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ATMOSPHERIC INPUT OF PERSISTENT ORGANIC POLLUTANTS TO THE MEDITERRANEAN SEA

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This series contains selected reports resulting from the various activities performed within the framework of the components of the Mediterranean Action Plan: Pollution Monitoring and Research Programme (MED POL), Blue Plan (BP), Priority Actions Programme (PAP), Specially Protected Areas (SPA), Regional Marine Pollution Emergency Response Centre for the Mediterranean Sea (REMPEC), Environment Remote Sensing Centre (ERS), and Cleaner Production Centre (CP).

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PREFACE

The MED POL Programme (acronym for *Mediterranean Marine Pollution Monitoring and Research Programme*) was created in 1975 by UNEP to answer the specific needs to better assess, qualify and quantify the marine environmental problems of the Mediterranean sea, already put in evidence by previous studies carried out by CIESM and FAO. The Progamme was the scientific and technical component of the **Mediterranean Action Plan (MAP)**, i.e. the activity framework of the Barcelona Convention. **MED POL-Phase I (1975-1980)** was formulated and coordinated by UNEP with the technical and scientific cooperation of five UN specialised Agencies (FAO, WHO, WMO, IOC of UNESCO and IAEA). Initially, about 200 research groups all around the Mediterranean carried out seven pilot projects. Later, a regional intercalibration exercise was also launched to ensure the quality of the data gathered. Assistance was provided to enable all laboratories in the region to fully participate in the Programme activities. This assistance, which cost UNEP 9 million USD, included the purchase of analytical instruments, maintenance service of the instruments and a full programme of training.

A second phase of MED POL **(MED POL Phase II)** was approved by the Mediterranean countries in 1981 and lasted until 1995. During this Phase the efforts concentrated on the establishment of **national monitoring programmes** in the Mediterranean countries, which included at the same time the provision of assistance for their implementation. A full data quality assurance programme was put in place covering not only intercalibration exercises but also other activities aiming at improving the quality of the data such as training of personnel, maintenance of instruments, good laboratory practice and the preparation of analytical reference methods. A **research programme** was also undertaken in support of the monitoring which resulted in more than 500 research projects carried out in 16 Mediterranean countries. During this Phase the countries collected a large number of marine pollution data. By the end of the Phase II, the **MED POL data bank** included a large inventory related to chemical contaminants in biota (over 15,000 samples for 50,000 analyses of heavy metals and halogenated hydrocarbons) and microorganisms in sea water (42,000 samples for 53,000 bacterial counts). Those data, along with others, directly contributed to a more in-depth assessment of the state of the Mediterranean and to the formulation of fifteen **pollution control measures**, which were later adopted by the Contracting Parties to the Barcelona Convention.

Towards the end of the phase II of the Programme, important events at the global and regional levels occurred. At the global level, the adoption of Agenda 21 in Rio and of the Global Plan of Action for pollution land-based sources and activities in Washington and, at the regional level, the signature of an amended and more comprehensive LBS Protocol followed by the creation of the Mediterranean Commission for Sustainable Development indicated the new directions and new priorities to be followed by MED POL. The MED POL Programme had to operate a gradual switch from pollution

assessment to pollution control and become a concrete tool for the Governments to apply the new texts and agreements and to ultimately control and eliminate marine pollution for an appropriate coastal zone management.

The new MED POL III, adopted by the Governments in 1995 and called **"Programme for the assessment and control of pollution in the Mediterranean region"**, presents a stronger emphasis on the managerial aspects of pollution control and a more direct link with the implementation of the relevant Protocols (Dumping and LBS). Under the *assessment component*, the Programme includes activities related to the establishment of trends in the levels of pollutants **(trend monitoring)** and effects of contaminants **(biological effects monitoring)** as well as the inventory of pollution sources and loads. Under the *control component*, the Programme includes the monitoring on a continuous basis of the effectiveness of action plans, programmes and measures for pollution control implemented by the Governments **(compliance monitoring)**. The monitoring activities are described in National Programmes agreed upon with the MED POL Secretariat and renewed every year.

While a research component is still foreseen to help solve methodological issues or better understand emerging pollution issues, the Programme includes an important **assistance component** related to data quality assurance, design of the monitoring programme, provision of equipment, training for the analysis and interpretation of the data and training for managerial aspects, such as operation of sewage treatment plants and systems of inspection. A report on the compliance with the existing national and international legislation is expected from the Governments each year.

The MED POL Phase III has become fully operational during the year 2000; in order to assess the needs of each country for a full participation in the activities, capacity building programmes have been prepared to assess the scientific and institutional resources of the participating laboratories, monitoring programmes have been prepared in several countries with the assistance of experts, and training has been organized for numerous scientists and technicians. In addition, equipment and materials have been purchased for a number of countries.

In 1980 the Mediterranean States had signed the Protocol related to the control of pollution from land-based sources **(LBS Protocol)**, committing themselves to take concrete measures to prevent and abate marine pollution. This Protocol was amended in Syracuse in 1996. It now covers all the polluting human activities and obliges the countries to formulate and implement regional and national action plans to reduce and eliminate pollution at source.

As a follow up to the provisions of the amended Protocol, In 1997 the MED POL Secretariat assisted the countries in the formulation and the formal adoption of a regional **Strategic Action Plan to address pollution from land-based activities (SAP)**. The Plan identifies, describes and analyses the main pollution land-based sources and activities, proposes remedial actions, costs them and formulates target dates for their

implementation. The SAP estimates that in order to solve the most urgent pollution problems of the region about 10 billion US $ need to be invested by countries and international sources. The text also contains a list of 103 **pollution "hot spots"** and 51 sensitive areas officially recognized by the Governments as needing special attention and intervention. The list is expected to be regularly updated in order to follow the progress made in the countries in resolving the problems, hot spot by hot spot, and assist them accordingly.

The MED POL Programme is also in charge of the follow up of the Protocol regulating all dumping operations at sea **(Dumping Protocol)** and the Protocol related to the protection from pollution by transboundary movements of toxic wastes **(Hazardous Wastes Protocol)**.

The present volume represents a contribution by WMO to the MED POL Programme and in particular to the component related to the assessment of the atmospheric input of pollution into the Mediterranean region.

SUMMARY

This report is the first attempt to estimate the quantity of the atmospheric input of some persistent organic pollutants (POPs) to the Mediterranean Sea. The calculations made are based on the available data and estimates of POP emissions to the atmosphere, on the meteorological information for 1987-1996, and on the available parameterization estimates for various processes related to the atmospheric transport, chemical transformation and atmosphere surface exchange of POPs.

The results of the modelling made in this report show that about 40 t of lindane and 1 t of PCBs deposit annually from the atmosphere on the Mediterranean Sea. The total (dry and wet) deposition density of lindane over the Mediterranean Sea amounts to 16$\mu g/m^2$ per year, and of PCBs – 0.3$\mu g/m^2$ per year with dry deposition being the prevailing deposition process for lindane (75%) and wet deposition for PCBs (70%). It was also shown that there are essential seasonal variations of POP fluxes and concentrations in air and precipitation connected with emission variations, and interannual variations in POP deposition connected with variability of meteorological conditions.

The lack or scarcity of POP measurements in the Mediterranean did not allow to compare the measurement and modelling results directly for this region and the comparison was made for Central and Northern Europe where the measurement data are available. Good agreement was received for lindane concentrations in rain water (precipitation). For lindane air concentrations the modelling results exceeded the measurements about 5 times. The PCBs the concentration and deposition estimates based on measurements were about 4 times of the modelling results.

At present there are no estimates of inputs of POPs to the Mediterranean Sea through rivers or direct discharges but taking into account the estimates available for the North Sea, which show for example, that the airborne input of lindane constitutes 98% of its total input to the sea, it is possible to assume that the similar occurs in the Mediterranean. Thus, the estimates presented in this report, despite that they are rather rough, are of principal importance for implementation of the Strategic Action Programme to address pollution from land-based activities in the Mediterranean, which require by the year 2005, to reduce 50% inputs of the priority POPs into the Mediterranean Sea.

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Chapter 1 INTRODUCTION

Persistent organic pollutants (POPs) are organic chemicals, which are stable to photochemical, chemical and biological decomposition. They are characterized by low solubility in water and high solubility in lipids. Therefore, they are readily accumulated in fat tissues. Being semi-volatile, these substances are predisposed to long-range transport. Contrary to other pollutants (for example acidifying compounds or heavy metals) the majority of POPs would not exist in the nature without human activity. Useful properties of these species for the sake of which they were synthesized turned out to be overbalanced by their negative effects on the environment and human being.

Obviously it is difficult to answer the question how many POPs exist even if we use conventionally complete list of their names because there are namesakes and a number of names are related to different species. Besides one cannot be sure that the list is complete since new compounds appear continuously. The world production of these chemicals was increased from 7 million tons in 1950 to 250 million tons in 1985 [*Geiss and Bourdeaux*, 1986]. At present chemical industry produces 5 million species of xenobiotics, 50 thousands of them are annually sold at the world market. However, data on toxicity available in scientific literature encompass only 10% of synthetic compounds [*Izrael and Tsyban*, 1989].

The following classification of POPs seems to be appropriate:

a) Products - are substances produced for certain purposes not connected with the impact on biological objects (for example, PCBs).

b) By-products - are substances which are not specially produced but they are formed as interim species in the process of a certain human activity. They include PAHs and dioxins/furans. By-products can be formed as a result of some natural processes.

c) Pesticides - are substances with selected toxic properties to affect certain biological objects.

Negative consequences of POP impacts are first of all connected with their toxicity. In some cases it is acute intoxication, in other cases - long-term impact on organisms with negative consequences including genetic ones. For example, PAHs are carcinogenic and mutagenic [*Izrael and Tsyban*, 1989], PCBs and DDT affect some biological functions such as reproduction of mammals. *S.Tanabe* [1986] considers that an essential part of PCBs in dolphins is transferred from mother to baby at the birth (4%) and by suckling (to 60-66%) [*Tanabe*, 1986]. Capability of POPs to bioaccumulation is of particular importance, because these substances as far as they transfer upward the food chains are accumulated by living organisms in growing concentrations beginning with negligible in water to dangerous ones at the top of a given trophic chain. The enrichment factor of PCBs reaches 10^8-10^9 for predatory birds [*Yufit and Klyuev*, 1997].

Finally, the third most important factor determining the POP harmful effect is their chemical stability, i.e. their capability not to be chemically transformed and/or to be degraded in various environmental compartments. Because of their stability POPs can be transported over long distances on the regional, continental and global scale mainly due to atmospheric transport.

Marine conventions (OSPAR, HELCOM, and Barcelona Convention) pay considerable attention to the problems of sea pollution by persistent organic compounds. Within the framework of OSPAR and HELCOM the lists of priority pollutants including POPs have been compiled and now they are refined.

In particular, the Hague conference on the North Sea (1990) approved a declaration on the reduction by 50% of the emission to the atmosphere and water of 36 harmful substances and by 70% of emission of dioxins, cadmium, mercury and lead [*Progress Report...*, 1995]. The PARCOM list of organic species consists of nine substances including PCBs and HCB in addition to solvents, pesticides and dioxins [*Axenfeld et al.*, 1991]. OSPAR Convention (1993) took also a decision to reduce by 50% or more anthropogenic inputs of PAHs [*Progress report*, 1995]. Helsinki Commission has taken a similar decision to reduce the emission of harmful species by 50%. The list of priority substances contains 11 persistent organic substances including PAHs, HCB, HCH, PCP and dioxins.

The 12 specific chemical compounds identified by UNEP Governing Council in May 1995, also represent one of the major groups of "chemical priority pollutants" of EPA, EEC and WHO. Their persistency, toxicity, capacity to bio-accumulate in the living tissues and endangering the living-beings for many generations, additionally being potentially hazardous even for the remote habitats because their capability to travel long range transboundary scales, obliged all the concerned people and organizations to consider POPs as a common threat. Hence, UNEP has affirmed the need to adopt a worldwide legally binding treaty for the elimination of POPs by the new millennium and the related text was prepared by the participation of 122 countries at 11 December 2000 in Nairobi which will be adopted in 22-23 May 2001 in Stockholm.

On regional basis, under the Convention for the Protection of the Mediterranean Sea against Pollution (Barcelona Convention) and the Mediterranean Action Plan (MAP) an amended Protocol for the Protection of the Mediterranean Sea against Pollution from Land-Based Sources and Activities (LBS Protocol) was signed in 1996. As a result of the international and regional concern for POPs, this Protocol specifically mentions the 12 POPs and, in its Article 5, the Contracting Parties undertake to phase out inputs of substances that are toxic, persistent and liable to bioaccumulate, giving priority to organohalogen compounds and specifically to the 12 POPs. These 12 POPs were divided into three groups: 1) Pesticides: DDT, Aldrin, Dieldrin, Endrin, Chlordane, Heptachlor, Mirex, Toxaphene and Hexachlorobenzene (HCB); 2) Industrial chemicals: PCBs and 3) Unwanted contaminants: Hexachlorobenzene, Dioxins and Furans. To facilitate the implementation of the LBS Protocol, the Parties agreed to develop a regional Strategic Action Programme (SAP) to address pollution from land-based activities which was adopted in 1997. In accordance with SAP the following targets have been established: by the year 2005, to reduce 50% inputs of the priority 12 POPs; by the year 2010, to phase out inputs of the 9 pesticides and PCBs and reduce to the fullest possible extent inputs of unwanted contaminants.

It is well known that besides some well-defined point sources of POPs like rivers and marine outfalls, diffuse sources difficult to evaluate carry a considerable amount of POPs to the marine environment. Atmospheric transport and deposition has evidently been accepted as the major input of POPs to the marine environment where it roughly comprises 80% of the total inputs to the Mediterranean. There exists a compartmental exchange of POPs between the

atmosphere, water column (via surface micro layer) and sediment. The majority of POPs tend not to persist in sea water or sediments but involved in a variety of biogeochemical pathways. The MED POL results have shown that the measured seawater concentrations of PCBs in the Mediterranean may be as high as about 550 ng/L and about 600 ng/L in the surface film [*UNEP*, 1996]. The average values, on the other hand, are of the same order of magnitude with the levels measured at other coastal and oceanic waters. The concentrations in the sediments of the Mediterranean vary in a wide range of <0.1-16000 µg/kg d.w indicating the possession of many hot spots correlating well with the anthropogenic inputs. The levels in biota, likewise, cover a wide range from <0.1 µg/kg d.w to 450 µg/kg w.w. The organochlorine levels measured in the Mediterranean pelagic fish were declared as to be higher than in the similar fish species in Atlantic [*Fowler*, 1985], however, the spatial and seasonal variability might have built this conclusion. The organochlorine concentrations in Mediterranean Tuna was reported as to be of the same order of magnitude as in elsewhere, however, higher concentrations were also reported in older individuals of Mediterranean Tuna [*Fowler*, 1985]. The mesopelagic fish from the Western Mediterranean has recently been reported as being exposed to POPs, however, to a much lower extent than the coastal fish [*Garcia et al.*, 2000]. Some recent studies have shown that the Mediterranean Risso's dolphins contain notably high DDT levels [*Storelli and Marcotrigiano*, 2000]. The common whale in the Western Mediterranean was also found to be significantly accumulated some POPs in the selected tissues [*Hernandez et al.*, 2000]. All the scientific studies in the region show that the Mediterranean is not less contaminated with POPs when compared to the other oceanic and coastal marine environments. Therefore, the atmospheric transport and deposition of these pollutants in the Mediterranean should be taken into consideration cautiously.

Within the framework of the Convention on Long-Range Transboundary Air Pollution (LRTAP) the protocol on persistent organic pollutants was adopted in June 1998. This protocol is focused on substances subject to complete prohibition (List A), substances of limited application (List B), and substances which emissions should be reduced (List E). Within the framework of the Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe (EMEP) a number of workshops on persistent organic pollutants has been held. At the workshop held in Moscow in 1996 [*WMO*, 1997] it was recommended that the following organic pollutants be measured in the first step: PAHs, PCBs, HCB, chlordane, lindane, HCH, DDT/DDE. As far as the atmospheric transport modelling of POPs is concerned, it was recommended that at the first stage modellers should concentrate their efforts on a small number of species with different physical-chemical properties. The following pollutants have been selected: HCB, B[a]P, PCBs and lindane [*WMO*, 1997].

The purpose of this report is to provide a brief survey of physical-chemical properties of selected POPs, available estimates of anthropogenic emissions to the atmosphere and measurement data. It gives a description of their behavior in different environmental compartments and the evaluation of PCB and lindane transport in the Mediterranean region using available models. The calculated data on the atmospheric pollution of the Mediterranean Sea are based on results of studies carried out with application of the model developed at the EMEP Meteorological Synthesizing Centre - East, Moscow (MSC-E) [*Pekar et al.*, 1998]. In addition the following works carried out in MSC-E were used [*Vozhzennikov et al.*, 1997; *Yufit and Klyuev*, 1997; *Purmal*, 1997].

The first estimates of PCB and lindane transport via atmosphere in the Mediterranean presented with this study is a quite useful tool for MAP which was built-in with the Barcelona

Convention. The related protocols for the protection of the Mediterranean Sea against pollution from Land-Based Sources and Activities (1980; 1996); Transboundary Movements of Hazardous Wastes and Disposal (1996); and from any kind of Incineration and Dumping Activities At Sea (1976; 1995) deal with POPs as one of the major group of pollutants as mentioned in the articles and the related annexes of these protocols.

It is believed that the combined effort of legally binding treaty and the scientific studies on this most toxic group of pollutants can promise a much better protection against POPs in the following decades.

Chapter 2 BEHAVIOR OF POPS IN DIFFERENT ENVIRONMENTAL COMPARTMENTS

The fate of POPs in the environment, their accumulation in and removal from environmental compartments as well as the intercompartment transfer significantly depend on their physical-chemical properties. These properties define their capability to partition between gaseous and particulate phase depending on characteristics of the environment, degradation rate in and scavenging rate from different compartments, characteristics of the transfer from one compartment to another.

Persistence of POPs (that is, low degradation and transformation rate) is understood as their capability for being stable in various compartments. For the atmosphere and (partially) water, persistence of a chemical means the capability for long-range transport, in particular, on a global scale. For soils, sediments, and (partially) water the persistence of a compound fosters creation of sources of secondary pollution.

Low solubility in water causes re-emission of a compound from water or soil to the atmosphere and can lead to the possibility of its flow into bottom sediments.

Temperature dependencies for air/water and air/particles partition coefficients give rise to strongly pronounced seasonal variations of POP concentrations in various compartments as well as of fluxes between these compartments. In particular, such temperature dependencies originate transport of POPs from warm regions to cold ones, for example, to the Arctic region [*Mackay and Wania*, 1995].

Lipophility of all POPs considered in the present work leads to their bioaccumulation, that is, accumulation of a chemical in vegetation and living beings (mainly in fat tissue), and biomagnification along food chains (that is, the increase of the concentration of POPs in a consumer organism compared with a consumed one).

Below, the peculiarities of the POP behavior in different environmental compartments and parameters governing this behavior is considered.

2.1 Atmosphere

The POPs enter the atmosphere as a result of human activity: industrial processes, fossil fuel combustion, waste destruction, application of various substances and pesticides. In addition, POPs can enter the atmosphere from other environmental compartments due to re-volatilization from soil, marine and fresh waters. The capability of POPs to re-volatilize from water and soil along with their persistence does create prerequisites for global pollution by POPs. Persistent organic pollutants are present in the atmosphere in gaseous and aerosol phase. They degrade in the atmosphere due to different physical-chemical processes and are removed by wet and dry deposition. The removal and degradation occur in different ways depending on the phase state of organic compound. The POPs partitioning between gaseous and aerosol phases depends on a number of factors such as their physical-chemical properties, ambient temperature, humidity and aerosol characteristics.

The following properties of POPs determine their behavior and/or concentration in the atmosphere:

1. Molecular weight .

2. Melting temperature - T_m (^{0}K).

3. Boiling temperature - T_b (^{0}K).

4. Emission/re-emission rate of a chemical from soils and water bodies to the atmosphere.

5. Saturated vapor pressure - p^0 (Pa). By definition given in [*Mackay et al.*, 1992] this parameter describes the "solubility of a chemical in air". The parameter p^0 shows which maximum partial pressure of a chemical in the atmosphere can be originated under given conditions by its transformation to the gaseous phase from solid (sublimation) or liquid one (evaporation). Consequently, the saturated vapor pressure for solid state - p^0_S and for subcooled liquid – p^0_L is considered. The values of p^0_L and p^0_S depend on air temperature and increase with increasing temperature for all compounds considered in this work. With the help of p^0_L one can characterize the partitioning of an organic compound between its aerosol and gaseous phase. The part φ of a compound in the aerosol phase is calculated according to C. Junge model [*Junge*, 1977] by the formula:

$$\varphi = c\,\theta/(p^0_L + c\,\theta), \qquad (2.1)$$

where c - is the constant depending on thermodynamic parameters of the adsorption process and on aerosol surface properties;

θ - concentration of aerosol surface area, m^2/m^3.

F. Wania and D. Mackay [1996] proposed a classification of compounds from the viewpoint of their partitioning between gaseous and aerosol phase based on p^0_L value at 25^0 C.

POPs with p^0_L (25^{0}C) above 1 Pa, in the temperature range usual for the lower troposphere, practically do not condense and are present in the atmosphere only in the gaseous phase.

POPs with p^0_L (25^{0}C) varying from 1 to 10^{-2} Pa, can condense at temperatures about 30^{0}C and are present in the aerosol phase mainly at high latitudes.

POPs with p^0_L (25^{0}C) varying from 10^{-2} to 10^{-4} Pa, can condense at temperatures higher than 0^0 C and can be found in the aerosol phase at middle latitudes.

POPs with p^0_L (25^{0}C) less than 10^{-4} PA, are present in the atmosphere mainly in the aerosol phase.

6. Solubility in water - S (units are weight (g/l) or molar (mol/l) concentrations). This parameter characterizes the capability of a chemical to permeate into water from solid phase (S_S) and from subcooled liquid state (S_L). Under given conditions, S_S and S_L are maximum concentrations in water of the solid phase of a chemical or, respectively, its overcooled liquid state. The S_S and S_L play essential role in the consideration of the transport of a chemical from the atmosphere to rain or cloud drops and/or underlying water surface. Solubility for a given chemical depends on water temperature, its salinity and organic matter content.

The dependence of solubility on temperature is not, in general, an increasing function of temperature, but for the chemicals considered here the solubility increases with temperature increase.

The dependence of solubility on salinity is different for different chemicals. For example, in *B.G.Whitehouse* [1984] paper the data are reported on several PAHs that show that their solubility decreases with salinity increase whereas for 1,2-phenantracene considered in the same paper the salinity increase leads to the increase of solubility.

7. Henry's law constant - H. The Henry's law constant plays an important role in the atmosphere/ sea exchange processes and in-cloud and below cloud scavenging for the gaseous phase of a compound. In real situations the maximum values of saturated vapor pressure or solubility are not, as a rule, achieved. However, according to the Henry's law the ratio of equilibrium partial pressure p_a of a chemical in the air and its water concentration C_w equals to that of its saturated vapor pressure p^0 and its solubility S. This ratio is known as the Henry's law constant - H:

$$\frac{p_a}{C_w} = \frac{p^0}{S} = H \tag{2.2}$$

The H units are $Pa \cdot m^3/mol$ under the assumption that the concentration of a chemical is measured in mol/m^3. Expressing saturated vapor pressure via its molar air concentration (according to the Mendeleev-Clapeyron equation), one can represent the Henry's law constant in the dimensionless form K_H:

$$\frac{C_a}{C_w} = K_{AW} = K_H = \frac{H}{RT}, \tag{2.3}$$

where K_{AW} is the dimensionless "air-water" partition coefficient, R is the universal gas constant, and T is an absolute temperature (^0K).

Note that the Henry's law constant is the same both for solid state and for overcooled liquid:

$$H = \frac{p_L^0}{S_L} = \frac{p_S^0}{S_S} \tag{2.4}$$

The Henry's law constant is temperature dependent. This dependence can be computed via temperature dependencies for p^0_L (p^0_S) and S_L (S_S).

The dependence of the Henry's law constant on salinity is connected with the dependence of solubility on salinity. For the majority of substances the Henry's law constant increases with salinity increase.

8. Octanol-air partition coefficient - K_{OA}. The "octanol-air" partition coefficient (K_{OA}) characterizes POP partitioning between air and organic films (cuticle, covering the plant leaves). It can be used for the description of exchange of POPs between the atmosphere and vegetation [*Bacci et al.*, 1990]. In the recent publications ([*Wania*, 1997] and [*Harner and Bidleman*, 1998]) it has been shown that the main mechanism of the POP sorption by atmospheric particles can be the process of absorption by the organic film covering particles. The POP partitioning between the gaseous phase and organic films of the atmospheric aerosol is described by K_{OA} coefficient [*Finizio et al.*, 1997].

Dimensionless K_{OA} is the equilibrium ratio of POP concentrations in octanol and air:

$$K_{OA} = C_O/C_A, \quad (2.5)$$

where C_O (ng/m^3) and C_A (ng/m^3) – concentrations of a substance in octanol and air respectively.

The K_{OA} value can be calculated from the following relationship:

$$K_{OA} = K_{OW}/ K_{AW}, \quad (2.6)$$

where K_{AW} – dimensionless "air-water" partition coefficient (see formula 2.3) and K_{OW} - "octanol-water" partition coefficient (see below section 2.2 "Water").

This estimate, however, leads to a significant error since K_{OW} characterizes POP partitioning between octanol saturated by water and water saturated by octanol whereas the Henry's law constant characterizes partitioning between pure water and air. Besides the error in the determination of the K_{OW} value, the Henry's law constant also introduces an error to the K_{OA} value (due to errors in determination of H by measuring solute concentrations in air and water). Therefore, it is better to use K_{OA} values obtained in direct measurements (for example, see the papers by *T.Harner et al.* [1995]; *T.Harner and T.F.Bidleman* [1996]).

9. Degradation in air. Degradation of organic chemicals is an important parameter affecting their behaviour in environmental compartments. Degradation of POPs in the atmosphere can be caused by photolysis and reactions with the hydroxyl-radical OH. As a rule, it can be described by the first-order reactions with degradation rate constant K_A. Degradation rates depend on a compound, its state (gaseous or aerosol) and a number of environmental characteristics: intensity of sunlight, temperature, concentration of the OH radical.

10. Molecular diffusion coefficient - D_A (m^2/s) determines the behaviour of a chemical in the gaseous phase in the quasi-laminar near surface air.

2.2 Water

The POP input to the lakes and seas takes place with rivers, direct discharges and from the atmosphere. The POPs enter the rivers due to runoff from watersheds and direct discharges of municipal and industrial wastes. In water POPs are present in a dissolved state and on particulate matter. The POPs can degrade in water and can be removed due to sedimentation, biosedimentation and re-volatilization to the atmosphere. Sedimentation and biosedimentation result in the fact that fresh-water bodies and the seas in particular can become the final sink of POPs [*Izrael and Tsyban*, 1989]. Biosedimentation processes are more intensive in biologically productive zones (in particular coastal and shelf regions). An important factor is the POP input to biota and their further bioaccumulation as far as they move up the food chain.

Behavior of POPs in water and their interaction with other compartments depend both on the parameters described in the section "Atmosphere" (Henry constants, solubility) and on the following parameters.

1. "Octanol-water" partition coefficient - K_{OW}

The "octanol-water" partition coefficient (K_{OW}) is a measure of substance hydrophobicity characterizing its partitioning between water and organic matter (lipids, waxes, and natural organic matter).

It is determined as a quotient of equilibrium concentrations of a chemical in octanol - C_O (mol/l) and in water - C_W (mol/l):

$$K_{OW} = C_O/C_W \qquad (2.7)$$

K_{OW} is used for the assessment both of the "organic carbon-water" partition coefficient (K_{OC}) and the "octanol-air" partition coefficient (K_{OA}) and bioconcentration factor (BCF).

2. "Organic carbon-water" partition coefficient

Sorption of POPs by particulate matter in water, bottom sediments and soil (section 2.3) is described by the "organic carbon-water" partition coefficient (K_{OC}, dm^3/kg) determined as a ratio of equilibrium concentrations of a POP in organic carbon - C_{OC} (ng/kg) and in water - C_W (ng/dm^3):

$$K_{OC} = C_{OC}/C_W \ [dm^3/kg] \qquad (2.8)$$

The K_{OC} value can be estimated by the "octanol-water" partition coefficient (K_{OW}) using the following relationships:

$$\log K_{OC} = 1.00 \log K_{OW} - 0.21 \qquad [\textit{Karikhoff et al.}, 1979] \qquad (2.9)$$

or

$$K_{OC} = 0.41 K_{OW} \qquad [\textit{Karikhoff}, 1981] \qquad (2.10)$$

3. Molecular diffusion coefficient - D_W. It determines the rate of substance dispersion in a thin surface water layer.

4. Degradation in water. Degradation of organic compounds in water can be caused by photolysis in surface layer, hydrolysis or biodegradation. It can be described by the first-order reactions with the degradation rate constant K_W.

2.3 Soil

The POPs enter the soil due to application of pesticides and municipal and industrial discharges. Besides, they come from the atmosphere due to wet and dry deposition. They are present in soil in dissolved, gaseous (in soil pores) phases and adsorbed on soil particles. On the one hand POPs are accumulated in soil and can penetrate to lower layers, on the other - they are removed from soil due to degradation, entering the biota and re-volatilization to the atmosphere.

Soil can be considered as a multi-compartment medium consisting of soil matter itself and pores filled by air and water. Redistribution of a chemical between these compartments as

well as the air/soil exchange can be described with the help of parameters discussed in subsections 2.1 and 2.2. The soil-related parameters are:

1. Degradation in soil. This parameter is determined by not only photolysis and/or reaction with the hydroxyl radical OH but mainly by microorganism's activity.
2. Soil/water partition coefficient - $K_p(dm^3/kg)$. The coefficient K_p is determined as a ratio of equilibrium concentrations of POPs in the solid compartment of soil (as well as bottom sediments and suspended particles) and the concentration of POPs in water compartment:

$$K_P = C_P/C_W \quad [ng/kg]/[ng/dm^3] \tag{2.11}$$

where C_P and C_w are the concentrations of a chemical in the sorbed and dissolved phase, respectively,

The K_P can be expressed via K_{OC} (see formula 2.8) as:

$$K_P = K_{OC} \cdot f_{OC}, \tag{2.12}$$

where f_{OC} is the mass fraction of organic carbon in soil (suspended particles/bottom sediments).

It is clear that for estimating the partitioning of a chemical between different soil compartments it is necessary to use some parameters described above, such as molecular diffusion coefficient and Henry's law constant.

Chapter 3 PHYSICAL-CHEMICAL PROPERTIES OF SOME POPs

This chapter is focused on physical-chemical properties of the organic compounds included in the priority list by the Moscow Workshop on Heavy Metals and POPs [*WMO*, 1997]. The following properties will be presented (detailed description of these properties was presented in Chapter 2):

p^0_S (Pa) - saturated vapor pressure for the solid state;

p^0_L (Pa) - saturated vapor pressure for the subcooled liquid state;

S_S(mol/m^3) - solubility of solid phase in fresh water;

S_L(mol/m^3) - solubility of liquid phase in fresh water;

S_S^*(mol/m^3) - solubility of solid phase in ocean water;

S_L^*(mol/m^3) - solubility of liquid phase in ocean water;

H(Pa .m^3/mol) - Henry's law constant for fresh water;

H^*(Pa .m^3/mol) - Henry's law constant for ocean water;

K_{OW}(-) - "octanol-water" partition coefficient (dimensionless);

K_{OC}(dm^3/kg) – "organic carbon-water" partition coefficient;

K_A(time^{-1}) - degradation rate in air;

T_A(time) - degradation half-live in air;

K_W(time^{-1}) - degradation rate in water;

T_W(time) - degradation half-live in water;

K_S(time^{-1}) - degradation rate in soil;

T_S(time) - degradation half-live in soil.

Estimations of these parameters were obtained both on the basis of experimental data and theoretical calculations using equations connecting different parameters. The uncertainty of these estimations is rather high. It can be due to the differences of the methods used and distinctions in assumptions. Therefore the discrepancies in these data accounted up to several times is quite usual.

3.1 Pesticides

Pesticides constitute a highly heterogeneous group of substances entering the environment in great quantities. They are divided into herbicides, insecticides, fungicides and rodentcides. A number of substances (aldrin, dieldrin, endrin, chlordane, mirex, toxophene, and chlordecone) are prohibited for production and sale.

Lindane (γ-HCH)

Lindane or γ-HCH is one of the conformers of 1,2,3,4,5,6-hexachlorocyclohexane. The HCH is produced by benzene chlorination under the impact of UV radiation. It was first synthesized by *M.Faradey* in 1825. In 1933 its insecticide properties were revealed and its industrial

production began. At the end of the 70-s - 80-s this substance was used extensively when stringent restrictions for the production, sale and application of DDT were set up [*Yufit and Klyuev*, 1997]. Lindane is an effective agent for the control of many pests. It is applied during sowing and germination of agricultural plants, for treating forests and gardens, to control locust and sprayed cotton plants, beat roots and potatoes during the growing season and for other purposes. It is used as dust, granules, oil, solutions, emulsions, and suspensions by spraying, surface application or ploughing in soil [*Gruzdev*, 1987]. By estimation, in the 80-s, 5900 tons of lindane was annually used in the world and 4000 tons – in the 90-s. The agricultural use of lindane was restricted in many European countries. Nevertheless it is still used as an insecticide [*Holoubek et al.*, 1993].

Lindane exhibits mutagenic activity and can cause chromosomic aberrations in leukocyte culture. It also causes irritative and allergic effect on organism. Lindane negatively affects reproductivity provoking death of embrions. Toxicity of lindane increases with increase of organism temperature [*Yufit and Klyuev*, 1997]. According to classification [*Holoubek et al.*, 1993] lindane can be considered as a possible human carcinogen.

The following physical-chemical properties of lindane are presented:

Molecular formula

$C_6H_6Cl_6$

Molecular weight

290.85

Melting (T_m) and boiling (T_b) temperature

$T_m = 113^0C$, $T_b = 323.4^0C$ [*Howard,* 1991]

Solubility (S, mol/m^3)

Solubility (S) at 25^0C is 2.6×10^{-2} mol/m^3 = 7.5 mg/l [*Schwarzenbach et al.,* 1993]

Solubility dependences on temperature –T(^{0}K) as follows: [*Kucklik et al.,* 1991]

for temperature range from 15^0C to 45^0C:

$$\log S\ (mol/m^3) = -(1918 \pm 656)/T + (4.75 \pm 2.16)$$

for sea water in temperature range from 0.5^0C to 23^0C:

$$\log S\ (mol/m^3) = -2787/T + 8.03$$

for deionized water in temperature range from 0.5^0C to 45^0C:

$$\log S\ (mol/m^3) = -3108/T + 9.18$$

Lindane solubility remains practically constant when concentrations of humic and fulvic acids increase from 0 to 100 mg/l and it does not depend on the nature and concentrations of the dissolved organic matter [*Chiou et al.,* 1986].

Saturated vapor pressure (P^0_S ,Pa)

for temperature range from 15^0C to 45^0C:

$\log p^0_S = -(5290 \pm 222)/T + (15.65 \pm 0.74)$ *Kucklik et al.* 1991]

for temperature range -30^0C - $+30^0$C:

$\log p^0_S = -5490/T + 16.72$ *Wania et al*., 1994]

The vapor pressure dependence on temperature for a subcooled liquid:

$\log p^0_L = -3680/T + 11.15$ *Hincley et al.,* 1990]

Henry`s law constant (H, Pa m^3/mol)

The H temperature dependencies (T- in ^{0}K):

for deionized water in the range from 0.5 to 45 ^{0}C:

$\log H = -(2382 \pm 160)/T + (7.54 \pm 0.54)$ [*Kucklik et al.,* 1991]

for sea water in the range from 0.5 to 23 ^{0}C:

$\log H = -(2703 \pm 276)/T + (8.68 \pm 0.96)$ [*Kucklik et al.,* 1991]

$\ln(H) = 19.99 – 6225/T$ [*Strand and Hov*, 1996]

for fresh water in the range from 0.5 to 45 ^{0}C:

$\ln(H) = 17.36 – 5486/T$ [*Strand and Hov*, 1996]

$H = 0.073 \exp(25.88-7329/T)$ [*Jacobs and van Pul*, 1996]

Sorption by soil, sediments and suspended particles

The sorption value is determined by the following coefficients: K_{OC} (dm^3/kg) – "organic carbon-water" partition coefficient; K_{OW} – "octanol-water" partition coefficient (see Chapter 2).

$\log K_{OC} = 2.99$ [*Kushi et al.,* 1990]

$\log K_{OC} = 2.96$ [*Kenaga and Goring*, 1980]

$\log K_{OC} = 3.03$ [*Lyman,* 1982]

$\log K_{OW} = 2.96$ [*Kenaga and Goring,* 1980]

$\log K_{OW} = 3.30$ - 3.89 with average value 3.60 [*Isnard and Lambert*, 1988]

Degradation half-life in soil (mainly due to biodegradation)

267 days [*Jacobs and van Pul*, 1996]

253 days [*Strand and Hov*, 1996]

2 years [*Mackay et al.,* 1991]

Lindane degradation half-lives in soils measured in the field experiments after the surface application varied in the range of 150-350 days [*Kononiuk,* 1986; *Lyman,* 1982; *Tzukerman*

1985]. However, under field conditions volatilization of lindane to the atmosphere plays a significant role for the evaluation of the lindane content in the soil. Therefore the degradation rate constant for this pesticide can be determined only under laboratory conditions where volatilization is suppressed or controlled. Based on the laboratory experiments data the lindane half-life in the soil was estimated to be 600 days [*Laskovski et al.,* 1984].

Degradation half-life in water (mainly due to hydrolysis and photolysis)

4.7 years in surface water	[*Strand and Hov*, 1996]
28 years in deep water	[*Strand and Hov*, 1996]
2 years	[*Mackay et al.,* 1991]

At pH = 7 and 25^0C the hydrolysis half-life is 6 years [*Elington et al.,* 1987].

Estimated values of the degradation half-live in water due to the reaction with hydroxyl radical are 1.3, 27, 530 days for fresh water, coastal sea water and open ocean, respectively [*Vozhzennikov et al.*, 1997].

Degradation half-life in air (mainly due to reaction with hydroxyl radicals in air)

32 days	[*Jacobs and van Pul*, 1996]
170 days	[*Mackay et al.,* 1991]

Hexachlorobenzene (HCB)

Hexachlorobenzene HCB is a selective fungicide that was first introduced in 1945 to control soils and plant diseases. Although in the majority of European countries its application is completely prohibited it still enters the environment because it is a component of many pesticides (as impurity) applied to agriculture [*Holoubek et al*., 1993; *Axenfeld et al.*, 1991]. In addition to agricultural application HCB is used as a flame retardant, in pyrotechnics, as a solvent and for garbage incineration [*Holoubek et al*., 1993; *Axenfeld et al.*, 1991; *Berdowski et al.*, 1997].

HCB is a toxic compound. Oral exposure to HCB can cause metabolic disturbances and diseases of internal organs. [*Axenfeld et al.*, 1991].

Below some of its physical-chemical properties are presented.

Molecular formula

C_6Cl_6

Molecular weight

284.78

Melting and boiling temperature

$T_m = 228.5^0$C, $T_b = 321^0$C [*Dannenfelser and Paric,* 1991]

Solubility

The HCB solubility at 25^0C is:

S (mol/L) = 2.0×10^{-8}; [*Dannenfelser and Paric,* 1991]

S (mg/L) = 5.7×10^{-3} (averaged values published).

The dependence of solubility on temperature (in ^{0}K) was obtained by dividing the vapor pressure [*Wania et al.,* 1994] by the Henry`s law constant for fresh water [*ten Hulscher et al.,* 1992]:

$$\log S\ (mol/m^3) = -1381/T + 0.18$$

The following equation was calculated by *F.Wania and D.Mackay* [1995] by dividing the vapor pressure [*Wania et al.,* 1994] by the Henry`s law constant for sea water [*ten Hulscher et al.,* 1992]:

$$\log S\ (mol/m^3) = -1314/T + 0.254$$

Saturated vapor pressure (p^0 , Pa)

The following experimental data for saturated vapor pressure of HCB are available:

$p^0_S = 1.35 \times 10^{-8}$ atm at 20^0C [*Dannenfelser and Paric,* 1991]

$p^0_S = 2.37 \times 10^{-8}$ atm at 25^0C [*Banerjjee et al.*, 1990]

$p^0_S = 1.72 \times 10^{-8}$ atm at 25^0C [*Wania et al.,* 1994]

The vapor pressure dependence on temperature (in ^{0}K) could be calculated as follows:

$\log p^0_S\ (Pa) = -3874/T + 10.23$ (-30 - +30^0C) [*Wania et al.,* 1994]

$\log p^0_L\ (Pa) = -3582/T + 11.11$ [*Hincley et al.*, 1990]

Henry`s law constant (H)

The Henry`s law constant depends on the temperature (^{0}K) as follows:

for fresh water:

$\log H\ (Pa\ m^3/mol) = -2493/T + 10.05$ [*ten Hulscher et al,* 1992]

for sea water:

$\log H\ (Pa\ m^3/mol) = -2560/T + 9.88$ [*ten Hulscher et al.,* 1992]

Sorption by soils, sediments and suspended particles

The sorption value is determined by the following coefficients: K_{OC} (dm^3/kg) – "organic carbon-water" partition coefficient; K_{OW} (-) – "octanol-water" partition coefficient (see Chapter 2).

$\log K_{OC} = 3.9$ [*Dannenfelser and Paric,* 1991]

$\log K_{OW} = 5.4$ (20 - 30^0C) [*Dannenfelser and Paric,* 1991]

$\log K_{OW} = 5.5$ [*Bayona et al.,* 1991]

Degradation half-live in soil

1500 days [*Mackay and Paterson,* 1991]

6.3 years [*Wania and Mackay*, 1995]

Measurement of the HCB degradation rate constant in soils is a difficult task due to its stability to microbiological degradation. Therefore there are few data about the HCB degradation half-lives in soils.

Degradation half-life in water

6.3 years [*Wania and Mackay,* 1995]

Estimated degradation half-lives due to reaction with hydroxyl-radical are 1.6, 32 and 640 days in fresh waters, coastal sea water and open ocean, respectively. These estimations were made for HCB fraction dissolved in water [*Vozhzennikov et al.*, 1997].

Degradation half-life in the atmosphere

700 days is the assessment of the half-life in the atmosphere in temperate and boreal air [*Wania and Mackay,* 1995].

An assessment of the half-lives in the surface layers of the atmosphere due to the reaction with hydroxyl radical is: 40 days in summer, 100 days in spring/autumn, 900 days in winter. These estimations were made for the gaseous HCB fraction [*Vozhzennikov et al.*, 1997].

3.2 Polychlorinated biphenyls (PCBs)

Polychlorinated biphenils (PCBs) is a group of organic compounds that were synthesized in 1929 in the USA and manufactured in developed countries until the late 1970s. Because of their properties - chemical stability and heat resistance - they were used worldwide in industry in condensers and transformers as a heat-transfer agent; in ballast resistance, luminescent lamps, hydraulic liquids; for insulation of electric wire, cable etc. PCB mixtures were used also as plasticizers, additions to hydraulic liquids and as flame retardant in various industrial and commercial products.

There are 209 possible PCB isomers, from three monochlorinated isomers to the fully chlorinated decachlorobiphenyl isomer. The properties and toxicity of PCB isomers are affected by the number and position of chlorine atoms. Polychlorinated biphenyls are possible carcinogens for people. PCBs can affect the reproductive system of adults. Being highly lipophilic PCBs is bioaccumulated in fatty tissues of animals, birds and aquatic live beings.

This paper considers the properties and behavior of PCB-153 as a reference compound, since it is a constituent of the calibration mixture used for identification and quantitative estimates of all 209 PCB congeners. PCB-153 is a hexaisomer (2,2',4,4',5,5' – hexachlorobiphenyl)

which is a constituent of polychlorinated biphenyls. There are 42 hexachlorobiphenyls. Although PCB-153 is not toxic it can be a modulator of toxic impacts of other PCB congeners. The most important fact is that PCB-153 is present practically in all PCB technical mixtures in sufficiently large quantities - from 5 to 17% (on the average - 10%). Therefore it can be used as an indicator of the PCB input to the environment and removal from it.

Below the physical-chemical properties of PCB-153 are presented.

Molecular weight

360.9

Melting (T_m) and boiling (T_b) temperature

$T_m = 103^0C$ [*Yalkowsky et. al.,* 1983]

$T_b = 405^0C$ [*Estimating exposure..*, 1994]

Solubility (S)

The data on solubility of PCB-153 at 25^0C found in literature are listed below:

Reference	S, mol/m^3	S, mg/l
D. Pal et al., 1980	24×10^{-6}	8.8×10^{-3}
W.Y. Shiu and D. Mackay, 1986	2.8×10^{-6}	1×10^{-3}
R. Haque and D.W. Schmedding, 1975	2.6×10^{-6}	0.95×10^{-3}
C.T. Chiou et al., 1977	2.6×10^{-6}	0.95×10^{-3}
S.H. Yalkowsky et. al., 1983	3.6×10^{-6}	1.3×10^{-3}
A. Opperhuizen et al., 1988	3.3×10^{-6}	1.15×10^{-3}
F.W. Dunnivant and A.M. Elzerman, 1988	2.4×10^{-6}	1.3×10^{-3}
D. Mackay et al., 1991	3×10^{-6}	1.1×10^{-3}

Solubility dependence on temperature (^0K)

The following equation is calculated using dissolution enthalpy data [*Doucette and Andren,* 1988]:

$$\log S\ (mol/m^3) = -2435/T + 2.65$$

Solubility dependence on salinity

The solubility of PCB-153 in sea water can be assessed as 20% of its solubility in distilled water.

Solubility dependence on the organic matter content in water

Solubility of the chlorinated biphenyls increases 5-7 times as the concentration of the humic acid increases from 0 to 100 mg/l, while the increase of fulvic acid concentration in the same range does not considerably affect the PCB-153 solubility [*Chiou et al.,* 1986].

Saturated vapor pressure (p^0, Pa)

$p^0_S = 3.2 \times 10^{-5}$ Pa (25^0C) [*Dunnivant and Elzerman*, 1988];

$p^0_S = 4.2 \times 10^{-5}$ Pa (20^0C) [*Murphy et al*., 1987];

$p^0_S = 2.6 \times 10^{-5}$ Pa (25^0C) [*Harner et al*., 1995];

$p^0_S = 1.2 \times 10^{-4}$ Pa (25^0C) [*Mackay et al.,* 1991].

Temperature dependence of vapor pressure p^0_S is determined as follows:

$\log p^0_S\,(\text{Pa}) = -5851/T + 15.10$ [*Vozhzennikov et al.*, 1997]

Temperature dependence of vapor pressure p^0_L is determined as follows:

$\log p^0_L\,(\text{Pa}) = -4798/T + 12.30$ [*Vozhzennikov et al.*, 1997]

Henry`s law constant (H)

The Henry`s law constant values for PCB-153 were estimated as follows:

References	t,^{0}C	H, Pa·m^3/mol
T.J. Murphy et al., 1987	20	9.9
F.M. Dunnivant and A.M. Elzerman, 1988	25	13.2
T. Harner et al., 1995	25	20
D. Mackay et al., 1991	25	42

Dependence of H on temperature T (^{0}K) is the following:

$\log H\,(\text{Pa}\cdot\text{m}^3/\text{mol}) = -3416/T + 12.61$ [*Vozhzennikov et al.*, 1997]

Sorption by soil, sediments and suspended particles

The sorption value is determined by the following coefficients: K_{OC} (dm^3/kg) – "organic carbon-water" partition coefficient; K_{OW} (-) – "octanol-water" partition coefficient (see Chapter 2).

$\log K_{OC} = 6.07$ [*Karikhoff et al.,* 1979]

$\log K_{OC} = 4.78 - 6.87$ with average value 5.70 [*Horzempa and Di Toro,* 1983]

$\log K_{OW} = 7.00$ [*Shiu and Mackay,* 1986]

$\log K_{OW} = 7.55$ [*Miller et al.,* 1984]

$\log K_{OW} = 6.9$ [*Bayona et al.,* 1991]

$\log K_{OW} = 6.9$ [*Risby et al.,* 1990]

Degradation half-life in soil

The degradation half-life in soils for hexachlorobiphenyls is 6 years [*Mackay et al.*, 1991].

Degradation half-life in water

Considered half-life values are 4, 80 and 1600 days for fresh water, coastal sea water and open ocean, respectively. These estimations were made for dissolved PCB-153 fraction [*Vozhzennikov et al.*, 1997].

The degradation half-life in soils for hexachlorobiphenyls is 6 years [*Mackay et al.*, 1991].

Degradation half-life in atmosphere

Assessment of the degradation half-life of PCB-153 in the atmosphere due to reaction with OH radical is: 13 days in summer, 34 days in spring/autumn, 300 days in winter. These estimations were made for the gaseous PCB-153 fraction [*Vozhzennikov et al.*, 1997].

Degradation half-life for hexachlorobiphenyls is 8 months [*Mackay et al.*, 1991].

3.3 Products of pyrosynthesis

Products of pyrosynthesis are mainly polycyclic aromatic hydrocarbons (PAHs) and dioxins/furans. In this section only PAHs, in particular benzo[a]pyrene, will be considered.

Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are compounds consisting of two or more fused aromatic carbon rings. PAHs are characterized by high stability to external impacts and by the accumulation in natural matrices including biota. PAHs having mutageneous and carcinogenic effect are especially dangerous. First of all it refers to benzo[a]pyrene - B[a]P [*Holoubek et al*., 1993; *Yufit and Klyuev*, 1997].

The environmental pollution by PAHs of anthropogenic origin is of a global character [*UN Environmental program...*, 1993; *Harvey*, 1991; *Rovinsky et al.*, 1988; *Maistrenko et al.*, 1996]. The bulk of PAHs is directly emitted to the air as a result of combustion. PAHs are produced when the organic matter containing carbon and hydrogen is heated to the temperature above 700^0C and subject to pyrolysis and/or incomplete combustion. Since the processes of pyrolysis and incomplete burning occur everywhere including natural processes it is evident that PAHs, their derivatives and analogs can be found everywhere [*Holoubek et al.*, 1993].

Benzo[a]pyrene (B[a]P)

Benzo[a]pyrene (B[a]P) is one of many PAHs. It can hardly represent the whole family of PAHs: it is not the most toxic, it is not the most abundant; in contrast to many PAHs it is rather unstable in the atmosphere. But it can be easily measured, and a great amount of the data on its concentrations is available.

B[a]P can have both natural and anthropogenic sources. In both cases it is emitted mainly to the atmosphere. The main anthropogenic sources are fuel combustion, coke production, oil

refining and aluminum production. Estimates of B[a]P emissions for different countries can vary within a factor of 3. The global emission is about 5000 t/yr [*Holoubek et al*., 1993; *Yufit and Klyuev*, 1997].

Below some physical-chemical properties of B[a]P are presented.

Molecular formula

$C_{20}H_{12}$

Molecular weight

252

Melting (T_m) and boiling (T_b) temperature

$T_m = 179^0C$; $T_b = 310^0C$ [*Yufit and Klyuev*, 1997].

Solubility - S

The B[a]P solubility data at 25^0C found in literature are listed below:

Reference	S, mol/L	S, mg/L
D. Mackay and W.Y. Shiu, 1984	1.5×10^{-8}	3.8×10^{-3}
S.H. Yalkowsky et. al., 1983*	2.1×10^{-8}	5.3×10^{-3}
B.G. Whitehouse, 1984	0.61×10^{-8}	1.5×10^{-3}
B.G. Whitehouse, 1984	0.61×10^{-8}	1.5×10^{-3}

* Calculated as an average of 12 independent literature S values.

Solubility dependence on temperature (^0K) for fresh water:

$\log S\ (mol/m^3) = -1790/T + 1.18$ [*Vozhzennikov et al.*, 1997].

Solubility dependence on temperature for sea water:

$\log S\ (mol/m^3) = -2355/T + 2.94$ [*Vozhzennikov et al.*, 1997].

Saturated vapor pressure (p^0 , Pa)

Data on saturated vapor pressure for B[a]P found in literature are presented below:

Vapor pressure	References	t, ^0C	p^0, Pa
p^0_S	*T.F. Bidleman and W.T. Foreman,* 1987**	20	3.2×10^{-7}
p^0_S	*S. Banerjjee et al.,* 1990*	25	7.2×10^{-7}
p^0_S	*D.A. Hincley et al*., 1990	25	7.2×10^{-6}
p^0_L	*D. Mackay et al.,* 1992	25	2.1×10^{-5}
p^0_L	*Y. Cohen and R.E. Clay,* 1994**	25	7.4×10^{-7}

* Average value of literature data

** Assessment based on literature data.

Dependence of saturated vapor pressure on temperature:

$\log p^0_L$ (Pa) = -4989/T + 11.59 [*Hincley et al.*, 1990]

$\log p^0_S$ (Pa) = -6319/T + 15.07

(the latter equation was obtained in [*Vozhzennikov et al.*, 1997] using the data of [*Hincley et al.*, 1990] and [*Bidleman and Foreman*, 1987]).

Henry's law constant (H)

H = 0.05 Pa m^3/mol (at 25^0 C) [*Mackay et al.*, 1992].

Temperature dependence of H for fresh water:

log H (Pa m^3/mol) = -4529/T(^{0}K) + 13.89 [*Vozhzennikov et al.*, 1997].

Temperature dependence of H for sea water:

log H (Pa m^3/mol) = -3964/T(^{0}K) + 12.13 [*Vozhzennikov et al.*, 1997].

Sorption by soil, sediments and suspended particles

The sorption value is determined by the following coefficients: K_{OC} (dm^3/kg) – "organic carbon-water" partition coefficient; K_{OW} (-) – "octanol-water" partition coefficient (see Chapter 2).

$\log K_{OW}$ = 6.13 [*Cohen and Clay,* 1994]

$\log K_{OW}$ = 6.2 [*Bayona et. al.,* 1991]

$\log K_{OW}$ = 6.04 [*Mackay et al.*, 1992]

The "organic carbon-water" partition coefficient K_{OC} can be estimated using K_{OW} (2.10). For instance, in the latter case, on the basis of $\log K_{OW}$ of [*Mackay et al.*, 1992], appropriate value of log K_{OC} will be equal to 5.65.

Degradation half-life in soil

825 days (biodegradation half-life) [*Mackay and Paterson*, 1991]

530 days [*Cohen and Clay*, 1994]

10-60 days (in sod-podsolic soil) [*Shilina et al.*, 1980]

20-50 days [*Tonkopiy et al.*, 1979]

Degradation half-life in water

1.1 hour [*Cohen and Clay*, 1994]

The values 1, 0.7, 0.5, and 0.8 hour are the calculated degradation half-lives of dissolved B[a]P due to direct photolysis in the surface water layer at 40°N at noon in winter, spring, summer and fall respectively [*Mill et al.*, 1981].

Other estimates:

4 days (rivers and lakes) [*Vozhzennikov et al.*, 1997]

80 days (coastal sea water) [*Vozhzennikov et al.*, 1997]

1600 days (ocean water)	[*Vozhzennikov et al.*, 1997]
2 months (average)	[*Mackay et al.*, 1992]

Degradation half-life in the atmosphere

Many authors believe that the B[a]P stability in the particulate phase is much higher than that in the gas phase. *Y.Cohen and R.E.Clay* [1994] used the value of degradation half-life of B[a]P in the gaseous phase equal to 1.1 hour whereas in the particulate phase - 8 days. According to the calculations made by *L.Blau and H.Güster* [1981] the degradation half-life under daily average intensity of the summer sun radiation in central Europe is equal to 5 hours. In the model calculations *D.Mackay et al.* [1991] recommend to use the value of 170 hours as an annual mean half-life degradation rate.

Gas/aerosol partitioning in the atmosphere

Gas/aerosol partitioning of B[a]P depends mainly on temperature. In winter the share of the aerosol fraction increases with the decrease of mean temperature [*Finlayson-Pitts et al.*, 1986]. *M.Afanasiev et al.* [1982] measured benzo[a]pyrene gas/particle partitioning in rural areas of the European USSR in 1982. The gas fraction varied from 2.3 to 18.2%. Similar results (6-20% of the gas fraction) were obtained in the suburbs of large cities in Belgium and the Netherlands [*Broddin et al.*, 1980].

Size distribution of particulate B[a]P

Size distribution is a factor of crucial importance, which determines the rate of dry and wet deposition. It was found in a transport tunnel experiment [*Venkataraman et al.*, 1994] that more than 85 % of PAH was sorbed on fine particles.

Washout ratio

A lot of experimental data on B[a]P concentrations both in air and precipitation were obtained by *F.Rovinskiy et al*. [1988] in the background regions of the European part of the former USSR. On this basis it is possible to assume that the washout ratio can be 10^4 -10^5 in summer and 10^3 - 10^4 in winter. It is natural that washout ratio values should be different for gaseous and particulate phases of B[a]P. For the particulate phase *A.Baart et al.* [1995] used the value of 3×10^5. The value for the gaseous phase can be estimated as a function of the Henry's law constant and temperature.

Diffusion coefficients

Molecular diffusion determines the intensity of the B[a]P exchange between air, water and soil. As estimated by *R.Schwarzenbach et al.* [1993] the B[a]P diffusion coefficients in air are 6.9×10^{-6} m^2/s and in water - 7.5×10^{-10} m^2/s. In model calculations *D.Bakker and W. de Vries* [1996] recommend to use the values of 4×10^{-6} and 4×10^{-9} m^2/s, respectively.

Chapter 4 EMISSION ESTIMATES OF SELECTED POPs

Estimates of POP emissions into the atmosphere are hampered because of the uncertainty of emission factors and gaps in knowledge on processes of POP inputs to the environment. *K.D.van den Hout (Ed.)* [1994] believes that the uncertainty of POP emission estimates is as much as 2-5 times and even more. Assessments of POP emissions made by different specialists prove this statement.

4.1 Pesticides

Lindane (γ-HCH)

Estimates of the European emission of lindane were made by various authors. Table 4.1 presents lindane emission estimates by *F.Axenfeld et al.* [1991], *K.D. van den Hout (Ed.)* [1994] and *A.Baart et al.* [1995] for the 1982 and the 1990 reference years.

Table 4.1 National total γ-HCH emission in Europe in 1982 [*Axenfeld et al*., 1991] and in 1990 [*van den Hout (Ed.)*, 1994; *Baart et al*., 1995], t/yr

Country	1990		1982
	A.C.Baart et al., 1995	*K.D. van den Hout (Ed.)*, 1994	*F.Axenfeld et al*, 1991
Albania	4.6	0.9	1.015
Austria	18	3.6	2.735
Belgium	5	1.0	1.565
Bulgaria	27	5.3	5.035
CSSR (former)	0.4	0.1	4.310
Denmark	5.1	1.0	1.500
Finland	12	2.3	0.200
France	281	56.3	12.818
E.Germany	{70	{14.0	6.605
W.Germany			36.005
Great Britain	71	14.3	26.704
Greece	26	5.2	4.945
Hungary	98	19.5	14.175
Iceland	-	0.0	0.050
Ireland	1.3	0.3	0.600
Italy	60	12.0	12.901
Luxembourg	1	0.0	0.180
Netherlands	9.7	3.8	3.051
Norway	5.5	1.1	0.465
Poland	1.6	0.3	14.520
Portugal	6.1	1.2	0.305
Romania	69	13.7	12.905
USSR (Europe) (former)	969	193.7	217.500
Spain	132	26.5	24.220
Sweden	4.1	0.8	0.435
Switzerland	1	0.2	1.065
Yugoslavia (former)	50	10.1	10.025
Europe	1930	387.0	415.833

As it can be seen from the table the contribution of the Mediterranean and some adjacent countries (including Portugal, Romania and Bulgaria) is about 30% of the total European emission in 1990.

HCB

Table 4.2 presents estimates of HCB in Europe for 1982 adapted from [*Axenfeld et al.*, 1991]. As it can be seen from the table emission of HCB was mainly due to its application as pesticide.

Table 4.2 HCB emission in Europe in 1982 - all sources, t/yr

Country	Production of Polychlorinated Hydrocarbons	Use of Pesticides	Use of PCP (pentachlorophenol)	Total HCB emission
Albania	-	0.072	0.043	0.114
Austria	0.011	0.151	0.114	0.276
Belgium	0.240	0.080	0.148	0.468
Bulgaria	-	0.413	0.137	0.550
CSSR (former)	0.208	0.515	0.231	0.953
Denmark	-	0.261	0.077	0.338
Finland	-	0.239	0.072	0.312
France	1.250	1.899	0.817	3.967
E.Germany	0.200	0.496	0.250	0.946
W.Germany	1.616	0.746	0.925	3.287
Great Britain	0.890	0.702	0.845	2.437
Greece	-	0.394	0.147	0.541
Hungary	-	0.529	0.161	0.689
Iceland	-	-	0.004	0.004
Ireland	-	0.078	0.052	0.130
Italy	1.416	1.219	0.850	3.484
Luxembourg	-	0.013	0.005	0.018
Netherlands	0.110	0.090	0.215	0.415
Norway	-	0.086	0.062	0.147
Poland	-	1.482	0.546	2.028
Portugal	-	0.275	0.150	0.425
Romania	0.200	1.066	0.338	1.603
Spain	0.595	2.042	0.569	3.207
Sweden	0.090	0.297	0.125	0.512
Switzerland	-	0.042	0.097	0.139
USSR (Europe) (former)	0.400	20.000	2.625	23.625
Yugoslavia (former)	-	0.778	0.339	1.117
Europe	7.226	33.964	9.942	51.132

The contribution of the Mediterranean and some adjacent countries (including Romania, Bulgaria and Portugal) to the total European emission is about 30%.

4.2 Industrial chemicals

Estimates of the European PCB emission are presented in table 4.3, adapted from [*Axenfeld et al.*, 1991] for the 1982 reference year and from [*Baart et al*., 1995] for the 1990 reference year.

Table 4.3 National total PCB emissions in Europe in 1982 [*Axenfeld et al*., 1991] and in 1990 [*Baart et al.*, 1995], t/yr

Country	Emission 1982	Emission 1990
Albania	5.720	0.134
Austria	15.142	1.410
Belgium	19.712	5.220
Bulgaria	18.200	0.355
CSSR (former)	30.780	2.920
Denmark	10.238	1.050
Finland	9.654	5.100
France	108.960	19.900
E.Germany	33.394	{ 43.500
W.Germany	123.276	
Great Britain	112.670	9.220
Greece	19.580	0.362
Hungary	21.400	0.398
Iceland	0.468	-
Ireland	6.966	0.182
Italy	113.278	6.420
Luxembourg	0.732	0.116
Netherlands	28.626	0.498
Norway	8.232	1.700
Poland	72.798	1.840
Portugal	19.938	0.572
Romania	45.054	1.100
Spain	75.922	9.220
Sweden	16.654	5.010
Switzerland	12.934	1.770
USSR (Europe) (former)	350.000	24.600
Yugoslavia (former)	45.260	1.050
Europe	1325.588	143.447

As it can be seen from the table 4.3, the contribution of the the Mediterranean and some adjacent countries (including Bulgaria, Portugal and Romania) to the total European emission of PCB is about 25%. Significant decrease of the European emission can be noted in the 1990 reference year in comparison with 1982.

4.3 By-products. PAHs

There are some data on the total PAH emission in Europe for 1982, (adapted from [*Axenfeld et al*., 1991]), on 6 Borneff PAH for 1990 (adapted from [*Baart et al*., 1995]) and on B(a)P for 1990 (adapted from [*van den Hout (Ed.),* 1994] and [*Baart et al*., 1995]). These estimates are compiled in Table 4.4. According to these estimates the contribution of the Mediterranean and some adjacent countries (including Bulgaria, Portugal, Romania) to the total European PAH (or B(a)P) emission is between 10 and 15%.

Table 4.4 National emission of total PAH in Europe in 1982 [*Axenfeld et al*., 1991], B(a)P in 1990 [*van den Hout (Ed.),* 1994; *Baart et al*., 1995], and 6 Borneff PAH in 1990 [*Baart et al*., 1995], t/yr

Country	*F.Axenfeld et al.*, 1991 Total PAH, 1982	*K.D.van den Hout (Ed.),* 1994 B(a)P, 1990			*A.C. Baart et al.*, 1995	
		Avg	Low	High	B(a)P, 1990	6 Borneff PAH, 1990
Albania	114.406	5	1	9	2	32
Austria	237.629	15	3	33	20	210
Belgium	157.050	15	3	32	12	143
Bulgaria	231.567	11	3	21	10	126
CSSR (former)	408.216	97	23	165	37	369
Denmark	48.982	1	0	2	4	64
Finland	267.430	4	1	11	8	102
France	1237.937	54	11	112	108	1230
E.Germany	409.782	{ 215	{ 51	{ 361	{ 103	{ 1340
W.Germany	1020.944					
Great Britain	767.628	49	11	92	54	730
Greece	208.277	5	1	11	10	146
Hungary	393.002	27	7	43	16	198
Iceland	43.868	5	1	9	-	-
Ireland	66.487	5	1	8	6	73
Italy	498.315	20	4	47	47	688
Luxembourg	4.914	3	0	6	<1	6
Netherlands	173.106	7	2	16	14	183
Norway	714.871	8	3	16	9	106
Poland	1962.757	155	38	261	69	704
Portugal	43.472	3	1	8	10	138
Romania	736.164	21	5	43	46	456
Spain	571.880	22	5	45	28	449
Sweden	1330.848	6	1	14	7	105
Switzerland	118.050	1	0	3	28	238
Turkey	-	59	14	95	-	-
USSR (Europe) (former)	13104.789	565	147	1007	465	5330
Yugoslavia (former)	548.591	36	11	73	27	346
Europe	25420.969	1409	347	2534	1140	13510

4.4 European emission inventory of POPs for 1990

On behalf of the PARCOM, HELCOM and LRTAP Conventions the European emission inventory of POPs and heavy metals was prepared on the basis of national data and expert estimates [*Berdowski et al*., 1997]. Table 4.5 presents emission data on selected POPs (6 Borneff PAH, lindane, PCBs, HCB) obtained from this inventory. According to different estimates presented here the emissions of some POPs, in particular PCBs and HCB, were significantly reduced during the decade from 1982 to 1990.

Table 4.5 Annual emission of POPs in Europe in 1990, t/yr [*Berdowski et al*., 1997]

Countries	PAH	PCB	Lindane	HCB
Albania	35.8	0.034	3.5	0
Austria	243	1.32	13.3	0.001
Belarus	191	0.6	47.2	0
Belgium	818	5.2	54.3	0.213
Bosnia & Herzegovina	47.8	0.128	6.23	0.02
Bulgaria	54.9	0.317	0	0
Croatia	54.0	0.132	11.0	0.03
Cyprus	0.182	0.044	-	-
Czech Republic	259	1.99	0.21	0.07
Denmark	76.7	0.987	3.80	0.103
Estonia	29.7	0.190	7.45	0
Finland	104	2.62	8.80	0
France	3479	19.5	211	0.011
Germany	420	43.0	-	0.086
Greece	153	0.251	19.4	0.000
Hungary	192	0.130	0.300	4.54
Iceland	6.33	0.047	0	0
Ireland	73.7	0.063	0.9	0
Italy	694	5.83	44.9	0.406
Latvia	38.4	0.162	13.6	0
Lithuania	52.3	0.221	25.1	0
Luxembourg	6.24	0.119	0	0
the FYR Macedonia	21.7	0.083	0.76	0
Moldova	58.0	0.269	13.2	0
Netherlands	184	0.251	15.0	-
Norway	140	0.384	4.10	0.001
Poland	372	2.37	0	0
Portugal	138	0.523	4.4	0
Romania	723	0.515	51.4	0.053
Russian Federation	3146	10.2	355	0.001
Slovak Republic	310	1.33	0.09	0.003
Slovenia	50.5	0.071	1.23	0
Spain	521	8.53	0	1.18
Sweden	282	1.93	0	0.03
Switzerland	96.1	1.64	0.8	0.004
the Ukraine	1137	3.74	265	0
United Kingdom	1437	3.45	114	1.24
Yugoslavia (Serbia and Montenegro)	172	0.435	18.6	0.05
Europe	15800	119	1310	8.04

Chapter 5 SELECTED POPs IN VARIOUS ENVIRONMENTAL COMPARTMENTS (MEASUREMENT DATA)

In this chapter the concentrations of selected POPs in various environmental compartments are presented. The number of measurements for the Mediterranean Sea is rather limited. For this reason measurements for other regions along with background levels of POP concentrations are presented. The following tables contain measured concentrations of B[a]P, PCBs, HCB, and HCH in air, precipitation, soil, sea and ocean water, and sediments.

B[a]P

Concentrations in air and in precipitation

Table 5.1 Concentrations of B[a]P in air and in precipitation. Figures in brackets represent mean values.

Region	*Concentration in air* (ng/m^3)	*Concentration in precipitation* (ng/l)	*Reference*
Background			
Western Europe	0.01 – 5.0 (0.5)		[*Maistrenko et al*., 1996]
Eastern Europe	0.04 – 5.0 (0.5)		[*Maistrenko et al*., 1996]
Arctic	(0.002)		[*Maistrenko et al*., 1996]
Pacific Ocean		5 – 209 (20)	[*Rovinsky et al*., 1988]
Norway		30 – 37	[*Rovinsky et al*., 1988]
Former USSR		0.4 – 40	[*Rovinsky et al*., 1988]
Industrial regions			
Cities of USA	(6)		[*Maistrenko et al*., 1996]

Concentrations in sea water

Table 5.2 Mean levels of marine pollution by B[a]P from [*Izrael and Tsyban*, 1989]

Water basin	*B[a]P concentration in different objects*		
	water, μg/l	*near bottom layer, μg/l*	*bottom sediments, μg/kg*
Pure basin, almost background	0.025 ± 0.003	0.125 ± 0.003	
Basin without specific PAH sources but with intensive shipping	0.052 ± 0.004		16.2 ± 1.17
Coastal water adjacent to industrial region	0.15 ± 0.01	2.24 ± 0.1	76.8 ± 3.25
Coastal waters in the region of waste water discharge from shale treating industry	0.27 ± 0.07	5.0 ± 0.2	7500 ± 125
Coastal waters in the region of oil production and waste water discharge of oil refining industry	0.10 ± 0.02	10.6 ± 0.39	8030 ± 146

Concentrations in sediments

Table 5.3 B[a]P content in marine sediments, μg/kg of dry mass [*Izrael and Tsyban*, 1989].

Region of sampling	*B[a]P content*
Le-saint Channel	1760
Dunkirk	400
Saint-Malo Bay	1320
Bay of Naples	
Near oil refinery plant	1000 – 3000
at the depth to 60 m	10 – 530
at the depth to 120 m	2 – 10
French coast of the Mediterranean Sea	2000 – 5000
Coastal zone of the Black and Baltic Seas	2 – 23
South-eastern coast of the Black Sea	60 – 304
Baltic Sea	8.51
Great Barrier Reef	0.01

Concentrations in soil

Table 5.4 B[a]P content in soil, μg/kg [*Rovinsky et al.*, 1987; *Rovinsky et al*., 1988].

Region	*Concentration in soil (μg/kg)*
Rural background	1 – 3
Iceland	0.1 – 5.8
Norway (Kirkenes)	10
Germany	1.5 – 22.6
France	2 - 170
Czech Republic	2 - 127

PCBs

Concentrations in air and in precipitation

Table 5.5 PCB mean concentrations in air and precipitation in background regions [*Yufit and Klyuev*, 1997; *Background monitoring...*, 1990; *Strachan and Huneanet*, 1979; *Schreitmüller et al.*, 1994]

Region	*PCBs*	
	air, ng/m^3	*precipitation, ng/l*
Western Europe	0.3	30
North America	3	60
Antarctic	0.061	
Arctic	0.005 - 0.02	

Table 5.6 PCB air concentrations in continental and coastal regions, ng m^{-3} [*Yufit and Klyuev*, 1997; *Background monitoring...*, 1990; *Izrael and Tsyban*, 1989; *Rovinsky et al.*, 1992; *Schreitmüller et al.*, 1994; *Korte*, 1996]

Region	*Year*	*Arochlor N 1254*
Sweden	1983 – 1985	0.056
USA: Houston	1977 – 1980	3
Boston	1978	3
Great Lake	1978	0.33
Michigan Lake	1977	0.22
Chicago	1978	1.21

According to the observations made during the cruise [*UNEP/FAO/WHO/IAEA*, 1989] the PCB mean air concentrations over the Mediterranean Sea were 0.23 ng/m^3 in 1975 and 0.07 ng/m^3 in 1977. The PCB content in the marine and oceanic atmosphere including the Mediterranean Sea is presented in Table 5.7.

Table 5.7 PCB air concentrations in the marine regions, ng/m^3 .

Region	*Year*	*Content*	*Mean*
Northern Atlantic, Newfoundland*	1981	0.042 – 0.15	0.12
Pacific ocean			
Enewetak Atoll*	1981	0.35 – 1.0	0.54
western part*	1982	0.089 – 0.74	0.25
western part*	1985	0.041 – 0.061	0.051
western part*	1985	0.022 – 0.095	0.043
Bering Sea*	1985	0.026 – 0.059	0.041
southern part*	1982	0.083 – 0.50	0.27
Indian ocean			
eastern part*	1982	0.066 – 0.33	0.15
western part*	1983	0.060 – 0.24	0.16
Antarctic			
western part*	1982	0.056 – 0.18	0.091
eastern part*	1983	0.076 – 0.11	0.091
Monaco coast**	1975	0.1 – 1.0	0.4
Monaco coast**	1976	0.03 – 0.08	0.06
Algero-Provencal Basin**	1975	0.2 – 0.3	0.25
Tyrrhenian Sea**	1975	0.1 – 0.3	0.2

* - [*Izrael and Tsyban*, 1989]

** - [*Fowler*, 1986] cited in [*Jeftic et al.*, 1989]

Concentrations in sea and ocean water

Tables 5.8 and 5.9 present measured concentrations of PCBs and HCH in sea and ocean water.

Table 5.8 PCB concentrations in the open ocean and seas, ng/l [*Izrael and Tsyban*, 1989]

Region	*Year*	*Number of samples*	*Range*	*Mean*
Northern Atlantic				
Sargasso Sea	1973	17	0.9 – 3.6	1.0
North Sea	1974	5	0.15 – 0.52	0.23
Bermuda Island	1978 – 80	5	0.15 – 0.40	0.20
Southern Atlantic				
eastern part	1975	8	0.3 – 3.7	1.0
Northern Pacific				
western region	1975 – 85	42	0.23 – 11	0.35
	1986	9	0.039 – 0.15	0.089
Bering Sea	1981 – 85	6	0.073 – 0.13	0.10
Southern Pacific				
western part	1981 – 85	5	0.081 – 0.21	0.12
Indian ocean	1980 – 85	6		
eastern part			0.057 – 0.25	0.14
South ocean	1980 – 85	10	0.035 – 0.075	0.055

Table 5.9 Concentrations of chlorinated hydrocarbons in sea water, ng/l

Region	*Year*	*HCH*	*PCBs*	*Reference*
Baltic Sea	1977	10 - 500	1.1	[*Izrael and Tsyban*, 1989]
	1978	3 - 20	0.5 - 1.1	-``-``-
	1979	5 - 20	0.5 - 1.0	-``-``-
	1987	1 - 15	0.5 - 4.5	-``-``-
Atlantic ocean	1977	3 - 180	< 1.0	-``-``-
Bering Sea	1984	0.5 - 1.3	0.1 - 0.8	-``-``-
	1988	1.2 - 4.9	0.2 - 0.3	-``-``-
Chukchi Sea	1988	1.5 - 5.0	0.1 - 0.2	-``-``-
Equatorial Pacific	1988	<0.5	0.02	-``-``-
Mediterranean				
North-western part	1974		1.5 - 38	[*Fowler*, 1986]
Ligurian	1975		1.3 - 8.6	-``-``-
Aegean	1975		0.2 - 1.3	-``-``-
Ionian	1975		0.2 - 2.0	-``-``-
Tyrrhenian and Algero-Provencal Basin	1975		0.2 - 5.9	-``-``-
Algero- Provencal basin	1975		0.6 - 19	-``-``-
			0.6 - 4.8	-``-``-
Tyrrhenian	1975		1.5 - 11.6	-``-``-
Eastern basin off-shore		0.06 - 0.12		[*Jeftic et al.*,1989]

The PCB concentrations in waters of the Mediterranean sea range from 0.2 to 38 ng l^{-1} (Table 5.9). The levels of other halogenated hydrocarbons are too low for a quantitative determination [*Elder and Villeneuve*, 1977]. *R.W.Risebrough et al.* [1976] found considerably lower PCB levels in sea water samples near the French coast showing the difficulties inherent

in comparing data of different authors without intercalibration. In the Northern Adriatic coastal waters in 50 samples analysed between 1977 and 1978 most of the concentrations were below the detection limit of 0.1 ng PCBs l^{-1} [*Picer and Picer*, 1979; *Jeftic et al.*, 1989].

Concentrations in sediments

According to [*Izrael and Tsyban*, 1989], total concentrations of chlorinated hydrocarbons in sediments amount to 10 - 100 ng/g of dry weight. In the Baltic Sea mean concentration of PCBs for 1977 was about 8 ng/g (with the maximum value being 20 ng/g for PCBs). According to [*Fowler*, 1986], concentrations of PCBs in the top centimeter layer of open sea core in the eastern and western Mediterranean range from 0.8 to 9.0 ng/g of dry weight (DW):

Ionian Sea:	0.8 - 5.1 (2.8), ng/g
Algero-Provencal basin:	0.8 - 9.0 (4.0), ng/g
Gibraltar sill and Siculo-Tunisian sill:	0.8, ng/g
Algerian marin:	9.0, ng/g

According to [*Jeftic et al.*, 1989], there were examples of "… high sediment concentrations near the sewage outfalls of Marseille (up to 16000 μg PCBs kg^{-1} DW) and Athens (up to 800 μg PCBs kg^{-1} DW), near larger towns such as Nice (up to 1165 μg PCBs kg^{-1} DW), Naples (up to 3200 μg PCBs kg^{-1} DW) and Augusta (up to 460 μg PCBs kg^{-1} DW). However, in the case of the Marseille outfall, these high levels drop to background levels at about 10 km from the source [*Fowler*, 1986]". It should be noted that according to [*Tolosa et al*., 1995] the total flux of 12 PCB congeners was found to be 14 - 60 ng/m^2/day. These estimates are obtained on the basis of analysis of surface sediment samples taken in the north-western Mediterranean coastal region. Typical concentrations of PCBs in natural objects and in human organism are presented in Table 5.10.

Table 5.10 Typical concentrations of PCBs in natural objects [*Yufit and Klyuev*, 1997]

Object studies	*PCB concentration*
Atmospheric air, ng/m^3:	
cities	5.0
rural regions	0.5
over ocean	0.05
Antarctic	0.05
Atmospheric precipitation, ng/l:	
over land	10 - 100
Hydrosphere, ng/l	
surface land water	1 - 10
seas, oceans	0.2 – 9
Soil, μg/kg:	
natural reserves far from agricultural regions	2 - 20
Terrestrial biota, μg/kg:	
plants	2 - 20
wild animals	20 - 400
Aquatic biota, μg/kg	
zooplancton	10 - 150
fresh water fish	10 - 300
fish of seas and oceans	10 - 100
sea mammals (under skin fat)	100 - 10000
Human body (fat), μg/kg	350

HCH and lindane

Concentrations in the atmosphere

Lindane concentrations in air over Europe range from 0.01 to 5 ng/m^3. Concentrations in precipitation can also vary in a wide range from 5 to 125 ng/l [*Rovinsky et al.*, 1992; *Lindane*, 1983; *Revich et al.*, 1995; *Background monitoring...*, 1990; *van den Hout (Ed.)*, 1994].

Concentrations in sea water

The concentrations of HCH in the sea water are presented in Table 5.9. In the Mediterranean sea the levels of lindane off shore in the eastern basin ranged from 0.06 to 0.12 ng/l. Elevated concentrations were found near terrestrial run-offs and river inputs. Concentrations in suspended particulate matter exceeded those in dissolved phase [*Jeftic et al.*, 1989].

Concentrations in sediments

Data on HCH concentrations in coastal sediments from the Central and Eastern Mediterranean are presented in Table 5.11.

Table 5.11 Concentrations of HCH in coastal sediments of the Central and Eastern part of the Mediterranean Sea, ng/g*

Area	*HCH total*	
	mean	*range*
IV	2.5	0.1 - 27.4
V	1.1	0.2 - 4.6
V	0.9	0.5 - 1.1
VI	0.1	0.1 - 2.6
VIII	0.6	0.4 - 0.8
IX	0.2	0.2 - 0.3
X	0.7	

* adapted from [*Jeftic et al*., 1989]

Measurement data on some POPs over the North and Baltic Seas are presented in Tables 5.12 and 5.13. Tables 5.14 and 5.15 contain measurement data of the EMEP monitoring network. Table 5.16 presents the list of the EMEP monitoring sites which presented measurement data on POPs.

Table 5.12 Mean air concentrations of some POPs 1987-1989 (Baltic and North Seas), pg/m^3 [*Wodarg and Reinhardt*, 1992]

	HCB	α-HCH	γ-HCH
Kiel Bight	260	250	440
Ship	98	53	69
measurements,	220	82	216
various	220	170	864
campaigns,	251	184	2780
88 - 89	165	46	176

Table 5.13 Concentrations of some POPs in precipitation over the North Sea*, ng/l

	PCB	α-HCH	γ-HCH
Collafirth	1.56	1.74	0.88
Rattray Hd.	5.6	2.64	2.14
Carnbee	2.8	3.81	3.06
Tantallon	4.13	4.78	5.25
Lindisfarne	7.62	4.55	4.91
Flamborough	10.1	4.82	6.49
Burnham	59.6	3.96	8.96
Average	13.1	3.76	4.53

* from [*Wells and Johnstone*, 1978]

Table 5.14 EMEP data on air concentrations of some POPs, pg/m^3 [*Berg et al.*, 1996]

	IS91/95*	NO42/93	NO42/94	NO42/95	NO99/92	NO99/93	NO99/94	NO99/95
HCB	7/6**	92/86	115/107	99/97	160/151	121/115	95/89	95/94
PCB-153	0.8/0.7	0.6/0.5	0.6/0.5	0.3/0.3	52/39	33/26	29/24	
α-HCH	17/12	77/69	61/58	63/60	93/82	74/67	65/56	52/50
γ-HCH	14/11	14/13	16/14	13/12	86/59	59/43	123/55	65/39
B(a)P	-	-	13/2	9/2				

* - site code / year

** - arithmetic mean/geometric mean

Table 5.15 EMEP data on concentrations of some POPs in precipitation (1990-1995), ng/l [*Berg et al.*, 1996]

	DE1			DK31		NO99				
	90	*92*	*93*	*91*	*92*	*91*	*92*	*93*	*94*	*95*
HCB		0.87	0.26			1.78	0.14	0.40	0.53	0.77
α-HCH	0.85	1.89	1.01	1.71	1.2	2.69	2.07	2.07	2.14	2.00
γ-HCH	4.54	18.22	9.28	11.91	15.8	4.05	5.02	8.45	9.98	5.54

Table 5.16 List of EMEP monitoring stations included in the POP data base [*Berg et al.*, 1996]

Country	*Station codes*	*Station name*	*Location*		*Height above sea, m*
			Lat.	*Long.*	
Czech Republic	CZ3	Kosetice	49o35'N	15o05'E	633
Denmark	DK31	Ulborg	56o17'N	8o26'E	10
Finland	FI96	Pallas	67o58'N	24o7'E	566
Germany	DE1	Westerland	54o55'N	8o18'E	12
	DE9	Zingst	54o26'N	12o44'E	1
Iceland	IS91	Stórhöfdi	63o24'N	20o17'W	118
Ireland	IE2	Turlough Hill	53o02'N	6o24'W	420
Norway	NO42	Zeppelinfjell	78o54'N	11o53'E	474
Norway	NO99	Lista	58o06'N	6o34'E	13
Sweden	SE2	Rörvik	57o25'N	11o56'E	10

Chapter 6 MSC-E MODEL

6.1 Description of the atmospheric module (ASIMD model)

A three-dimensional Eulerian transport model ASIMD (**AS**ymmetric **I**mproved **M**o**D**el) used for calculations of the long-range transport of persistent organic pollutants was developed in EMEP/MSC-E by M.Pekar [*Pekar*, 1996].

The vertical grid consists from four layers with non-uniform heights (Figure 6.1). The surface layer, Δz =100 m is distinguished and is treated differently from other layers. The depths of the following layers are chosen according to the levels of meteorological data. The calculated levels along z correspond to cell centers.

The horizontal transport in ASIMD is described with application of an asymmetric advection scheme. Compensation of numerical diffusion is made by correction of the advection velocity depending on local gradients.

The vertical diffusion is calculated by an explicit scheme with the preservation of 3 moments developed for unequal grid intervals.

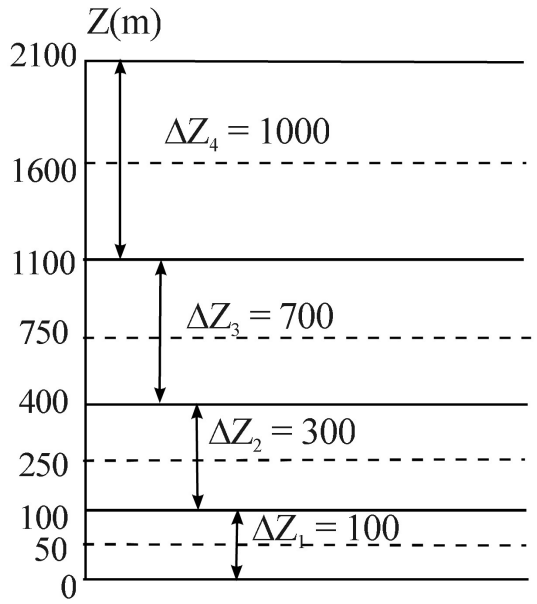

Figure 6.1 *Vertical scheme of the model.*

A system of parameters required for the description of local conditions of pollution dispersion consists of friction velocity u_* (m/sec), Monin-Obukhov length scale L (m), mixing layer height h (m), vertical diffusion coefficient profiles $K_z(z)$ (m^2/sec) which are determined on the basis of data on 1000 mb wind, temperature and roughness z_0. The roughness data are taken from the archive "Global Data Set for Land-Atmosphere Models" (ISLSCP). The database contains global data on roughness with resolution $1^o x 1^o$ averaged over a month.

The meteorological pre-processor is based on the energetic balance evaluation with further application of results of the similarity theory [*Holtslag and van Ulden*, 1983; *van Ulden and Holtslag*, 1985]. Calculations of the parameter are made for each 6-hour interval (03, 09, 15, 21 UTC).

Detailed description of the ASIMD model is given in [*Pekar*, 1996].

6.2 Input data

Emission

Figure 6.2 presents a map of the lindane emission distribution over the EMEP grid in 1990 [*Berdowski et al.*, 1997]. The total lindane emission amounts to 1310 t/yr. Taking into account seasonal variation of the lindane application it was assumed that 10% of its emission took place in February, 15% - in March and 25% - in April, May and June.

Spatial distribution of the PCB emission in 1990 is shown in Figure 6.3 [*Berdowski et al.*, 1997]. The PCB total emission amounts to about 119 tons. For calculations it was assumed that the PCB emission has no seasonal variations.

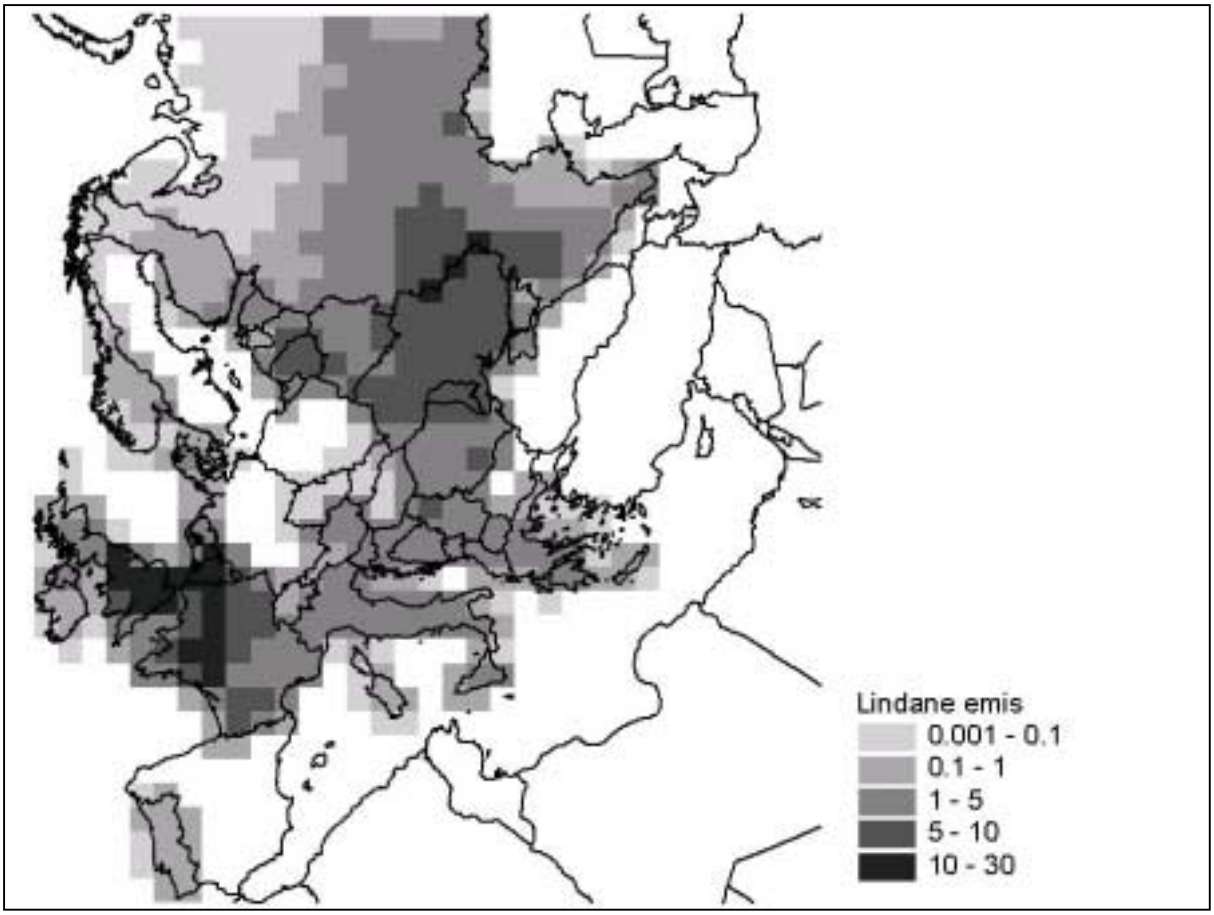

Figure 6.2 Distribution of lindane emissions with the 150 x 150 km^2 EMEP grid in Europe for 1990, t/yr.

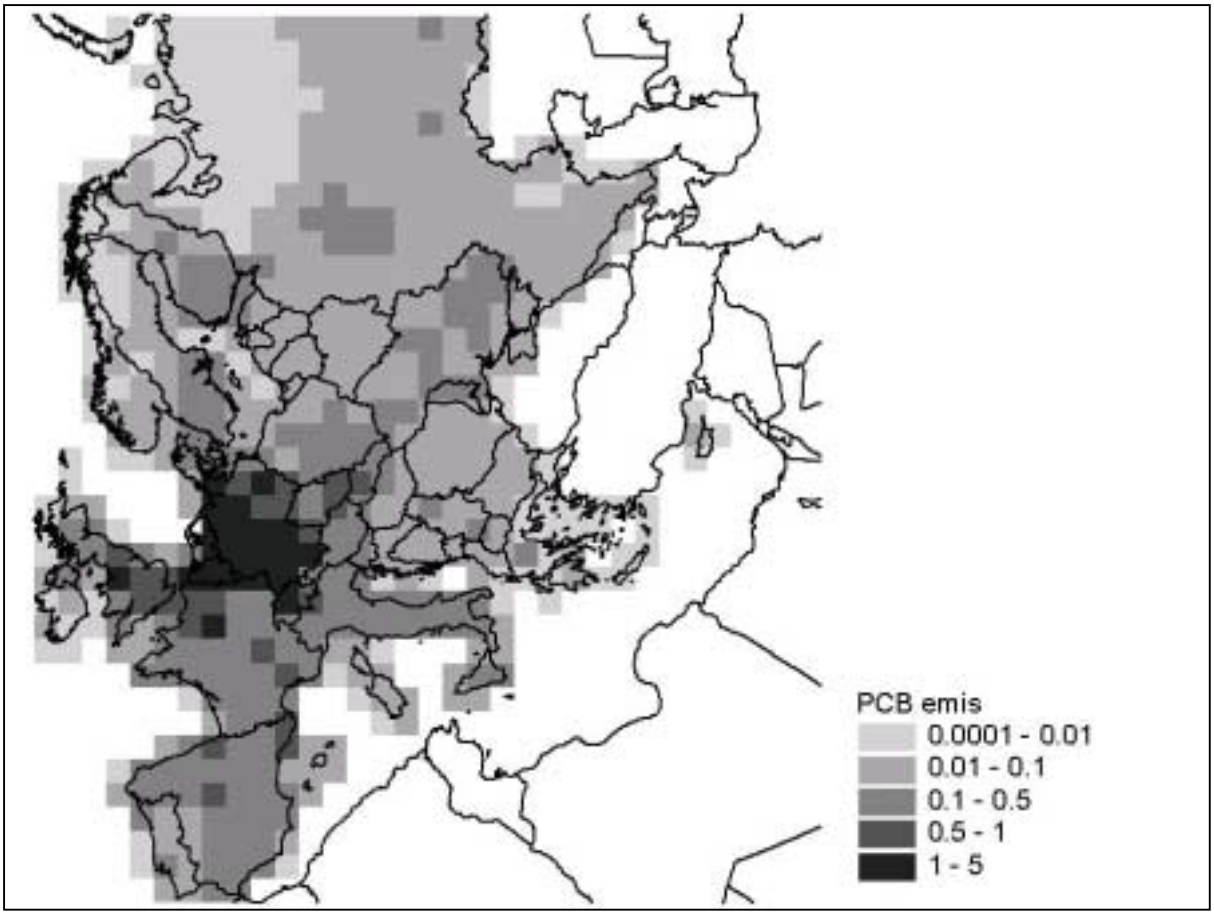

Figure 6.3 Distribution of PCB emissions with the 150 x 150 km^2 EMEP grid in Europe for 1990, t/yr.

Meteorology

The following input meteorological data for 1987-1996 were used: orthogonal wind components u and v, temperature at 850 and 1000 mB levels (925 mB for 1995,1996 years), and precipitation amount. These data were provided by the Russian Hydrometeorological Centre.

6.3 Surface-atmosphere exchange module

For description of the exchange of gaseous POPs between the atmosphere and underlying surface, the surface-atmospheric exchange modules developed by *C.M.J.Jacobs and W.A.J.van Pul* [1996] were used.

6.4 Model parameterization

6.4.1 Lindane

Parameterization for the lindane model is made on the basis of the parameterization described in [*Jacobs and van Pul*, 1996]

Henry`s law constant $H = \frac{0.073}{8.314 \cdot T} \exp\left(-7329 \left(\frac{1}{T} - \frac{1}{283.15} \right) \right)$ (dimensionless)

Soil/water partition coefficient $K_p = f_{oc} \times K_{oc}$, m^3/kg

f_{oc} - fraction of organic carbon in soil f_{oc} *(dimensionless)*

K_{oc} - "organic carbon-water" partition coefficient $K_{oc} = 1.3$, m^3/kg

Degradation rate:

Soil	$K_s = 3.0 \times 10^{-8}$, s^{-1}
Sea	$K_w = 4.66 \times 10^{-9}$, s^{-1}
Atmosphere	$K_a = 2.5 \times 10^{-7}$, s^{-1}

Molecular diffusion coefficients:

Atmosphere	$D_g = 5.0 \cdot 10^{-6}$, m^2/s
Water	$D_w = 5.0 \times 10^{-10}$, m^2/s

Volumetric fractions in soil:

Porosity	$\varphi = 0.5$, m^3/m^3
Volumetric Air Content	$a = 0.2$, m^3/m^3
Volumetric Water Content	$\theta = 0.3$, m^3/m^3
Soil Bulk Density	$\rho_s = 1350$, kg/m^3

Molecular diffusion layer thickness $d_{zwm} = 4.0 \times 10^{-5}$, m

Accumulating layer depth for water $d_{wz} = 25$, m

Characteristics of the calculation grid for soil:

Number of layers $K_{max} = 5$

Layer depths :

DSZ(1) = 0.005, m
DSZ(2) = 0.005, m
DSZ(3) = 0.01, m
DSZ(4) = 0.02, m
DSZ(5) = 0.11, m

6.4.2 PCB-153

Henry`s law constant $H = \frac{1}{RT} \cdot 10^{13.42-3625/T}$ *(dimensionless)*

Vapor Pressure $p^0_L = 10^{1285-4775/T}$, PA

Soil/water partition coefficient $K_p = f_{oc} \cdot K_{oc}$, m^3/kg

f_{oc} - fraction of organic carbon in soil f_{oc} *(dimensionless)*

K_{oc} - "organic carbon-water" partition coefficient $K_{oc} = 3236$ m^3/kg

Degradation rate:

Soil	$K_s = 3.5 \times 10^{-9}$, s^{-1}
Sea	$K_w = 3.5 \times 10^{-9}$, s^{-1}
Atmosphere	$K_a = 3.5 \times 10^{-8}$, s^{-1}

Molecular Diffusion Coefficients:

Atmosphere	$D_g = 4.58 \times 10^{-6}$, m^2/s
Water	$D_w = 5.14 \times 10^{-10}$, m^2/s

Volumetric Fractions in Soil:

Porosity	$\varphi = 0.5$, m^3/m^3
Volumetric Air Content	$a = 0.2$, m^3/m^3
Volumetric Water Content	$\theta = 0.3$, m^3/m^3
Soil Bulk Density	$\rho_s = 1350$, kg/m^3

Molecular Diffusion Layer Thickness $d_{zwm} = 4.0 \times 10^{-5}$, m

Accumulating Layer Depth for Water $d_{wz} = 25$, m

Characteristics of the Calculation Grid for Soil:

Number of layers	$K_{max} = 5$
Layer depths:	DSZ(1) = 0.005, m
	DSZ(2) = 0.005, m
	DSZ(3) = 0.01, m
	DSZ(4) = 0.02, m
	DSZ(5) = 0.11, m

Chapter 7 ESTIMATES OF POP DEPOSITIOINS AND CONCENTRATIONS IN AIR

7.1 Lindane

7.1.1 Calculation results

Calculations of the lindane transport were made within the EMEP grid (Figure 7.1) using 3D Eulerian model ASIMD [*Pekar*, 1996] and atmosphere-soil and atmosphere-water exchange modules [*Jacobs and van Pul*, 1996] with the temporal resolution of 1 hour. The calculations covered the period of ten years (1987-1996) in order to reveal trends of lindane accumulation in various compartments. Parameterization for the lindane model is made on the basis of the parameterization described in the section 6.4.1. It is assumed that lindane is present in the atmosphere in the gas phase only. Modelling results contain air concentrations, deposition and fluxes between environmental compartments.

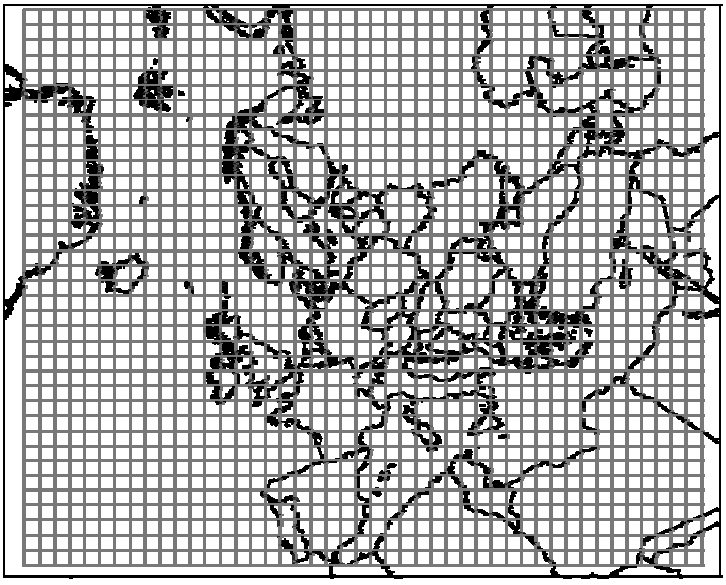

Figure 7.1 The EMEP grid

Figure 7.2 shows mean annual air concentration of lindane for 1996. Maximum mean annual air concentrations of lindane are amounted to 3-4 ng/m^3 in Belgium, France and the Ukraine. Regions of maximum concentrations correspond to the regions of maximum emissions. In the Mediterranean region the air concentrations of lindane decrease in the southern direction. Mean annual air concentrations in this area are about 0.5 ng/m^3.

Figure 7.3 presents densities of lindane total depositions for 1987-1996. Regions of the maximum deposition coincide with regions of the maximum emission. The maximum density of total deposition reaches 80μg/m^2 /year. For the Mediterranean sea the mean annual deposition density is accounted to approximately 16 μg/m^2 /year and during the simulation period, on the average, 41 tonnes of lindane (about 3% of the annual European emission of lindane) deposited on the Mediterranean Sea each year.

Figure 7.4 presents the budget of lindane within the whole EMEP region for the 10 years` calculation period. For this period about 13,000 t of lindane were emitted to the atmosphere in Europe (see Table 4.5 for annual emissions). The major part of that lindane deposited on the continental part of the EMEP grid. About 20% degraded in the soil and 2% - 240 tonnes were retained in the soil after the 10 year simulation period. About 9% degraded in sea water

and 8% - 1000 tonnes remained in the seas. About 14% of lindane degraded in the atmosphere due to rather rapid degradation in air and 45% of lindane was transported outside of the EMEP grid.

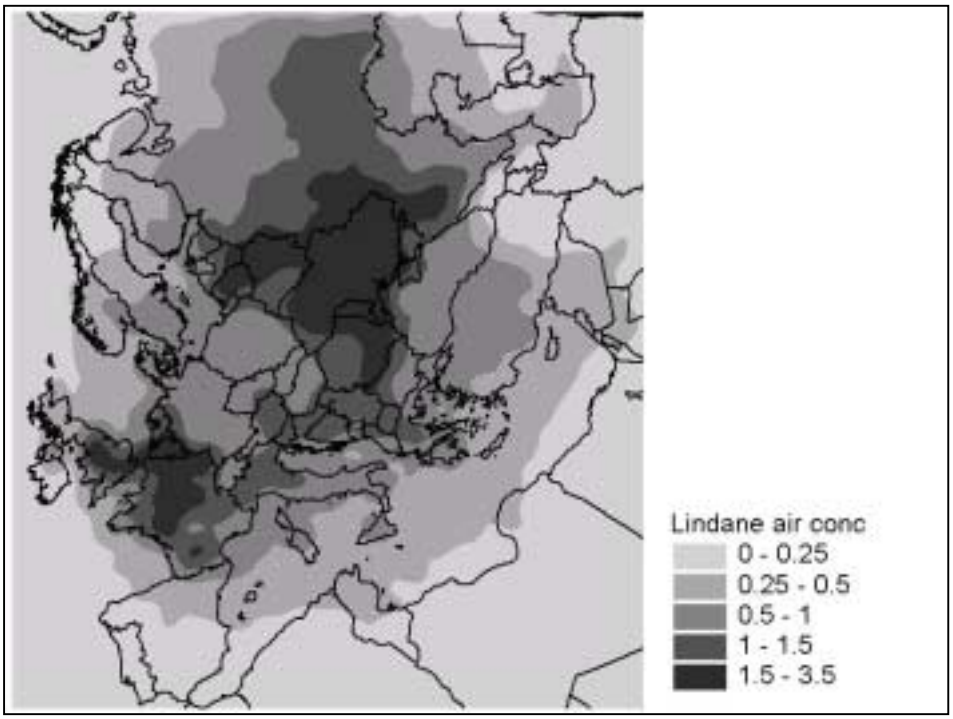

Figure 7.2 Calculated mean annual air concentrations of lindane over the 150x150 km^2 EMEP grid in Europe in 1996, ng/m^3

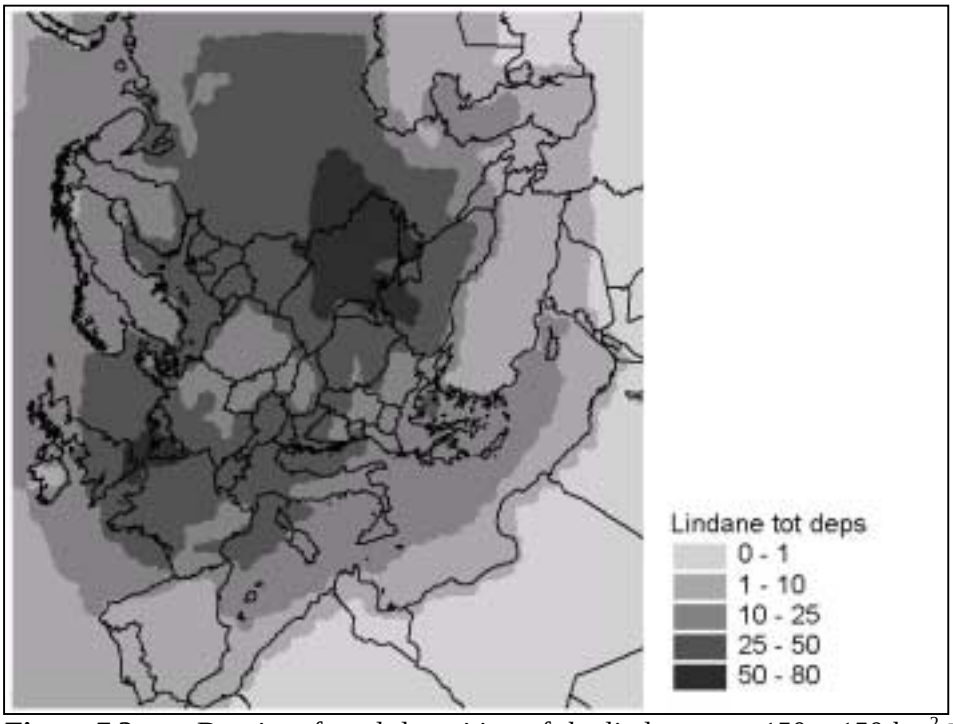

Figure 7.3 Density of total deposition of the lindane over 150 x 150 km^2 EMEP grid in Europe for 1987-1996, $\mu g/m^2$ /year.

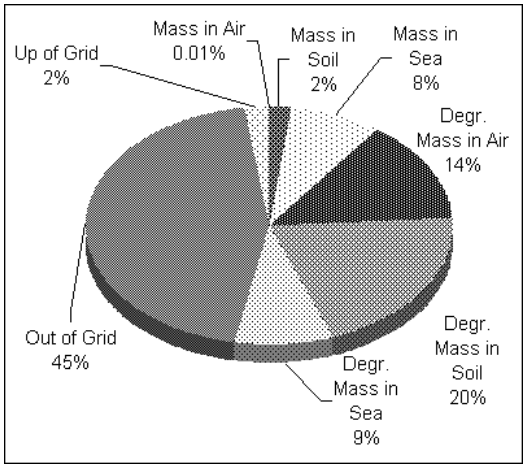

Figure 7.4 Mass balance of lindane after 10 years

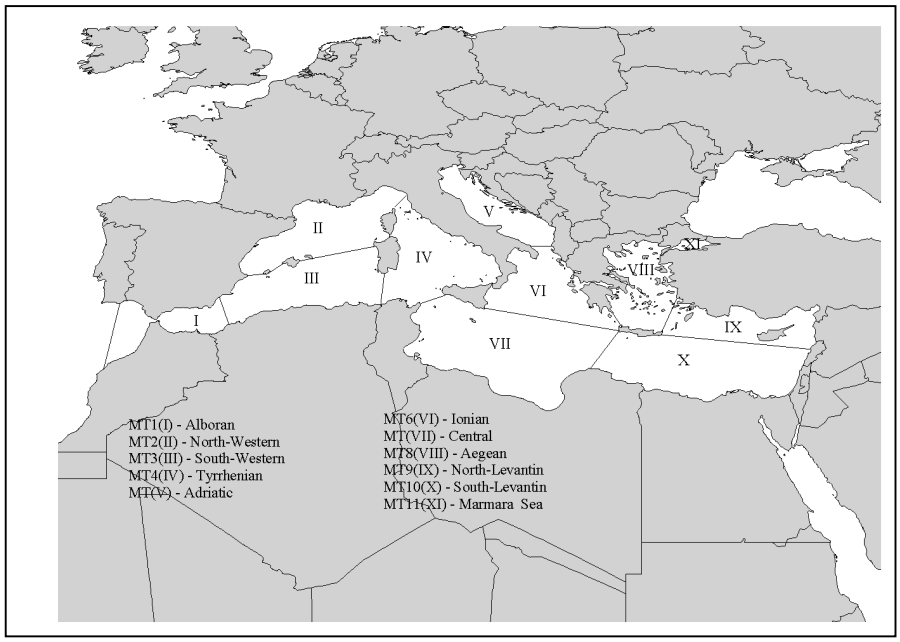

Figure 7.5 Division of the Mediterranean Sea waters according to MED-POL (data from UNEP, 1980)

Figure 7.5 presents the division of the Mediterranean Sea into sub-basins as it is accepted in MED POL. The sub-basins are as follows: MT1 – Alboran, MT2 – North-Western, MT3 – South-Western, MT4 – Tyrrhenian, MT5 – Adriatic, MT6 – Ionian, MT7 – Central, MT8 – Aegean, MT9 – North-Levantin, MT10 – South-Levantin, MT11 – Sea of Marmora.

Tables 7.1-7.4 and Figure 7.6 present deposition on the Mediterranean sub-basins: net dry deposition (Table 7.1, Figure 7.6A), wet deposition (Table 7.2, Figure 7.6B) and total deposition (Table 7.3, Figure 7.6C). Net dry deposition and its density imply an algebraic sum of dry deposition (downward flux) and re-emission from the underlying surface (upward flux).

Table 7.1 Lindane net dry deposition on the Mediterranean Sea and its sub-basins, kg/yr.

Sub-basins	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	Mean
mt1	190	182	174	127	430	406	39	77	60	174	186
mt2	7237	6039	5480	3576	4723	5789	3504	3351	4855	3652	4821
mt3	3488	2116	2655	1823	2928	3715	879	1839	1468	2323	2324
mt4	7172	3803	6504	2924	4444	5132	4305	3194	2641	3820	4394
mt5	4576	3192	4037	2236	3337	3030	3289	1817	2683	2347	3055
mt6	4406	2437	3701	2605	3209	3202	2858	2656	1095	2784	2895
mt7	8302	4162	6082	3704	5061	6200	4869	4373	1581	5747	5008
mt8	4890	3394	3575	3054	3627	3913	2920	2192	2195	2444	3220
mt9	2502	1915	1961	1812	1786	2655	1531	1072	1118	1590	1794
mt10	5527	3243	3286	3558	4284	5172	4030	3069	2045	3414	3763
mt11	349	345	268	231	221	299	201	171	312	235	263
Total	48640	30828	37724	25650	34050	39513	28426	23813	20052	28530	31723

Table 7.2 Lindane wet deposition on the Mediterranean Sea and its sub-basins, kg/yr.

Sub-basins	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	Mean
mt1	22	49	36	52	65	98	47	25	52	40	49
mt2	1760	2384	1596	1629	2520	2656	1507	1580	1877	2405	1991
mt3	635	630	508	581	1098	1140	489	529	413	965	699
mt4	1493	1455	1278	1081	1651	1528	1440	1186	1423	2106	1464
mt5	1566	1404	1685	1157	2276	1570	1556	1368	2223	1898	1670
mt6	1137	720	667	590	809	876	1287	777	611	1259	873
mt7	1157	601	764	524	679	1063	1006	658	527	1358	834
mt8	1036	925	526	591	990	955	1074	815	966	1615	949
mt9	307	343	163	274	356	668	574	394	288	586	395
mt10	517	447	241	290	347	577	541	530	366	778	463
mt11	107	115	75	85	118	124	119	89	167	140	114
Total	9737	9073	7540	6854	10909	11253	9638	7949	8913	13150	9502

Table 7.3 Lindane total deposition on the Mediterranean Sea and its sub-basins, kg/yr.

Sub-basins	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	Mean
mt1	212	231	210	179	495	504	86	103	112	214	235
mt2	8997	8422	7077	5205	7243	8445	5011	4932	6732	6057	6812
mt3	4123	2746	3163	2404	4026	4855	1368	2368	1881	3287	3022
mt4	8665	5258	7783	4006	6095	6660	5744	4380	4064	5927	5858
mt5	6142	4597	5722	3393	5613	4599	4844	3185	4906	4245	4725
mt6	5544	3158	4368	3195	4017	4078	4145	3432	1706	4043	3769
mt7	9459	4763	6846	4228	5740	7263	5876	5031	2108	7106	5842
mt8	5926	4319	4101	3644	4617	4868	3994	3007	3161	4059	4170
mt9	2808	2257	2124	2086	2142	3323	2104	1466	1406	2176	2189
mt10	6044	3691	3527	3848	4631	5749	4570	3599	2411	4192	4226
mt11	456	460	343	316	339	423	320	260	479	375	377
Total	58376	39902	45264	32504	44959	50767	38064	31762	28966	41680	41224

Table 7.4 Lindane deposition density for the Mediterranean Sea and its sub-basins, $\mu g/m^2/yr = g/km^2/yr$

Sub-basins	Net dry deposition	Wet deposition	Total deposition
mt1	2.7	0.7	3.3
mt2	19.0	7.8	26.8
mt3	9.0	2.7	11.6
mt4	17.2	5.7	22.9
mt5	24.1	13.2	37.2
mt6	13.5	4.1	17.6
mt7	9.2	1.5	10.7
mt8	17.9	5.3	23.1
mt9	11.8	2.6	14.4
mt10	8.5	1.0	9.6
mt11	23.0	9.9	32.9
Total	**12.6**	**3.8**	**16.4**

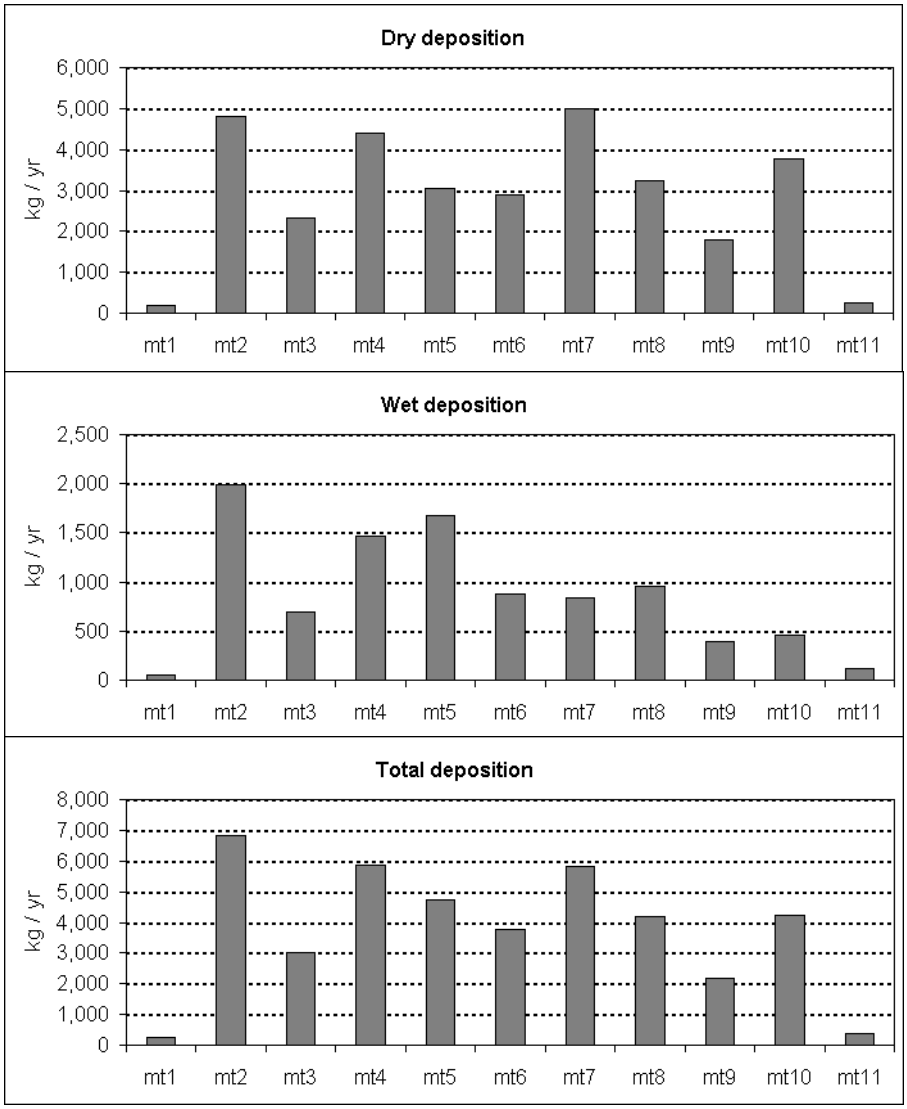

Figure 7.6 Depositions of lindane on the Mediterranean sea sub-basins, kg/yr.

As indicated in Figure 7.6 the maximum net dry deposition and total deposition falls on MT7 (central Mediterranean) since the area of this sub-basin is the largest one. Deposition on MT1 is lowest due to its small area and remote location. The area MT2 is smaller than MT3 but dry deposition on MT2 is greater than on MT3 since its location is closer to the emission sources. The total input of lindane to the Mediterranean Sea due to net dry deposition is around 32 tonnes each year.

Maximum densities of dry and wet deposition are characteristic of the sub-basin MT5 (Adriatic), because of its nearest location to emission sources. The value of total deposition density onto MT5 is about 40 $\mu g/m^2$/year. The average density of deposition onto Mediterranean Sea is 13 $\mu g/m^2$/year for dry deposition, 4 $\mu g/m^2$/year – for wet deposition, and 16 $\mu g/m^2$/year – for total deposition.

As it follows from Tables 7.1-7.3 the depositions on a number of the Mediterranean sub-basins have considerable interannual variability. For example, for MT1 (the Alboran Sea) the minimum value of total deposition is 86 kg/yr (1993) and the maximum value – 504 kg/yr (1992). To a certain extent it is likely connected with the interannual trend of the atmospheric transport direction.

Air concentrations and fluxes of lindane have significant seasonal variations. It is connected with application of lindane, which takes place mainly in spring and at the beginning of summer, and its physical-chemical characteristics (especially the Henry's constant) which are strongly dependent on temperature. The pattern of these variations for the calculation period is shown in Figures 7.7 and 7.8. Mean monthly concentrations in air and fluxes were averaged separately for land and sea cells over the whole EMEP grid.

Values of air concentrations in the surface layer are presented in Figures 7.7A and 7.8A (over land), in Figures 7.7D and 7.8D (over sea); total gaseous flux is shown in Figures 7.7B and 7.8B (over land) and 7.7E and 7.8E (over sea); wet depositions - in Figures 7.7C and 7.8C (over land) and in Figures 7.7F and 7.8F (over sea). Figure 7.7 shows the listed values for 3 chosen years and Figure 7.8 shows the same values for the whole calculation period.

The plots A and D in Figures 7.7 and 7.8 demonstrate that the lindane air concentration increases over land and sea up to June in compliance with the emission variation. Since June, when emission is ceased, the concentrations rapidly decrease. By August-September the concentrations are two orders of magnitude lower than its maximum. It should be mentioned that mean concentrations over the sea are approximately three times lower than over land. It is explained by the fact that the seas are far from the strongest lindane emission sources.

Seasonal variations of wet depositions (C and F in Figures 7.7 and 7.8) are practically a replica of concentrations in air (since wet depositions almost linearly depend on concentrations in air). Like in the case of air concentrations the wet depositions on land are three times higher than the wet deposition on the sea.

Distributions of net gaseous fluxes (B and E in Figures 7.7 and 7.8) are most interesting, since these values are an algebraic sum of dry deposition (downward flux) and re-emission (upward flux). As lindane is accumulated by the underlying surface the re-emission becomes more significant, reducing the resulting flux from the atmosphere to the underlying surface.

Since re-emission of lindane from land exceeds that from the sea surface its effect is revealed earlier than the effect of marine re-emission. Hence maximum of the net gaseous flux over

land is reached not in May, as it could be expected, but in March-April (Figures 7.7B and 7.8B). Beginning with July, when sources stop emitting, the net gaseous flux becomes negative, i.e. re-emission predominates and its maximum effect is observed in July-August. Then re-emission decreases (but not up to zero) by February next year when sources start to function. Over the sea (Figures 7.7E and 7.8E) the impact of re-emission is not so significant during the first year of simulation period. But from year to year the re-emission over the sea becomes stronger due to accumulation of lindane in marine water. The maximum of re-emission from the sea is reached in August.

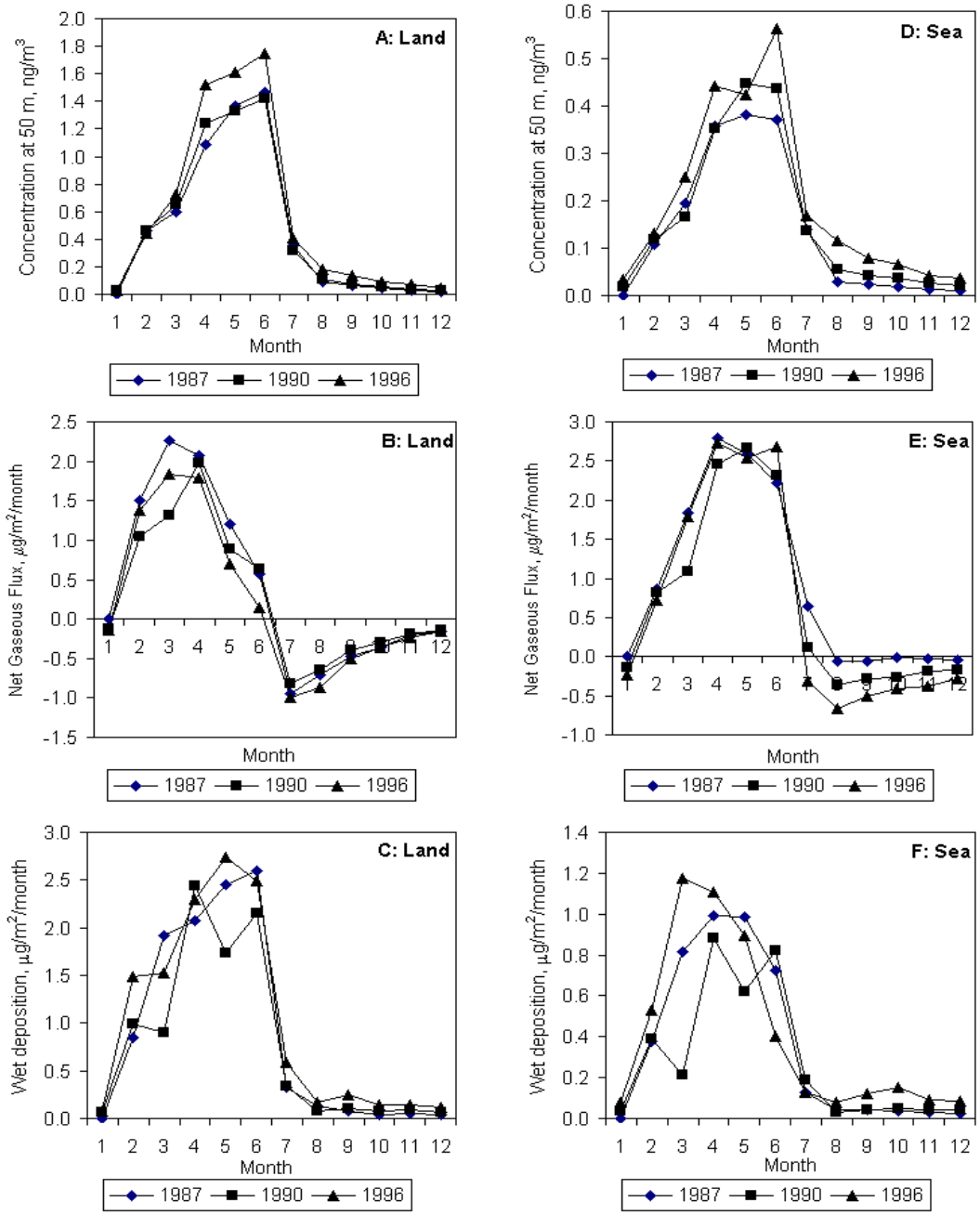

Figure 7.7 Monthly averaged concentration (A and D), monthly net gaseous flux (B and E) and wet deposition (C and F) of lindane.

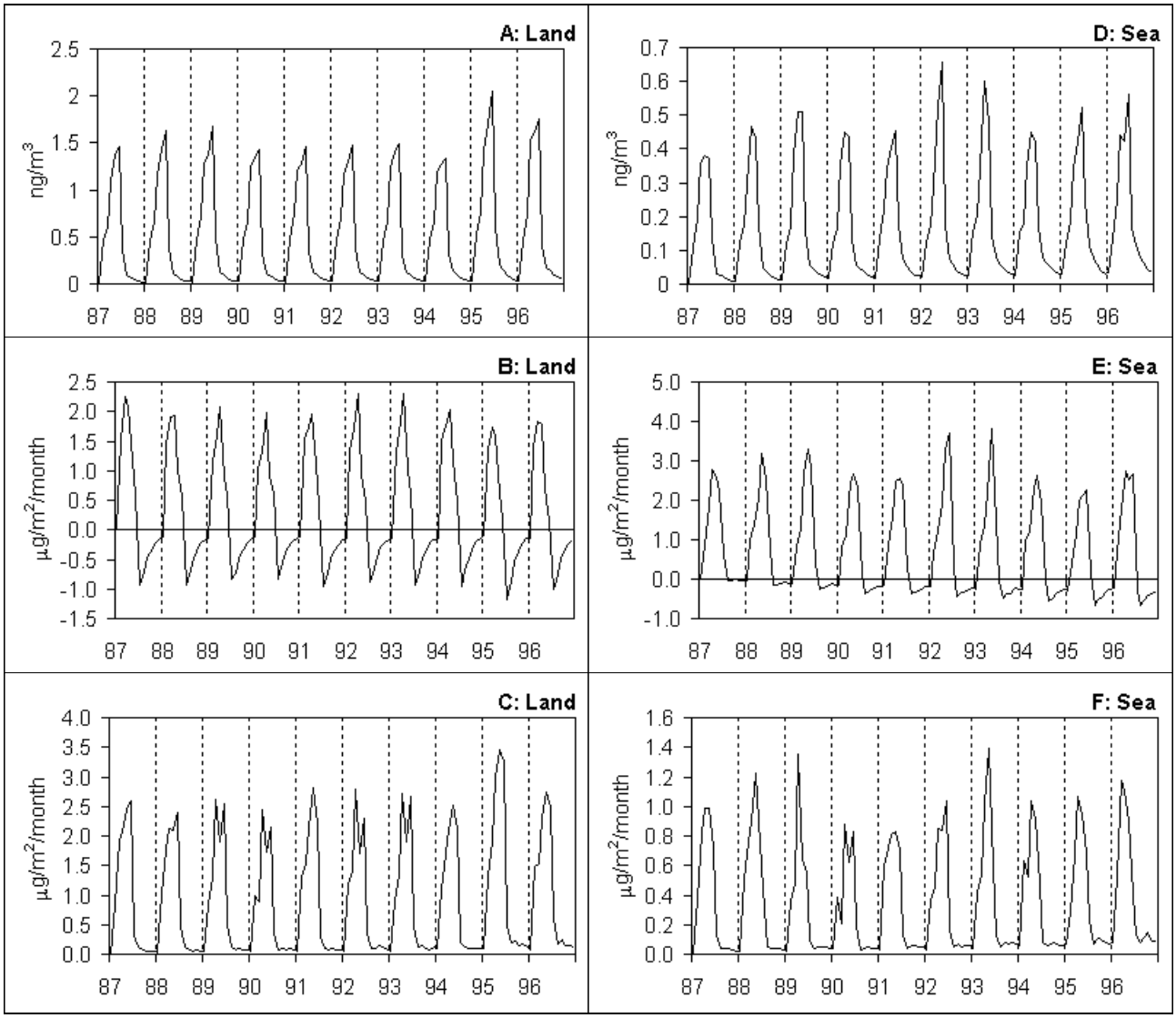

Figure 7.8 Monthly averaged concentration (A and D), monthly net gaseous flux (B and E) and wet deposition (C and F) of lindane.

7.1.2 Comparison with measurement data

Measurements of lindane in the Mediterranean region are rather scarce. For this reason measurement data of the EMEP monitoring network were used [*Berg et al.*, 1996]. Figures 7.9 and 7.10 present the comparison of calculated and measured concentrations of lindane in precipitations and in air. Mean values of measured (7.37 ng/l) and calculated (13.03 ng/l) concentrations in precipitation are rather close. Correlation between measured and calculated values is equal to 0.3. Mean value of simulated lindane concentration in air (234.08 pg/m^3) overestimates the measured one (41.25 pg/m^3) by a factor of 5.7. Correlation between measured and calculated values is about 0.5.

Table 7.5 Comparison of modelling results with measurements of lindane.

Lindane concentration in precipitation, ng/l

Station	Year	Measured	Calculated
DE1	1990	4.54	13.96
DE1	1992	18.22	11.26
DE1	1993	9.28	10.97
DE1	1995	6.32	17.91
DE1	1996	10.38	20.79
DK31	1990	16.98	14.32
DK31	1991	11.91	16.92
DK31	1992	15.82	10.71
NO99	1991	4.05	10.28
NO99	1992	5.02	5.60
NO99	1993	8.45	11.11
NO99	1994	9.98	12.87
NO99	1995	5.54	11.64
NO99	1996	8.01	24.31
DE9	1995	6.52	36.16
IE2	1994	1.43	8.36
IE2	1995	2.15	6.36
IE2	1996	2.04	9.51
IS91	1995	0.44	3.12
IS91	1996	0.27	4.36
Mean		7.37	13.03
Correlation			0.30

Lindane concentration in air, pg/m^3

Station	Year	Measured	Calculated
IS91	1995	14.19	73.07
NO42	1993	14.41	31.11
NO42	1994	16.06	31.61
NO42	1995	13.13	27.77
NO42	1996	12.85	42.52
NO99	1992	86.25	243.2
NO99	1993	58.52	349.99
NO99	1994	122.89	316.11
NO99	1995	64.98	274.62
NO99	1996	60.72	369.05
FI96	1996	10.67	213.09
SE2	1994	51.2	441.89
SE2	1995	26.82	367.61
SE2	1996	24.8	495.47
Mean		41.25	234.08
Correlation			0.48

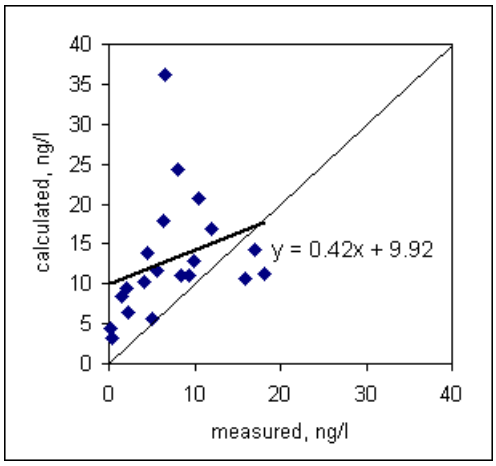

Figure 7.9 Lindane concentration in precipitation, ng/l (comparison of measured data and modelling results).

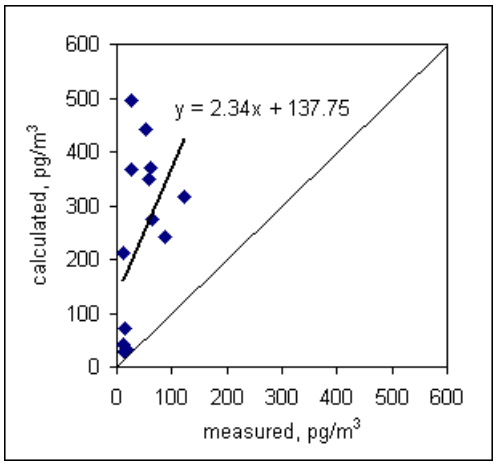

Figure 7.10 Lindane concentration in air, pg/m^3 (comparison of measured data and modelling results)

7.2 PCBs

7.2.1 Calculation results

The PCB simulation was performed for the period of 10 years. Meteorological data for 1987-1996 were used. The model used for the PCB simulation was identical to that one for the lindane simulation with the exception that PCBs were assumed to be in the atmosphere in two phases – in the gaseous phase and in the aerosol phase. The parameterization of physical-chemical properties was fulfilled on the basis of PCB-153. Total emissions of all PCB congeners within the EMEP grid were used in order not to underestimate the contamination effect. This can lead to some uncertainties due to differences in physical-chemical properties of different congeners. Therefore these results can be considered as indicative only.

Spatial distribution of PCB emissions is presented in the Figure 6.2 with the maximum of emissions in the centre of Europe and the total emission of 112 tonnes per year. Figures 7.11 and 7.12 represent calculated mean annual PCB concentrations in air (in 1996), ng/m^3, and PCB total deposition densities (averaged over 10 year), μg/m^2 per year.
Mean annual PCB concentration in air reaches its maximum (0.8 ng/m^3) in the centre of Europe. Over the Mediterranean Sea mean annual air concentrations are about 0.1 ng/m^3. Maximum density of total deposition (5 μg/m^2 per year) is also connected with the centre of Europe. Over the Mediterranean Sea total deposition densities are about 0.1 – 1 μg/m^2 per year.

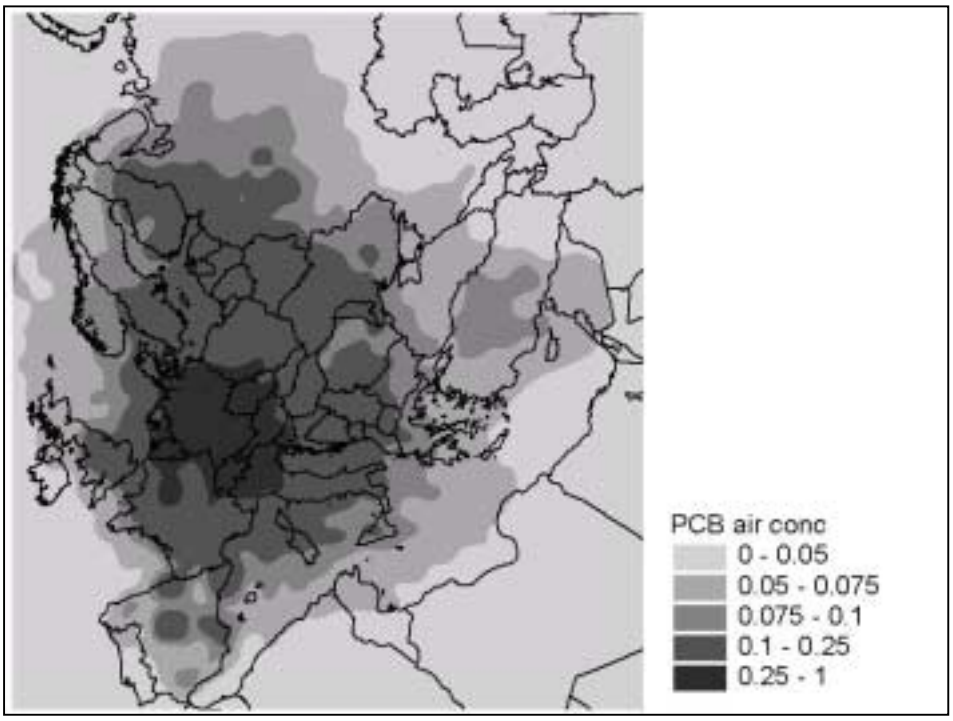

Figure 7.11 Calculated mean annual air concentrations of PCB over the 150 x 150 km^2 EMEP grid in Europe, ng/m^3

During the simulation period, on average, 1 tonn of PCB, which is about 1% of the annual PCB European emissions, deposited on waters of the Mediterranean Sea each year.

Figure 7.13 presents the budget of PCBs within the EMEP region after 10 years. For this period about 1200 t of PCBs were emitted to the atmosphere in Europe (see Table 4.5 for annual emissions). Input to soil amounts to 16%. About 6% degraded in the soil and 10% - 112 tonnes were retained in soil after 10 years. Input to the seas amounts to 6%. About 2% degraded in the seas and 4% - 40 tonnes remained in the seas after 10 years. About 2% of PCBs degraded in the air and 76% of PCBs were transported outside of the EMEP grid.

Atmospheric input to the Mediterranean Sea due to dry and wet deposition amounts to 8.2 tonnes for 10 years. About 30% of it degraded in the sea but about 6 tonnes remained and originated the source of further environmental contamination due to evaporation of PCB from the sea surface.

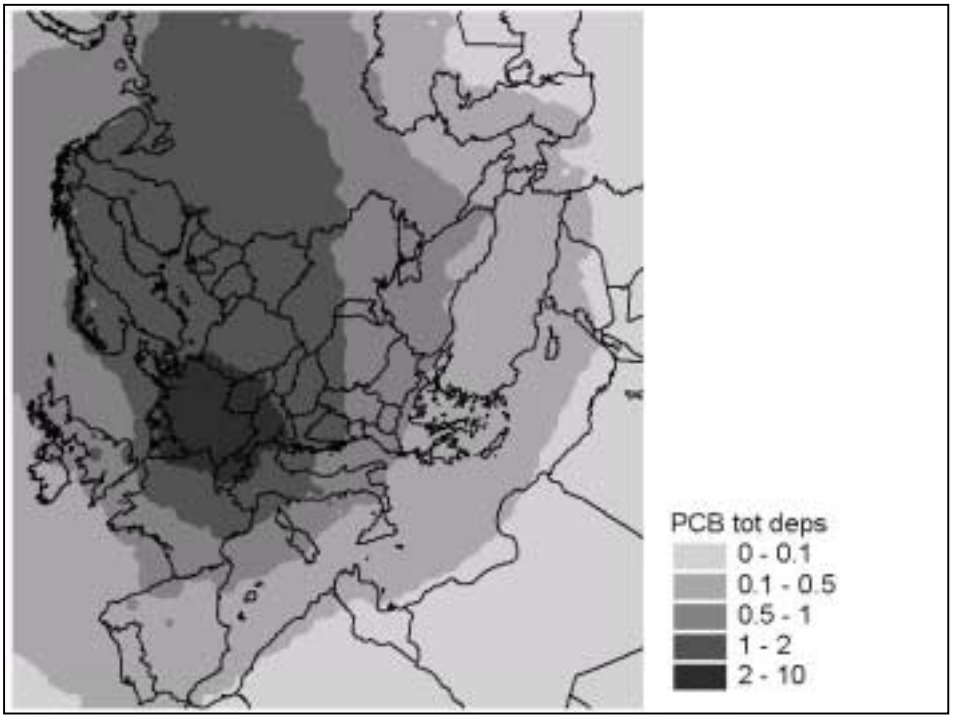

Figure 7.12 Calculated total deposition densities of PCB over the 150 x 150 km^2 EMEP grid in Europe, μg/m^2/yr.

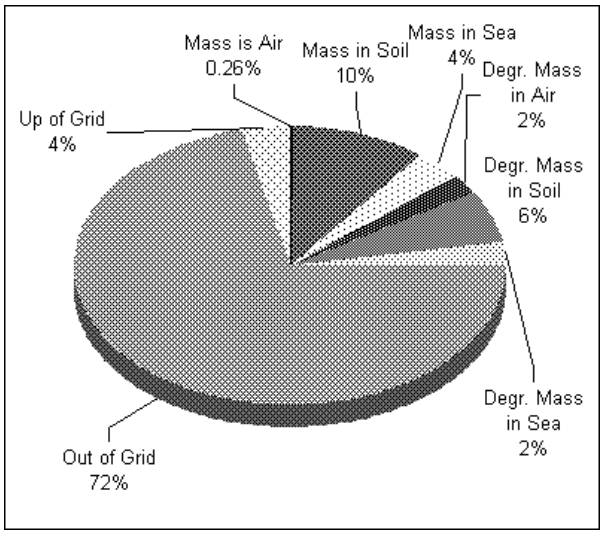

Figure 7.13 Mass balance of PCB after the 10 years period of simulation.

Tables 7.6-7.9 and Figure 7.14 present PCB depositions on the Mediterranean sub-basins: dry depositions (Table 7.6, Figure 7.14A), wet depositions (Table 7.7, Figure 7.14B) and total depositions (Table 7.8, Figure 7.14C). Dry deposition is an algebraic sum of dry deposition (gaseous and aerosol phase) (downward flux) and re-emission from the underlying surface (gaseous phase) (upward flux). Due to high values of the Henry`s law constant PCBs evaporate from water to air more intensively than lindane. That is why PCB dry deposition fluxes are sometimes negative (see Table 7.6).

Figure 7.14 presents the inputs of PCB into each sub-basins, kg/yr. Averaging is made over 10 years. The distribution of the inputs with the sub-basins is similar to that of lindane (Figure 7.6). The averaged density of dry, wet and total deposition onto each sub-basin is shown in Table 7.9. As for lindane, the PCB maximum density of deposition is observed in MT5, and the minimum – in MT1.

Figures 7.15 and 7.16 show seasonal variations of mean air concentrations of PCB over the continent (7.15A, 7.16A) and over the sea (7.15E, 7.16E); net gaseous fluxes over the continent (7.15B, 7.16B) and over the sea (7.15F, 7.16F); dry deposition fluxes of aerosol bounded PCB over the continent (7.15C, 7.16C) and over the sea (7.15G, 7.16G); and wet deposition fluxes over the continent (7.15D, 7.16D) and over the sea (7.15H, 7.16H).

Figure 7.15 presents the above listed values for 3 selected years and Figure 7.16 presents the same values for the whole calculation period. It should be mentioned here that in our calculations emissions are distributed uniformly over each year. Seasonal variations of the characteristics shown in Figures 7.15 and 7.16 are connected with seasonal variations of meteorological parameters, mainly with temperature.

Table 7.6 PCB dry deposition on the Mediterranean Sea and its sub-basins, kg/yr.

Sub-basins	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	Mean
mt1	11	4	-7	14	-1	1	2	1	-2	8	3
mt2	208	60	-8	102	-10	18	58	0	40	40	51
mt3	102	58	-38	94	-10	-3	29	10	-14	45	27
mt4	175	73	-4	66	17	-38	55	20	-4	44	41
mt5	103	36	-5	34	9	-11	20	14	22	54	28
mt6	93	27	3	35	13	-27	12	29	-12	35	21
mt7	157	122	-57	71	66	-67	12	82	-38	67	42
mt8	59	26	5	12	14	-2	-2	26	-1	20	16
mt9	41	22	-3	8	22	-5	-19	18	6	10	10
mt10	94	59	-25	6	60	-14	-24	55	-21	36	23
mt11	5	2	0	1	1	0	0	2	1	0	1
Total	1049	490	-137	444	181	-147	142	259	-22	360	262

Table 7.7 PCB wet deposition on the Mediterranean Sea and its sub-basins, kg/yr.

Sub-basins	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	Mean
mt1	4	4	3	5	5	6	3	2	4	4	4
mt2	143	102	80	80	120	133	129	84	110	146	113
mt3	52	40	37	45	61	59	54	32	44	85	51
mt4	110	108	78	68	95	73	99	62	91	160	94
mt5	87	84	67	74	97	58	76	59	106	137	85
mt6	58	68	41	37	53	39	68	45	32	70	51
mt7	71	64	60	46	67	62	66	45	44	109	63
mt8	36	55	23	26	36	28	38	38	65	56	40
mt9	15	26	15	14	33	36	22	26	20	40	25
mt10	27	44	24	19	33	36	27	36	22	57	32
mt11	3	5	3	3	4	3	3	3	8	5	4
Total	605	600	432	417	603	533	586	432	546	869	562

Table 7.8 PCB total deposition on the Mediterranean Sea and its sub-basins, kg/yr.

Sub-basins	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	Mean
mt1	15	8	-3	19	4	7	6	3	1	12	7
mt2	351	163	72	182	109	151	187	84	149	186	163
mt3	153	98	-1	139	50	56	82	42	30	130	78
mt4	285	182	75	134	112	35	154	82	87	203	135
mt5	190	121	62	108	106	48	96	73	129	192	112
mt6	151	95	43	71	66	12	80	74	20	105	72
mt7	228	186	4	117	133	-6	79	127	6	176	105
mt8	96	80	29	38	51	26	36	64	64	76	56
mt9	56	47	12	22	56	32	3	45	26	50	35
mt10	121	103	-1	26	92	22	3	91	2	93	55
mt11	8	7	3	4	5	3	3	6	9	5	5
Total	1653	1090	294	861	785	385	729	691	524	1229	824

Table 7.9 PCB deposition density on the Mediterranean Sea and its sub-basins, $\mu g/m^2/yr = g/km^2/yr$

Sub-basins	Net dry deposition	Wet deposition	Total deposition
mt1	0.05	0.06	0.10
mt2	0.20	0.44	0.64
mt3	0.10	0.20	0.30
mt4	0.16	0.37	0.53
mt5	0.22	0.67	0.89
mt6	0.10	0.24	0.33
mt7	0.08	0.12	0.19
mt8	0.09	0.22	0.31
mt9	0.07	0.16	0.23
mt10	0.05	0.07	0.13
mt11	0.12	0.35	0.46
Total	**0.10**	**0.22**	**0.33**

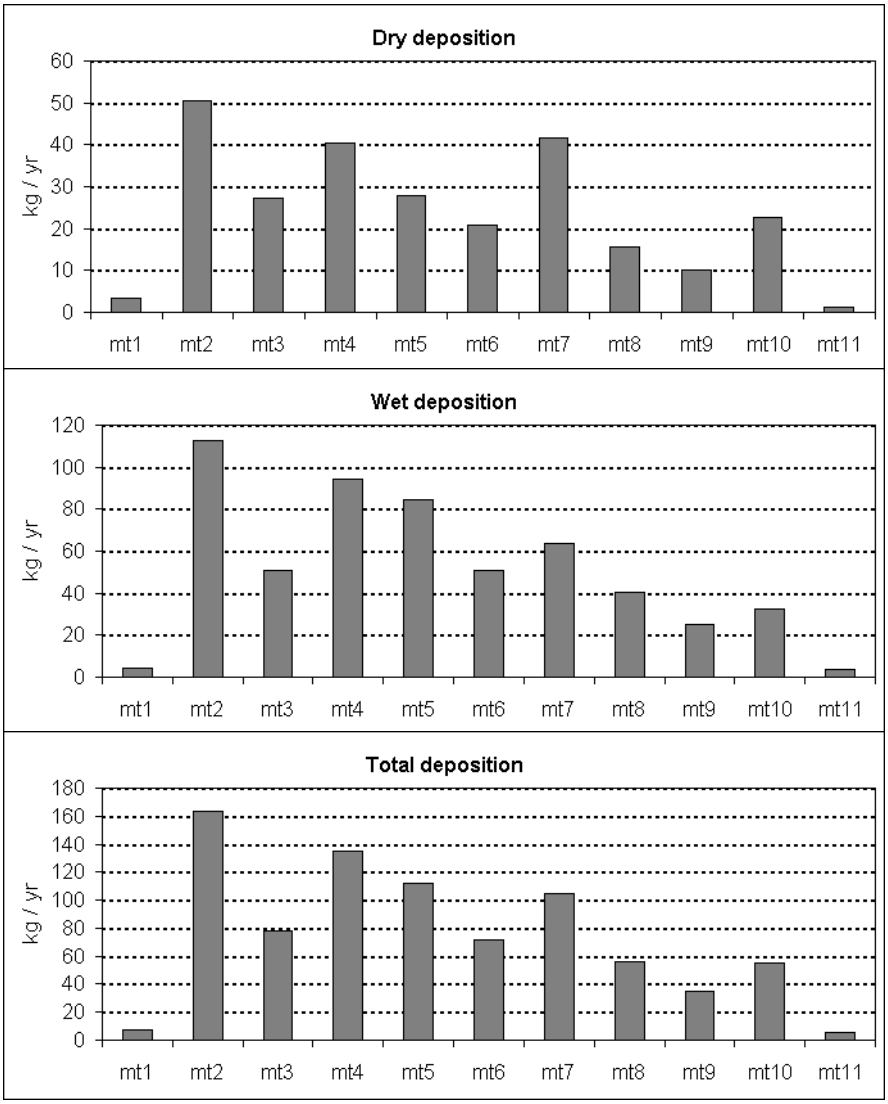

Figure 7.14 Depositions of PCBs on waters of the Mediterranean sea, kg/yr.

For example, dry deposition fluxes of the aerosol phase decrease in summer and increase in winter. This is caused by the fact that at high temperatures PCB-153 exists in air mainly in the gas-phase and at low temperatures – mainly in the aerosol phase. Net gaseous fluxes over

sea become negative in summer because at high temperatures the Henry`s law constant increases and PCBs evaporate from the sea surface more willingly.

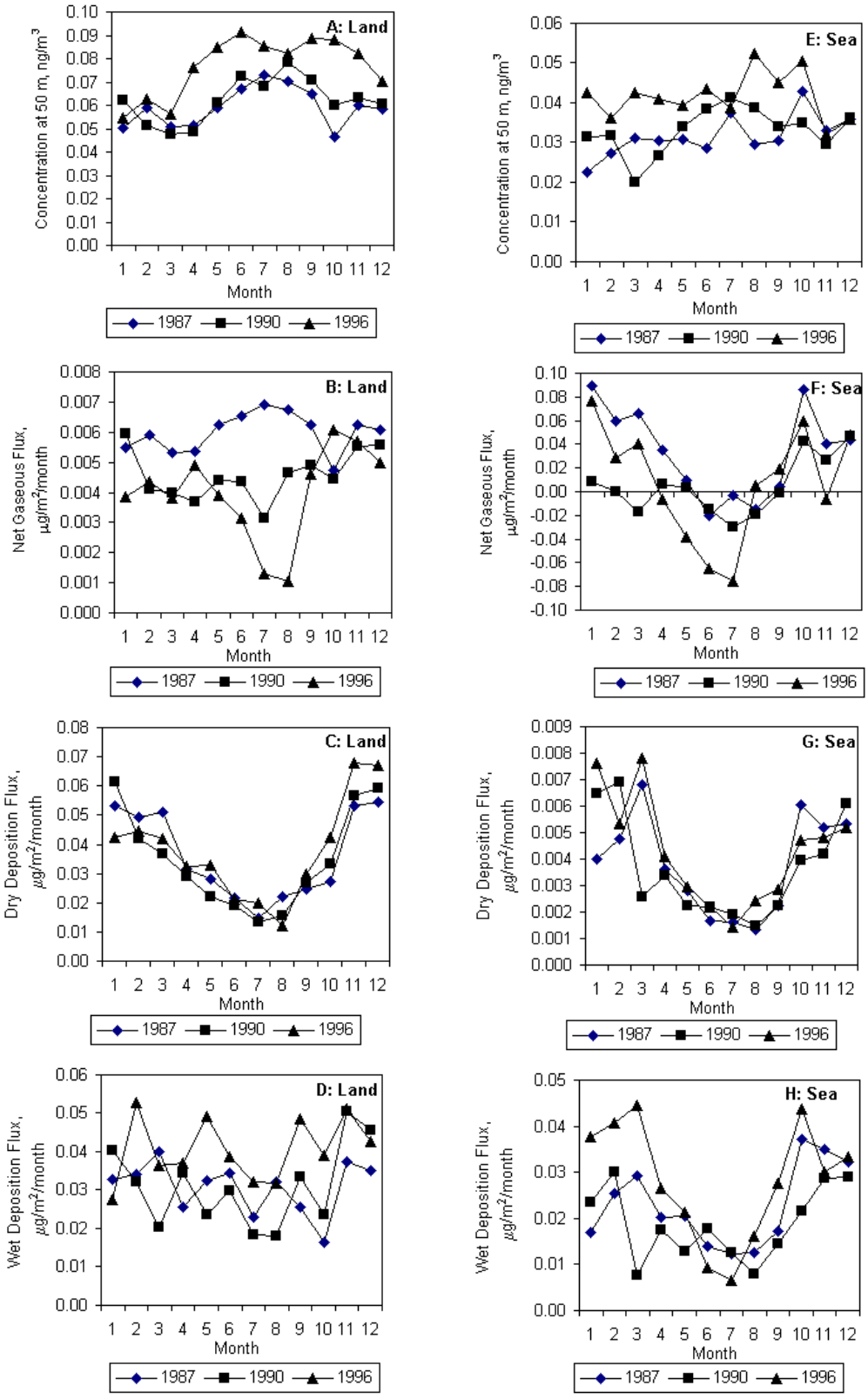

Figure 7.15 Monthly averaged air concentration (A and E), monthly net gaseous flux (B and F), monthly aerosol phase dry deposition flux (C and G) and wet deposition (D and H) of PCBs

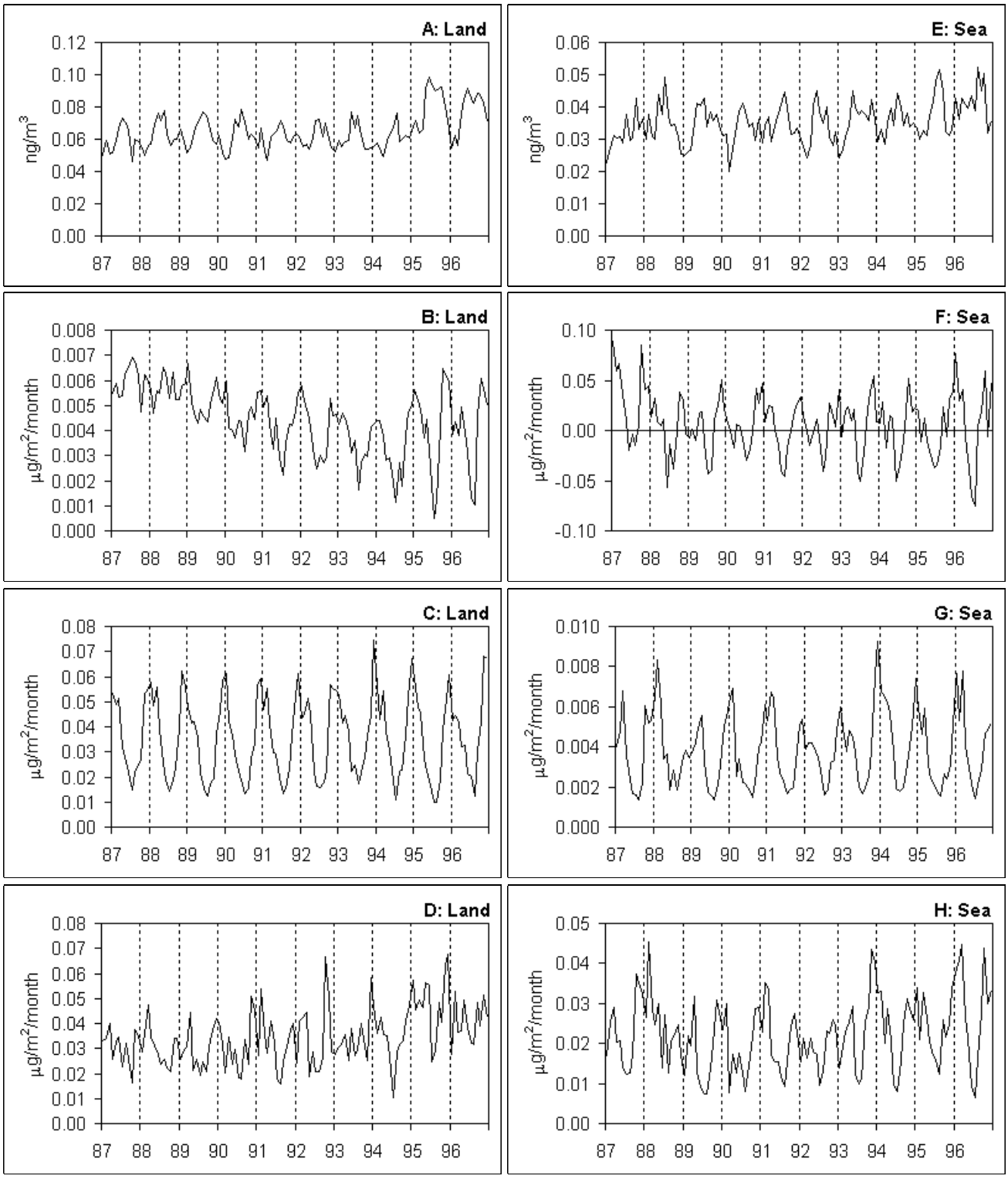

Figure 7.16 Monthly averaged air concentration (A and E), monthly net gaseous flux (B and F), monthly aerosol phase dry deposition flux (C and G) and wet deposition (D and H) of PCBs

7.2.2 Comparison with measurement data

For comparison with modelling results the available measurement data of the EMEP monitoring network [*Berg et al.*, 1996] for PCB-153 were used. Modelling results of the total PCB were recalculated for the PCB-153 using coefficient 0.04 on the basis of expert estimates of the PCB-153 fraction in the total PCB emission.

Table 7.10 and Figure 7.17 show the comparison of calculated and measured data of PCB in air, pg/m^3. Calculated values of PCB-153 air concentrations are 4 times less than measured ones.

Measurements of PCBs in precipitation are available for 4 stations. The comparison of calculated and measured data on PCB wet deposition is present in Table 7.11.

Table 7.10 Comparison of calculated air concentrations of PCBs with measurements.

Station	Year	Measured, pg/m^3	Calculated, pg/m^3
IS91	1995	0.69	1.40
NO42	1993	0.61	0.84
NO42	1994	0.62	0.80
NO42	1995	0.32	1.04
NO42	1996	2.29	0.71
NO99	1992	51.9	2.18
NO99	1993	32.8	3.09
NO99	1994	28.9	4.08
FI96	1996	1.52	2.87
SE2	1994	5.81	5.36
SE2	1995	4.67	5.44
SE2	1996	2.15	5.00
Mean		11.02	2.73

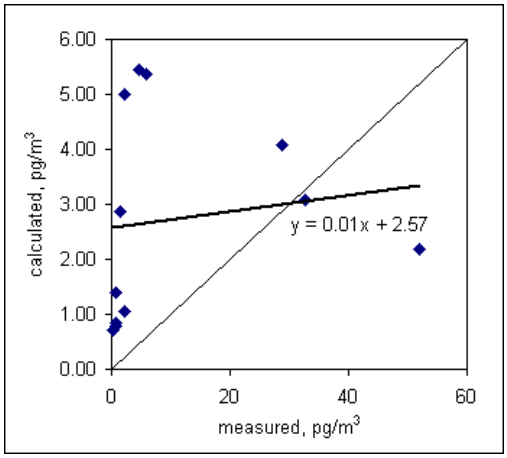

Figure 7.17 PCB-153 concentration in air, pg/m^3 (comparison of measured data and modelling results)

Calculated values of the PCB-153 wet depositions are 3 times less than measured ones.

Table 7.11 Comparison of calculated and measured concentrations of PCBs in precipitation.

Station code	Year	Measured, ng/m^2/year	Calculated, ng/m^2/year
DE9	1996	40.98	54.56
FI96	1996	175.2	24.86
IS91	1995	46.812	22.35
IS91	1996	100.52	24.37
SE2	1996	91.25	33.60
Mean		90.95	31.95

Chapter 8 CONCLUSIONS

1. According to the model calculations presented in this report it was estimated for the first time, that deposition of POPs to the Mediterranean Sea from the atmosphere (atmospheric input) amount to 41 t/y for lindane and 1 t/y for PCBs. Mass balance calculations made earlier for the North Sea showed that direct atmospheric deposition of lindane was 13.3 t/y (60% of its total input), direct discharges and riverine input were 3.9 t/y (with 3.5 t/y being of atmospheric emission origin) and the Atlantic inflow was 5.0 t/y (all of atmospheric origin). In total for the North Sea the airborne input of lindane constituted 98% of its total input to the sea. Similar estimates might also be assumed for the Mediterranean but the lack of input estimates for rivers and other pathways did not allow to compare them with the atmospheric input.

2. Other basic calculation results could be summarized as follows:

- Lindane deposition on the Mediterranean Sea is about 3% of the total European emission;

- PCB deposition on the Mediterranean Sea is about 1% of the total European emission;

- Mean annual air concentration of lindane over the Mediterranean Sea is about 0.5 ng/m^3, and of PCBs – 0.1 ng/m^3.

- Total (dry and wet) deposition density of lindane over the Mediterranean Sea is about 16 μg/m^2 per year, and of PCBs – 0.3 μg/m^2 per year. Dry deposition constitutes about 75% of the total deposition for lindane and 30% for PCBs.

- Maximum deposition densities have been calculated for the following Mediterranean regions: 1) for lindane-Adriatic, Marmara Sea, North-Western part, Aegean Sea and Tyrrhenian Sea, and 2) for PCBs – Adriatic, North-Western part, Tyrrhenian Sea and Marmara Sea;

- Atmospheric deposition of POPs on the Mediterranean Sea from sources located in the Mediterranean countries constitutes a considerable part of the total deposition on the sea since the emission of POPs to the atmosphere from these countries is about 25-30% of the total European emission.

3. The analysis of the results revealed essential seasonal variations of fluxes and concentrations in air and precipitation over the Mediterranean Sea. Similar variations were detected over other seas. There are noticeable interannual variations of the lindane and PCB deposition on the Mediterranean subbasins, which are probably connected with a variability of meteorological situations.

4. The marine compartment to a considerable degree accumulates POPs and, after accumulation, re-emits POPs back to the atmosphere. The ability of PCBs to re-emission from the sea to air exceeds that of lindane.

5. There is scarcity of official emission data from the Mediterranean countries and in this study a wide spectrum of expert estimates of emission is presented. For the calculations of atmospheric inputs of POPs to the Mediterranean Sea presented in this report the emission

assessments made by the Netherlands Organization for Applied Scientific Research (TNO) [*Berdowski, et al., 1997*] were used.

6. Physical-chemical properties of lindane, PCB, B(a)P, and HCB available in literature have been summarized in this report. It should be noted that the available estimates of a number of parameters vary within a wide range leading to uncertainties in deposition calculations.

7. For the evaluation of the Mediterranean pollution by lindane and PCBs the ASIMD model developed in MSC-E with the integrated atmosphere/surface exchange module devised in RIVM was used. The following assumptions were made: lindane was considered in the atmosphere only in the gaseous phase while PCBs were considered as combination of two phases: gaseous and aerosol bounded with the partitioning between these two phases being dependent on temperature and aerosol concentration in air.

8. The analysis of measurements indicated their paucity for the Mediterranean and they are of a campaign character. In this connection available data for Central and Northern Europe were used to compare the calculations with measurement results.

9. Comparison of model calculations with available measurement results showed good agreement for lindane concentrations in precipitation (13 and 7.4 ng/l respectively). The calculated mean lindane concentration in air (234pg/m^3) overestimated the measured one (41 pg/m^3). For PCB-153 the calculated concentrations in air were 4 times less than the measured ones and the calculated wet deposition was 3 times less than the measured one. The main reason for these discrepancies are the inaccuracy of emission data, shortage and unknown quality of measurements, and uncertainties in parameterization of physical-chemical properties of POPs.

10. Comparison of modelling results with experimental data shows that to improve the model the following is needed:

- More accurate emission data;
- Improvements in modelling the removal processes from the atmosphere to underlying surface. These processes are: gaseous exchange with the surface, dry deposition of particle bounded POPs onto the surface, precipitation scavenging of gaseous and aerosol phases of POPs, and degradation in air;
- Consideration of processes which are not presently included in the model, namely the POP absorption by plants, sedimentation in the sea and runoff from watersheds;
- More accurate parameterization of physical-chemical properties;
- More measurement data of known quality.

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ABBREVIATIONS

B(a)P	-	Benzo[a]pyrene
DDE	-	1,1-Bis(4-chlorophenyl)-2,2-dichloroethane
DDT	-	1,1-Bis(4-chlorophenyl)-2,2,2-trichloroethane
Dioxins	-	Polychlorinated dibenzo-p-dioxins and dibenzofurans
EMEP	-	Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe
HCB	-	Hexachlorobenzene
HCH	-	Hexachlorocyclohexanes (several isomers such as γ-HCH)
γ-HCH	-	Lindane
MSC-E	-	EMEP Meteorological Synthesizing Centre – East, Moscow
PAHs	-	Polycyclic aromatic hydrocarbons
PCBs	-	Polychlorinated biphenyls
PCP	-	Pentachlorophenol

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