 6 PCBs)	Liem and Theelen 1997
	246	M	1995-97	550	118-1810		Schade and Heinzow 1998
Hungary	20	M	1992-3	61		Budapest (Sum 6 PCBs)	Liem and Theelen 1997
	10	M	1992-3	45		Scentes (Sum 6 PCBs)	
Ireland							
Latvia							
Lichtenstein							
Lithuania	12	M	1992-3	361		Palanga (Sum 6 PCBs)	Liem and Theelen 1997
	12	M	1992-3	287		Anykshchiai (Sum 6 PCBs)	
Luxemburg							
Netherlands	195	M	1990-92	409		(Sum 6 PCBs)	Liem and Theelen 1997
	104	M	1992-3	273	102-606	20 regions	
Norway	10	M	1992-3	273		Tromso (Sum 6 PCBs)	
	10	M	1992-3	265		Hamer (Sum 6 PCBs)	
Poland	277	A	1989-92	860	36000 max		Holoubek et al., 2000
	158	M		0.02	0.001-0.32	More industrialised areas (mg l)	
	199	M		0.03	0.002-0.19	Less industrialised areas (mg l)	
Moldova							
Romania							
Russian F.	1	M	1992-3	197		Arkhankelsk(Sum 6 PCBs)	Liem and Theelen 1997
	1	M	1992-3	102		Karhopol (Sum 6 PCBs)	
Slovakia	50	M	1993-4	785		6 PCBs	Kocan et al., 1995
Sweden	192	B	1996	160	20-780	PCB-153 only	Rylander et al., 1997
Switzerland							
Ukraine	5	M	1992-3	264		Kiev (Sum 6 PCBs)	Liem and Theelen 1997
	5	M	1992-3	191		Kiev (Sum 6 PCBs)	
UK	57	M	1990-91	232	6 PCBs	Wales	Duarte-Davidson et al., 1992
	20	M	1992-3	129		Birmingham (Sum 6 PCBs)	Liem and Theelen 1997
	23	M	1992-3	131		Glasgow (Sum 6 PCBs)	
	75	A	1990-91	788	242-1794	Welsh	Duarte Davidson et al., 1994

Liem and Theelen 1997 Dioxins: Chemical Exposure and Risk Assessment (PhD Thesis) all data $ng.g^{-1}$ lipid

3.4.3. PCDD/Fs

Human background exposure to PCDDs and PCDFs predominantly occurs through the diet, with food of animal origin being the major source. It is estimated that more than 95% of human exposure to dioxins is through the food supply importantly, past and present human exposure to PCDD/Fs and PCBs results primarily from their transfer along the pathway: atmospheric emissions – air – deposition – terrestrial/aquatic food chains – human diet.

Information is available throughout the Region concerning which components of the diet contribute most to exposure for 'typical consumers', namely lipid-rich foods such as milk, dairy products, meat and fish. Concentrations of PCDD/Fs in these products are themselves a complex function of many variables. Ultimately, however, they are controlled by concentrations in the diet of the animal (i.e. vegetation, feed, sediment etc), which itself will be controlled by levels in the surrounding environment (i.e. the air, water, soil).

The European Commission initiated a study to collect information on concentrations of dioxin-like PCBs in food, feed and in environmental samples on a Europe-wide scale (Hosseinpour et al., 2002). Samples have been taken Europe-wide between April and October 2001 on a product-oriented approach representing 8 European regions. 231 compound samples were prepared from ~ 2 600 individual samples, representing 42 different types of products including meat and meat products, milk and milk products, eggs, fish and fish oil, cereals, oil seeds, vegetables, vegetable oils, feed stuff, fruits, further plant products and bone- and blood meal. With respect to the dry matter based samples, all matrices were below the 0.1 pg WHO-PCB-TEQ.g^{-1} d.m. with the exception of some green crop samples included in the feed stuff category.

Information from food surveys in industrialized countries indicates a daily intake of PCDDs and PCDFs in the order of 50-200 pg I-TEQ.$person^{-1}$.day^{-1}, or 1-3 pg I-TEQ.kg^{-1} bw.day^{-1} for a 60 kg adult. If dioxin-like PCBs are also included, the daily total TEQ intake can be a factor of 2-3 higher. Data from Germany shows a decrease of around 64% in mean PCDDs/Fs levels in blood lipid from 1988-1996. Measurements from Sweden for human milk also show a large reduction in levels of around 65% from the early 1970s to the mid-1980s.

Compared to adults, the daily TEQ intake of PCDDs/Fs and PCBs for breast fed babies is 1-2 orders of magnitude higher. The latest WHO field study showed higher mean levels of PCDDs/Fs and PCBs in human milk in industrialized areas (10-35 pg I-TEQ.g^{-1} milk fat) and lower levels in developing countries (< 10 pg I-TEQ.g^{-1} milk fat) (WHO 1998).

Although human exposure to PCDDs/Fs and PCBs has generally declined in Europe (see Table 3-89) over recent years, the general reductions in the TDI limit value mean that a proportion of the population continues to exceed the current TDI. Concern surrounding human exposure to persistent compounds revolves around exposure in early childhood, and breast-fed infants are the sub-group of the population where exceedance of the limit is greatest. The diet and hence the pollutant exposure of infants are very different than adults: as long as the child is breast-fed, its mothers milk is the sole source of compound intake. Concentrations of contaminants in milk can be significant, since it has a relatively high fat content and derives from an individual who has accumulated compound via food intake over decades. Per kilogram of body weight, we are exposed to a greater amount of pollutants in the first few months of life than at any later stage. It is questionable if this has an impact in terms of adverse effects and research is underway to attempt to elucidate this.

The most recent data from a study in the UK followed the consumption of human milk by 48 infants over an eight-month period to give estimates of the mean consumption of human milk by nursing infants between 2 and 10 months of age (see Table 3.21).

Table 3.21: Estimated mean dietary intakes of PCDD/Fs and PCBs from human milk by breast-fed infants (data from MAFF, 1997)

Age [months]	Mean consumption milk [g.kg^{-1} bw day]	Mean intakes [pg TEQ.kg^{-1} bw.day^{-1}]		
		PCDD/Fs	PCBs	PCDDFs+PCB
2	160	112	58	170
3	140	100	51	150
4	124	88	45	130
5	103	73	37	110
6	79	56	29	84
7	63	44	23	67
8	42	30	15	45
10	37	26	13	39

Multiplication of milk consumption databy average levels of PCDD/Fs and PCBs in human milk samples collected in 1993-94 gave estimated intakes from human milk of 170 pg TEQ.kg^{-1} B.W.day^{-1} at age 2 months. This fell to 39 pg TEQ.kg^{-1}.day^{-1} at 10 months of age, due to an increased bodyweight and the move to a mixed diet. Clearly these values are considerably in excess of the current TDI

Table 3.22: Dioxins in human tissues throughout the Northern European Region [as pg TEQ.g^{-1}]

Country	n	Media	Year of collection	Mean	Range	Comments	References
Austria	13	M	1992-3	10.7		Urban	Liem and Theelen 1997
	21	M	1992-3	10.9		Rural	
	13	M	1992-3	14		Industrial	
Belgium	8	M	1992-3	20.8		Brabant	
	20	M	1992-3	27.1		Liege	
	6	M	1992-3	26.6		Brussels	
	9	M	1992-3	34.4		Flanders	
	200	B	1999	48	44-54	Flanders women	Covaci et al., 2001
Czech Republic	10	M	1992-3	12.1		Kladno	Holoubek et al., 2000
	13	M	1992-3	18.4		Uh. Hradiste	
	7	M	1999	29.1		Uh. Hradiste	
	15	M	1999	21.4		Praha	
	27	A	?	35.7	13.9-92		
Denmark	48	M	1992-3	15.2		7 cities	Liem and Theelen 1997
	4	M	1992-3	17.1			
	?	M	1995	16.7			Hilbert et al., 1996
Estonia	?	M	1991		13.5-21.4		Mussalo-Lindstom 1995
	?	M	1993	14.4		Urban	Vartiainen et al., 1997
	?	M	1993	12.4		Rural	
Finland	10	M	1992-3	21.5		Helsinki	Liem and Theelen 1997
	24	M	1992-3	12		Kuopio	
	?	M	1986-87		16-17.9		Mussalo-Lindstom 1995
	37	M	1995	34		Urban	Vartiainen et al., 1997
	33	M	1995	20		Rural	
Germany	10	B	1988	46.3			Holoubek et al., 2000
	102	B	1989	40.8	11.6-93.6		
	44	B	1992	26	12-61		
	70	B	1993	21.7	10.3-49		
	134	B	1994	19.1	5.2-44		
	180	B	1996	15.6	16.5-70		
	10	M	1992-3	16.5		Berlin	Liem and Theelen 1997
	185	M	1990	27			Schecter et al., 1991
	112	M	1992-3?	30	10-72		Beck et al., 1994
Hungary	20	M	1992-3	8.55		Budapest	Holoubek et al., 2000
	10	M	1992-3	7.8		Scentes	
Netherlands	10	M	1988	34.3	31-40		Liem et al., 1995
	104	M	1992-3	23.5	8.4-63.1	20 regions	Liem and Theelen 1997
	176	M	1992-3	30.2		Rotterdam	

Country	n	Media	Year of collection	Mean	Range	Comments	References
Norway	10	M	1992-3	10.1		Tromso	
	10	M	1992-3	9.3		Hamer	
Lithuania	12	M	1992-3	16.6		Palanga	
	12	M	1992-3	14.4		Anykshchiai	
Russia	23	M	1990	12		Siberia	Schecter et al., 1991
	1	M	1992-3	15.2		Arkhankelsk	Liem and Theelen 1997
	1	M	1992-3	5.9		Karhopol	
	?	M	1993	16.4		Urban	Vartiainen et al., 1997
	44	B	1997	45.5		Ufa	Amirova and Kruglov
	1	B	1998	14.8		Angarsk	Amirova et al., 2002
	11	B	1998	27.7		Sayansik	
	8	B	1998	24		Irkutsk	
	15	B	2000	37.8		Ufa	Amirova and Kruglov, 2001
Slovakia	10	M	1992-3	15.1		Michalovce	Liem and Theelen 1997
	10	M	1992-3	12.6		Nitra	
	30	B	?	20			Holoubek et al., 2000
	2	B	?	75		Chemko Co	
Sweden	?	M	1987		20.8-23.8		Mussalo-Lindstom 1995
Ukraine	5	M	1992-3	11		Kiev	Liem and Theelen 1997
	5	M	1992-3	13.3		Kiev	
	20	M	1992-3	17.9		Birmingham	
	23	M	1992-3	15.2		Glasgow (Sum	

WHO Breast milk monitoring

Since the mid-1980s, the WHO Regional Office for Europe, in collaboration with other international organisations and national institutions, has coordinated a comprehensive programme on possible health risks of PCBs and PCDDs/Fs, especially in infants, due to exposure through contaminated breast milk, and aiming to prevent and control environmental exposure to these chemicals (Van Leeuwen and Malish, 2002). International exposure studies on levels of these contaminants in breast milk were of special interest for this programme. The first WHO-coordinated exposure study took place in 1987-1988, the second round in 1992-1993 and the most recent in 2001-2002.

The third round of the WHO-coordinated exposure study was organised in order to collect data on more countries, including those beyond the European region, and was organised with the co-operation with IPCS and GEMS Food. The results of this round show that, in general, variation between countries is much higher that within countries. In some countries specific sites of contamination could be identified. As far as evaluated region III, industrialised countries like the Netherlands, show relatively high levels of PCDDs/Fs (median values range about 12-18 pg WHO-TEQ.g^{-1} fat). Low PCDDs/Fs levels have been found in Bulgaria, Hungary and Ireland (median values range about 6-7 pg WHO-TEQ.g^{-1} fat). Elevated levels of dioxin-like PCBs were found in human milk from Ukraine, Russia and the Czech Republic (median values range about 15-20 pg WHO-TEQ.g^{-1} fat). Low dioxin=like PCBs (< 4 pg WHO-TEQ.g^{-1} fat) were found in pooled samples from Hungary (Table 3.23).

Table 3.23: Levels of PCDDs/Fs and dioxin-like PCBs in human milk (2001-2002) [pg WHO-TEQ.g^{-1} fat]

Country	PCDDs/Fs		PCBs		Number of pools
	median	range	median	range	
Bulgaria	6.14	5.08-7.11	4.21	3.74-4.70	3

Czech Republic	7.78	7.44-10.73	15.24	14.32-28.48	3
Finland	9.44	9.35-9.52	5.85	5.66-6.03	2
Hungary	6.79	5.26-7.46	2.87	2.38-4.24	3
Ireland	6.91	6.19-8.54	4.66	2.72-5.19	3
Norway	7.30	7.16-7.43	8.08	6.56-9.61	2
Romania	8.86	8.37-12.00	8.06	8.05-8.11	3
Russia	8.88	7.46-12.93	15.68	13.38-22.99	4
Slovak Republic	9.07	7.84-9.87	12.60	10.72-19.49	4
Sweden	9.58	-	9.71	-	1
The Netherlands	18.27	17.09-21.29	11.57	10.90-13.08	3
Ukraine	10.04	8.38-10.16	19.95	14.10-22.00	3

Temporal trends in levels of PCDDs/Fs in human milk for countries participating in the current study as well as in one of the previous rounds confirmed that the declining trend continues. On average, the decline between the levels found in 2nd round in 1993 and those found in current study is about 40 %. In addition, levels of indicator PCBs in human milk vary widely between the countries, with lowest levels in Ireland and Bulgaria (median values 34 and 42 pg WHO-TEQ.g^{-1} fat, respectively), and highest levels in Slovak and Czech Republic (median values 443 and 502 pg WHO-TEQ.g^{-1} fat, respectively) (Table 3.24).

Table 3.24: Levels of indicator PCBs in human milk (2001-2002) [ng.g^{-1} fat]

Country	**Sum indicator PCBs**	
	median	**range**
Bulgaria	42	32-52
Czech Republic	502	496-1 009
Finland	91	84-98
Hungary	34	29-59
Ireland	61	41-64
Norway	119	106-132
Romania	173	165-198
Russia	138	83-311
Slovak Republic	443	331-621
Sweden	146	-
The Netherlands	191	178-210
Ukraine	136	102-148

3.4.4. HCB

Owing to its persistence and lipophilicity, HCB is present at low levels in the fatty tissues of virtually all members of the general population. Mean levels in adipose tissue of the human general population in various countries range from tens to hundreds of ng.g^{-1} wet weight (IPCS 1997). In general, concentrations of HCB in breast milk in various countries or regions range widely, and appear to be related to the degree of industrialization and/or urbanization within the survey area. Results of most studies on the levels of HCB in foods and human tissues over time indicate that exposure of the general population to HCB declined from the 1970s to the mid-1990s in many locations. Based on representative levels of HCB in air, water and food, the total intake of HCB by adults in the general population is estimated to be between 0.0004 and 0.003 ng.g^{-1} body weight per day. This intake is predominantly from the diet. Owing to the presence of HCB in breast milk, mean intakes by nursing infants have been estimated to range from < 0.018 to 5.1 ng.g^{-1} body weight per day in various countries.

Table 3.25: Levels of HCB in breast milk [ng.g^{-1} lipid] (Holoubek et al., 2000)

Country	n	Media	Year of collection	Mean	Range	Comments
Poland	277	A	1989-92	0.31	9 max	
	158	M		0.002	0.0002-0.01	More industrialised areas (mg l)
	199	M		0.002	0.0002-0.02	Less industrialised areas (mg l)
Slovakia		S	1992	5.4	0.16-23	ng.g^{-1}
UK						

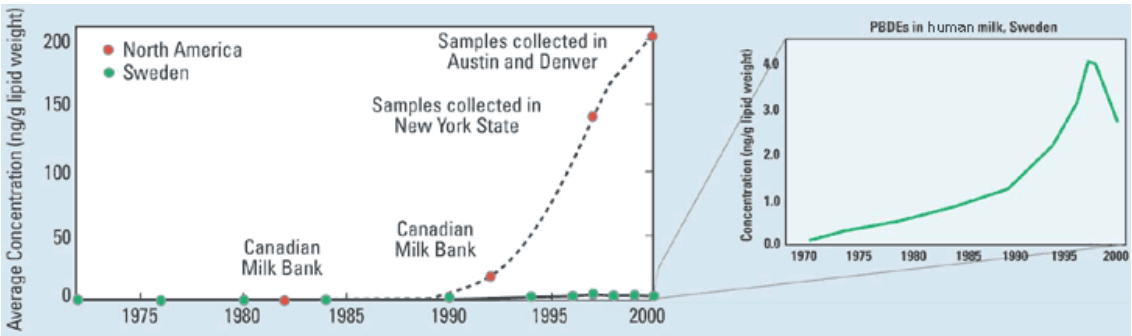
3.4.5. Polybrominated diphenyl ethers

Some persistent pollutants have not shared the overall decline in concentrations seen in recent years for PCBs, PCDDs/Fs and OC pesticides. Brominated fame retardants came into general use in the 1970s, when the 'classic' pollutants were being phased out. Data from Sweden sounded the first alarm about the potential for breast-milk contamination from PBDEs. In the Swedish study, archived samples collected between 1972 and 1997 were analysed for the presence of PBDEs to get an overall summed total of PBDEs in milk (see Figure 3.29 below). Levels of these compounds in human milk in Sweden shows an exponential rise in concentrations throughout 1980s. A single congener, 2,2´,4,4´-tetra-BDE (BDE-47) was the major component (60-70%), and was present at approximately 2.3 ng.g^{-1} lipid in 1997.

At present there are no other European data to confirm these trends in human tissues. The BgVV in Germany is launching a study (beginning 2002) aiming to supply up-to-date German data on the extent to which PBDEs are present in human breast milk. This study aims to clarify how these substances reach the human body, whether a diet without any animal products can improve the situation or whether the PBDE levels reflect general environmental contamination irrespective of eating habits.

An assessment of polybrominated diphenyl ethers (PBDEs) in the breast milk of North American women indicates that the body burden of Americans and Canadians is the highest in the world, 40 times greater than the highest levels reported for women in Sweden (ES&T News September 2001). The levels of PBDEs in North Americans appear to be doubling every two to five years as the Figure 3.10 below demonstrates. Only certain PBDE isomers have been detected in breast milk, and the level detected in Sweden has fallen by 30% every two years since 1997. The PBDE isomers/congeners detected in human breast milk are largely composed of tetra-, penta- and hexaBDE congeners with a single isomer, 2,2',4,4'-TeBDE, generally contributing 50-70% of the total. The predominant BDE congeners which were detected in human tissues, are the three *ortho-para*-(2,4-) substituted congeners: 2,2´,4,4´-tetra-BDE (PBDE-47); 2,2´,4,4´,5-penta-BDE (PBDE-99); and 2,2´,4,4´,5,5´-hexa-BDE (PBDE-153).

Figure 3.10: PBDEs in human milk: North America versus Europe



3.4.6. Conlusions

In summary, human exposure to PTS compounds in dominated by intake via terrestrial and aquatic food products which have a high lipid content and have been subject to bioaccumulation within agricultural foodchains e.g. milk, meat, eggs and fish (particularly oily and/or long-lived species). Exposure is generally well characterized and quantified for PCBs and PCDD/Fs and a range of organchlorine pesticides. The vast

majority of adult exposure will be below current WHO guideline values. Individuals exceeding the guideline value will be dominated by subsistence fishermen and their families, individuals who consume several meals of oily fish each week in addition to those consuming locally produced foods in the vicinity of an on-going sources of contamination.

Human lipid concentrations of well characterized compounds such as PCBs and PCDD/Fs have been declining significantly in recent years throughout the Region at a rate of approximately 5% per year since the early 1990s. This decline coincides with European restrictions on the manufacture and release of these compounds into the environment and in particular, into the atmosphere. For some PTS compounds of emerging concern such as PBDEs, there is some evidence of increasing trends in human breast milk during the last 20 years.

Breast-fed infants represent a distinct sub-group of the population whose exposure to PCDD/Fs and Dioxin-like PCBs will exceed current guideline values based on bodyweight for the first few months of life. In view of the significant declining trends in TEQ concentrations in breast milk over the last 20 years, WHO strongly recommend that breast feeding is encouraged and promoted for the child benefit.

3.4.7. References

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4. ASSESSMENT OF MAJOR PATHWAYS OF CONTAMINANTS TRANSPORT

4.1. GENERAL FEATURES

As many PTS compounds are semivolatile, their atmospheric transport can occur either in the gas phase or in the particle phase of the atmosphere. Due to their low vapour pressure, PTS tend to partition mainly into organic carbon containing media, such as soil, sediment, biota or aerosols. However, their volatility is often high enough to allow for long-range transport in a way that has been described as the ”grasshopper effect” (Wania and Mackay 1993, 1996). This means that the chemical is trapped in an organic phase without being degraded, and is then released back into the atmosphere, allowing for a short transport, after which it is trapped again and the procedure continues until the chemical is ultimately degraded. This “grasshopper effect” allows persistent chemicals of low vapour pressure to be transported long distances to areas where they have never been used, which is of concern both for ethical and environmental reasons. Transboundary movement may also be possible via large water bodies, where chemicals of low water solubility can be transported a long way via water particles and suspended sediment material or chemicals with high water solubility can be very effectively transported in the dissolved state. Migrating fish could also contribute to this phenomenon.

Regardless of the medium of chemical transport, what ultimately determines a chemical’s potential of long-range transport and thus transboundary movement are its partitioning properties in combination with the nature of the environmental media in or between which such transport occurs. Therefore, in order to achieve an adequate description of a chemical’s movement, it is crucial to create a picture which accurately describes the possible transport pathways that a chemical substance can undergo. This is a complicated task, since the complexity of the environment cannot be underestimated. As a first approach, the environment can however be divided into basic units, or compartments, which might include air with aerosols, water with water particles, soil, sediment and vegetation, or other significant media. The aim is then to achieve a description of transport processes and to derive a full picture of the movement of chemicals within the region being assessed. Figure 4.1 shows an example of how a general environment can be described and the direction of possible transport processes that a chemical might undergo in that environment.

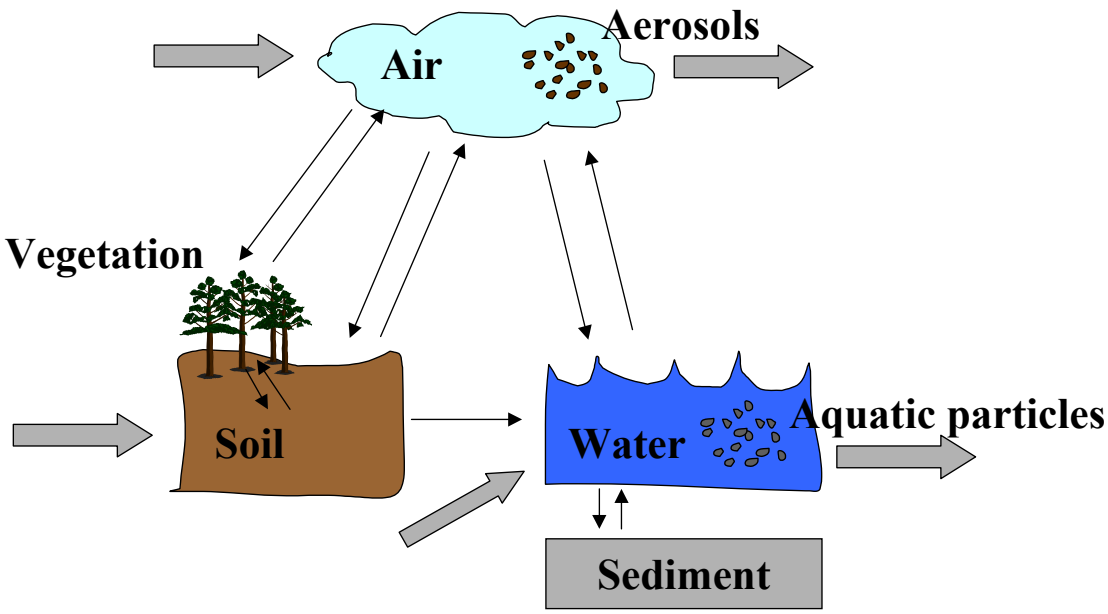


Figure 4.1: Example of compartments and transport processes that can be included in a general description of chemical movement in the environment.

4.2. REGION SPECIFIC FEATURES

Today, most PTS are banned and not "primarily" emitted in the European region. Transboundary air transport has been shown to be important for the occurrence of these chemicals in northern Europe. Atmospheric deposition is an important pathway for PTSs to both aquatic and terrestrial ecosystems. The cold climate in the northern part of the region may favour the deposition of the PTS.

Environmental compartments, such as vegetation, soil and sediments, will act as reservoirs for PTSs. In this region, contaminated sites, so-called "hot spots", will also constitute as significant reservoirs . PTSs may be re-emitted back from the ecosystem to the atmosphere and be transported both within and from the region into the arctic areas (grasshopper effect, see above).

4.3. OVERVIEW OF EXISTING MODELLING PROGRAMMES AND PROJECTS

4.3.1. Introduction

It is now increasingly accepted that successful management of chemicals in the environment requires quantitative information on major sources, environmental concentrations, transport pathways and routes of exposure to humans and wildlife. Essential also are assessments of risk as determined by the proximity of measured concentrations or body residues to those at which effects are observed. This quantitative information concerning chemical fate cannot be assembled from monitoring data alone, and is best captured in mass balance models. As a result, environmental fate models are widely used to predict contaminant fate and behaviour profiles and are becoming essential tools in the risk assessment process. The reliability of such models, however, is paramount if they are to be used successfully. There has also been considerable interest in developing screening models to cope with a range of geographical scales. Until recently much of the research carried out into the fate and behaviour and the likely effects of contaminants in the environment was carried out on a local scale. This usually involved an assessment of the impact of a single point source on the local vicinity. However, as a result of the measurement of contaminants in areas remote from their sources e.g. the arctic there has been increasing interest in the atmospheric transport of contaminants on a regional and global scale. Indeed there has been a suggestion that remote areas such as the arctic may become sinks for semi-volatile contaminants as they are preferentially deposited in cold climes where degradation processes are extremely slow. It is therefore clear that for successful management of contaminants an understanding of their long-term fate and ability to undergo long-range transport is required. As a result, there have been many international meetings of expert groups to discuss these problems and protocols for the control of contaminants that undergo long-range transport have been developed, e.g. UN ECE or UNEP. The fate and behaviour of contaminants within the environment is an extremely complex issue. Development of predictive models requires an understanding of the release of a contaminant (both quantity and emission route), its migration pathway through a multi-media environment, the dynamics of inter-compartmental exchange (e.g. clearance rates) and its ultimate fate. As the end use of such models is to protect humans or wildlife then ideally, these models need to be linked to food-chain models that can be used to predict exposure.

4.3.2. Steady state models

The Mackay suite of fugacity based models are good examples of steady state mass balance models, with the simple models relying on equilibrium partitioning and the more complex assuming that equilibrium is not achieved between compartments. The Level I model describes how a given amount of chemical partitions itself at equilibrium between six media; air, water, soil, bottom sediment, suspended sediment and fish. The area of the unit world into which the chemical is added is 100 000 km^2, which is about the size of England. Simple models such as this require few input parameters and are able to provide a likely distribution pattern for the chemical in a typical environment. However, this model obviously represents an oversimplification of the environment. For example, reactivity is not taken into account. The Level II model structure is similar but includes loss processes such as degradation. Moving up in complexity, and hence realism, is the ChemCan model. ChemCan is a Level III model and, unlike Level I and Level II calculations, does not assume that the compartments are in equilibrium, although the unit world is still at steady state. The model is divided into four compartments; air, water soil and sediment. In order to improve the sophistication of the model, 12 intermedia transport parameters are included which describe the ease of transfer of the chemical between compartments. As a result, the data input requirements are higher, although the potential output is of a higher quality. ChemCan divides Canada into regions - each complete with a geographical description, e.g. mean temperature, percentage water coverage etc. Each region can be given defined emission data into air, water, soil or sediment

compartments (or a combination). Background emission data can also be included to simulate chemical input from other regions. The output from the model provides a useful indication of the fate and behaviour of a chemical in a defined environment. It can also provide information on the relative importance of chemical loadings as a result of point sources, compared to advected input from neighbouring regions. TaPL3 is another example of a Level III steady state fugacity based environmental fate model which is intended to evaluate the persistence of chemicals and to assess potential for long-range transport in a mobile medium, either air or water.

4.3.3. Dynamic models

Most dynamic models are highly complex and location specific such as the EUROS atmospheric transport model developed by RIVM in the Netherlands and the EMEP (MSC-East) multi-media POP transport model (see below).

The MPI-MCTM (multicompartment chemistry-transport model of the Max Planck Institute for Meteorology, Hamburg) is designed to describe the environmental fate of semivolatile organic substances consistently with the geospheric transports and transformations including their geographic distribution and temporal variability. In the present state of model development it comprises atmosphere (3D), vegetation, soils and ocean (2D distribution of single layer boxes, each). It is based on an atmospheric general circulation model (GCM). The surface properties (vegetation and soil type distributions, land and sea ice, soil hydrological status) and the large-scale atmospheric circulation patterns are well represented in GCMs. The atmosphere is a three phase system (gas, particles, cloudwater), with the mass exchange between them being controlled by instantaneous equilibria. Degradation is controlled by the hydroxyl and nitrate radical concentrations (3D fields varying with time of day and month). Wet and dry deposition processes are considered for various types, each. Deposition of the gaseous molecules to ground surfaces is described by fixed deposition velocities or by accounting for the atmospheric and surface resistances. The soil is a multiphase system. The ocean is a single phase (neglecting the hydrosol), two layer system (locally and seasonally varying depth of well-mixed surface layer). A 3D ocean GCM will be coupled for the study of the environmental fate of substances, which on the long term might accumulate in the ocean. The model accounts for first-order degradation processes in the compartments and volatilization processes from the ground compartments into the atmosphere. The model is fully dynamic and can be run either in a climatological mode (then generating its own but realistic climate) or simulating historic climate (then driven by weather and sea surface observations).

There are few examples of dynamic fugacity based models. A primary emission driven fugacity model of the historical fate, behaviour and distribution of PCBs in the UK environment has been developed (Sweetman et al. 2002). The model attempts to re-create the temporal release trend of PCBs over the last 40 years and to replicate the observed historical trends in soils and sediments. One from the most known dynamic fugacity based model is POPCYCLING-Baltic (Pacyna et a., 1999). Many very useful results from this model were recently published for example the study by Breivik and Wania on the fate of HCHs in Northern Europe (Breivik and Wania, 2002a,b).

Table 4.1 lists examples of currently existing modelling tools and descriptions of their field of application and Table 4.2 lists of some currently existing models and examples of their fields of application.

Table 4.1: Examples of existing models and their fields of application

Model name	Description/Field of application	Reference
	Global Models	
MPI-MCTM	Multicompartmental chemistry transport model	Max Planck Institute for Meteorology, Hamburg
ChemRange	Distribution model for the assessment of long-range transport and persistence of chemicals	Scheringer (1996, 1997)
Globo-POP	Multi-compartmental mass balance model for evaluation of fate in the global environment	Wania & Mackay 1995
	Regional Models	
Level I,II,III models	Initial fate assessment of chemicals, e.g. for comparative reasons	Mackay et al., 1992
EQC model	Level I, II, III models in one package	Mackay et al.,1996a,b,c
CalTox	Regional multi-media model	T McKone
ChemCAN	Level III fugacity model containing site-specific parameters for the states of Canada	CEMC, Trent University

Model name	Description/Field of application	Reference
SimpleBox	Commonly used tool for risk assessment of chemicals within the European Union	van de Meent 1993; EC 1996
CoZMo-POP	A generic, dynamic coastal zone fugacity model, which can be modified by the user	Wania et al., 2000b
TaPL3	Level III model especially aimed at calculating potential for long-range transport	Beyer et al., 2000
ELPOS	Adapted version of EUSES-SimpleBox aiming to evaluate long-range transport potential and persistence of POPs	Beyer & Matthies, 2001
POPCYCLING-Baltic	Dynamic 85-compartment model used for assessment of the fate of POPs in the drainage basin of the Baltic Sea	Wania et al., 2000a
EUROS	Eulerian transport model	RIVM
EUTREND	Lagrangian atmospheric transport model	RIVM
MSCE-POP multi-compartment models	Models for the assessment of POP fate within the EMEP region and at hemispheric scale	Shatalov & Malanichev 2000
BETR North America	Segmented multicompartmental model for North America	MacLeod et al., 2001
Local Models		
ChemUK	Level IV UK scale multi-media model	Sweetman et al (2002)
MUM	Level III Urban 6-compartment model parameterized to Downtown Toronto	Diamond et al, 2001
CeStoc	Level III Urban 5-compartment model parameterized to centre of Stockholm	Palm, 2001
QWASI	A water-air-sediment exchange model that can be applied to a lake-or river system	Mackay et al., 1983 a,b
GREAT-ER	Riverine catchment model (GIS based)	Unilever and friends

Table 4.2: Detailed information about model time-scales, spatial resolution and main field of application.

Model name	Time Scale	Spatially resolved (yes/no or resolution)	Purpose	Input requirements	Media
MPI-MCTM	months/decades	300 km x 300 km	B,C,D,E,F		
ChemRange					
Globo-POP	decades	zonally divided	D,E,F	Properties, time-dependent emission rates	air/water/soil/sediment
Level I,II,III models	steady state			Key properties	air/water/soil/sed/fish
EQC model	steady state			Key properties	air/water/soil/sed/fish
CalTox			B		air/water/soil/sediment/veg
ChemCAN	steady state			Properties, emission rates	air/water/soil/sediment/veg
SimpleBox	steady state	Nested	A,B,C,D,F	Properties, emission rates	air/water/soil/sediment/veg .
CoZMo-POP	decades	No		Properties, time-dependent emission rates	air/water/soil/sediment/veg
TaPL3	steady state	No	A,E,F	Key properties	air, water, soil, sediment, fish
ELPOS					
POPCYCLING-Baltic	decades	Yes		Properties, time-dependent emission rates	air/water/soil/sediment/veg
EUROS					
EUTREND					
MSCE-POP multi-compartment models					
BETR North America	steady state				
Sweet model					
MUM					
CeStoc	steady state	No	B,D	properties, emissions	air/water/soil/sediment/urban film
QWASI					
GREAT-ER					

4.4. EMEP/MSCE-POP MODEL – A MODEL USED IN THE REGION

4.4.1. Introduction

For the systematic assessment of PTS contamination in the European region, a complex monitoring/modelling approach is used. This approach includes the arrangement of a superstation network, model assessment of contamination levels and national measurement campaigns. Apart from direct assessment of contamination measurement data can be used for model verification and formulation.

The EMEP/MSCE-POP model is a multicompartment model describing processes in and exchange between basic environmental compartments (atmosphere, soil, seawater, vegetation). The spatial resolution of the model is 50 × 150 km.

Figure 4.2 presents the structure of the model showing environmental media and processes included.

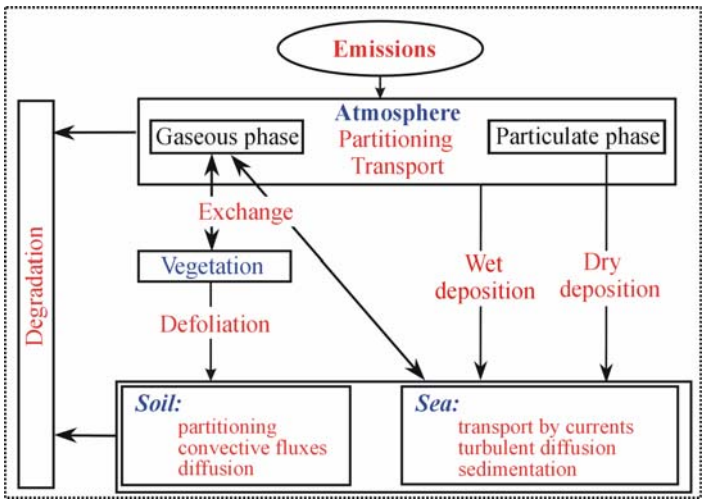


Figure 4.2: Scheme of the multicompartment transport model MSCE-POP

Apart from atmospheric transport the model particularly takes into account the transport of pollutants by sea currents. Vegetation is considered to describe their transport from vegetation to soil, and forest litter was introduced as an intermediate media between vegetation and soil.

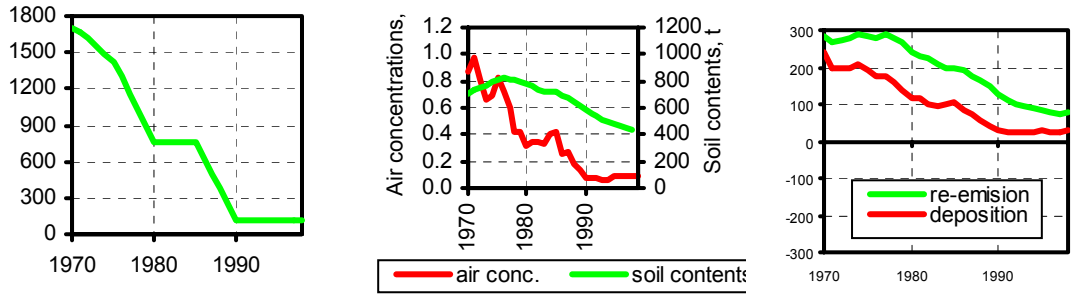
Model parameterizations have been elaborated for PAHs (B(a)P), HCHs (γ-HCH), PCBs, HCB, and PCDDs/Fs. The structure of description for each pollutant is:

- Emissions (official EMEP data, expert estimates and emission prepared for modelling);
- Distribution of pollution between basic environmental media;
- Model assessment of environmental levels;
- Transboundary transport (for B(a)P).

At present there exists a modification of the model for evaluation of B(a)P transboundary transport by country-to-country scheme with resolution 50 × 50 km.

In the model, atmosphere, soil, and sea are separated vertically into a number of layers to describe the vertical transport of a pollutant in question. To describe the variability of soil and vegetation properties in the horizontal direction the corresponding land-use and leaf area index information is taken into account.

Due to large accumulation capacities of the soil and sea compartments and the long periods required for equilibrium to be established, long-term calculations have to be performed in order to achieve a correct evaluation of POP environmental pollution levels. This can be illustrated by plots of long-term dynamics of PCB accumulation in various media (Fig. 4.3) calculated for the period from 1970 to 2010 under the assumption, that emissions from 1995 have remained on a constant level.



a emissions [t.y^{-1}] **b** air and soil **c** depositions over land [t.y^{-1}]

Figure 4.3: Long-term dynamics of emissions (a), air concentrations and soil content (b), and re-emission and particle deposition over land (c) for PCBs during the period from 1970 to 2010 under the assumption that emissions have remained constant since 1995

Figure 4.3 shows that the contamination levels in soil are determined by a long-term process and can act as secondary sources for PTSs for a long period of time.

The distribution of POPs between environmental compartments has been calculated and assessments of environmental levels, transboundary transport have been carried out for the EMEP region (Shatalov et al., 2000). Model calculations have been performed for the following POPs: PAHs (B(a)P), HCHs (γ-HCH), PCBs, HCB, and PCDDs/Fs. At present the discrepancies between measured and calculated data for all the pollutants considered are within an order of magnitude. The results are summarised below. More detailed information on comparison of calculated data against measurements can be found in (Shatalov et al., 2000; Shatalov et al., 2001). Detailed description of MSCE-POP model is published in MSC-E Report 4/2000 (vol.1) and in MSC-E web site: www.msce@msceast.org.

4.4.2. Benzo(a)pyrene (B(a)P)

The percentage of the total environmental content of B(a)P for each media calculated for 1997 is shown in Figure 4.4. Both terrestrial (soil and forest litter) and marine environments seem to accumulate B(a)P in essential quantities. A large fraction of B(a)P is predicted to accumulate in forest litter which is conditioned by filtration of B(a)P aerosol phase (which contains about 90% of the B(a)P present in the atmosphere) by forests. About 30% of the B(a)P annually emitted in the region is predicted to be transported out of the EMEP region. The spatial distribution of B(a)P contamination in different media has been calculated, see Figures 4.5 and 4.6.

The comparison of the spatial distributions of the air concentrations with the emissions shows good correlation. Countries with high air concentrations are also characterised by high B(a)P concentrations in soil (Fig. 4.5a). The model predicts high soil concentrations of B(a)P (30-60 ng.g^{-1}) in Germany, Poland, the Czech Republic, Slovakia, Belgium, the Netherlands, Luxembourg and in parts of the Ukraine and Russia.

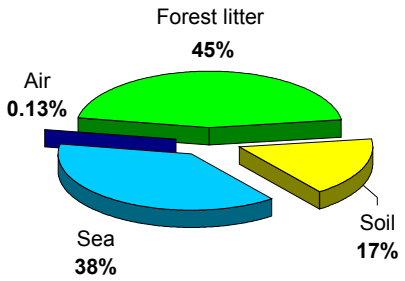
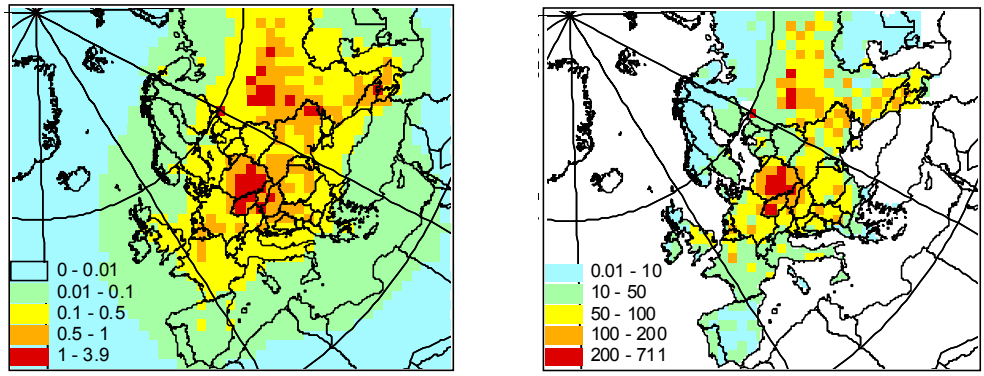


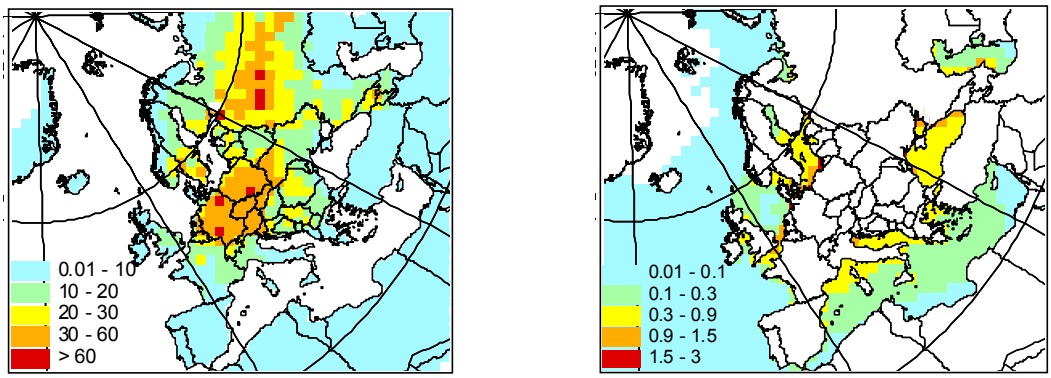
Figure 4. B[a]P redistribution between basic compartments by 1997 calculated by EMEP/MSCE-POP model using emission expert estimates

Figure 4.4: B(a)P redistribution between basic compartments by 1997 calculated by EMEP/MSCE-POP model using emission expert estimates

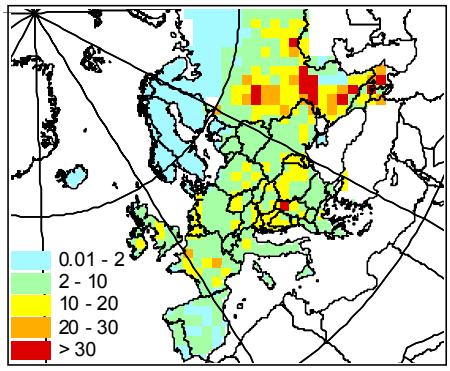


a **b**

Figure 4.5: a - B(a)P air concentrations [ng.m^{-3}]; b - B(a)P emission in 1997 used in calculations, [g.km^{-2}.y^{-1}]



a - soil concentrations [ng.g^{-1}] **b** - concentrations in sea [µg.m^{-3}]



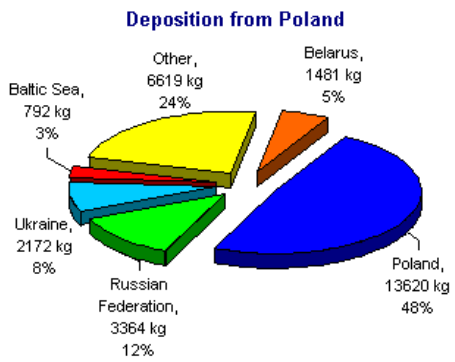
c - concentrations in vegetation [ng.g^{-1}]

Figure 4.6: Spatial distribution of B(a)P contamination in main environmental compartments by 1997

The regions for which the model gave high concentrations of B(a)P in sea water (up to 3 µg.m^{-3}) are located in the Black Sea bordering Georgia, Russia and the Ukraine, in the Baltic Sea, and in the North Sea near Belgium and Germany (Figure 4-6b). The concentration distribution in vegetation (Figure 4-6c) indicated high concentrations of B(a)P in vegetation (above 10 ng.g^{-1}) in Austria, Belgium, Bosnia and Herzegovina, Georgia, Republic of Moldova, Romania, and Yugoslavia.

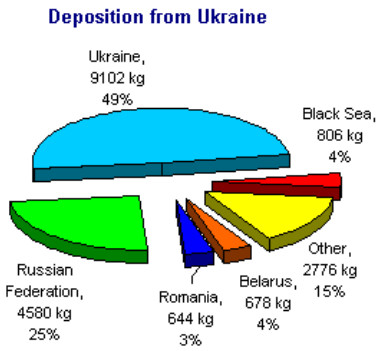
According to emission expert estimates, Poland, Russian Federation and the Ukraine make the greatest contribution to European pollution of B(a)P (28, 91 and 18.6 t.y^{-1} respectively, which cover over 90% from total European deposition). The distribution of deposition from these countries between other European countries and regions (export charts) was constructed on the basis of calculations by EMEP/MSCE-POP model for 1998, Figure 4.7.

Figure 4.7 shows that for Poland and Ukraine about half of their emissions of B(a)P is finally deposited in other countries. This shows the role of transboundary transport in assessment of B(a)P contamination in the European region.



a

b



c

Figure 4.7: Export charts for deposition from Poland (a), Russian Federation (b) and Ukraine (c) for 1998 calculated by EMEP/MSCE-POP model on the basis of expert estimates

Model calculations have also been used in order to estimate the contribution of B(a)P to other countries via deposition These calculations allow us also to evaluate contributions of European countries to depositions to a particular countries. Figure 4.8 presents this information (import charts) for the above three countries. It can be seen that for these countries an essential part of deposition is caused by transboundary transport from other European countries.

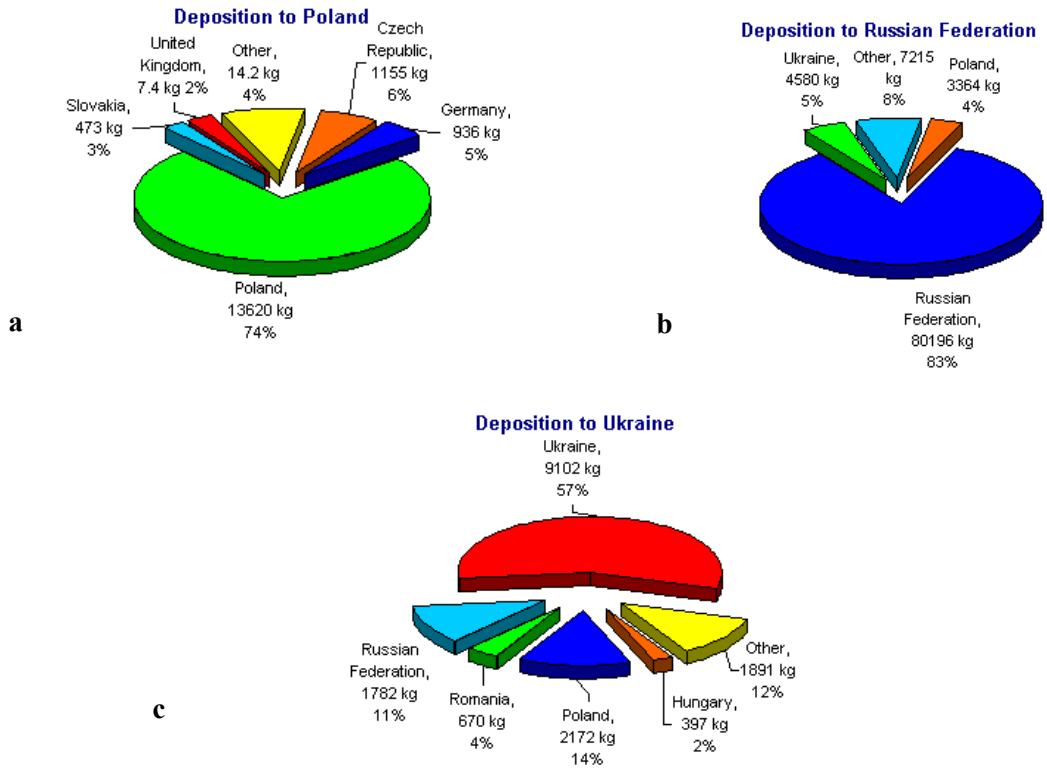


Figure 4.8: Import charts for deposition from Poland (a), Russian Federation (b) and Ukraine (c) for 1998 calculated by EMEP/MSCE-POP model on the basis of expert estimates

4.4.3. γ-HCH

Modelling of γ-HCH transport have been performed for the period from 1970 to 1997 with **expert emission estimates** since the amount of official data available is very small.

The calculated distribution of γ-HCH contamination between environmental compartments in 1997 is presented in Figure 4.9, where the percentage of total environmental content is given for each media.

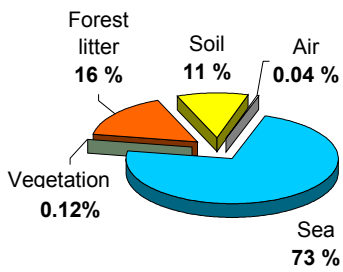
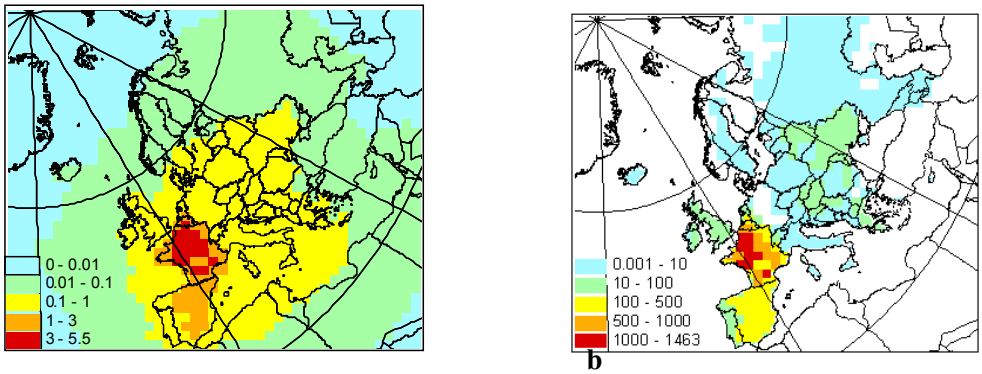


Figure 4.9: Redistribution of environmental pollution by γ-HCH between basic compartments by 1997 calculated by EMEP/MSC-E

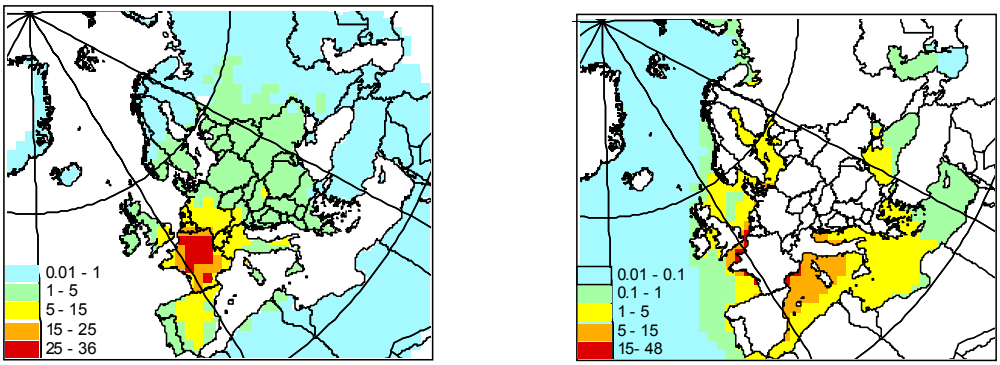
The highest content of γ-HCH is fixed in seawater (about three fourths of the whole content). The content in soil and forest litter constitutes together about one fourth of the total amount. The air and vegetation content of γ-HCH seems to be minor. Thus the results from this calculation indicates that the marine environment plays an appreciable role in γ-HCH long-range transport.

The spatial distributions of γ-HCH contamination in different media are presented in Figures 4.10 and 4.11. The spatial distributions of γ-HCH in air show good correlation with the regions where emissions occurs.

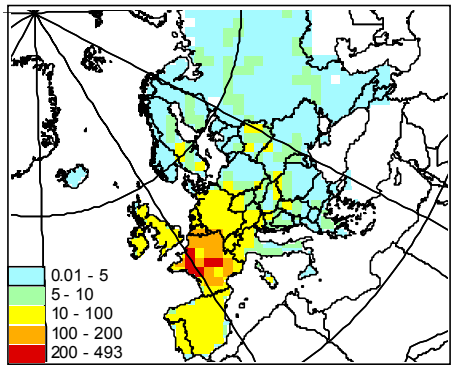


a b

Figure 4.10: a γ-HCH air concentrations [ng.m^{-3}]; b γ-HCH emission in 1997 used in calculations, [g.km^{-2}.y^{-1}].



a - soil concentrations [ng.g^{-1}] b - concentrations in sea [µg.m^{-3}]



c - concentrations in vegetation [ng.g^{-1}]

Figure 4.11: Spatial distribution of γ-HCH contamination in main environmental compartments by 1997

As was the case for air concentrations, maximum soil concentrations for γ-HCH coincide with the maximum emission region. The highest soil concentrations (1-36 ng.g^{-1}) were estimated for Luxembourg and Belgium, while slightly lower (5-15 ng.g^{-1}) were estimated for Switzerland, the Netherlands, Germany and Austria.

The maximum seawater concentrations (up to 50 µg.m^{-3}) were achieved in sea regions located close to major emission sources. γ-HCH is entering seawater near emission sources and is then transported by sea currents up to the northern coast of Scandinavia.

Maximum concentrations γ-HCH in vegetation (100-500 ng.g^{-1}) were estimated for Luxembourg and Belgium. Concentrations in Switzerland, the Netherlands, Ireland, Germany, the UK and Austria were in the range from 20 to 100 ng.g^{-1}.

4.4.4. Polychlorinated biphenyls

Modelling of PCB transport was performed for the period from 1970 to 1998 with **expert emission estimates**. We remark that the discrepancies between official data and emission expert estimates for majority of European countries vary from 1% to 60% with exceptions for Hungary and the Netherlands.

The distribution of PCB contamination between different environmental compartments for 1998 is given in Figure 4.12.

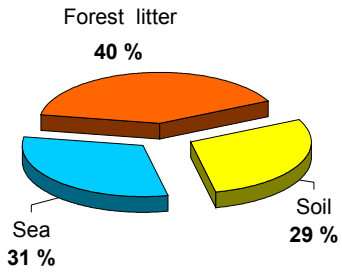


Figure 4.12: Redistribution of environmental pollution by PCB between basic compartments by 1998 calculated by EMEP/MSCE-POP model using emission expert estimates

The PCB mass distribution between main media shows that about 29% of total PCB contents in the environment is contained in soil, 40% – in forest litter, and 31% – in seawater. Fractions of PCB in air and vegetation are not shown in the diagram since their values are insignificant in comparison with other media. So, for PCBs the main accumulating media is soil (since forest litter can be treated as the upper soil part). As seen from calculation results re-emission from soils is essential for the description of PCB behaviour in the environment. About 50% of annual emissions are transported outside the calculation domain, EMEP-region.

The spatial distribution of PCB contamination in different media has been estimated. Figure 4.13 shows the PCB air concentration distribution (a) in comparison with that of the emissions (b).

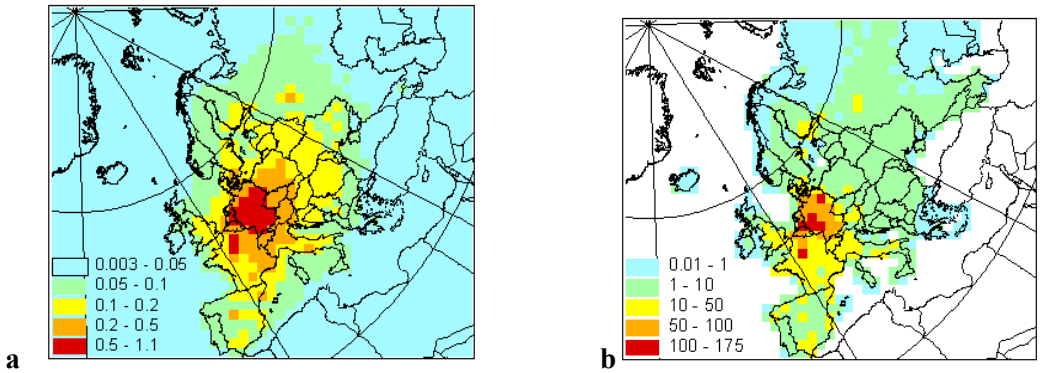
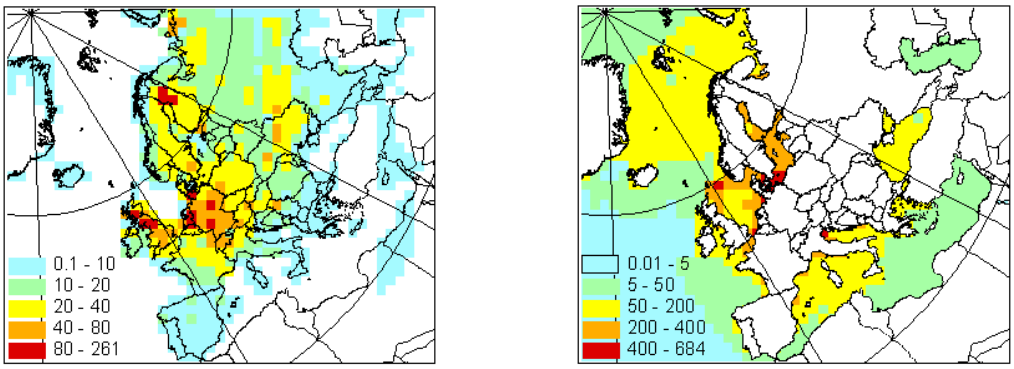
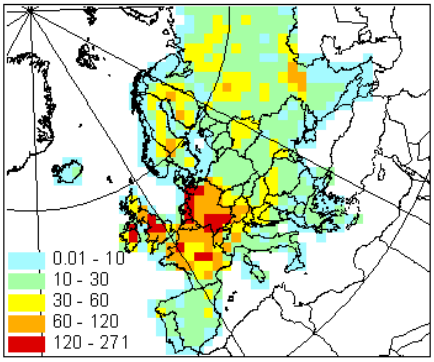


Figure 4.13: a - PCB air concentrations [ng.m^{-3}]; b - PCB emission in 1998 used in calculations, [g.km^{-2}.y^{-1}] Calculations made by EMEP/MSCE-POP model using emission expert estimates.

Figure 4.14 shows concentration levels of PCB in main environmental compartments other than atmosphere (soil, sea, and vegetation).



a - soil concentrations [ng.g^{-1}] **b** - concentrations in sea [ng.m^{-3}]



c - concentrations in vegetation [ng.g^{-1}]

Figure 4.14: Spatial distribution of PCB contamination in main environmental compartments by 1998

Like in the case of air concentrations the maximum soil concentrations for PCB coincide with the maximum emission region. Maximum soil concentrations were estimated in the middle part of Europe. However, soil concentrations in some parts of the Scandinavian Peninsula were also relatively high. Possibly, such concentrations can be explained by influence of forests. Similar to concentrations in soil, the estimated maximum concentrations in vegetation (up to 270 ng.g^{-1}) were found in the central part of Europe and in some parts of the Scandinavian Peninsula. The maximum calculated seawater concentrations (up to 680 ng.m^{-3}) were achieved in sea regions located close to major emission sources.

Model reliability. At present the discrepancies between measured and calculated data for all the pollutants considered are within an order of magnitude but in many cases are less. As an example, the results of the comparison between measured and calculated concentrations in the lower atmospheric layer for PCB-153 are presented (see Figure 4.15).

It can be seen that while measurements vary by two orders of magnitude, over 75% of comparisons are within a factor of three. This is in an agreement with emission uncertainties. These results show that the model reasonably reflects the spatial distribution of contamination. More detailed information on comparisons of calculated data versus measurements can be found in (Shatalov et al., 2000, 2001).

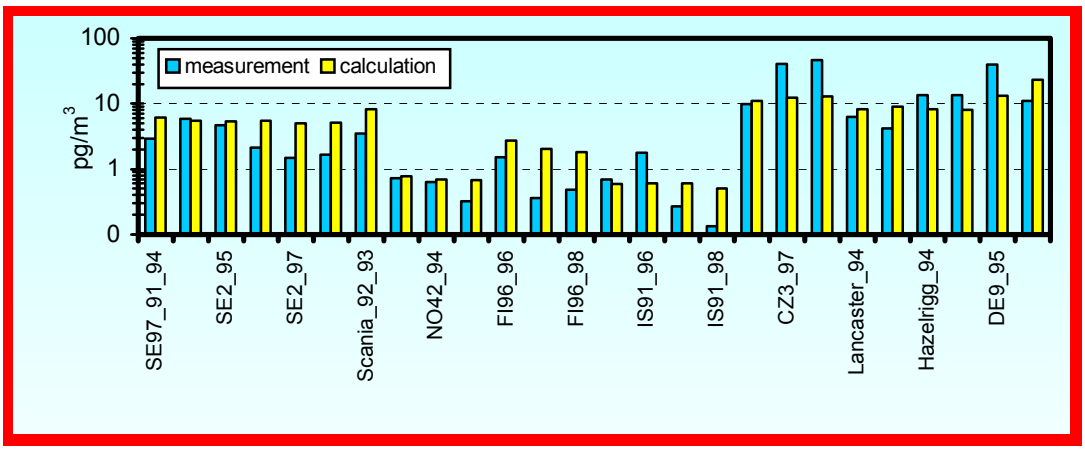


Figure 4.15: PCB 153 mean annual air concentrations [pg.m^{-3}]

4.4.5. Hexachlorobenzene (HCB)

Modelling was performed with **expert emission estimates** for the period from 1970 to 1998 since in present the main aim of the research was investigation of long-term trends of HCB contamination.

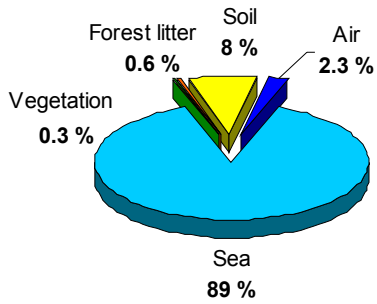
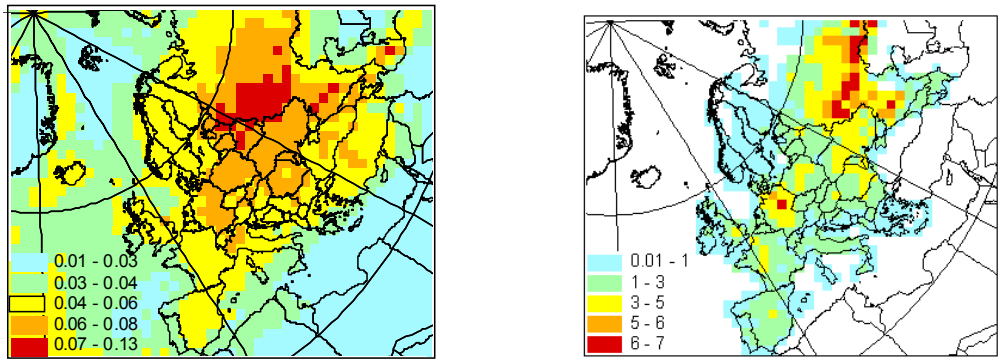


Figure 4.16: Redistribution of environmental pollution by HCB between basic compartments in 1998

The distribution of HCB between different environmental compartments is presented in Figure 4.16. This distribution shows that more than 80% of total HCB content in the environment is contained in seawater. Thus, HCB is mainly accumulated in the marine compartment. Further, according to the model calculations, vegetation plays insignificant role in HCB long-range transport and accumulation in the environment. This conclusion is also confirmed by measurement results (see Shatalov et al., 2001). Calculations show that more than 80% of annual emissions are transported outside the calculation domain.

Here spatial distributions of HCB contamination of different media are characterised. Figure 4.17 shows the HCB air concentration distribution (a) in comparison with emissions (b).



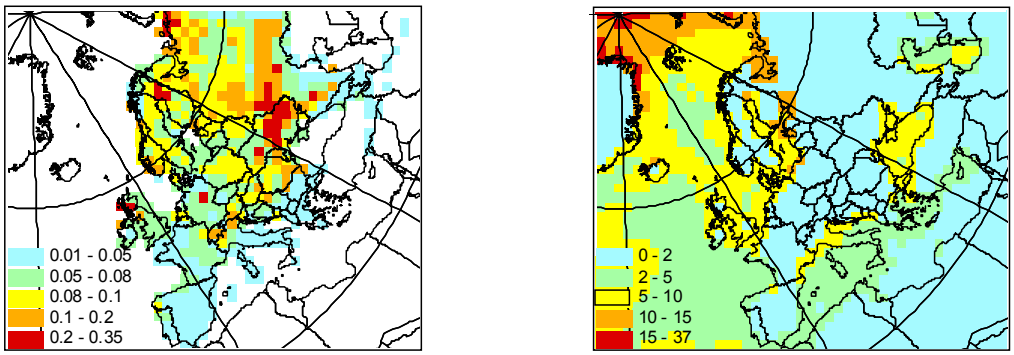
a b

Figure 4.17: a - HCB air concentrations [ng.m^{-3}]; b - HCB emission in 1998 used in calculations [g.km^{-2}.y^{-1}] Calculations made by EMEP/MSCE-POP model using emission expert estimates

The distribution of atmospheric concentrations of HCB over the European region is much more uniform than for other considered pollutants. This is conditioned by high HCB persistence in the atmosphere (the corresponding half-life is about 1.8 year) and, as a consequence, high ability to the long-range transport.

The concentration levels of PCB in soil and seawater are shown in Figure 4.18 (vegetation is not considered since the content in this compartment is comparably small). A map of HCB concentration distribution in soil is presented in Figure 4.18a. The comparison of this map with that of emission allows to draw a conclusion that soil pollution levels are not defined by the emissions of the current year and they are formed in the process of long-term accumulation.

The map of sea concentration distribution (Fig. 4.18b) shows that HCB is emitted both by European sources and that there is an inflow to the calculation grid through its northern and western boundaries. Clearly, like to the case of air concentrations the hemispheric model can essentially correct spatial distribution of HCB share transported by sea currents to the EMEP region from outside. These results are preliminary and are to be refined by usage of hemispheric version of the model.



a - soil concentrations [ng.g^{-1}] b - concentrations in sea [ng.m^{-3}]

Figure 4.18: Spatial distribution of HCB contamination in soil and seawater by 1998. Calculations by EMEP/MSCE-POP model using emission expert estimates

Due to the high persistence and volatilization ability of some PTS, the may be transported from the European region and will contribute to the contamination of other regions. The spatial distribution of HCB air contamination from European sources over the Northern Hemisphere calculated by hemispheric version of MSCE-POP model is exemplified in Figure 4.19 (Malanichev et al., 2002). The figure shows that European sources can contribute to HCB air contamination in such remote regions as Asia, the Arctic and North America.

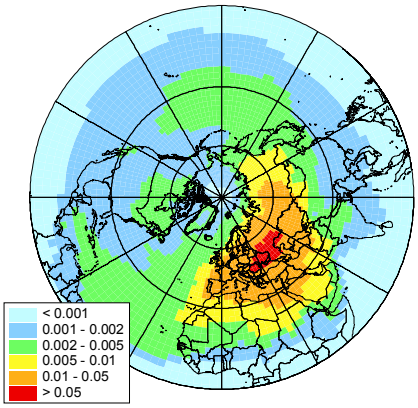


Figure 4.19: Spatial distribution of HCB air concentrations from European sources [ng.m^{-3}]. Calculations made by hemispheric version of MSCE-POP model for 1990.

4.4.6. PCDDs/Fs

Modelling of PCDDs/Fs transport was performed for the period from 1970 to 1999. Note that all the calculations were made in I-TEQ.

The distribution of PCDDs/Fs contamination between environmental compartments in 1999 is presented in Figure 4.20 which gives the percentage of total environmental content for each media.

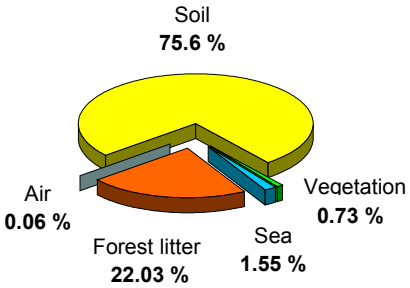


Figure 4.20: Redistribution of environmental pollution by PCDDs/Fs between basic compartments by 1999

This distribution shows that similar to the case of PCBs the main accumulating compartment for PCDDs/Fs is soil. The calculations show that about 60% of PDCC/F annual emissions are transported outside the calculation domain.

The spatial distributions of PCDD/F contamination of different media have been estimated. Figure 4.21 shows PCDD/F air concentration distribution together with emission distribution for 1999.

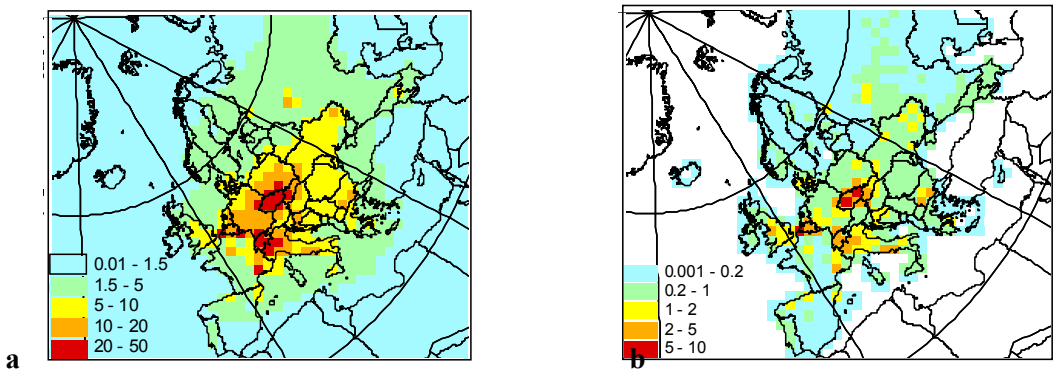


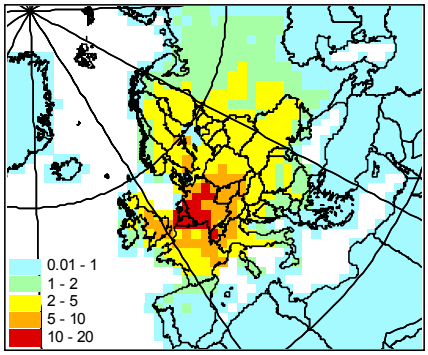
Figure 4.21: a – PCDDs/Fs air concentrations [fg I-TEQ.m^{-3}]; b – PCDDs/Fs emission in 1999 used in calculations [ng I-TEQ.m^{-2}.y^{-1}]

According to calculations, maximally polluted countries (with average concentration level above 20 fg.m^{-3}) are Czech Republic (concentration range is 12 – 52 fg.m^{-3}), Switzerland (8 – 31 fg.m^{-3}), Luxembourg (23 fg.m^{-3}), Belgium (10 – 27 fg.m^{-3}), and Slovakia (10 – 28 fg.m^{-3}).

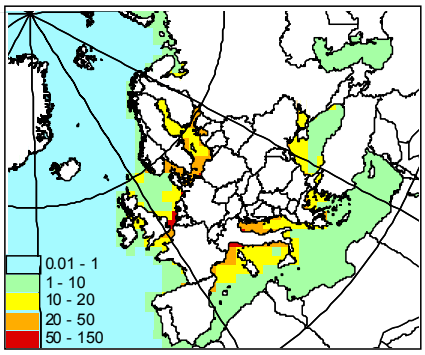
Soil concentrations vary from 0 to 20 pg.g^{-1} (Fig. 4.22a). Maximally polluted countries (with average concentration level above 10 pg.g^{-1}) are Luxembourg (15 pg.g^{-1}), Belgium (11 – 22 pg.g^{-1}), the Netherlands (0.5 – 22 pg.g^{-1}), and Germany (0.5 – 22 pg .g^{-1}).

Seawater concentrations (Fig. 4.22b) range between 0.01 and 150 fg.l^{-1}. Maximum concentrations (above 30 fg.l^{-1}) are achieved in waters washing Belgium (66 – 159 fg.l^{-1}), the Netherlands (18 – 159 fg.l^{-1}), and Poland (32 – 67 fg.l^{-1}).

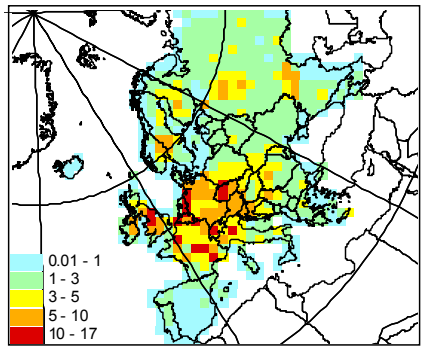
Maximum concentrations (with average concentration level above 10 pg.g^{-1}) are found in the following countries: Luxembourg (19 pg.g^{-1}), Belgium (2 – 19 pg.g^{-1}), and Czech Republic (4 – 19 pg.g^{-1}).



a - soil concentrations [pg I-TEQ.g^{-1}]



b - concentrations in sea [fg I-TEQ.l^{-1}]



c - concentrations in vegetation [pg I-TEQ.g^{-1}]

Figure 4.22: Spatial distribution of PCDDs/Fs contamination in main environmental compartments in 1999

4.5. EXPERIMENTAL EVIDENCE FOR LONG-RANGE TRANSPORT (LRT)

As previously discussed, atmospheric and multimedia transport models are useful tools for estimating the potential of a chemical to be transported long distances. However, in order to provide experimental evidence, measurements are required. Reliable experimental data that support model predictions for a number of POPs, can encourage application of models to other substances. Lack of experimental data however, makes it impossible to validate or evaluate model predictions.

Measurements of POPs have been carried out in areas in the European region far from any potential point sources of the chemical. POPs have been detected in background and remote areas in Europe (See Chapter Levels 3.1).

Detection of a substance at remote locations where it has never been used provides evidence for long-range transport, since it means that the chemical has actually managed to get there in one way or another. However, the precise analytical methods we possess today enable us to detect any substance almost anywhere and pure detection may not necessarily be an evidence for high transport potential.

In order to obtain experimental evidence for the LRT potential of POPs in a particular region more extensive investigations are required. For example, such an investigation could include sampling along a vertical (or horizontal) transect in one or more environmental media with the aim to provide information on changes in concentrations when moving away from identified point sources or larger source areas.

If concentrations decline quickly, then LRT is unlikely to occur, but if a shallow slope of the concentration curve is obtained, then LRT might be an issue. For some compounds and media an increase in concentration might even be possible when moving away from the source, due to the so-called “global fractionation effect”,

which suggest that persistent low volatile substances are transported from temperate regions to regions with colder climate (e.g. Simonich and Hites, 1995; Wania and Mackay, 1996).

Airborne concentrations of polychlorinated biphenyls (PCBs) and hexachlorobenzene (HCB) were measured by using passive air samplers (SPMDs) along a latitudinal transect from the south of the UK to the north of Norway during 1998-2000 (Meijer et al, in prep)

Spatial trends of the 1998-2000 data show a decrease in absolute sequestered amounts of the heavier PCBs with increasing latitude / distance from the source area, whereas the lighter PCBs were more equally distributed along the transect. However, relative sequestered amounts (expressed as % of total PCB) show a clear latitudinal trend with the relative contribution of the lighter congeners increasing with increasing latitude, providing evidence of latitudinal fractionation. Absolute amounts of HCB are increasing with increasing latitude, suggesting this compound is undergoing cold condensation / grass hopping.

Similarly, the spatial variation of PCB concentrations in soil has recently been investigated along the same transect mentioned above, but at 41 sampling stations evenly distributed from the southern UK to Bear Island off the coast of northern Norway (Meijer et al., 2002). The results indicated that the relative concentrations of more volatile PCBs (tri-and tetrachlorinated) increased with latitude, which supports the idea of global fractionation and long-range transport of PCBs.

Grimalt et al. (2001) studied the variation of fish and sediment concentration of various organochlorine compounds (OCs; e.g. PCBs, DDT, HCHs) in European mountain lakes. The study showed that concentrations of less volatile organochlorines in fish and sediment increased with altitude, which was assigned the effect of a decrease in temperature. These findings also support the theory of global fractionation and long-range transport.

Agrell et al (1999) found a negative relationship between latitude and concentration of POPs, such as PCBs, in the atmosphere of the Baltic Sea area. This south to north gradient of semivolatile POPs could be the result of a ”regional distillation” process, where POPs used in the warmer climate regions of the Baltic (or further south, in the equatorial region) are volatilised and driven by temperature gradients to colder areas.

Table 4.3 lists the modelled or measured indications for long-range transport of selected substances.

Table 4.3: List of modelled or measured indications for long-range transport of selected substances. Substances in italic font have not been assessed. A: More than 10 times higher potential than DDT (LEQ >10) B: 1<LEQ<10 C: 0.1<LEQ<1 D: LEQ<0.1 LEQ = Long-Range Transport Equivalents; reference substance p,p’-DDT

Substance	**Air LRT potential (modelled)**	**Water LRT potential (modelled)**	**LRT potential (Expert judgement)**	**Measurements indicating LRT?**	**Main transport medium**	**References**
Aldrin	D	C		No	water	
Chlordane	C	C		Yes	air, water	Brorström-Lundén, regular monitoring
DDTs	C	C		Yes	air, water	Calamari, 1991, Muir et al., 1995
Dieldrin	C	B		yes	water	Muir et al., 1995?
Endrin	C	B		yes	water	
Heptachlor	C	D			air	
HCB	A	C		yes	air	Calamari, 1991, Simonich & Hites, 1995
Mirex			*A+*			
Toxaphene	B	B		yes	air, water	
PCBs	B-C	C		yes	air	Iwata et al., 1993, Muir et al., 1996; Simonich & Hites, 1995
Dioxins	B-C	C		yes	air	

Substance	Air LRT potential (modelled)	Water LRT potential (modelled)	LRT potential (Expert judgement)	Measurements indicating LRT?	Main transport medium	References
Furans	B-C	B-C		yes	air,water	
HCHs	A-B	B		yes	air	Iwata et al., 1993; Simonich & Hites, 1995
PCP	B	B		?	air, water	
PAHs	C-D	B-C		yes	water	numerous...
Org. Mercury Compunds				*?*		
Org. tin compounds			*D*	*no*		
Org. lead comp.			*D*	*no*		
PBDE	B-C	C		yes	air	several...
Phthalates	B-C	C-D		?	air	
Endosulphan	C	B-C		no	water	
Atrazine	D	A		no	water	
Chlordecone						
Octylphenols			*D*	*no*		
Nonylphenols			*D*	*no*		
Chlorinated Paraffins			*B*	*no*		

Main purpose of model: A: Ranking B: PECs C: Budgets D: Distribution E: TBT F: Persistence

4.6. CONCLUSIONS

Transboundary transport is important for the occurrence of PTS in the European region. Atmospheric transport processes are important pathways for PTS to both aquatic and terrestrial ecosystems.

The evidence of LTR in the region has been investigated both with measurements and modelling.

An integrated monitoring/modelling approach is applied for assessment of PTS contamination in the European region. This approach includes arrangement of superstation network, model assessment of contamination levels and national measurement campaigns. In modelling activities accumulation in the compartments other than atmosphere is important.

At present there exist a lot of multicompartment PTS transport models both steady-state and dynamic describing PTS fate in the environment (see Tables 4 – 1 and 4 – 2 above). In the framework of LRTAP Convention the EMEP/MSCE-POP model is used for assessment of PTS contamination in the region.

Modelling activities are useful for evaluation of PTS redistribution between various environmental compartments, long-term trends of environmental contamination, spatial distribution of concentrations in different media (atmosphere, soil, seawater, vegetation) and transboundary transport.

Some PTS possess very high long-range transport potential and hemispheric/global scale is reasonable for them to assess European contamination. The hemispheric version of EMEP/MSCE-POP model indicates the ability of some PTS to transport to and from the European region.

PTS often possess very high long-range transport potential and hemispheric/global scale is reasonable to assess European contamination. The results of EMEP/MSCE-POP model indicate the ability of some PTS such as PCBs, PCDDs/Fs, γ-HCH.

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5. PRELIMINARY ASSESSMENT OF THE REGIONAL CAPACITY AND NEED TO MANAGE PTS

5.1. INTRODUCTION

Region III has 29 countries, 22 of them signed and 8 already ratified SC. Many countries of the Region also signed (24 from 36 which signed this Protocol in that time) and ratified (11 from 12) the Aarhus Protocol to the Convention on Long-Range Transboundary Air Pollution on POPs.

The production and use of PCBs and OCPs are restricted or banned with very few exceptions. Air, water, soils, plants and foods are legally protected against hazardous substances in the Region. The PTS inventories of releases to air, water, land and products are an ongoing process. Few countries have complex emission inventories based on the measurement of real emission factors, all countries based on EMEP and CORINAIR activities are using the European Atmospheric Emission Guidebook for annual inventory, but lack of actual inventories exist as far as water and land releases and the products contents of PTS. The most "open" problem is PTS by-products such as PCDDs/Fs, PAHs, HCB. Also the inventory of obsolete pests is on the acceptable level. The evidence of PTS hot spots remains a problem in CEECs.

5.2. MONITORING CAPACITY

5.2.1. Introduction

The use of chemicals almost inevitably means that in many cases some portion of the used volumes ends up in the environment. It is thus essential that the levels of some of these substances in the environment be measured to check that the use does not result in concentrations that are unacceptable to human health or to the environment.

A large number of measurements are being performed every year on environmental pollutants in monitoring and survey type programs. To some extent these activities are harmonised in regional programmes, such as the water quality (GEMS/WATER) and the marine programs for the Northeast Atlantic (OSPAR), but a lot remains to be done in order to produce consistent and comparable results that may be used for a wide variety of purposes e.g. emission controls, remediation, physical planning and regulatory purposes. Furthermore, many of the data are neither publicly available nor accessible, which makes them useful only for limited purposes. This situation is far from ideal and there is room for improvement. At present several new activities are being initiated e.g. the water quality control programme in Europe under the Water Framework Directive.

A measurement is normally designed to answer a specific question and often the possibility to use the results for other purposes are not considered. Measurements are often labour and instrument intensive and the results are therefore expensive to obtain. It is thus essential that they can be used as effectively and as broadly as possible. Measured data can be used for many purposes, e.g. to study:

- the emission strength of a specific source
- the distribution of such an emission
- the presence of a chemical in pristine or background areas
- the geographic distribution of a chemical
- temporal trends of a chemical in the environment
- specific exposure situations.

These are the most commonly expressed aims with monitoring programmes, but it should be kept in mind that the data may also be used for a number of other purposes e.g. to determine the bioaccumulation, biomagnification and other specific parameters of a chemical. The risk assessment of a chemical or chemicals is also heavily dependent on existing exposure data and there is normally no time and few resources to start new targeted measurements and the assessor has to rely on existing data.

The quality of the result of a measurement depends on a number of factors, both for the sample itself and for the measurement. The major problem in sampling is obtaining "representative" samples. The quality of the

measurement is also influenced by a number of factors. The accuracy, which describes the difference between the result and true value, is often difficult to determine, as the latter is not known. Repeatability (inter-laboratory variation) and reproducibility (intra-laboratory variation) can be determined in calibration exercises. Data produced within an individual monitoring program are often, but not always, comparable due to the design of the program and calibrations performed within the program. Differences may occur over time as new analytical methods or sampling techniques are introduced to the programme. Comparing data from different programs is more difficult for a number of reasons. Different sample matrices (different fractions of a sediment, different species, different ages etc) can make it almost impossible to compare results without extensive investigations of the origin etc. of the data. Also different types of calculations (wet or dry weight basis, wet weight or lipid weight basis, etc) may inadvertently make the results difficult to compare if not all the necessary information for recalculations are available.

There is obviously room for increased harmonisation of measurements of chemicals in the environment. Ongoing monitoring programmes are to some extent harmonised and data from e.g. national activities are often fed into regional or global programmes an operation for which harmonisation is a prerequisite. Smaller programmes and surveys may be less well planned and thus the results are often difficult to compare with those from other, more systematic, investigations.

5.2.2. Existing regional monitoring programmes

- Since 1976, the **Global Environment Monitoring System - Food Contamination Monitoring and Assessment Programme**, which is commonly known as **GEMS/Food**, has informed governments, the **Codex Alimentarius Commission** and other relevant institutions, as well as the public, on levels and trends of contaminants in food, their contribution to total human exposure, and significance with regard to public health and trade. GEMS/Food-EURO made a major contribution to the preparation of the book "Concern for Europe's Tomorrow", one of the most comprehensive surveys on environmental health ever carried out in Europe. The book includes assessment of exposure to several important chemical contaminants in food.
- The GEMS/Water programme is a multi-faceted water science programme oriented towards understanding freshwater quality issues throughout the world. Major activities include **monitoring, assessment,** and **capacity** building. The implementation of the GEMS/Water programme involves several United Nations agencies active in the water sector as well as a number of organizations around the world.
- The EMEP programme (Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air pollutants in Europe) has been established to regularly provide Governments and subsidiary bodies under the LRTAP Convention with qualified scientific information to support the development and further evaluation of the international protocols on emission reductions negotiated within the Convention. The Aarhus Protocol on POPs was signed by 36 countries in 1979, among which, many European countries, Canada and United States of America. The POPs protocol sets out provisions for 16 persistent pollutants.
- The Convention on the Protection of the Marine Environment of the Baltic Sea Area was agreed in 1992. The governing body of the Convention is the Helsinki Commission - Baltic Marine Environment Protection Commission - also known as HELCOM. The Commission publishes every five years a "Periodic Assessment of the State of the Environment of the Baltic Marine Area" based on monitoring activities going on in the area.
- The Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR Convention) was signed in 1992. In 1994 the OSPAR Commissions agreed to develop a new joint monitoring programme for the maritime area of the Oslo and Paris Conventions and to update the Joint Monitoring Programme of the Oslo and Paris Commissions and the Monitoring Master Plan of the North Sea Task Force. The new joint monitoring programme is called the 'Joint Assessment and Monitoring Programme (JAMP)'. The region covered by the monitoring programme is the North-East Atlantic which, in turn, is divided in five regions: Arctic Waters (Region I), the Greater North Sea (Region II), the Celtic Seas (Region III), the Bay of Biscay and Iberian Coast (Region IV) and the Wider Atlantic (Region V). Persistent pollutants are measured to a varying extent in the different regions. The most commonly represented are PCBs, tributyltin, mercury and PAHs. The Commission has published an extensive Quality Status Report in 2000.

- The Caspian Environment Programme (CEP) is a regional programme developed for and by the five Caspian Littoral States, Azerbaijan, Iran, Kazakhstan, Russia and Turkmenistan, aiming to halt the deterioration of environmental conditions of the Caspian Sea and to promote sustainable development in the area. Similarly at the region of Black Sea, a lot of research and monitoring projects, which cover also PTS, was initiated (NATO, EC).

5.2.3. Local monitoring

A lot of measurements were done in countries such as UK, Sweden, Germany, the Netherlands, the Czech Republic. On the other hand, a lot of countries mainly from the Eastern part of Region III (Moldova, Belarus, Ukraine) have no ambient air measurements and limited information concerning other environmental compartments. The main regional rivers such as Elbe, Rhine or Danube and their main tributaries are frequently and regularly monitored, but a worse situation in the case of Russian and some other rivers, where alack of information still exists. Lakes are very useful for trend analysis, the study of historical development of contamination, but these topics are the subject of various research projects mainly. Soil contamination is also determined mainly on the national level as typical local problems. In some cases, more complex projects covering more than one country exist. For example, the study of spatial and temporal variation or contamination of boarder regions (UK, Germany, Czech Republic), were performed during last ten years.

All countries of the region have some national programme concerning thestudy of human exposure and food contamination. Of course, there are a lot of differences as far as the size and scopeof these programmes.

5.3. EXISTING REGULATION AND MANAGEMENT STRUCTURES

5.3.1. International

Pollution issues are covered by several international agreements or arrangements that form an important focus for political efforts aimed at reducing impacts of PTS contamination on the environment and its ecosystems in the Region III. The following have particular relevance to the UNEP assessment of the Region III:

- Convention on Long-range Transboundary Air Pollution (CLRTAP), 1998
- Convention for the Protection of the Marine Environment of the North East Atlantic (OSPAR), 1992
- International Convention for the Prevention of Pollution from Ships, 1973, as modified by the Protocol of 1978 (MARPOL 73/78)
- Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade,
- Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal
- Stockholm Convention on Persistent Organic Pollutants
- WHO Environmental Health Criteria

5.3.2. Regional

EC Directives relevant for the regional PTS Strategy:

- Council Directive 91/414/EEC provides the framework for the authorisation, the placing of plant protection products on the market and its use in the European Union.

  A working programme for all existing active substances, is set up by the Directive (Art. 8(2)). All active substances on the market in Member States on 25 July 1993 must undergo a full evaluation verifying whether they fulfil the obligations of Art. 5 and therefore can be listed in Annex I of the Directive. This list contains active substances whose use in plant protection products is considered safe. Substances addressed proposed ban of organotins as plant protection products non-inclusion of Quintozene and Lindane in Annex I.
- Council Directive 98/8/EC on placing on the market of biocides.

  After full implementation of this Directive, all active substances have to be assessed and approved on the Community level and all the biocidal products have to be authorised by the Member States. If the result of the assessment is that an active substance can be used in a biocidal product, it will be put on a positive list accompanied with the requirements on that use. Substances addressed PeCP, PAHs (creosote), TBT, Lindane

- Council Directive 79/117/EEC prohibiting the placing on the market and use of plant protection products containing certain active substances.
  Substances addressed DDT, Lindane, Aldrin, Chlordane, Dieldrin, Endrin, HCH, Hexachlorobenzene, Camphechlor, Mercury.

- Council Directive 76/769/EEC on the approximations of the laws, regulations, and administrative provisions of the Member States relating to restrictions on the marketing and use of certain dangerous substances and preparations. According to Council Regulation 793/93/EEC on the systematic evaluation and control of the risks of existing substances risk assessments are carried out and risk reduction strategies are developed, possibly resulting in amendments under Council Directive 76/769/EEC.

  National information on the import, production, stockpiling, use and export of substances is requested. Marketing and use restrictions based on evaluation of risk as well as socio-economic considerations. 4 priority lists (containing about 150 substances and identified Rapporteur Member States) have been established for carrying out the risk assessment work under regulation no 793/93 (2001).

  Substances addressed 9th amendment: 91/173/EEC: restricts use (with exceptions) of pentachlorophenol (PCP) for wood preservation in concentrations greater than 0.1% by mass. 1999/51/EC: PCP and its salts and esters shall not be used in concentrations equal to or greater than 0.1 % by mass in substances or preparations placed on the market. Member States shall apply appropriate provisions as from 1st September 2000. The use of PCP, NaPCP and PCPL will cease by the end of 2008 in all EU Member States. 94/60/EC: PAH (Creosote).

- 2000/76/EEC on waste incineration.
  Emission limit values on emissions of particles and total organic matter from incineration of all type of waste. This is of relevance when e.g. incinerating obsolete pesticides. Substances addressed e.g. PAH, PCDD/PCDF, mercury.

- Directive 1999/31/EEC on the landfill of waste provides that only treated waste can be landfilled.
  Provides measures, procedures and guidance to prevent or reduce pollution of surface waters, ground water, soil and air from landfills of waste This could be of relevance when e.g. landfilling obsolete pesticides. Waste containing HELCOM Hazardous substances needs appropriate treatment before landfilling; in particular relevant for metals where there may be borderline cases.

- Council Directive 2000/60/EC of the European Parliament and of the council establishing a framework for Community action in the field of water policy (Water Framework Directive).
  This Directive contains provisions on measures aimed at progressively reducing (for priority substances) and at ceasing or phasing out (for priority hazardous substances, within 20 years) discharges, emissions and losses as well as identification of these priority substances and hazardous priority substances (emission inventories according to Article 13(4)). This is the same objective as for Recommendation 19/5 substances. Of special relevance to the work of the Project Team on Hazardous Substances are Article 1 (c) (…cessation of discharges, emissions and losses of priority hazardous substances), Article 2 (29-31), Article 4 (a (iv)), Article 16 (Strategies against pollution of water) and Annexes VIII-X). The EC has two years to propose control measures necessary to reach the objectives for priority (hazardous) substances. These substances will have to be monitored as mandatory parameters under the WFD. Non-compliance with the requirements of the WFD leads to penalties.

  - ✓ Substances addressed:
    - proposed priority hazardous substances: pentaBDPE, Cd, SCCPs, HCB, HCHs, Hg, NP/NPEs, PAHs, Petachlorobenzene, Tributyltin compounds, Hexachlorobutadiene;
    - proposed possible priority hazardous substances: other brominated diphenylether (PBDP) Dibutylphthalate and Diethylhexylphtalate, Pb, PsCP, Naphthalene, Anthracene, Atrazine, Chlorpyrifos, Endosulfan, Trifluralin, Trichlorobenzenes, Octylphenols);
    - proposed other priority substances: Alachlor; Benzene; Chlorfenvinphos; Dichloromethane; 1,2-Dichloromethane; Diuron; Isoproturon; Nickel; Simazine; Trichloromethane (also subject to emission controls and quality standards in accordance with Article 16 of the Water Framework Directive)

- Council Directive 76/464/EEC on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community.
  Established two lists of substances classified as hazardous. List I identified 129 substances to be eliminated from the environment because of their toxicity and their bioaccumulation. List II contained those, which have a detrimental impact on the environment but which may be contained within a given area depending on the characteristics and location of the area. The Directive required Member States to draw up authorisation limits for

emissions of substances on both lists and set up pollution programmes. The Directive set up a framework for the elimination or reduction of discharges of dangerous substances to inland and coastal waters through six daughter directives, which established emission limits for specific substances on List I of the Annex to the Directive.

- Council Directive 86/280/EEC on limit values and quality objectives for discharges of certain dangerous substances included in List I of the Annex to Directive 76/464/EEC (Council Directive 76/464/EEC of 4 May 1976 on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community).

  This Directive lays down, pursuant ot Article 6 of Directive 76/464/EEC, limit values for emission standards for the substances referred to in Article 2 in discharges from industrial plants, quality objectives in the aquatic environment, time limits for compliance, reference methods of measurement. It establishes a monitoring procedure, requires Member States to cooperate and to draw up programmes to avoid or eliminate pollution arising from the sources referred to in Article 5. The Directive applies to the waters referred to in Article 1 of Directive 76/464/EEC, with the exception of ground water. Substances addressed: DDT, the Drins, PCP, Hexachlorobenzene.

- Council Directive 80/68/EEC on the protection of ground water against pollution caused by certain dangerous substances.

  Replaces Article 4 of Council Directive 76/464/EEC. Its aim is to prevent the direct or indirect introduction of substances in List I and limit the substances in List II of the Annex to groundwater supplies. It will become part of the overall approach of the draft Community Water Policy Framework Directive.

- Council Directive 67/548/EEC concerning the classification and labelling of dangerous substances and preparations.
  Dangerous substances, which are placed on the market have to be labelled according to their classification in Annex I of Directive 67/548/EEC, which in 2001, contains approximately 2350 existing and 214 new substances. For dangerous substances not in Annex I, the manufacturer, distributor and importer is obliged to apply a provisional classifications and labelling following the criteria in Annex VI of this directive. Substances addressed 2350 existing and 214 new substances.

- Council Directive 96/61/EC concerning integrated pollution prevention and control (IPPC).
  The objective is to prevent or minimise air, water and soil pollution by emissions from industrial installations in the Community, with a view to achieving a high level of environmental protection. This Directive requires the assessment of chemicals used in certain production processes and certain conditions for the licensing of industrial installations. In the context of the execution of the Directive so called BAT notes are elaborated laying down requirements for progressive technologies. Such BAT notes are foreseen e.g. for PCB sources such as certain combustion sources (for power generation and waste incineration) and production and processing of metals. Article 15 (3) of the Directive requires Member States to inventory and supply data on principal emissions and responsible sources, that is from all large facilities with one or more activities as mentioned in Annex I to this Directive. According to this Article 15 the Commission decided on the implementation of an European Pollutant Emission Register (EPER). Substances addressed e.g. PCP, HCB, HCH, PCDD + PCDF (dioxins and furans), Organotin compounds, sectors, where hazardous substances are emitted: energy industries, production and processing of metals, mineral industry, chemical industry and chemical installations for the production of basic organic chemicals, basic inorganic chemicals or fertilisers, biocides, pharmaceuticals; pulp and paper industry, textile pre-treatment and finishing, etc.

5.4. WHITE PAPER ON THE COMMISSION ON A NEW CHEMICALS POLICY IN EUROPE

Related activities aim to:

- Place more responsibility on down stream users of dangerous chemicals
- To phase out PTBs except for application for which a safe use can be demonstrated in an authorisation procedure
- Establishing substitution as one of the guiding principles for the future EU chemicals policy

Enabling activities, as defined in the GEF Operational Strategy, represent a basic building block of GEF assistance to developing countries and countries with economies in transition as far as the implementation of Stockholm Convention. They are a means of fulfilling essential communication requirements to a Convention, providing a basic and essential level of information to enable policy and strategic decisions to be made, or assisting planning that identifies priority activities within a country. Countries thus enabled will have the

ability to formulate and direct sectoral and economy-wide programs to address global environmental problems through cost-effective approaches within the context of national sustainable development efforts. Country-driven enabling activities will normally qualify for full agreed costs funding from the GEF when they are directly related to global environmental benefits and/or consistent with the guidance of a Convention. In the interim period, developing countries and countries with economies in transition signatory to the Convention will be eligible for funding for enabling activities. After entry into force of the Convention, the COP would provide guidance on eligibility criteria.

The GEF's initial assistance will have two main components. The first component will cover the Preparation of a National Implementation Plan (NIP) in each eligible country. The second component, Capacity Building Support for Enabling Activities, will provide assistance to strengthen the ability of countries to implement a systematic and participatory process for the preparation of the NIPs.

A GEF Implementing Agency or Executing Agency, selected by a country, will provide assistance for the development and implementation of enabling activities, including submitting the funding proposal to the GEF Secretariat on its behalf (World Bank, UNDP, UNEP, FAO, UNIDO, and regional development banks).

5.4.1. National

All countries of the Region have the legal framework for environmental protection in general, Laws on chemicals and chemical products and adequate legislature concerning to PTS. The production and use of PCBs and OCPs are restricted or banned with very few exceptions. Air, water, soils, plants and foods are legally protected against hazardous substances in the Region.

5.5. STATUS OF ENFORCEMENT

The countries of Region III should take all necessary steps to ensure that their national responsibilities and arrangements to reduce contaminant inputs to the regional and global environment are fully implemented. If these responsibilities and arrangements are not addressed in an appropriate manner, the justification for recommending actions aimed at reducing transboundary contaminants with sources outside of the Region will be accordingly diminished. There is a need for actions to clean up contaminants from heavily contaminated regional hot spots such as former industrial and military sites which could support ongoing release and emission of compounds into the environment. A control of primary source inputs strengthen the relative importance of secondary recycling inputs will become more important and should be targeted for clean-up.

Levels of many contaminants in the Region have been deeclining based on decreasing emissions and releases which are partly the results of long term strategies focused on reduction and elimination of emissions and releases of hazardous chemicals, and partly the result of political and economic changes in Central and Eastern European countries.

5.6. ALTERNATIVES OR MEASURES FOR REDUCTION

It is generally accepted that newer pesticides are more expensive than older ones, particularly when the newer ones are still protected by patents. Many of the encountered "POPs alternatives" are however by now also rather old, resulting indevelopment costs beingalready recovered (Mörner, 1996). In certain applications, such as termite protection, POP pesticides will nevertheless have a cost advantage through their long residual effect. On the other hand, many of the identified non-POP pesticides are in fact more toxic than the POPs (PTS). In general, the problem of POP pesticides is not apparent in Region III. The main part of these compounds have never been used in the region or were banned many years ago in most countries. The problem is focussed on obsolete pesticides in the Region, mainly in Central and Eastern Europe, where hundred thousands of tons of old wastes with unquantified contents of organochlorine pesticides remainin various storage facilities.

Many countries of Region III have produced and all countries of Region have used the PCBs technical mixtures in various forms. The production of PCBs and use of PCBs in the Western part of Region has been restricted during the first part of the 1970´s. Adifferent situation existedin the former communistic countries, where this ban was realised later in the first part of the 1980´s. As a result the present level of contamination of abiotic, biotic and human samples in this part of the Region is higher (but with decreasing tendency). The use of transformers and capacitors with lower contents of PCBs continues in the countries of CEE.

A lot of various technical alternatives of PCB use were developed and tested. For example, the common chemical alternative to PCB in transformers is mineral oil with different additives or as the capacitor fluid is most frequently used a mixture of various alkyl and aryl benzenes (Öberg, 1996). Also, alternatives to HCB (pesticides, by-product and chemical product which was used in military pyrotechnics, aluminium smelting, graphite electrode production, rubber industry) are intensively developed and used (Öberg, 1996).

Although many results from various measurements at potential sources of PCDDs/Fs have become available, the data that are required to assess the contribution of these sources do in many cases still have a large margin of uncertainty (Björndal, 1996). There are several possibilities for the control or prevention of PCDDs/Fs release emissions. Measures for the reduction of PCDDs/Fs release focus on the substitution of relevant raw and starting materials, process modifications (including maintenance and operational control) and on the retrofitting of the existing plants. The following available measures, which may be implemented either separately or in combination include:

- materials-related primary measures
- process-related primary measures
- measures in the waste gases
- waste gas purification techniques
- procedures for treating the residues.

Based on the preliminary prioritisation of PTS in Region III, it is possible to summarize that the regional priorities are chemicals such as polychlorinated biphenyls, polybrominated diphenyl ethers, short chains chlorinated paraffins or by products such polychlorinated dibenzo-p-dioxins and furans or polycyclic aromatic hydrocarbons. The remaining pollutants from the basic list - mainly pesticides – are at the present time mainly local problems of obsolete pesticides, old stockpiles, etc. But regional transport of these pesticides such as DDTs, HCHs, HCB through the air, waters or biota exists and also transport onto/out of region could be important.

For the common regional strategy (including European part of Region IV), the basic approaches are done by the European Community strategy for dioxins, furans and polychlorinated biphenyls (COMMUNICATION FROM THE COMMISSION TO THE COUNCIL, THE EUROPEAN PARLIAMENT AND THE ECONOMIC AND SOCIAL COMMITTEE: Community strategy for dioxins, furans and polychlorinated biphenyls (2001/C 322/02) (COM(2001) 593 final)), which was adopted EU and which is a very useful tool for Accession countries including all Commonwealth of New Independent States.

Over the past two decades the Commission has proposed wide ranging legislation aimed at directly or indirectly reducing the release of these compounds into the environment, with the objective of reducing human exposure and protecting human health and the environment. Recent exposure data show that measures introduced to control dioxin releases have resulted in a substantial reduction in intake of these compounds: levels in humans are decreasing since the mid eighties. Since 1995 this tendency is levelling out, even slightly rising levels have been observed.

The enlargement of the European Union to include accession countries is likely to increase the average exposure in EU. Indeed, the accession countries are likely to produce higher emissions than the EU at the present time through variation in legislation and due to the vast abundance of worn industrial plants. They are probably high contributors to the total dioxin emissions into the European environment. This puts an emphasis on the need to ensure compliance with the relevant environmental legislation in the accession countries.

The objectives of the strategy are:

- To assess the current state of the environment and the ecosystem,
- To reduce human exposure to dioxins and PCBs in the short term and to maintain human exposure at safe levels in the medium to long term,
- To reduce environmental effects from dioxins and PCBs.

The quantitative objective is:

- To reduce human intake levels below 14 picograms WHO-TEQ per kg bodyweight per week.

According to the "European dioxin emission inventory, Stage II" (LUA-NRW (1), 2001), launched by the Commission, considerable improvement of the general situation concerning emissions to air during the last decade has occurred which is due to comprehensive abatement measures carried out in the most industrialised Member States. This improvement is reflected by decreasing dioxin concentrations in ambient air and declining depositions. Furthermore, the above-mentioned report assessed the emission trend 1985-2005 and foresees that for those industrial processes which are considered as the most relevant emission sources a 90 % reduction of dioxin emissions to air will be nearly realised in 2005. This is to a large part due to the successes regarding particular emission sources which already by 1985/1990 were targets of active dioxin-abatement policy.

In order to get a clearer insight and to be able to address the problem in an efficient way the Commission has financed several studies and has proposed a number of Directives, which reduce the releases of dioxins and PCBs into the environment thereby reducing human exposure to these compounds.

These Directives are focused on:

- Waste incineration
- Integrated pollution prevention and control (IPPC)
- The Seveso Directives on the control of major accident hazards
- Releases to water
- Restrictions on marketing and use of chemicals
- Shipment and disposal of PCB-containing waste
- Animal nutrition

Although a lot of progress has been achieved in reducing the releases of dioxins/PCBs in the environment, the following facts have been stated:

- The target set in the 5th EAP will not be achieved: for the industrial sources a considerable emission reduction has been attained (based on current trends and activities it is foreseen that the target set in the 5th EAP of a 90 % reduction will be nearly realised in 2005 compared to the levels in 1985) BUT, for the non-industrial sources (domestic solid fuel burning, domestic waste burning, fires, etc.) the rate of emission reduction is much lower. The relation between industrial and non-industrial sources is shifting towards growing importance of non-industrial sources.
- One million tons of PCBs have been produced and used during the 20th century until their ban in 1985. The main part of these products, which are highly resistant to degradation (> 30 years) and bioaccumulable in fat of biota, is now spread in soils, sediments and the whole aquatic ecosystem ("historical pollution").
- Much equipment and material containing PCBs will be reaching in the coming years, if they have not done so yet, their waste stage, and a correct disposal has to be ensured to avoid additional releases in the environment.

Therefore, and in combination with the new elements described in the introduction, there is a need to further address the problem in order to protect human health. To reduce human intake it is important to reduce the levels in the food chain because food consumption is the most important route for human exposure (90 % of total exposure). The most efficient way to reduce the levels in the food chain is to reduce the contamination in the environment. This should be done by:

1. avoiding "new releases" in the environment;
2. addressing "historical pollution".

5.7. TECHNOLOGY TRANSFER

Based on the EC Strategy to reduce the presence of dioxins and PCBs in the environment, all assessments have stressed the urgent need to reduce the sources of environmental contamination with these compounds to the lowest possible as the most appropriate way to reduce human exposure. Therefore, a set of actions has to be identified for the short- to medium-term and for the long-term.

The set of the short- to medium-term (5 years) actions relates to hazard identification, risk assessment, risk management, research, communication to the public and cooperation with third countries and international organisations.

A. Hazard identification

Further identification of dioxin and PCB sources:

A complete inventory of sources and more knowledge on the share of the different dioxin sources is essential. "The European dioxin emission inventory, Stage II", (LUA-NRW, 2001), launched by the Commission, identified the need for further investigation or actions on specific sources. The Commission will therefore take special activities in the following sectors:

- Hospital waste incinerators:
- Iron ore sintering
- Electric arc furnaces
- Non-ferrous metal industry
- Miscellaneous industrial sources such as secondary smelters for non-ferrous metals (aluminium, copper), iron foundries (cupola furnaces), cement production.
- Non-industrial emission sources concerning the domestic solid fuel combustion, domestic waste burning burning of animal carcasses

The Inventory of releases to land and water is still incomplete. Further research and data collection will be carried out to verify the scale of releases from the source sectors which have a high potential for release. Not just measurements on concentrations, but also further research on details of activity and processes will be included.

B. Risk assessment

- Non dioxin-like PCBs
- Development of measurement methods
- Establishment of environmental indicators, including bio-indicators

C. Risk management

- Prevention measures
- Control of emissions
- Control of the quality of the environment

D. Research

The Commission, member state and accession countries will encourage all types of research that will contribute to reduce the impact of dioxins and PCBs. It will also bring together researchers across projects to exchange information and will facilitate coordination among Member States (as a part of 6th Framework Programme). In order to 1. Further identify measures to reduce the contamination; 2. Predict the effects of regulatory controls; and 3. Be able to monitor the environment (both on ecotoxicological and epidemiological aspects) in the future

an integrated approach to research, thus ensuring value for money and appropriate coverage of the key issues is needed.

E. Communication to the public

To allay public concern, to raise awareness and to inform the public, reliable, accurate, clear and comprehensible information will be provided on activities of the Commission, on possible effects and risks, on uncertainties, etc. To educate the public: the general public has not only to be informed, but has to play an active role in the prevention of releases into the environment.

F. Cooperation with third countries and international organisations

Emissions in the accession countries are likely to be higher than in the EU. The Commission intends to launch a project in order to identify important dioxin sources and to carry out measurements in the accession countries. Cooperation with WHO is essential to avoid duplication of work and will continue in the future. As a contracting party to several conventions in the field of dioxins and PCBs the Commission will continue international cooperation on this subject.

An important part of the long-term strategy (10 years) will be a long-term preparation to 1. Further identify source directed actions; and 2. Evaluate the efficacy of existing legislation. In order to implement the "environment health" objectives in the 6th EAP a set of actions are identified which relates to data collection, monitoring and surveillance and further identification of measures:

- Data collection on the level of dioxin/PCB contamination in air, water (sediment) and soil:
- Monitoring and surveillance of the level of dioxin/PCB contamination in air, water (sediment) and soil
- Identification of measures

Dioxins and PCBs are occupying a predominant situation in the consciousness of the European citizens because these compounds are known to cause severe and far-reaching environmental and health effects. In spite of the existing legislation and of the progress already achieved in reducing emissions and human exposure deficiencies still remain. An integrated and systematic approach is missing. There is an urgent need for action to further reduce emissions and avoid environmental and adverse health effects from dioxins and PCBs. Therefore it is essential that the Commission adopt a strategy to reduce the presence of those compounds in the environment, in feed and food, including short- to medium-term and long-term actions. Such an integrated approach would have to guarantee that the dioxin and PCB problem is totally under control in 10 years. At that point this strategy will have to be assessed and eventually revised to take account of the latest progress. The results of this strategy could then be applied to reduce the presence of other persistent hazardous substances in the environment.

5.8. IDENTIFICATION OF NEEDS

Remaining gaps have been identified upon which an action plan may be developed. These gaps can be classified as gaps in knowledge, gaps in legislation and gaps in implementation of Community legislation.

1. Gaps in knowledge:
    - Sources and inventories: regarding the emission sources data gaps still exist causing considerable uncertainties of the emission estimates. The inventory of releases to land and water is not complete: further research and data collection is needed to verify the scale of releases from the source sectors which have a high potential for release.
    - Emissions in the accession countries: important dioxin and PCB sources should be identified in the accession countries, which may be high contributors to the total dioxin and PCB emissions into the European environment.
    - Monitoring programmes should be developed in order to control compliance with existing legislation and to monitor the effects of this strategy, the state of the environment and the trends. These programmes will be essential in order to further identify measures.

- Measurement methods and standards: a necessary condition for effective control and monitoring mechanisms is the availability of appropriate measurement methods and the comparability of data. At present, methods for analyses of dioxins and dioxin-like PCBs are expensive and slow. Therefore low-cost and fast methods have to be developed allowing to analyse in routinely manner a great number of samples and provide quick, cheap, and reliable results on the presence of those compounds in the environment, feed and food. In order to obtain comparable, consistent, reliable and high quality measurement results it is necessary to implement a high quality measurement standard at Community level.

- Dioxin-like PCBs: measurement programmes performed in the past focused mostly on dioxins. Yet a variety of other compounds probably having similar adverse health effects have been identified, the so-called dioxin-like PCBs. The available database is insufficient to assess the current situation with respect to dioxin-like PCBs. Therefore the Commission recently launched a study to collect information on concentrations of dioxin-like PCBs in food, feed and in environmental samples across Europe.

- Risk assessment: the European Scientific Committee on Animal Nutrition (SCAN) adopted an opinion on "Dioxins in feed" on 6 November 2000 and the Scientific Committee on Food (SCF) adopted an opinion on "Risk assessment of dioxins and dioxin-like PCBs in food" on 22 November 2000. The SCF updated its opinion on 30 May 2001 based on new scientific information available since the adoption of the SCF opinion of 22 November 2000. However, for the non dioxin-like ("classical" or "non-coplanar") PCBs which have another toxicological profile, which circulate more easily through muscles and blood and affect directly the nervous system and brain development (namely for foetus and young children) and which could be several orders of magnitude more concentrated than dioxins in aquatic biota such as fish and shellfish a risk assessment should be carried out.

- Public information is needed to inform the public, to allay public concern, to raise awareness about the risks associated with exposure to these compounds and about the role they have to play to prevent further contamination of the environment. It is also important to allow "self identification" of at-risk groups.

- Further research is needed on environmental fate and transport, ecotoxicology and human health, agrofood

- industry, source inventories, analytical aspects, decontamination measures and monitoring. The most important gaps in knowledge concern: 1) transfer and degradation processes (a better understanding and quantification of the fundamental transfer processes by which dioxins and PCBs move between the different environmental media and of the degradation processes occurring within these media is needed); 2) bio-accumulation and bio-magnification processes; 3) domestic incineration of wood (there is an information deficit concerning the amount and the composition of wooden fuels used for room heating and cooking purposes); 4) reservoir sources (the contribution to human exposure, the behaviour and degradation processes and decontamination methods require examination); 5) open uses of PCBs; 6) carry-over rates and transfer factors for dioxins and PCBs from soil and feed to animal tissues and products (milk, eggs).

2. Gaps in legislation

   - Legislation in order to limit and control the presence of dioxins and PCBs in feed and food.

3. Gaps in implementation of the Community legislation

   - The PCB Directive has not been adequately implemented and several infringement cases have been launched against Member States for failure to implement the obligations under this Directive. In the case of PCBs there is currently a deadline of 2010 for destruction and disposal (pursuant to Council Directive 96/59/EC on the disposal of PCBs and PCTs) of big equipment. However, Member States are experiencing problems for establishing the mandatory inventories of PCB-containing equipment and to prevent the illegal dumping and inadequate disposal of PCBs.

To secure better protection of human health and of the environment from the effects of dioxins and PCBs an integrated and systematic approach is needed. Therefore the Commission proposes a strategy:

1) To reduce the presence of dioxins and PCBs in the environment;

2) To reduce the presence of dioxins and PCBs in feed and food.

This strategy aims to fill the identified gaps, to improve the link between data collection and a consistent Community response system, to adjust the existing sectoral legislation in order to achieve the Environment health objectives of the 6th EAP and to develop incentive measures promoting exchange of information and experience between Member States. Full enforcement of existing Community legislation by the Member States is a prerequisite to achieve the objectives pursued by this strategy. Furthermore the success of the strategy will critically depend on the action taken at local and regional level by communities and Member States.

5.9. CONCLUSIONS

The production and use of PCBs and OCPs are restricted or banned with very few exceptions. The region has legal, economical and political capacity for solution of PTS environmental problems mainly based on the EU strategy and co-operation between EU and accession countries.

5.10. REFERENCES

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CONCLUSIONS

This report summarises information concerning PTS sources, levels and effects in the Region III – Europe. Here the main results have been selected from previous chapters.

✎ General Comments:

- ✓ Most countries within the Region have the legal framework for environmental protection in general, Laws on chemicals and chemical products and adequate legislature concerning to PTS;

- ✓ The production and use of PCBs and OCPs are restricted or banned with very few exceptions. Air, water, soils, plants and foods are legally protected against hazardous substances in the Region;

- ✓ Although monitoring indicates that the loads of some hazardous substances have been reduced considerably over the past ten years in all parts of Region, problems still persist;

- ✓ As a result of former production, long term and widespread use and also long-range transport from other parts of Globe, OCPs, PCBs, PCDDs/Fs and PAHs and also some newer PTS are found in all environmental compartments including remote high mountain European sites. In general, decreasing trends in concentrations are observed.

✎ Limitations of presented data and information:

- ✓ Comparisons between the present analytical results and available older data can be questionable because:

- of differences in the analytical procedures;
- lower versus higher precision and accuracy;
- total PCBs or PCDDs/Fs versus congener specific analysis;
- different sampling and analytical methodology;
- different ways of calculation, expression of results;
- lack of the additional information concerning to the nature of the samples (biological parameters, organic carbon contents, lipid contents;

✓ Consequently, some of the data presented in this study should be treated as indicating general levels and trends in environmental contamination and human exposure to PCBs and certain OCPs.

✓ Lack of a European-scale PTS monitoring system.

↳ Sources of PTS in the Region III:

✓ Hotspots:

- old dumpsites or soil contaminated as a result of (bad) industrial practice (whole region);
- more problematic situations in the Central and Eastern part of Region, where particular hot spots still exist (e.g. Neratovice, Bitterfeld, Strazske, Ufa, Chapaevsk) along with many old dumpsites;
- old technologies;
- flooded areas in the Central part and some others;
- territories of the former agricultural airfields (Russia, Ukraine, Moldova).

✓ The relative contribution from hotspots to the current cycling fraction is unknown;

✓ It's likely that diffuse sources (including LRTP) are often dominating.

↳ Sources, inventories:

✓ Within the Region as a whole there is a large amount of data relating to industrial point source emissions to the atmosphere;

✓ Sources to air of well studied compounds such as PAHs, PCBs, and PCDDs/Fs are generally well characterised and inventories have been calculated and updated regularly via EMEP;

✓ Due to restrictions on the manufacturing, more stringent control of releases and the substantial decrease of industrial production in the CIS, emissions from primary sources have been declining during the last 20 years;

- ✓ Understanding of secondary source inputs and the potential for environmental recycling of individual compounds continues to be limited and few measurements are available;

- ✓ Obsolete stocks of pesticides represent a potential source of PTS material particularly within the Central European Countries and Newly Independent States;

- ✓ Exact quantities and components of the stockpiled wastes are unknown at present but quantities are thought to be in excess of 80 000 t;

- ✓ The evidence of PTS hot spots is still a problem in CEECs;

- ✓ For the compounds of emerging concern (e.g. PBDEs, chlorinated parrafins) emission sources to all environmental compartments are very poorly characterised, few formal inventories have been established and there is limited understanding of the principal contemporary source catagories;

- ✓ Unlike sources to air, sources to land and water are very poorly quantified for all the PTS compounds;

- ✓ Prioritization of sources inputs within the Region as a whole highlight that the following compounds represent ongoing releases in the Region which are of most concern with respect the environment and health:
  - Hexachlorobenzene
  - PCBs
  - PCDD/Fs
  - PeCP
  - PBDEs
  - Chlorinated paraffins

➪ General strategy in Region III on unintentional emission of PTS:

- ✓ Individual judgements rather than limits or guideline values;

- ✓ Operating permits for 5 – 10 years;

- ✓ Dioxin emission to air from MWI and other sources were reduced in many countries of EU during last 15 years;

- ✓ Exposure limitation rather than limit values.

➪ General strategy on POPs pesticides and industrial chemicals:

- ✓ Ban;

- ✓ General information to:

  - The public including politicians;
  - Industry;
  - Agriculture.

- ✓ Detailed information to consumers.

➪ Levels:

- ✓ Region III has a wealthof information concerning environmental levels of PTS, but geographic distribution of the available data is not equal for all parts of Region. A better situation exists in some countries of EU and Central Europe;

- ✓ Monitoring system concerning PTS exists (UN ECE EMEP, OSPAR, HELCOM) which are oriented to air and deposition (EMEP), seas (OSPAR, HELCOM); some new are ongoing (Caspic Sea, Black Sea);

- ✓ As far as rivers, monitoring is mainly based on the national level, but a lot of multinational or regional activities also exist (Rhine, Danube);

- ✓ The measurements of PTS levels in some other compartments such as lakes, soils or vegetation is partly performed on the international programmes (ICP IM, EMEP), national monitoring programmes (soils) or pilot /research projects (biota, lakes); up to now different research projects are important for data collection in this region;

- ✓ Human exposure is measured and studied on the European levels (activities of WHO Europe) and very frequently on the national levels;

- ✓ Harmonisation of methods for sampling and analysis in the Region is initiated by different organisation EU (for example PECO Projects) and EMEP etc.

➪ The data could be divided into 3 groups:

- ✓ DDTs, HCHs, HCB, PCBs, PAHs for which there is quite wide data availability, and at significant concentrations;

- ✓ heptachlor, chlordanes, aldrin, dieldrin, endrin, toxaphene, mirex for which there is limited data;

- ✓ PCDDs/Fs for which there is wide data availability in some countries (mainly EU members) and for some matrices (emissions, human samples, foods).

↳ Ecotoxicological Effects:

- ✓ Analysis of the observed ecotoxicological effects of PTS on birds, mammals and fish in Europe has shown, that although a wide number of laboratory and manipulated *in situ* studies with various organisms and effects were conducted and are documented in the literature, one has to carefully and critically evaluate these data.

- ✓ On one hand, the controlled laboratory toxicological studies with individual compounds or carefully prepared mixtures usually allow to define clear dose-response causality between chemical exposure and observed effects.

- ✓ On the other hand, the laboratory tests alone seldom adequately describe what is likely to occur in the environment.

- ✓ The often complex and subtle effects of chronic, low-level environmental exposure to PTS are less well understood.

- ✓ In the environment, the universal exposure of organisms to low levels of a wide range of chemical contaminants 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 more chemicals to include for further research and possibly legislative measures depending on their persistency and bioaccumulative properties without focusing too much on their toxicity.

- ✓ The PBT criteria are useful for identification of "new" chemicals of concern but there is, in fact, a large number of environmental pollutants for which data on their PBT characteristics are partly known and still not used for prioritisation of research and legal actions.

↳ Toxicological effects:

- ✓ Analysis of the results of environmental epidemiological studies shows, that correlations do exist between the chemical contamination of air, water and soil and human health.

- ✓ To elucidate the particular effects of individual toxicants (genotoxicity, estrogenic effects, carcinogenicity, neurotoxicity, immunotoxicity, etc.) it is important to compare the above mentioned results with the data, obtained from experiments with the laboratory animals.

- ✓ There are more chemicals to include for further research and possibly legislative measures depending on their persistency and bioaccumulative properties without focusing too much on their toxicity.

↳ Human exposure:

- ✓ In summary, human exposure to PTS compounds is dominated by intake via terrestrial and aquatic food products which have high lipid content and have been subject to bioaccumulation within agricultural foodchains e.g. milk, meat, eggs and fish, (particularly oily and/or long-lived species) (WHO GEMS/FOOD).

- ✓ Exposure is generally well characterized and quantified for PCBs and PCDD/Fs and a range of organochlorine pesticides; the vast majority of adult exposure will be below current WHO guideline values.

- ✓ Individuals exceeding the guideline value will be dominated by subsistence fishermen and their families, individuals who consume several meals of oily fish each week in addition to those consuming locally produced foods in the vicinity of an on-going source of contamination.

- ✓ Human lipid concentrations of well characterized compounds such as PCBs and PCDD/Fs have been declining significantly in recent years throughout the Region at a rate of approximately 5% per year since the early 1990s.

- ✓ This decline coincides with European restrictions on the manufacture and release of these compounds into the environment and in particular, into the atmosphere.

- ✓ For some PTS compounds of emerging concern such as PBDEs, there is some evidence of increasing trends in human breast milk during the last 20 years.

- ✓ Breast-fed infants represent a distinct sub-group of the population whose exposure to PCDD/Fs and Dioxin-like PCBs will exceed current guideline values based on bodyweight for the first few months of life.

- ✓ In view of the significant declining trends in TEQ concentrations in breast milk over the last 20 years, WHO strongly recommend that breast feeding is encouraged and promoted for the childs benefit.

↳ Monitoring:

- ✓ Selected PTS in air and deposition are frequently measured in the EMEP observatories;

- ✓ Many measurements were and are currently carried out in countries such as UK, Sweden, Germany, Netherlands, Czech Republic;

- ✓ On the other hand, a lot of countries mainly from Eastern part of the Region III (Moldova, Belarus, Ukraine) have no ambient air measurements and limited information concerning other environmental compartments,;

- ✓ The main regional rivers such as Elbe, Rhine or Danube and their main tributaries are frequently and regularly monitored, but the situation is worse for Russian and some other rivers, where a lack of information still exists;

- ✓ Lake sediments and biota are very useful for trend analysis and the study of historical development of contamination, but these topics are the subject of various research projects;

- ✓ Soil contamination is determined mainly on the national level as specific local problems;

- ✓ All countries within the region have some national programme concerning to the study of human exposure and food contamination Differences exist in terms of the scope and size of these programmes.

➪ Trends:

- ✓ Results of monitoring programmes and research projects have confirmed that environmental levels and biotic contamination of industrial PTS such as PCDDs/Fs, PCBs or PAHs are declining in urban/industrialized centres and also on the regional level;

- ✓ These trends are observed in Western Europe and are believed to be largely due to emission abatement actions taken in the early nineties;

- ✓ These observed trends in the case of PAHs and PCDDs/Fs are the results of a lot of industrial changes during recent decades (e.g. cars equipped with catalyst engines, improvement of the fuel and the increased use of district heating, cleaner industrial technology ..);

- ✓ Towns in the former communistic countries have not seen these changes, in particular a high number of cars are still not equipped with the converters;

- ✓ Larger cities in CEE countries all have similar problems after the political changes. These include an extremely high increase of town traffic and decreasing contribution from former industrial sources as the results of declining production.

➪ Transport:

- ✓ Transboundary transport is an important mechanism for the occurrence of PTS in the European region;

- ✓ Atmospheric transport processes are important pathways for PTS to both aquatic and terrestrial ecosystems;

- ✓ The evidence of LTR in the region has been investigated both with measurements and modelling;

- ✓ An integrated monitoring/modelling approach is applied for assessment of PTS contamination in the European region;

- ✓ This approach includes arrangement of a 'superstation network', model assessment of contamination levels and national measurement campaigns - a better cover of monitoring stations is however needed and especial more data concerning to water and soils is essential for model validation;

- ✓ At present there are numerous multicompartment PTS transport models - both steady-state and dynamic - describing PTS fate in the environment which are used for assessment of PTS contamination in the region;

- ✓ Modelling activities are useful for evaluation of PTS redistribution between various environmental compartments, long-term trends of environmental contamination, spatial distribution of concentrations in different media (atmosphere, soil, seawater, vegetation) and transboundary transport;

- ✓ Some PTS possess very high long-range transport potential and hemispheric/global scale is reasonable to assess European contamination; the hemispheric version of EMEP/MSCE-POP model indicates the ability of some PTS to transport to and from the European region.

↳ Future topics:

- ✓ We need integrated and systematic risk assessment and research and monitoring for new and existing chemicals and their metabolites and products of degradation, because we have frequent lack of data which are needed for comprehensive risk assessment;

- ✓ Comprehensive knowledge about the impact of most available chemicals, and their combinations, on human health and the environment is still lacking;

- ✓ We have a frequent lack of sub regional, regional and global coordinated control measures;

- ✓ There is a lack of data of environmental levels of new PTS which may be important for the Region, e.g. PBDEs and SCCPs. We need to include "new" PTS in monitoring programmes. It is essential also for assessment of transport processes and for model validation.

↳ **The following barriers were identified:**

- ✓ Lack of knowledge on PTS issues in some part of the Region (background information, health effects, implications of conventions);

- ✓ Systems in regional countries for PTS/chemicals information collection, handling storage and use;

- ✓ More data on fate and transport of PTS in the region;

- ✓ Regional and national inter-agency collaboration/cooperation in PTS management, including information sharing;

- ✓ Public participation in PTS management activities and opportunities for such involvement;

- ✓ Public education concerning to PTS;

- ✓ Knowledge on alternatives to PTS use, and few, if any, practical demonstrations of alternatives.

ANNEX I

Priority Setting

Scoring for Prioritising PTS for Sources, environmental Levels, Effects and Data Gaps

Region: III

SCORING BY MATRIX					
Chemical	**Sources**	**Environmental Levels**	**Ecotoxicological Effects**	**Human Effects**	**Data gaps**
Aldrin	0	0	1	0	0
Chlordane	0	0	1	0	1
DDTs	1	1	1+	0	0
Dieldrin	1	1	1	0	0
Endrin	0	0	1	0	0
Heptachlor	1	1	1	0	0
Hexachlorobenzene	2	2	2	1	1
Mirex	0	0	0	0	0
Toxaphene	1	1	No data	No data	2
PCBs	2	2	2	1	1
Dioxins	2	2	2	1	2
Furans	2	2	2	1	2
HCHs	2	2	1	0	1
PeCP	2	2	1	1	2
PAHs	2	2	2	2	2
Organic Mercury Compounds	1	1	2	1	2
Organic Tin Compouds	1	1	2	No data	2
Organic Lead Compounds	1	1	1	2	1
PBDE	2	2	1	1	2
Phthalates	-	-	-	-	-
Endosulphan			-	-	-
Atrazine	1	1	1	1	1
Chlordecone			-	-	-
Octylphenols			-	-	-
Nonylphenols			-	-	-
Short chain chlorinated paraffins	2	2	1	1	2

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