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**ATMOSPHERIC INPUT OF PERSISTENT ORGANIC  
COMPOUNDS TO THE MEDITERRANEAN SEA**

L.Erdman, A.Gusev, N.Pavlova

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**METEOROLOGICAL SYNTHESIZING CENTRE - EAST**

Kedrova str.8-1, Moscow, 117292, Russia

Tel.: 007 095 124 47 58

Fax: 007 095 310 70 93

E-mail: msce@glasnet.ru

## CONTENTS

Chapter 1.	Introduction	1
Chapter 2.	POP behavior in different environment in different environmental compartments	3
2.1.	Atmosphere	3
2.2.	Water	6
2.3.	Soil	7
Chapter 3.	Physical-chemical properties of some persistent organic compounds	9
3.1.	Pesticides	9
3.2.	Polychlorinated biphenyls	14
3.3.	Products of pyrosynthesis	17
Chapter 4.	Emission estimates of selected POPs	21
4.1.	Pesticides	21
4.2.	Industrial chemicals	23
4.3.	By-products. PAHs	24
4.4.	European emission inventory of persistent organic pollutants for 1990	25
Chapter 5.	Selected POPs in various compartments (measurement data)	26
Chapter 6.	MSC-E model	34
6.1.	Description of the atmospheric module (ASIMD model)	34
6.1.1.	Input data	34
6.2.	Surface-atmospheric exchange module	36
6.3.	Model parametrization	36
6.3.1.	Lindane	36
6.3.2.	PCB-153	37
Chapter 7.	Preliminary results	38
7.1.	Lindane	38
7.2.	PCBs	47
Chapter 8.	Conclusions	54
	References	56

## 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 accumulated in fat tissues. Being semivolatile these substances are predisposed to long-range transport. Contrary to other pollutants (for example acid 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. In 1995 the world production of these chemicals amounted to 7-63 million tons [Geiss and Bourdeaux, 1986]. At present chemical industry produces 5 millions of species of xenobiotics, 50 thousands of them are annually sold at the world market [Izrael and Tsyban, 1989]. However, data on toxicity available in scientific literature encompass only 10% of synthetic compounds.

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 mutagenous [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 trophic chain 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 polychlorobiphenyl 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 (PARCOM, OSPARCOM, HELCOM, Barcelona Convention and its and MED POL) pay considerable attention to the problems of sea pollution by persistent organic compounds. Within the framework of PARCOM, OSPARCOM, 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 mercury, cadmium and dioxins [*Progress Report...*, 1995]. The PARCOM list of organic species consists of 9 substances including PCBs and HCB in addition to solvents, pesticides and dioxins [*Axenfeld et al.*, 1991]. OSPARCOM (1994) took also a decision to reduce by 50% and more PAH emission [*Progress report...*, 1995]. A similar decision has been taken by the Helsinki Commission - 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.

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), on substances of limited application (List B), and on substances the emission of which should be reduced (List E). Within the framework of 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 compounds has been held. At the workshop in Moscow (1996) it was recommended to measure the following organic pollutants: PAHs, PCBs, HCB, chlordan, lindane, HCH, DDT/DDE since these substances can be recorded in single series of measurements. 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 the report was to provide a brief survey of physical-chemical properties of selected POPs, available estimates of anthropogenic emissions to the atmosphere and measurement data, a description of their behaviour 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 in MSC-E [*Pekar et al.*, 1998]. In addition the following works carried out in MSC-E were used [*Vozhennikov et al.*, 1997; *Yufit and Klyuev*, 1997; *Purmal*, 1997].

## **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 depends 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.

*Persistency* 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, persistency of a chemical means the capability for long-range transport, in particular, on a global level. For soils, sediments, and (partially) water the persistency of a compound gives rise to 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 sediment.

*Temperature dependencies* for air/water and air/particles partition coefficients give rise to strongly pronounced season variations of concentrations of a chemical 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 (so called cold condensation) [Mackay and Wania, 1995].

*Lipophilicity* 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 trophic chains (that is, increasing of the concentration of POPs in a consumer organism compared with a consumed one).

Below, the peculiarities of POPs behavior in different environmental compartments and parameters governing this behavior will be considered.

### **2.1. Atmosphere**

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 persistency 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. POPs partitioning between gaseous and aerosol phases depends on a number of factors and first of all on their physical-chemical properties as well as on ambient temperature, humidity and aerosol characteristics.

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

1. Molecular mass  $M$ .
2. Melting temperature  $T_m$  ( $K^{\circ}$ ).
3. Boiling temperature  $T_b$  ( $K^{\circ}$ ).
4. Emission/re-emission rate of a chemical from soils and water bodies to the atmosphere.
5. Saturated vapor pressure  $P^0$ . By definition given in [Mackay *et al.*, 1992] this parameter describes the "solubility of a chemical in air". Units are Pa or Atm. 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  $P^0_L$  are considered. The quantities  $P^0_L$  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  $\varphi$  of a compound in the aerosol phase is calculated according to C. Junge model [Junge, 1977] by the formula:

$$\varphi = c \theta / (P^0_L + c \theta), \quad (2.1)$$

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

$\theta$  - concentration of aerosol surface area,  $m^2/m^3$ .

*F. Wania and D. Mackay* [1996] proposed the classification of compounds from the viewpoint of their partitioning between gaseous and aerosol phase based on  $P^0_L$  value at  $25^{\circ}C$ .

For  $P^0_L(25^{\circ}C)$  more than 1 Pa, in the temperature range usual for the lower troposphere, chemicals practically are not condensed and present in the atmosphere only in the gaseous phase.

For  $P^0_L(25^{\circ}C)$  varying from 1 to  $10^{-2}$  Pa chemicals are condensed at temperatures about  $30^{\circ}C$  and present in the aerosol phase mainly at high latitudes.

For  $P^0_L(25^{\circ}C)$  varying from  $10^{-2}$  to  $10^{-4}$  Pa chemicals can be condensed at temperatures higher than  $0^{\circ}C$  and can be found in the aerosol phase at middle latitudes.

For  $P^0_L(25^{\circ}C)$  less than  $10^{-4}$  Pa chemicals present in the atmosphere in the aerosol phase only.

6. Solubility in water  $S$  (units are weight (g/l) or molar (mol/l) concentrations). This quantity 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.  $S_s$  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-phenanthracene considered in the same paper the salinity increase leads to the increase of solubility.

7. Henry's law constant  $H$ . Henry's law constant plays an important role in the atmosphere/underlying water surface exchange processes and in cloud and subcloud washout 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 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 Henry's law constant  $H$ :

$$\frac{P_a}{C_w} = \frac{P^0}{S} = H \quad (2.2)$$

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

$$\frac{C_a}{C_w} = K_{AW} = K_H = \frac{H}{RT}, \quad (2.3)$$

here  $K_{AW}$  is the dimensionless air/water partition coefficient,  $R$  is a universal gas constant, and  $T$  is an absolute temperature ( $\text{K}^\circ$ ).

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

$$H = \frac{P^0_L}{S^L} = \frac{P^0_s}{S^s} \quad (2.4)$$

Henry's law constant is temperature-dependent. This dependence can be computed via temperature dependencies for  $P^0$  и  $S$ .

The dependence of Henry's law constant on salinity is connected with the dependence of solubility on salinity. For the majority of substances 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 film (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]. Besides in the literature of recent years ([Wania, 1997] and references of this paper; [Harner and Bidleman, 1998]) it is shown that the main mechanism of POP sorption by atmospheric particles can be the process of sorption by the organic film covering particles. It is true for urban aerosol characterized by a high content of organic matter. POP partitioning between the gaseous phase and organic film 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<sup>3</sup>) and  $C_a$  (ng/m<sup>3</sup>) – chemical concentrations in octanol and air respectively.

Value  $K_{OA}$  can be calculated from the following relationship:

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

where  $K_{AW}$  – dimensionless Henry's law constant and "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 Henry's law constant characterizes partitioning between pure water and air. Besides the error in the determination of  $K_{OW}$  value and Henry's law constant introduces an error to  $K_{OA}$  value. Therefore it is better to use  $K_{OA}$  values obtained in direct measurements (for example, presented in 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 hydroxyl-radical OH. As a rule, degradation processes can be described by the first-order reactions and degradation constants  $K_a$  determine these reaction rates. Degradation rates depend on the compound and a number of environmental characteristics: intensity of sunlight, temperature, concentration of OH radical and also the compound phase (gaseous or aerosol).

10. Molecular diffusion coefficient  $D_a$  (m<sup>2</sup>/s) determines the behaviour of a chemical in the gaseous phase in 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. 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. POPs degrade in water and they are 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 POPs input to biota and their further bioaccumulation as far as they move up the trophic chain.

Behaviour of POPs in water and the 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 media (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):

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

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

### 2. "Organic carbon-water" partition coefficient

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

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

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

$$\log K_{OC} = 1.00 \log K_{OW} - 0.21 \quad [\text{Karickhoff et al., 1979}] \quad (2.9)$$

or

$$K_{OC} = 0.41 K_{OW} \quad [\text{Karickhoff, 1981}] \quad (2.10)$$

3. Molecular diffusion coefficient  $D_W$  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 degradation rate  $K_W$ .

## 2.3. Soil

POPs enter the soil due to the application of pesticides and municipal and industrial discharges. Besides they come from the atmosphere due to wet and dry deposition. They occur 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. Purely soil parameters are:

1. Degradation in soil. This parameter is determined not only by photolysis and/or reaction with the hydroxyl radical OH but mainly by microorganism's activity.
2. Soil/water partition coefficient  $K_p$  ( $\text{dm}^3/\text{kg}$ ). 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:

$$K_p = C_p/C_w \quad [\text{ng}/\text{kg}]/[\text{ng}/\text{dm}^3] \quad (2.11)$$

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

$K_p$  can be expressed via  $K_{OC}$  (see formula 2.8) as:

$$K_p = K_{OC} \cdot f_{OC}, \quad (2.12)$$

where  $f_{OC}$  is the organic matter content in soil (suspended particles/bottom sediments).

Clearly, for 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 PERSISTENT ORGANIC COMPOUNDS

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<sup>3</sup>) - solubility in fresh water;

$S_s^*$  (mol/m<sup>3</sup>) - solubility in ocean water;

$H$  (Pa m<sup>3</sup>/mol) - Henry's law constant for fresh water;

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

$K_{ow}(-)$  - "octanol-water" partition coefficient;

$K_{oc}$  (dm<sup>3</sup>/kg) - organic carbon-water partition coefficient;

$K_a$  (time<sup>-1</sup>) - degradation rate in air;

$T_a$  (time) - degradation half-live in air;

$K_w$  (time<sup>-1</sup>) - degradation rate in water;

$T_w$  (time) - degradation half-live in water;

$K_s$  (time<sup>-1</sup>) - 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 are highly heterogeneous group of substances entering the environment in great quantities. They are divided into herbicides, insecticides, fungicides and rodenticides. A number of substances (aldrin, dieldrin, endrin, chlordane, mirex, toxophene, and chlordecone) are prohibited for production and sale.

## Lindane ( $\gamma$ -HCH)

Lindane or  $\gamma$ -HCH is one of 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. Faraday* 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 were 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*



### *Molecular weight*

290.85

### *Melting ( $T_m$ ) and boiling ( $T_b$ ) temperature*

$$T_m = 113^{\circ}\text{C}, T_b = 323.4^{\circ}\text{C} \quad [\text{Howard}, 1991]$$

### *Solubility (S, mol/m<sup>3</sup>)*

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

Solubility dependence on temperature [*Kucklik et al.*, 1991]

for sea water at  $T = 0.5 - 23^{\circ}\text{C}$ :

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

for deionized water at  $T = 0.5 - 45^{\circ}\text{C}$ :

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

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* ( $P^0$ , Pa)

for  $t = 15 - 45^{\circ}\text{C}$ :

$$\log P^0_s = -(5290 \pm 222)/T(\text{K}) + (15.65 \pm 0.74) \quad [\text{Kucklik et al. 1991}]$$

for  $T = -30 - +30^{\circ}\text{C}$ :

$$\log P^0_s = -5490/T(\text{K}) + 16.72 \quad [\text{Wania et al., 1994}]$$

Vapor pressure dependence on temperature for a subcooled liquid:

$$\log P^0_L = -3680/T(\text{K}) + 11.15 \quad [\text{Hincley et al., 1990}]$$

*Henry's law constant* ( $H$ , Pa  $\text{m}^3/\text{mol}$ )

Temperature dependencies:

for deionized water in the range from 0.5 to  $45^{\circ}\text{C}$ :

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

for sea water in the range from 0.5 to  $23^{\circ}\text{C}$ :

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

$$\ln(H) = 19.99 - 6225/T \quad [\text{Strand and Hov, 1996}]$$

for fresh water in the range from 0.5 to  $45^{\circ}\text{C}$ :

$$\ln(H) = 17.36 - 5486/T \quad [\text{Strand and Hov, 1996}]$$

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

*Sorption by soil, sediments and suspended particles*

The sorption value is determined by the following coefficients:  $K_{oc}$  ( $\text{dm}^3/\text{kg}$ ) – organic carbon distribution coefficient;  $K_{ow}$  – octanol-water partition coefficient (see chapter 2).

$$\log K_{oc} = 2.99 \quad [\text{Kushi et al., 1990}]$$

$$\log K_{oc} = 2.96 \quad [\text{Kenaga and Goring, 1980}]$$

$$\log K_{oc} = 3.03 \quad [\text{Lyman, 1982}]$$

$$\log K_{ow} = 2.96 \quad [\text{Kenaga and Goring, 1980}]$$

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

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

$$267 \text{ days} \quad [\text{Jacobs and van Pul, 1996}]$$

$$253 \text{ days} \quad [\text{Strand and Hov, 1996}]$$

$$2 \text{ years} \quad [\text{Mackay et al., 1991}]$$

Lindane degradation half-lives in soils measured in the field experiments after the surface application varied in the range of 150-350 days [Koniuk, 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<sup>0</sup>C 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 [Vozhennikov 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 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 will be presented.

*Molecular formula*



*Molecular weight*

284.78

*Melting ( $T_m$ ) and boiling ( $T_b$ ) temperature*

$$T_m = 228.5^{\circ}\text{C}, T_b = 321^{\circ}\text{C} \quad [\text{Dannenfelsler and Paric, 1991}]$$

*Solubility (S, mol/m<sup>3</sup>)*

The HCB solubility at 25<sup>0</sup>C is:

$$\begin{aligned} S \text{ (mol/l)} &= 2.0 \times 10^{-8}; & [\text{Dannenfelsler and Paric, 1991}] \\ S \text{ (mg/l)} &= 5.7 \times 10^{-3} & \text{(averaged values published).} \end{aligned}$$

The dependence of solubility on temperature was obtained by dividing the vapor pressure [Wania *et al.*, 1994] by Henry's law constant for fresh water [ten Hulscher *et al.*, 1992]:

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

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

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

*Saturated vapor pressure ( $P^0$ , Pa)*

The following experimental data for saturated vapor pressure of HCB is available.

$$\begin{aligned} P^0_s &= 1.35 \times 10^{-8} \text{ atm at } 20^{\circ}\text{C} & [\text{Dannenfelsler and Paric, 1991}] \\ P^0_s &= 2.37 \times 10^{-8} \text{ atm at } 25^{\circ}\text{C} & [\text{Banerjee et al., 1990}] \\ P^0_s &= 1.72 \times 10^{-8} \text{ atm at } 25^{\circ}\text{C} & [\text{Wania et al., 1994}] \end{aligned}$$

Vapor pressure dependence on temperature:

$$\begin{aligned} \log P^0_s \text{ (Pa)} &= -3874/T(\text{K}) + 10.23 \text{ (-30 - +30}^{\circ}\text{C)} & [\text{Wania et al., 1994}] \\ \log P^0_L \text{ (Pa)} &= -3582/T(\text{K}) + 11.11 & [\text{Hincley et al., 1990}] \end{aligned}$$

*Henry's law constant (H, Pa m<sup>3</sup>/mol)*

Henry's law constant (H) depends on the temperature as follows:

for fresh water:

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

for sea water:

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

*Sorption by soils, sediments and suspended particles*

The sorption value is determined by the following coefficients:  $K_{oc}$  (dm<sup>3</sup>/kg) – organic carbon partition coefficient;  $K_{ow}$  – octanol-water partition coefficient (see chapter 2).

$\log K_{oc} = 3.9$  [Dannenfesler and Paric, 1991]

$\log K_{ow} = 5.4 (20 - 30^{\circ}\text{C})$  [Dannenfesler and Paric, 1991]

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

#### *Degradation half-life 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 [Vozhennikov 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 [Vozhennikov et al., 1997].

### **3.2. Polychlorinated biphenyls (PCBs)**

Polychlorinated biphenyls (PCBs) is a group of organic compounds that were specially 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. The degree of toxicity is a function of the chlorination degree.

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 modulator of toxic impacts of other PCB congeners. The most important is the fact that PCB-153 is present practically in all technical mixtures in sufficiently large quantities - from 5 to 17% (on the average - 10%). Therefore it can be 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<sub>m</sub>) and boiling (T<sub>b</sub>) temperature*

T<sub>m</sub> = 103<sup>0</sup>C

[Yalkowsky et. al., 1983]

T<sub>b</sub> = 405<sup>0</sup>C

[Estimating exposure..., 1994]

*Solubility (S, mol/m<sup>3</sup>)*

The data on solubility of PCB-153 at 25<sup>0</sup>C found in literature are listed below:

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

*Solubility dependence on temperature*

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

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

*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 organic matter content in water*

Solubility of the chlorinated biphenyls increases in 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 PCB-153 solubility [Chiou *et al.*, 1986].

### *Saturated vapor pressure at 25(20)<sup>0</sup>C*

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

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

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

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

Temperature dependence of vapor pressure  $P_s^0$  is written as follows:

$$\log P_s^0 \text{ (Pa)} = -5851/T(\text{K}) + 15.10 \quad [\text{Vozhennikov et al., 1997}]$$

Temperature dependence of vapor pressure  $P_L^0$  is written as follows:

$$\log P_L^0 \text{ (Pa)} = -4798/T(\text{K}) + 12.30 \quad [\text{Vozhennikov et al., 1997}]$$

### *Henry`s law constant (H, Pa·m<sup>3</sup>/mol)*

Henry`s law constant H values at 25<sup>0</sup>C for PCB-153:

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

Dependence of H on temperature is as follows:

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

### *Sorption by soil, sediments and suspended particles*

The sorption value is determined by the following coefficients (see chapter 2):

$K_{oc}$ (dm<sup>3</sup>/kg) – organic carbon partition coefficient;

$K_{ow}$  – octanol-water partition coefficient.

$$\log K_{oc} = 6.07 \quad [\text{Karikhoff et al., 1979}]$$

$$\log K_{oc} = 4.78 - 6.87 \text{ with average value equal to } 5.70 \quad [\text{Horzempa and Di Toro, 1983}]$$

$$\log K_{ow} = 7.00 \quad [\text{Shiu and Mackay, 1986}]$$

$$\log K_{ow} = 7.55 \quad [\text{Miller et al., 1984}]$$

$$\log K_{ow} = 6.9 \quad [\text{Bayona et al., 1991}]$$

$$\log K_{ow} = 6.9 \quad [\text{Risby et al., 1990}]$$

#### *Degradation half-life in soil*

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].

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 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 mutagenous 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 the 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<sup>0</sup>C and subject to pyrolysis and/or incomplete combustion. Since processes of pyrolysis and incomplete burning occur everywhere including natural processes it is evident that PAHs, its derivatives and analogs can be found everywhere too [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 physical-chemical properties of B(a)P are presented.

*Molecular formula*



*Molecular weight*

252

*Melting ( $T_m$ ) and boiling ( $T_b$ ) temperature*

$T_m = 179^{\circ}C$ ;  $T_b = 310^{\circ}C$  [Yufit and Klyuev, 1997].

*Solubility (S, mol/m<sup>3</sup>)*

B(a)P solubility data at 25<sup>0</sup>C found in literature are listed below:

References	S, mol/L	S, mg/L
<i>D. Mackay and W.Y. Shiu, 1984</i>	$1.5 \times 10^{-8}$	$3.8 \times 10^{-3}$
<i>S.H. Yalkowsky et. al., 1983*</i>	$2.1 \times 10^{-8}$	$5.3 \times 10^{-3}$
<i>B.G. Whitehouse, 1984</i>	$0.61 \times 10^{-8}$	$1.5 \times 10^{-3}$
<i>B.G. Whitehouse, 1984</i>	$0.61 \times 10^{-8}$	$1.5 \times 10^{-3}$

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

Solubility dependence on temperature for fresh water:

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

Solubility dependence on temperature for sea water:

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

*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, <sup>0</sup> C	P <sup>0</sup> , Pa
P <sup>0</sup> <sub>S</sub>	<i>T.F. Bidleman and W.T. Foreman, 1987**</i>	20	$3.2 \times 10^{-7}$
P <sup>0</sup> <sub>S</sub>	<i>S. Banerjee et al., 1990*</i>	25	$7.2 \times 10^{-7}$
P <sup>0</sup> <sub>S</sub>	<i>D.A. Hincley et al., 1990</i>	25	$7.2 \times 10^{-6}$
P <sup>0</sup> <sub>L</sub>	<i>D. Mackay et al., 1992</i>	25	$2.1 \times 10^{-5}$
P <sup>0</sup> <sub>L</sub>	<i>Y. Cohen and R.E. Clay, 1994**</i>	25	$7.4 \times 10^{-7}$

\* Average value of literature data

\*\* Assessment based on literature data.

Dependence of saturated vapor pressure on temperature:

$$\log P^0_L \text{ (Pa)} = -4989/T(\text{K}) + 11.59 \quad [\text{Hincley et al., 1990}]$$

$$\log P^0_S \text{ (Pa)} = -6319/T(\text{K}) + 15.07$$

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

*Henry's law constant* (H, Pa m<sup>3</sup>/mol)

$$H = 0.05 \text{ Pa m}^3/\text{mol} \text{ (at } 25^0\text{C)} \quad [\text{Mackay et al., 1992}].$$

Temperature dependence of H for fresh water:

$$\log H \text{ (Pa m}^3/\text{mol)} = -4529/T(\text{K}) + 13.89 \quad [\text{Vozhennikov et al., 1997}].$$

Temperature dependence of H for sea water:

$$\log H \text{ (Pa m}^3/\text{mol)} = -3964/T(\text{K}) + 12.13 \quad [\text{Vozhennikov et al., 1997}].$$

*Sorption by soil, sediments and suspended particles*

The sorption value is determined by the following coefficients (see chapter 2):

$K_{oc}$  (dm<sup>3</sup>/kg) – organic carbon partition coefficient;

$K_{ow}$  – octanol-water partition coefficient.

$$\log K_{ow} = 6.13 \quad [\text{Cohen and Clay, 1994}]$$

$$\log K_{ow} = 6.2 \quad [\text{Bayona et al., 1991}]$$

*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 [Tonkopiyy et al., 1979]

*Degradation half-life in water*

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

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

1600 days (ocean water) [Vozhennikov et al., 1997]

2 months [Mackay et al., 1992]

*Degradation half-life in atmosphere*

Many authors believe that 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] 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.Afanasyev 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 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  $3 \times 10^5$ . The value for the gaseous phase can be estimated as a function of 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] B(a)P diffusion coefficients in the air are  $6.9 \times 10^{-6}$  m<sup>2</sup>/s and in the water -  $7.5 \times 10^{-10}$  m<sup>2</sup>/s. In model calculations *D.Bakker and W. de Vries* [1996] recommend to use the values of  $4 \times 10^{-6}$  and  $4 \times 10^{-9}$  m<sup>2</sup>/s, respectively.

## Chapter 4. EMISSION ESTIMATES OF SELECTED POPs

Estimates of POP emissions are hampered because of the uncertainty of emission factors and gaps in knowledge on processes of POP input 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 ( $\gamma$ -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  $\gamma$ -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
	<i>A.C.Baart et al.</i> , 1995	<i>K.D. van den Hout (Ed.)</i> , 1994	<i>F.Axenfeld et al.</i> , 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			6.605
W.Germany	{ 70	{ 14.0	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 Mediterranean 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 Mediterranean 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	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 Mediterranean countries (including Bulgaria, Portugal and Romania) to the total European emission of PCB is about 25%. Significant decrease of European emission can be noted in the 1990 reference year in comparison with 1982.

### 4.3. By-products. PAHs

There are some data on total PAH emission (1982, adapted from [Axenfeld *et al.*, 1991], 6 Borneff PAH\* (1990, adapted from [Baart *et al.*, 1995]) and B(a)P (1990, adapted from [van den Hout (*Ed.*), 1994] and [Baart *et al.*, 1995]). These estimates are compiled in table 4.4. According to the table the contribution of the Mediterranean 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 1982 [Axenfeld *et al.*, 1991], B(a)P in 1990 [van den Hout (*Ed.*), 1994; Baart *et al.*, 1995], 6 Borneff PAH\* in 1990 [Baart *et al.*, 1995], t/yr

Country	<i>F.Axenfeld et al.</i> , 1991 Total PAH, 1982	<i>K.D.van den Hout (Ed.)</i> , 1994 B(a)P, 1990			<i>A.C. Baart et al.</i> , 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

\* 6 of Borneff PAH: Fluoranthene, Benzo[a]pyrene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[ghi]perylene, Indeno[1,2,3-c,d]pyrene.

#### 4.4. European emission inventory of persistent organic pollutants for 1990

On behalf of 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 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]

Country	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 COMPARTMENTS (MEASUREMENT DATA)

There are very few data on POP measurements. With regard to the Mediterranean Sea there are some data on air pollution in [UNEP/FAO/WHO/IAEA, 1989] and on the contamination by chlororganic compounds (PCBs, HCH) in [Jeftic *et al.*, 1989]. Below concentrations of selected POPs in air, precipitation, marine water, sediments and biota are presented. Figures in brackets represent mean values.

### B(a)P

<i>Air concentrations</i> *, ng/m <sup>3</sup>		[Maistrenko <i>et al.</i> , 1996]
background	West Europe	0.01 – 5.0 (0.5)
	East Europe	0.04 - 5.0 (0.5)
	Arctic	10 <sup>-4</sup> – 10 <sup>-3</sup> (0.002)
industrial regions		10 <sup>-1</sup> - 10 <sup>2</sup>
mean value for cities of USA		6

<i>Concentrations in precipitation</i> * (ng/l)		[Rovinsky <i>et al.</i> , 1988]
background monitoring sites of the former USSR	Pacific ocean	5 – 209 (20)
	Norway	30 – 37
		0.4 – 40

\* See also EMEP and GKSS data (tables 5.10 - 5.13)

### *Concentrations in sea water*

**Table 5.1.** Mean levels of marine pollution by benzo(a)pyrene 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 5.2.** B(a)P content in marine sediments from [Izrael and Tsyban, 1989], µg/kg of dry mass

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 (µg/kg)*

rural background	1 - 3	[Rovinsky et al., 1987; Rovinsky et al., 1988]
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 precipitation*

**Table 5.3.** 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	ΣPCB	
	air, ng/m <sup>3</sup>	precipitation, ng/l
Western Europe	0.3	30
North America	3	60
Antarctic	0.061	
Arctic	0.005 - 0.02	-
Northern Pacific	0.41 - 1	0.6

**Table 5.4.** PCB air concentrations in continental and coastal regions, ng m<sup>-3</sup> [Yufit and Klyuev, 1997; *Background monitoring...*, 1990; *Izrael and Tsyban*, 1989; *Rovinsky et al.*, 1992; *Schreitmüller et al.*, 1994; *Korte*, 1996]

Region	Year	Arochlorine 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

Over the Mediterranean Sea PCB mean concentrations in air are 0.23 ng/m<sup>3</sup> in 1975 and 0.07 ng/m<sup>3</sup> in 1977 cruise [UNEP/FAO/WHO/IAEA, 1989]. PCB content in marine and oceanic atmosphere including Mediterranean Sea is presented in table 5.5.

**Table 5.5.** PCB content in marine and oceanic atmosphere, ng/m<sup>3</sup> [*Izrael and Tsyban*, 1989]

Region	Year	Content	Mean
Northern Atlantic, Newfoundland	1981	0.042 - 0.15	0.12
Pacific ocean	1981	0.35 - 1.0	0.54
Enewetak Atoll	1982	0.089 - 0.74	0.25
western part	1985	0.041 - 0.061	0.051
	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	0.91
eastern part	1983	0.076 - 0.11	0.091
Monaco coast *	1975	0.1 - 1.0	0.4
	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

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

#### *Concentrations in sea and ocean water*

Tables 5.6 and 5.7 present concentrations of PCBs and chlorinated hydrocarbons in sea and ocean water.

**Table 5.6.** PCB concentration 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 eastern part	1980 - 85	6	0.057 - 0.25	0.14
South ocean	1980 - 85	10	0.035 - 0.075	0.055

**Table 5.7.** Concentration of chlorinated hydrocarbons in sea waters, ng/l

Sea	Year	HCH	PCB	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	0.2	''''
<i>Mediterranean</i>				
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]

In the Mediterranean sea water samples have the concentration range from 0.2 to 38 ng PCBs l<sup>-1</sup> (table 5.7). The levels of the 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 from different authors without intercalibration. In the Northern Adriatic coastal waters in 50 samples analysed between 1977 and 1978 most concentrations were below the detection limits of 0.1 ng PCBs l<sup>-1</sup> [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 is about 8 ng/g (maximum value is 20 ng/g for PCBs). According to [Fowler, 1986], concentrations of PCBs in the top centimeter 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], «the examples concern high sediment concentrations near the sewage outfalls of Marseille (up to 16000 µg PCBs kg<sup>-1</sup> DW) and Athens (up to 800 µg PCBs kg<sup>-1</sup> DW), near larger towns such as Nice (up to 1165 µg PCBs kg<sup>-1</sup> DW), Naples (up to 3200 µg PCBs kg<sup>-1</sup> DW) and Augusta (up to 460 µg PCBs kg<sup>-1</sup> 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] total flux of 12 PCB congeners was found to be 14 - 60 ng/m<sup>2</sup>/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 5.8.

**Table 5.8.** Typical concentrations of PCBs in natural objects and in human organism [Yufit and Klyuev, 1997]

Object studies	PCB concentration
Atmospheric air, ng/m <sup>3</sup> :	
City	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:	
reserves far from agricultural regions	2 - 20
Surface biota, µg/kg:	
Plants	2 - 20
wild animals	20 - 400
Aquatic biota, µg/kg	
Zooplankton	10 - 150
fresh water fish	10 - 300
fish of seas and oceans	10 - 100
sea mammals (under skin fat)	100 - 10000
Man, body (fat), µg/kg	350

## HCH and lindane

### *Concentrations in the atmosphere*

Lindane concentrations in air over Europe range from 0.01 to 1.4 ng/m<sup>3</sup>. 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]. According to [van den Hout (*Ed.*), 1994], lindane concentrations over the North Sea amount to 4-5 ng/m<sup>3</sup>.

### *Concentrations in fresh water*

Typical concentrations are 10 - 40 ng/l of lindane. Its concentration in bottom sediments can be 100 times higher (1800 - 2400 ng/kg) [Yufit and Klyuev, 1997].

### *Concentrations in sea water*

See table 5.7. In the Mediterranean "lindane levels off shore in the eastern basin ranged from 0.06 to 0.12 ng/l. Higher concentrations were observed near terrestrial run-off and river inputs. Particulate matter had higher concentration than the sea water dissolved phase" [Jeftic *et al.*, 1989].

### *Concentrations in sediments*

Data on HCH concentrations in coastal sediments from the Central Mediterranean are presented in table 5.9, adapted from [Jeftic *et al.*, 1989].

**Table 5.9.** 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]

Below measurement data on some POPs in regions of the North and Baltic Seas are presented (tables 5.10, 5.11). Tables 5.12, 5.13 contain measurement data of EMEP monitoring network. Table 5.14 presents the list of EMEP sites used here and further in the report.

**Table 5.10.** Air concentrations of some POPs 1987, 1988 (Baltic and North Seas), pg/m<sup>3</sup>  
[Wodarg and Reinhardt, 1992]

	PCB	HCB	α-HCH	γ-HCH
Kiel Bight	40 – 600	60 - 1300	80 - 3000	50 - 10000
Ship measurements, various campaigns 88 - 89	(61) (133) (116) (117) (60)	(98) (220) (220) (251) (165)	(53) (82) (170) (184) (46)	(69) (216) 864 (2780) (176)

**Table 5.11.** Concentrations in precipitation of some POPs (North Sea)\*, ng/l

	vol (l)	PCB	pp`DDE	op`DDT	pp`DDT	α-HCH	γ-HCH
Collafirth	29.3	1.56	0.07	0.04	0.16	1.74	0.88
Ratray Hd.	19.4	5.6	0.79	0.52	4.06	2.64	2.14
Carnbee	19.5	2.8	0.37	0.18	1.45	3.81	3.06
Tantallon	12.3	4.13	0.41	0.18	1.11	4.78	5.25
Lindisfarne	15.9	7.62	0.48	0.1	0.84	4.55	4.91
Flamborough	15.3	10.1	0.8	0.39	3.35	4.82	6.49
Burnham	9.5	59.6	4.43	2.73	36.5	3.96	8.96
Average	17	13.1	1.05	0.59	6.79	3.76	4.53

\* from [Wells and Johnstone, 1987]

**Table 5.12.** EMEP data on air concentrations of some POPs, pg/m<sup>3</sup> [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				
pp`DDT			1/0.8	0.5/0.35				
pp`DDT			0.9/0.7	0.3/0.2				
op`DDE			1.4/1.2	0.2/0.1				
pp`DDE			1.9/1.5	0.9/0.6				

\* site code / year

\*\* arithmetic mean/geometric mean

**Table 5.13.** 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
DDT		9.23	4.41							
DDE			1.13							

**Table 5.14.** List of EMEP monitoring stations submitted data on concentrations of some POPs  
[Berg *et al.*, 1996]

Country	Station codes	Station name	Location		Height above sea, m
			Lat.	Long.	
Czech Republic	CZ3	Kosetice	49°35'N	15°05'E	633
Denmark	DK31	Ulborg	56°17'N	8°26'E	10
Finland	FI96	Pallas	67°58'N	24°07'E	566
Germany	DE1	Westerland	54°55'N	8°18'E	12
	DE9	Zingst	54°26'N	12°44'E	1
Iceland	IS91	Stórhöfði	63°24'N	20°17'W	118
Ireland	IE2	Turlough Hill	53°02'N	6°24'W	420
Norway	NO42	Spitsbergen, Zeppelinfjell	78°54'N	11°53'E	474
Sweden	SE2	Rörvik	57°25'N	11°56'E	10

## Chapter 6. ASIMD MODEL

### 6.1. Description of the atmospheric module (ASIMD model)

A three-dimensional Eulerian transport model ASIMD (ASymmetric Improved Model) 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 of four layers with non-uniform heights (Figure 6.1). The surface layer,  $\Delta z = 100$  m is distinguished, the depths of the following layers are chosen with orientation to the levels of meteorological data. The calculated levels along  $z$  correspond to cell centers.

Horizontal transport in ASIMD is realized with the application of asymmetric advection scheme. Compensation of numerical diffusion is made by correction of advection velocity depending on local gradients.

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

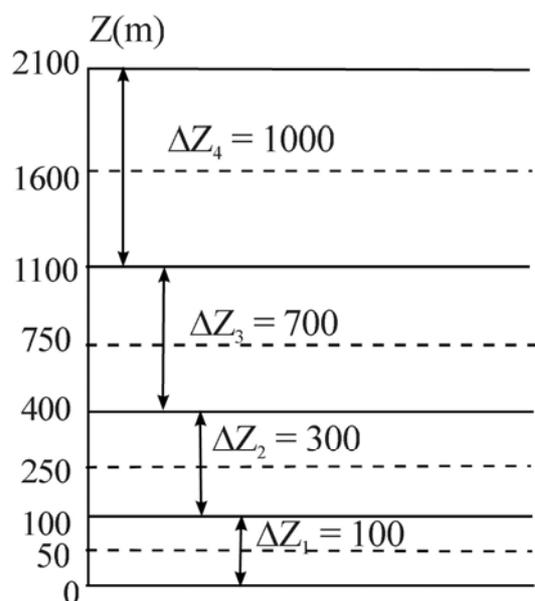


Figure 6.1. Vertical scheme of the model

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 devised 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  $1^\circ \times 1^\circ$  averaged over a month.

The meteorological pre-processor is based on the method of energetic balance evaluation with further application of results of similarity theory [Holtslag and

van Ulden, 1983; van Ulden and Holtslag, 1985]. The parameter calculations are made for each 6-hour interval (03, 09, 15, 21 UTC).

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

#### 6.1.1. Input data

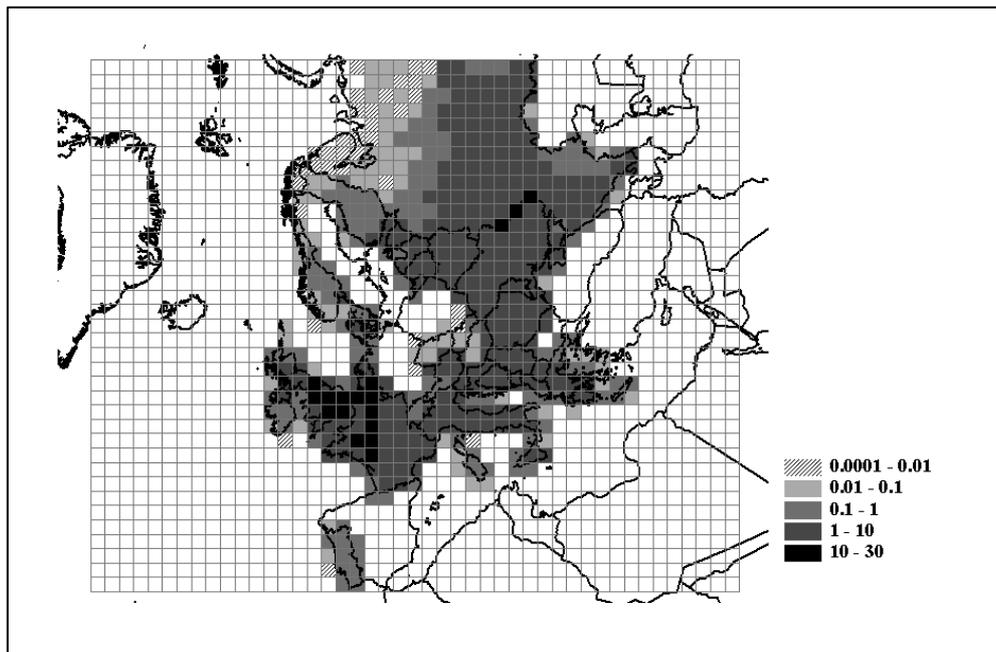
##### Emission

Fig.6.2 presents a map of the lindane emission distribution over the EMEP grid in 1990 [Berdowski et al., 1997]. Total lindane emission amounts to 1307 t/yr. Taking into account seasonal variation of lindane application it was assumed that 10% of its emission took place in February, 15% - in March and 25% - in April, May and June.

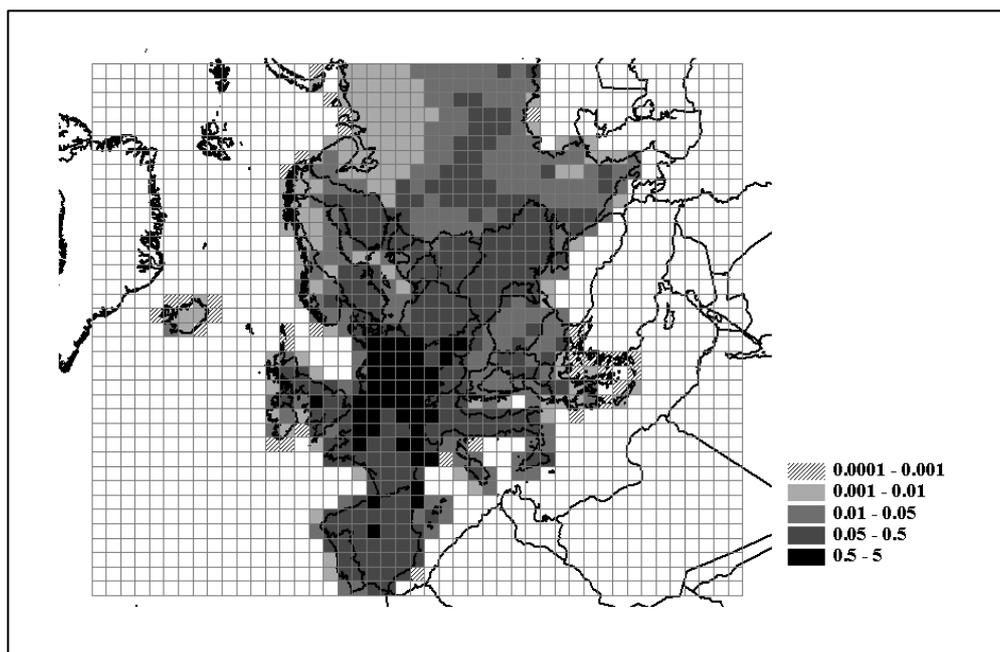
Spatial distribution of PCB emission in 1990 is shown in fig.6.3 [Berdowski *et al.*, 1997]. PCB total emission amounts to about 112 tons. For calculations it was assumed that PCB emission has no seasonal variations.

### Meteorology

The following input meteorological data for 1987-1994 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 Russian Hydrometeorological Centre.



**Figure 6.2.** Distribution of lindane emission with 150 x 150 km<sup>2</sup> EMEP grid in Europe for 1990, t/yr



**Figure 6.3.** Distribution of PCB emission with 150 x 150 km<sup>2</sup> EMEP grid in Europe for 1990, t/yr

## 6.2. Surface-atmospheric exchange module

For the description of the exchange with 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.

## 6.3. Model parameterization

### 6.3.1. 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<sup>3</sup>/kg

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

$K_{oc}$  - organic carbon distribution coefficient  $K_{oc} = 1.3$ , m<sup>3</sup>/kg

#### **DEGRADATION RATE:**

**SOIL**  $K_s = 3.0 \times 10^{-8}$ , s<sup>-1</sup>

**SEA**  $K_w = 4.66 \times 10^{-9}$ , s<sup>-1</sup>

**ATMOSPHERE**  $K_a = 2.5 \times 10^{-7}$ , s<sup>-1</sup>

#### **MOLECULAR DIFFUSION COEFFICIENTS:**

**ATMOSPHERE**  $D_g = 5.0 \cdot 10^{-6}$ , m<sup>2</sup>/s

**WATER**  $D_w = 5.0 \times 10^{-10}$ , m<sup>2</sup>/s

#### **VOLUMETRIC FRACTIONS IN SOIL:**

**POROSITY**  $\varphi = 0.5$ , m<sup>3</sup>/m<sup>3</sup>

**VOLUMETRIC AIR CONTENT**  $a = 0.2$ , m<sup>3</sup>/m<sup>3</sup>

**VOLUMETRIC WATER CONTENT**  $\theta = 0.3$ , m<sup>3</sup>/m<sup>3</sup>

**SOIL BULK DENSITY**  $\rho_s = 1350$ , kg/m<sup>3</sup>

#### **MOLECULAR DIFFUSION LAYER THICKNESS**

$$d_{zwm} = 4.0 \times 10^{-5}, \text{ m}$$

#### **AND ACCUMULATING LAYER DEPTHS FOR WATER**

$$d_{wz} = 25, \text{ m}$$

#### **CHARACTERISTICS OF THE CALCULATION GRID FOR SOIL:**

**NUMBER OF LAYERS**  $K_{max} = 5$

**DEPTHS OF LAYER:** 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

### 6.3.2. PCB-153

#### HENRY`S LAW CONSTANT

$$H = \frac{1}{RT} \cdot 10^{13.42 - 3625/T} \text{ (dimensionless)}$$

#### VAPOR PRESSURE

$$P_{OL} = 10^{1285 - 4775/T}, \text{ PA}$$

#### SOIL/WATER PARTITION COEFFICIENT

$$K_p = f_{oc} \cdot K_{oc}, \text{ m}^3/\text{kg}$$

$f_{oc}$  - fraction of organic carbon in soil

$f_{oc}$  (dimensionless)

$K_{oc}$  - organic carbon distribution coefficient

$$K_{oc} = 3236 \text{ m}^3/\text{kg}$$

#### DEGRADATION RATE:

SOIL  $K_s = 3.5 \times 10^{-9}, \text{ s}^{-1}$

SEA  $K_w = 3.5 \times 10^{-9}, \text{ s}^{-1}$

ATMOSPHERE  $K_a = 3.5 \times 10^{-8}, \text{ s}^{-1}$

#### MOLECULAR DIFFUSION COEFFICIENTS:

ATMOSPHERE  $D_g = 4.58 \times 10^{-6}, \text{ m}^2/\text{s}$

WATER  $D_w = 5.14 \times 10^{-10}, \text{ m}^2/\text{s}$

#### VOLUMETRIC FRACTIONS IN SOIL:

POROSITY  $\varphi = 0.5, \text{ m}^3/\text{m}^3$

VOLUMETRIC AIR CONTENT  $a = 0.2, \text{ m}^3/\text{m}^3$

VOLUMETRIC WATER CONTENT  $\theta = 0.3, \text{ m}^3/\text{m}^3$

SOIL BULK DENSITY  $\rho_s = 1350, \text{ kg}/\text{m}^3$

#### MOLECULAR DIFFUSION LAYER THICKNESS

$$d_{zwm} = 4.0 \times 10^{-5}, \text{ m}$$

#### AND ACCUMULATING LAYER DEPTHS FOR WATER

$$d_{wz} = 25, \text{ m}$$

#### CHARACTERISTICS OF THE CALCULATION GRID FOR SOIL:

NUMBER OF LAYERS  $K_{max} = 5$

DEPTHS OF LAYER: DSZ(1) = 0.005, m

DSZ(2) = 0.005, m

DSZ(3) = 0.01, m

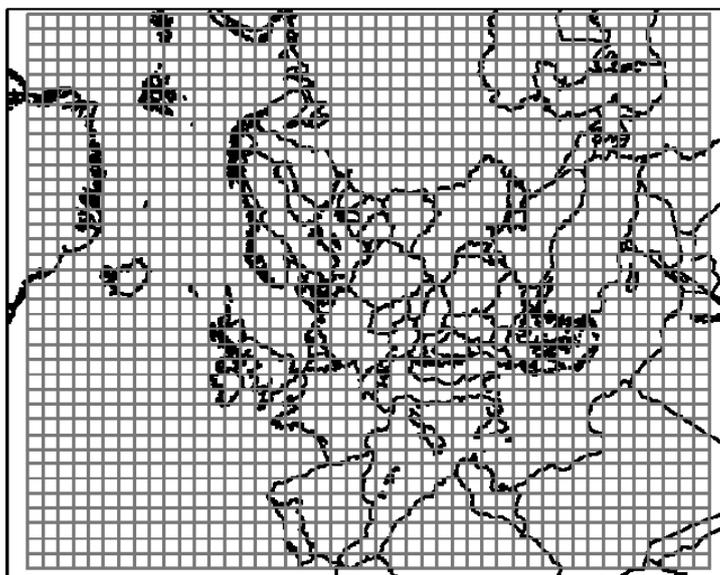
DSZ(4) = 0.02, m

DSZ(5) = 0.11, m

## Chapter 7. CALCULATION RESULTS

### 7.1. Lindane

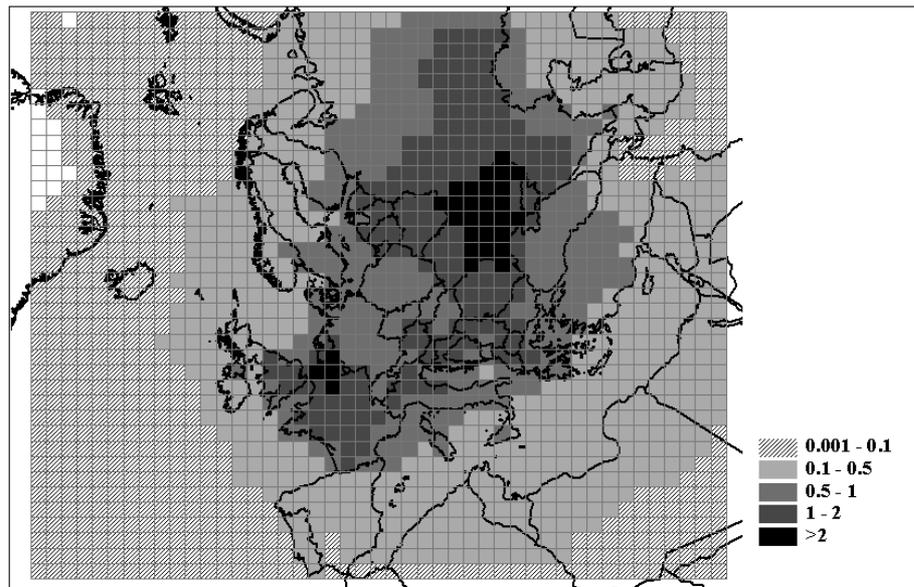
Calculations of lindane transport were made within the EMEP grid (fig.7.1) using Eulerian multi-layer model ASIMD [Pekar, 1996] and atmosphere-soil and atmosphere-water exchange modules [Jacobs and van Pul, 1996] with temporal resolution 1 hour. Calculations covered the period of ten years (1987-1996) 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 [Jacobs and van Pul, 1996]. It is assumed that lindane is present in the atmosphere in the gas phase only. Calculation results present air concentrations, deposition and fluxes between environmental compartments.



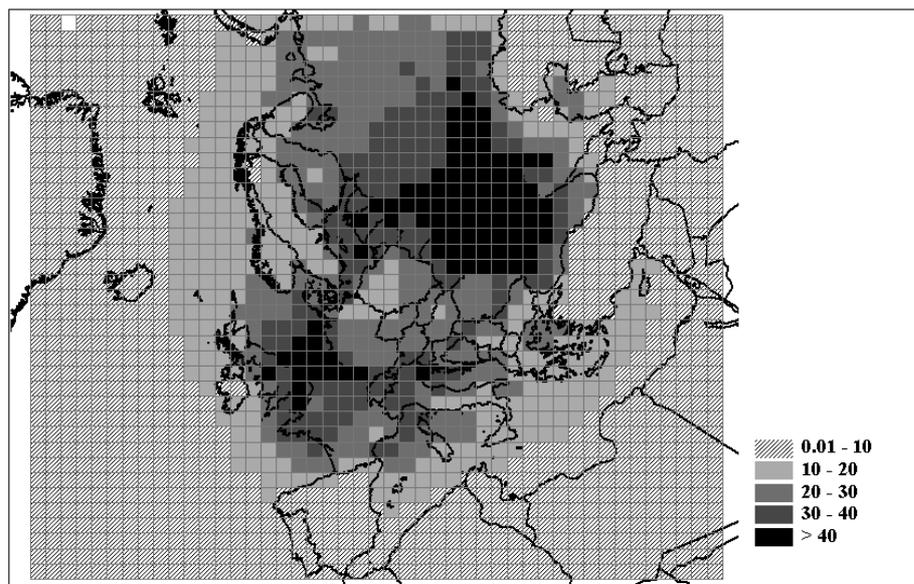
**Figure 7.1.** The EMEP grid

Lindane emission map is presented on the Fig. 6.1. Total European emission of lindane in 1990 was about 1310 t (Table 4.5). Fig.7.2 shows mean annual air concentration of lindane for 1996. Maximum annual concentrations of lindane in air are 3-4 ng/m<sup>3</sup> in France and the Ukraine. Regions of maximum concentrations correspond to the regions of maximum emissions. As moving off emission sources, concentrations decrease. In the Mediterranean air concentrations of lindane decrease in the southern direction. Mean annual concentrations in the Mediterranean are about 0.5 ng/m<sup>3</sup>. As it will be shown later concentrations increase in summer and decrease in winter. It is connected with the annual trend of emissions. Fig.7.3 presents a lindane deposition map for 1987-1996. Regions of the maximum deposition coincide with regions of the maximum emission. The maximum density of total deposition is up to 80 µg/m<sup>2</sup>/year.

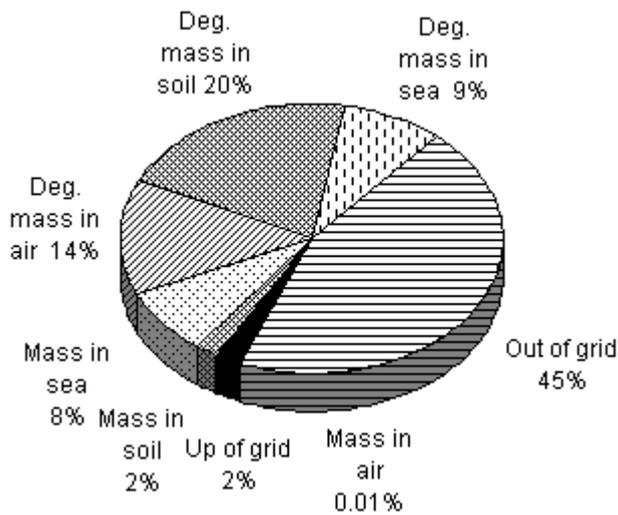
During the calculation period on the average about 55 tons of lindane (about 4% of annual emission of lindane), deposited on the Mediterranean Sea each year. Fig.7.4 presents the budget of lindane within the EMEP region during the calculation period. The major part of lindane falls at the continental part of the EMEP grid (20% was degraded in the soil and 2% - 240 tons were retained in the soil after 10 years of calculations). The large part of lindane is a share of the sea area of the EMEP grid (9% was degraded inside the sea and 8% - 1000 tons were remained in the sea after 10 years). 14% of lindane was degraded in the atmosphere due to rather rapid degradation in air and 47% was transported outside the EMEP grid.



**Figure 7.2.** Calculated mean annual air concentrations of lindane on 150x150 km<sup>2</sup> EMEP grid in Europe, ng/m<sup>3</sup>



**Figure 7.3.** Calculated total deposition of lindane on 150 x 150 km<sup>2</sup> EMEP grid in Europe, µg/m<sup>2</sup>/year

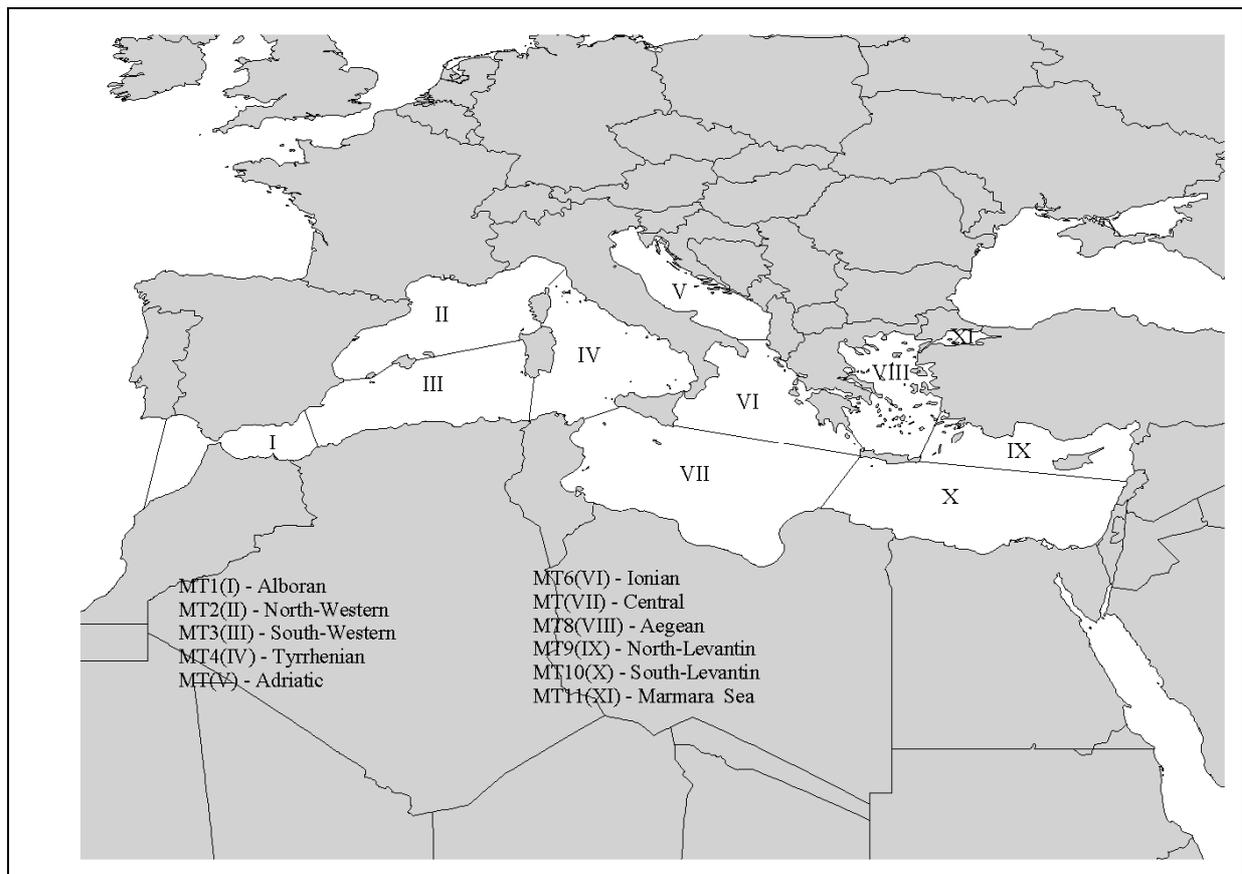


**Figure 7.4.** Mass balance of lindane after 10 years

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

Tables 7.1-7.4 and fig.7.6 present deposition on the Mediterranean subbasins: net dry deposition (table 7.1, fig.7.6A), wet deposition (table 7.2, fig.7.6B) and total deposition (table 7.3, fig.7.6C). Net dry deposition and its density imply an algebraic sum of dry deposition and re-emission from the underlying surface.

Net dry deposition and its density imply an algebraic sum of dry deposition and re-emission from the underlying surface.



**Figure 7.5.** MED-POL areas (data from UNEP, 1980)

**Table 7.1.** Lindane net dry deposition on the Mediterranean Sea and its subbasins, kg/yr

Subbasins	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	Mean
mt1	269	260	245	182	611	574	55	108	84	244	263
mt2	7401	6457	5457	3758	4932	6081	3593	3394	5280	3870	5022
mt3	4816	3265	3863	2662	4325	5376	1386	2624	2244	3306	3387
mt4	9856	5150	8770	4002	5961	6867	5645	4346	3672	5141	5941
mt5	5158	3612	4552	2541	3722	3374	3647	1967	3091	2560	3422
mt6	5423	3113	4601	3132	4087	3971	3715	3270	1535	3390	3624
mt7	12393	6217	9119	5674	7592	9217	7294	6588	2334	8546	7497
mt8	5934	4086	4259	3686	4398	4643	3538	2683	2581	3003	3881
mt9	3134	2308	2447	2204	2163	3258	1778	1256	1455	1892	2189
mt10	9586	5716	5849	6189	7437	9006	6933	5264	3436	5826	6524
mt11	841	831	654	557	525	688	472	395	757	574	629
Total	64812	41015	49815	34585	45754	53055	38057	31896	26468	38353	42381

**Table 7.2.** Lindane wet deposition on the Mediterranean Sea and its subbasins, kg/yr

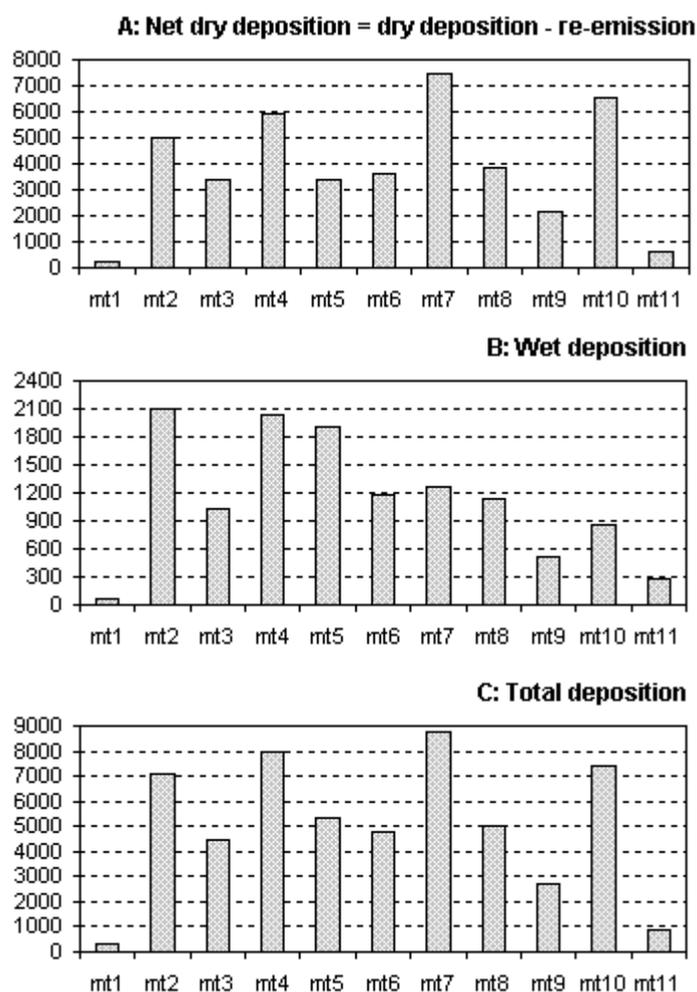
Subbasins	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	Mean
mt1	32	70	51	73	91	139	66	36	73	56	69
mt2	1819	2535	1645	1734	2691	2892	1611	1647	1956	2520	2105
mt3	907	949	764	879	1634	1718	737	790	605	1399	1038
mt4	2075	2029	1802	1549	2345	2131	1960	1678	1974	2886	2043
mt5	1742	1608	1927	1334	2620	1777	1713	1549	2611	2091	1897
mt6	1484	975	922	775	1160	1161	1750	1043	838	1756	1186
mt7	1783	918	1150	795	1022	1605	1548	1016	807	2036	1268
mt8	1267	1118	628	708	1196	1129	1287	977	1137	2004	1145
mt9	408	437	219	343	475	861	718	491	376	751	508
mt10	926	819	453	534	656	1090	1053	969	706	1441	865
mt11	252	271	181	205	278	289	279	211	405	343	271
Total	12695	11729	9743	8929	14169	14792	12721	10406	11488	17284	12396

**Table 7.3.** Lindane total deposition on the Mediterranean Sea and its subbasins, kg/yr

Subbasins	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	Mean
mt1	300	330	296	255	702	714	122	144	157	300	332
mt2	9220	8992	7102	5491	7622	8973	5204	5041	7236	6391	7127
mt3	5723	4214	4627	3541	5959	7094	2123	3414	2849	4706	4425
mt4	11931	7179	10572	5551	8306	8998	7606	6023	5646	8028	7984
mt5	6900	5220	6479	3875	6342	5151	5360	3516	5702	4650	5320
mt6	6907	4088	5523	3906	5247	5132	5465	4313	2373	5147	4810
mt7	14177	7135	10270	6469	8614	10822	8841	7604	3141	10582	8765
mt8	7201	5204	4887	4394	5594	5772	4825	3660	3718	5007	5026
mt9	3541	2745	2666	2547	2638	4119	2496	1747	1831	2642	2697
mt10	10512	6535	6302	6723	8094	10096	7986	6234	4142	7267	7389
mt11	1093	1102	835	761	803	977	750	606	1162	918	901
Total	77507	52744	59559	43514	59923	67847	50778	42301	37957	55637	54777

**Table 7.4.** Lindane deposition density for the Mediterranean Sea and its subbasins,  $\mu\text{g}/\text{m}^2/\text{yr} = \text{g}/\text{km}^2/\text{yr}$

Subbasins	Net dry deposition	Wet deposition	Total deposition
Mt1	3.06	0.80	3.85
Mt2	20.37	8.54	28.90
Mt3	9.03	2.77	11.80
Mt4	16.57	5.70	22.26
Mt5	24.81	13.75	38.57
Mt6	15.76	5.16	20.92
Mt7	8.82	1.49	10.31
Mt8	18.43	5.44	23.87
Mt9	12.52	2.90	15.43
Mt10	8.82	1.17	9.99
Mt11	22.93	9.89	32.82
Total	12.33	3.61	15.94



**Figure 7.6.** Lindane deposition onto MDT, kg/yr

As indicated in figures 7.6 the maximum net dry deposition and total deposition falls on MT7 (central Mediterranean) since the area of this subbasin is the largest one. Deposition on MT1

is lowest due to its small area and remote location. The area of MT2 is smaller than that of MT3 but dry deposition on MT2 is greater than on MT3 since MT2 is located nearer to the emission sources. The total input of lindane to the Mediterranean Sea due to net dry deposition is around 40 tons each year.

Maximum densities of dry and wet deposition are characteristic of subbasin MT5 (Adriatic), because of its nearest location to emission sources. The value of total deposition density onto MT5 is about  $40 \mu\text{g}/\text{m}^2/\text{year}$ . The average density of deposition onto Mediterranean Sea is  $12 \mu\text{g}/\text{m}^2/\text{year}$  for dry deposition,  $4 \mu\text{g}/\text{m}^2/\text{year}$  – for wet deposition, and  $16 \mu\text{g}/\text{m}^2/\text{year}$  – for total deposition.

As it is shown in tables 7.1-7.3 interannual variability of deposition for on a number of Mediterranean subbasins is considerable. For example, for MT1 (the Alboran Sea) the minimum value of total deposition is  $122 \text{ kg}/\text{yr}$  (1993) and the maximum value –  $714 \text{ kg}/\text{yr}$  (1992). To a certain extent it is probably connected with the interannual trend of the atmospheric transport direction.

Since lindane is applied mainly in spring and at the beginning of summer and its physical-chemical characteristics (especially Henry's constant) are strongly dependent on temperature seasonal variations of its concentrations and fluxes are essential. The pattern of these variations for the calculation period is shown in fig.7.7 and 7.8 as mean monthly concentrations in air and fluxes averaged separately for land and sea cells not only for the Mediterranean Sea but also over the whole grid.

Values of air concentration at the height of 50 m above the ground surface are presented in fig.7.7A and 7.8A (over land), in fig.7.7D and 7.8D (over sea); total gaseous flux is shown in fig.7.7B and 7.8B (over land) and 7.7E and 7.8E (over sea); wet deposition - in fig.7.7C and 7.8C (over land) and in fig.7.7F and 7.8F (over sea).

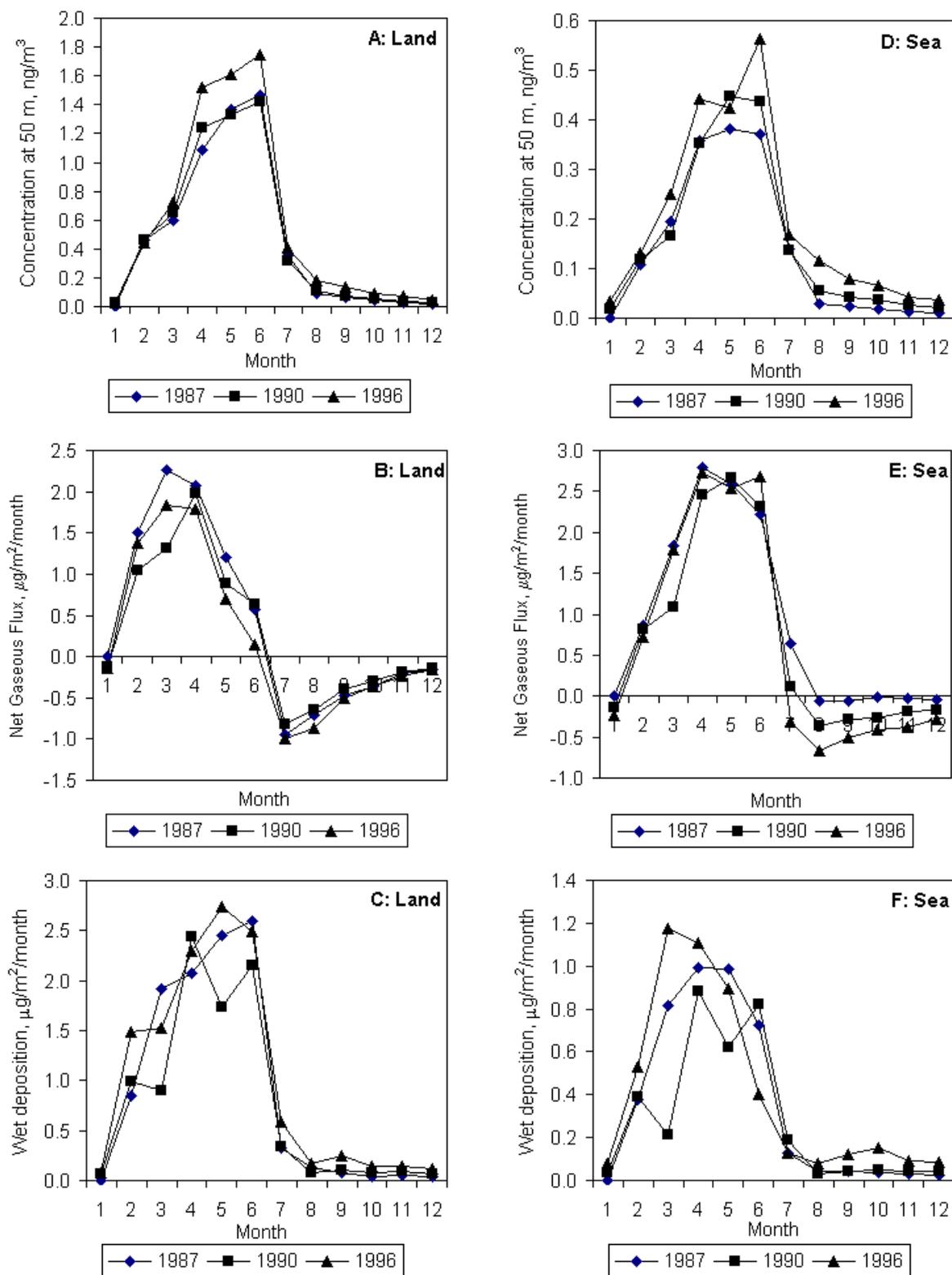
The plots demonstrate (A and D in fig.7.7 and 7.8) that lindane air concentration increases over land and sea up to June in compliance with the emission dynamics. Since June when emission is ceased the concentration rapidly decreases. By August-September concentration is two orders of magnitude lower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

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

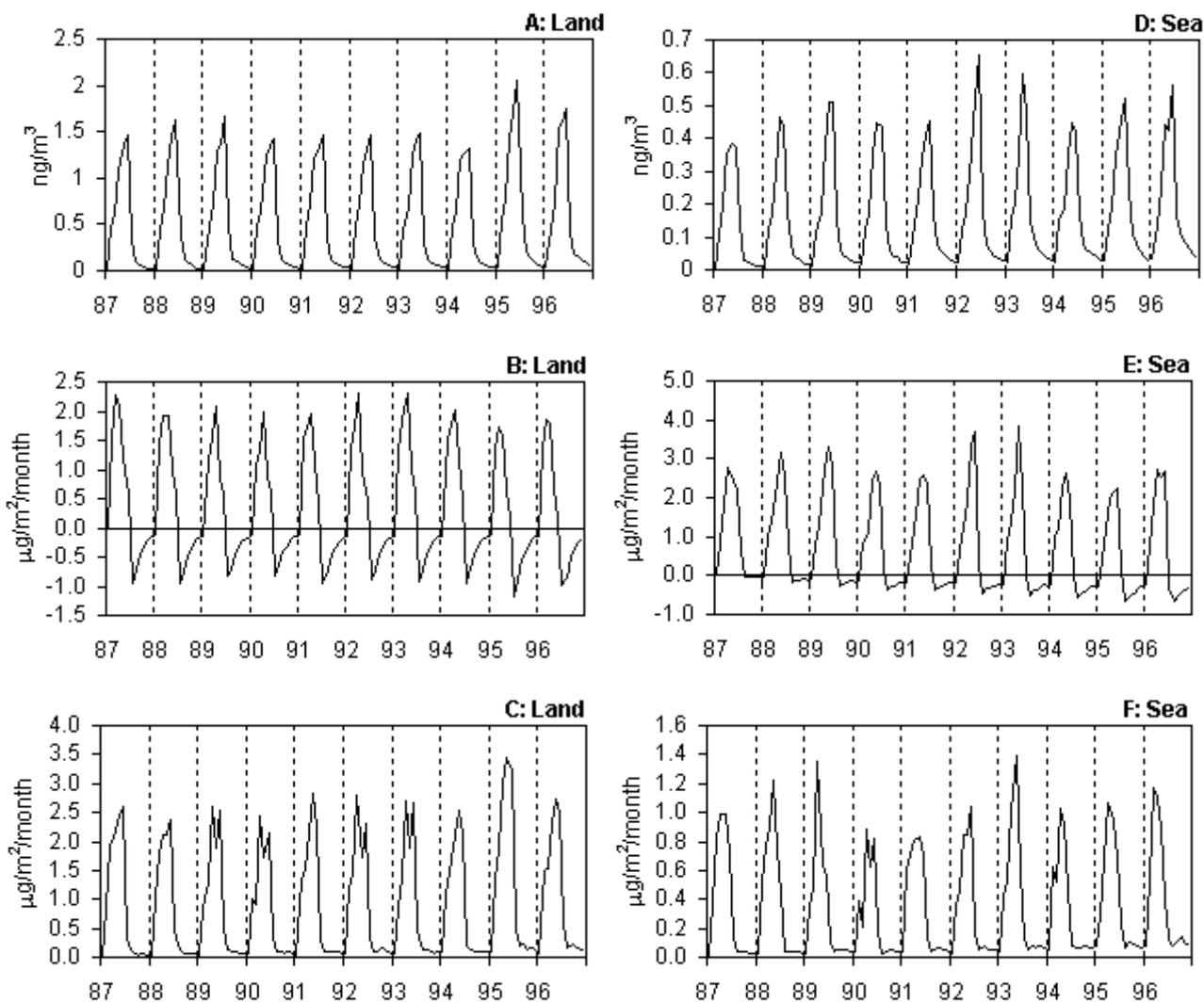
Distributions of net gaseous fluxes (B and E in fig.7.7 and 7.8) are most interesting, since these values are an algebraic sum of dry deposition and re-emission. As lindane is accumulated by the underlying surface re-emission becomes more significant, reducing the resulting flux from the atmosphere to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

Since re-emission from land exceeds that from the sea surface (for lindane) its effect is revealed earlier than the effect of marine re-emission, hence maximum net gaseous fluxes over land is reached not in May (as it could be expected) but in March-April (fig.7.7 and 7.8B). When sources stop emitting (beginning with July) net gaseous flux becomes negative, i.e. re-emission predominates and its maximum effect is observed in July-August. Then re-

emission decreases (but it is not zero) up to February next year when sources start to function.



**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

Over sea (fig.7.7 and 7.8E) the impact of re-emission is less during the first year of simulation. But from year to year the re-emission over sea becomes stronger due to accumulation of lindane in marine water. The maximum of re-emission from sea is reached in August.

A general pattern of concentrations and fluxes of lindane over the Mediterranean Sea is almost the same as for the whole sea part of EMEP grid shown on fig.7.7 and 7.8, though, on the average, values considered are 2-3 times higher over the Mediterranean Sea.

#### *Comparison with measurement data*

Measurements of lindane in the Mediterranean region are scarce. There are some measurements data for the Baltic and North Seas.

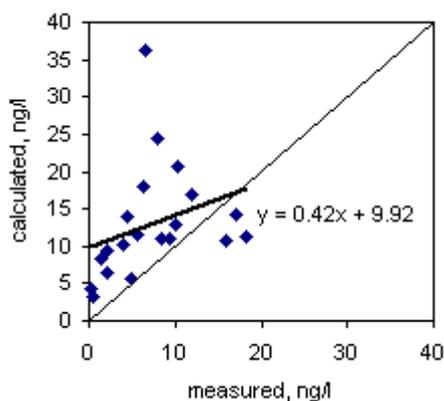
Fig.7.9 shows the comparison of calculated and measurement data of lindane in precipitation and fig. 7.10 represents the comparison of calculated and measured data of lindane

concentration in air. Mean values of measured (7.37 ng/l) and calculated (13.03) concentrations in precipitation are close. Correlation between measured and calculated values is 0.30. Mean value of simulated lindane concentration in air (234.08  $\text{pg}/\text{m}^3$ ) overestimates the measured one (41.25) by a factor of 5.7. Correlation between measured and calculated values is 0.48.

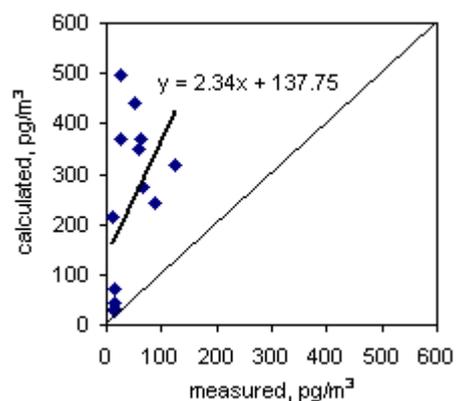
Lindane concentration in precipitation, ng/l

Lindane concentration in air,  $\text{pg}/\text{m}^3$

Station	Year	Measured	Calculated	Station	Year	Measured	Calculated
DE1	1990	4.54	13.96	IS91	1995	14.19	73.07
DE1	1992	18.22	11.26	NO42	1993	14.41	31.11
DE1	1993	9.28	10.97	NO42	1994	16.06	31.61
DE1	1995	6.32	17.91	NO42	1995	13.13	27.77
DE1	1996	10.38	20.79	NO42	1996	12.85	42.52
DK31	1990	16.98	14.32	NO99	1992	86.25	243.2
DK31	1991	11.91	16.92	NO99	1993	58.52	349.99
DK31	1992	15.82	10.71	NO99	1994	122.89	316.11
NO99	1991	4.05	10.28	NO99	1995	64.98	274.62
NO99	1992	5.02	5.60	NO99	1996	60.72	369.05
NO99	1993	8.45	11.11	FI96	1996	10.67	213.09
NO99	1994	9.98	12.87	SE2	1994	51.2	441.89
NO99	1995	5.54	11.64	SE2	1995	26.82	367.61
NO99	1996	8.01	24.31	SE2	1996	24.8	495.47
DE9	1995	6.52	36.16	Mean		41.25	234.08
IE2	1994	1.43	8.36	Correlation			0.48
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				



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

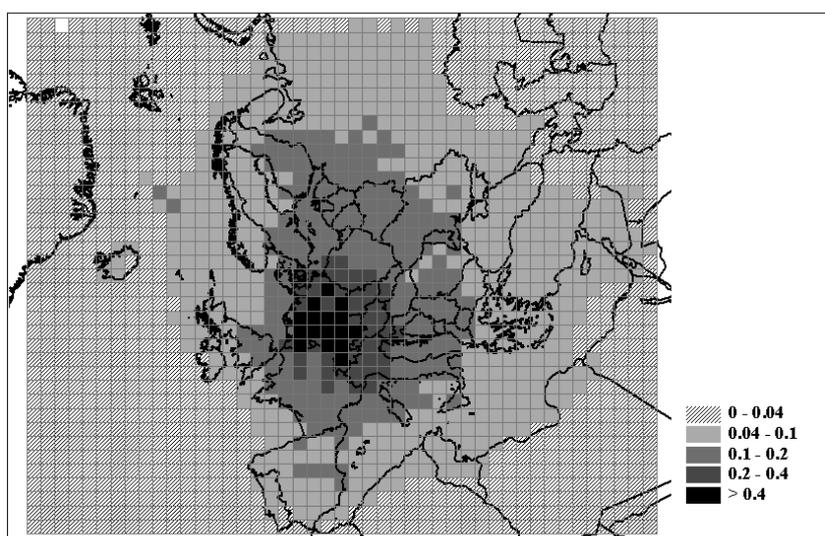


**Figure 7.10.** Lindane concentration in air,  $\text{pg}/\text{m}^3$  (comparison of measured data and calculated results)

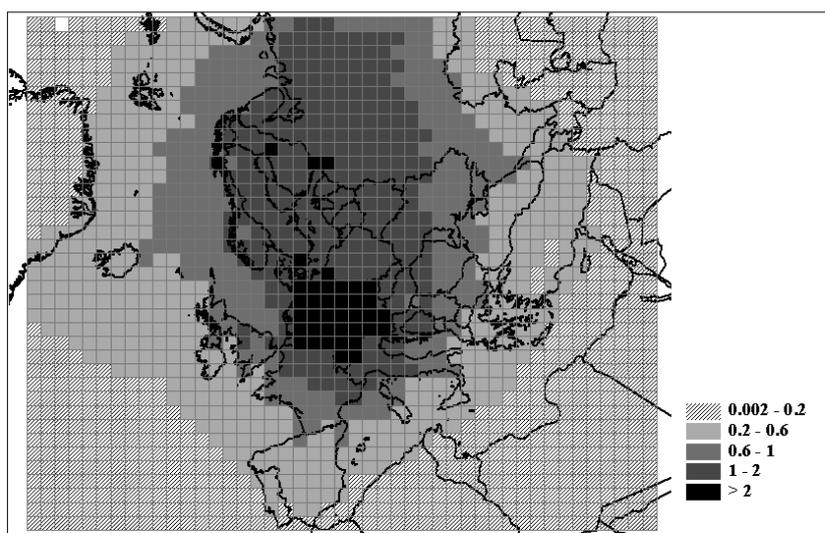
## 7.2. PCBs

PCB simulation was performed for the period of 10 years. Meteorological data for 1987-1996 were used. The model for PCB simulation was identical to that of 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 in the EMEP grid were used, not only that of PCB-153, 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.

PCB emission map is presented on the Figure 6.2 with the maximum of emissions in the center of Europe and total emission of 112 tons per year. Figures 7.11 and 7.12 represent calculated mean annual PCB concentration in air (1996),  $\text{ng/m}^3$ , and PCB total deposition density (averaged over 10 year),  $\mu\text{g/m}^2$  per year.



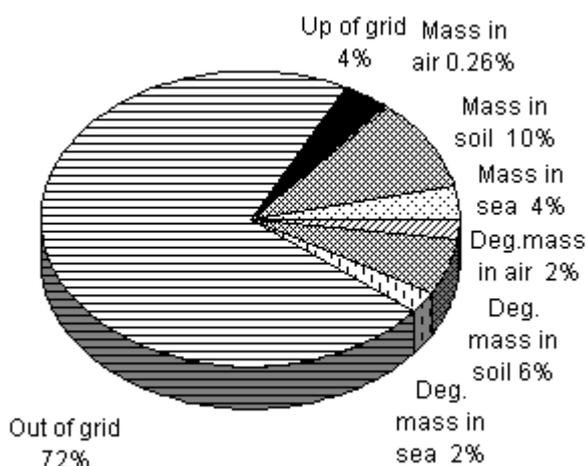
**Figure 7.11.** Calculated mean annual air concentrations of PCB on 150 x 150 km<sup>2</sup> EMEP grid in Europe,  $\text{ng/m}^3$



**Figure 7.12.** Calculated total deposition of PCB on 150 x 150 km<sup>2</sup> EMEP grid in Europe,  $\mu\text{g/m}^2/\text{year}$

Mean annual PCB concentration in air reaches its maximum ( $0.8 \text{ ng/m}^3$ ) in the center of Europe. Over the Mediterranean Sea mean annual concentration in air is about  $0.1 \text{ ng/m}^3$ . Maximum density of total deposition ( $5 \text{ } \mu\text{g/m}^2$  per year) is also connected with the center of Europe. Over the Mediterranean Sea total deposition density is about  $0.1 - 1 \text{ } \mu\text{g/m}^2$  per year.

During the calculation period about 1 ton of PCB (about 1% of annual PCB emission) deposited on the Mediterranean Sea each year.



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

remained and originated the source of further environmental contamination due to evaporation of PCB from sea surface.

Tables 7.5-7.8 and fig.7.14 present deposition on the Mediterranean subbasins: dry deposition (table 7.5, fig.7.14A), wet deposition (table 7.6, fig.7.14B) and total deposition (table 7.7, fig.7.14C). Dry deposition is an algebraic sum of dry deposition (gaseous and aerosol phase) and re-emission from the underlying surface (gaseous phase). Due to high values of the Henry's law constant PCBs are evaporated from water to air more intensively than lindane. That is why PCB dry deposition fluxes are sometimes negative (see table 7.5).

Figure 7.14 shows input of PCB into each subbasins, t/yr. Averaging is made over 10 years. The distribution of the inputs with the subbasins is similar to that of lindane (figure 7.6). The averaged density of dry, wet and total deposition onto each subbasin is shown in table 7.8. As for lindane, 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 concentration of PCB over continent (7.15A, 7.16A) and over sea (7.15E, 7.16E); of net gaseous flux over continent (7.15B, 7.16B) and over sea (7.15F, 7.16F); of dry deposition flux of aerosol bounded PCB over continent (7.15C, 7.16C) and over sea (7.15G, 7.16G); and of wet deposition flux over continent (7.15D, 7.16D) and over sea (7.15H, 7.16H). Concentrations in air are measured in  $\text{ng/m}^3$ , and fluxes – in  $\mu\text{g/m}^2/\text{month}$ .

Figure 7.15 shows listed values for 3 chosen years and figure 7.16 shows 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

Fig.7.13 presents the budget of PCBs within the EMEP region after 10 years. Input to soil is 16% (6% was degraded in the soil and 10% - 112 tons were retained in soil after 10 years). Input to sea was about 6% (2% was degraded inside the sea and 4% - 40 tons were remained in sea after 10 years). 2% of PCBs was degraded in the air and 76% of PCBs were transported outside the EMEP grid.

Input to the Mediterranean Sea due to dry and wet deposition from air amounts to 11 tons for 10 years. Some part of this amount (1/3) was degraded in sea but 7 tons

figures 7.15 and 7.16 are connected with seasonal variations of meteorological parameters, mainly with temperature.

**Table 7.5.** PCB dry deposition on the Mediterranean Sea and its subbasins, kg/yr.

Subbasins	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	Mean
mt1	16.5	6.3	-9.3	20.5	-1.4	1.3	3.4	0.8	-3.2	11.4	4.6
mt2	216.2	56.0	-4.9	108.4	-13.1	24.2	55.6	0.9	46.1	40.9	53.0
mt3	156.6	76.8	-50.6	137.2	-14.2	1.0	45.9	11.1	-20.6	66.2	40.9
mt4	238.3	104.4	-10.3	93.5	21.6	-49.5	75.8	24.3	-0.5	59.7	55.7
mt5	116.5	41.9	-6.9	37.6	10.7	-10.3	22.2	14.4	25.9	62.0	31.4
mt6	117.0	27.8	7.8	46.1	12.2	-32.8	17.5	35.5	-11.1	42.1	26.2
mt7	235.5	180.2	-82.6	104.6	97.0	-99.1	16.5	122.5	-56.1	100.2	61.9
mt8	70.9	28.4	6.8	17.1	14.3	-2.4	-1.3	29.5	-0.3	24.3	18.7
mt9	47.9	25.6	-2.9	10.6	23.4	-3.8	-22.6	22.5	7.8	10.8	11.9
mt10	161.5	100.8	-39.3	11.2	102.5	-24.8	-41.1	92.5	-33.9	62.5	39.2
mt11	11.4	5.1	0.9	1.7	2.5	0.1	-0.2	5.9	3.6	1.0	3.2
Total	1388.2	653.3	-191.4	588.5	255.3	-196.0	171.6	359.9	-42.3	481.2	346.8

**Table 7.6.** PCB wet deposition on the Mediterranean Sea and its subbasins, kg/yr.

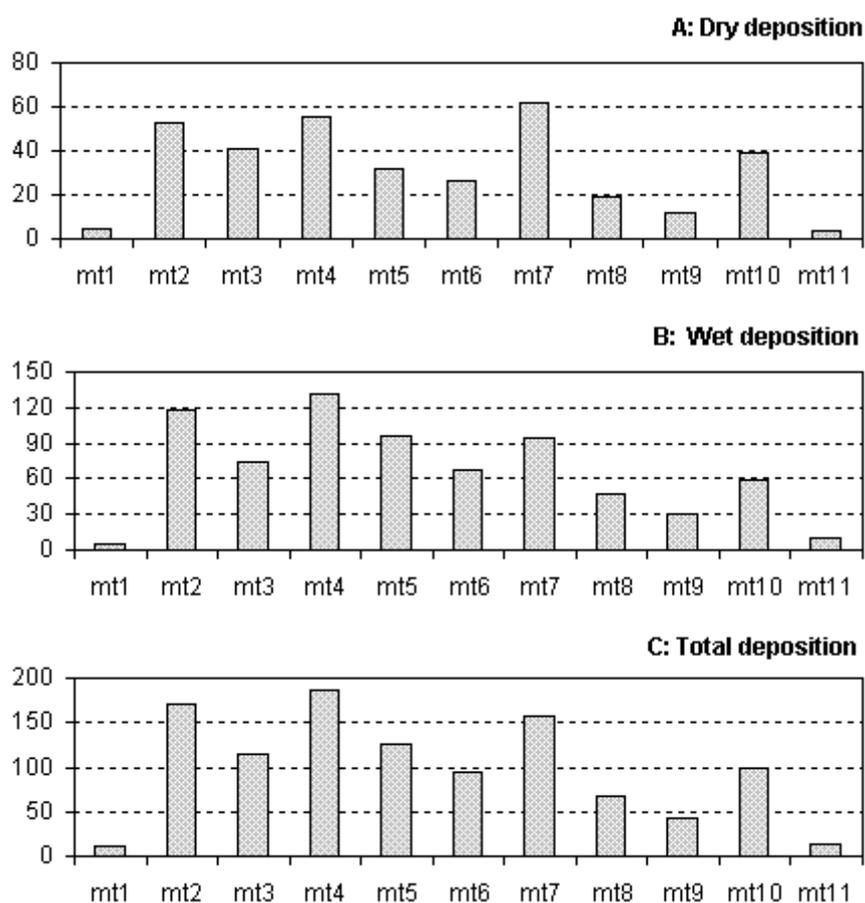
Subbasins	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	Mean
mt1	5.2	5.0	4.6	7.1	7.5	8.7	4.9	3.0	5.0	6.3	5.7
mt2	148.5	103.7	82.2	83.0	124.3	143.3	136.1	88.9	113.1	149.4	117.3
mt3	76.7	59.5	55.9	65.9	90.4	89.9	82.0	47.7	55.3	120.5	74.4
mt4	152.6	148.1	106.9	95.7	133.8	102.5	135.5	86.6	132.6	220.3	131.5
mt5	98.3	94.6	76.4	84.2	110.6	67.1	85.3	65.7	119.2	153.5	95.5
mt6	75.1	88.8	51.6	50.0	68.5	46.3	88.4	58.5	51.7	98.9	67.8
mt7	106.4	98.4	90.7	67.7	101.1	92.9	101.1	68.7	63.2	160.7	95.1
mt8	44.1	66.3	27.2	30.9	43.9	33.1	46.1	44.7	78.1	65.5	48.0
mt9	19.7	30.6	18.8	17.8	40.7	45.2	27.7	32.9	27.4	48.8	31.0
mt10	48.2	80.4	43.3	34.9	61.5	64.4	49.9	64.2	41.8	104.7	59.3
mt11	6.9	11.2	6.1	7.1	8.4	6.9	8.0	7.9	20.4	11.9	9.5
Total	781.7	786.6	563.6	544.5	790.8	700.5	764.9	568.8	707.8	1140.5	735.0

**Table 7.7.** PCB total deposition on the Mediterranean Sea and its subbasins, kg/yr.

Subbasins	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	Mean
mt1	21.7	11.4	-4.8	27.7	6.1	10.0	8.2	3.8	1.8	17.7	10.4
mt2	364.7	159.7	77.3	191.4	111.2	167.6	191.7	89.7	159.2	190.4	170.3
mt3	233.3	136.3	5.2	203.1	76.1	90.9	127.9	58.8	34.7	186.7	115.3
mt4	390.9	252.5	96.6	189.3	155.4	53.0	211.3	110.9	132.2	280.0	187.2
mt5	214.8	136.4	69.5	121.8	121.2	56.9	107.4	80.1	145.1	215.5	126.9
mt6	192.1	116.6	59.4	96.0	80.6	13.5	105.9	94.0	40.7	141.0	94.0
mt7	341.8	278.6	8.1	172.3	198.1	-6.2	117.6	191.2	7.1	260.9	157.0
mt8	115.0	94.8	34.0	48.0	58.2	30.8	44.9	74.2	77.8	89.8	66.7
mt9	67.6	56.3	15.9	28.4	64.2	41.4	5.1	55.4	35.2	59.6	42.9
mt10	209.7	181.2	4.0	46.1	163.9	39.6	8.8	156.7	7.9	167.1	98.5
mt11	18.3	16.2	7.0	8.9	11.0	7.1	7.8	13.9	23.9	12.9	12.7
Total	2170.0	1439.9	372.2	1133.0	1046.1	504.5	936.5	928.7	665.5	1621.7	1081.8

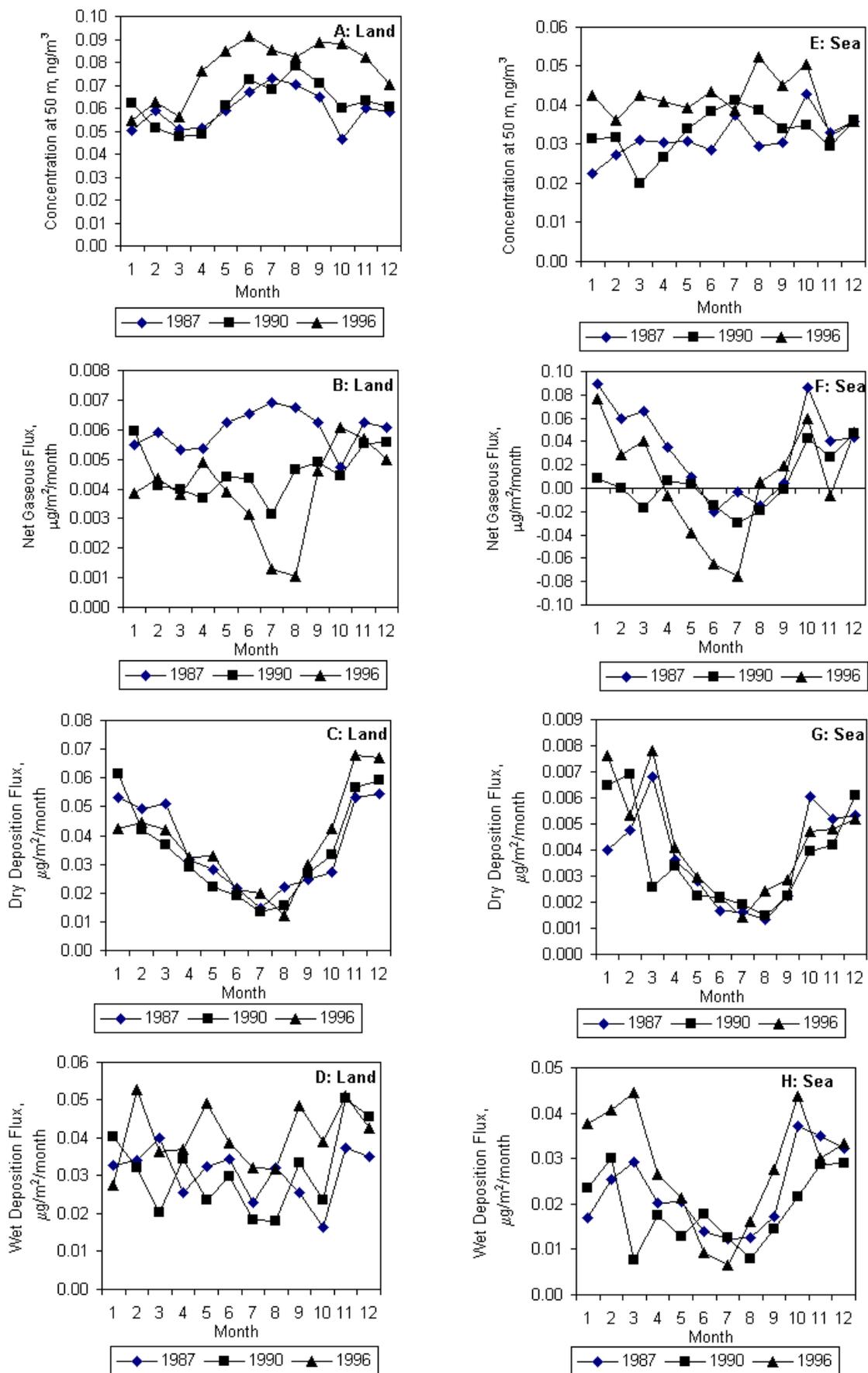
**Table 7.8** PCB deposition density on the Mediterranean Sea and its subbasins,  $\mu\text{g}/\text{m}^2/\text{yr} = \text{g}/\text{km}^2/\text{yr}$

Subbasins	Net dry deposition	Wet deposition	Total deposition
mt1	0.054	0.067	0.120
mt2	0.215	0.475	0.691
mt3	0.109	0.198	0.308
mt4	0.155	0.367	0.522
mt5	0.228	0.692	0.920
mt6	0.114	0.295	0.409
mt7	0.073	0.112	0.185
mt8	0.089	0.228	0.317
mt9	0.068	0.177	0.245
mt10	0.053	0.080	0.133
mt11	0.117	0.346	0.462
Total	0.101	0.214	0.315

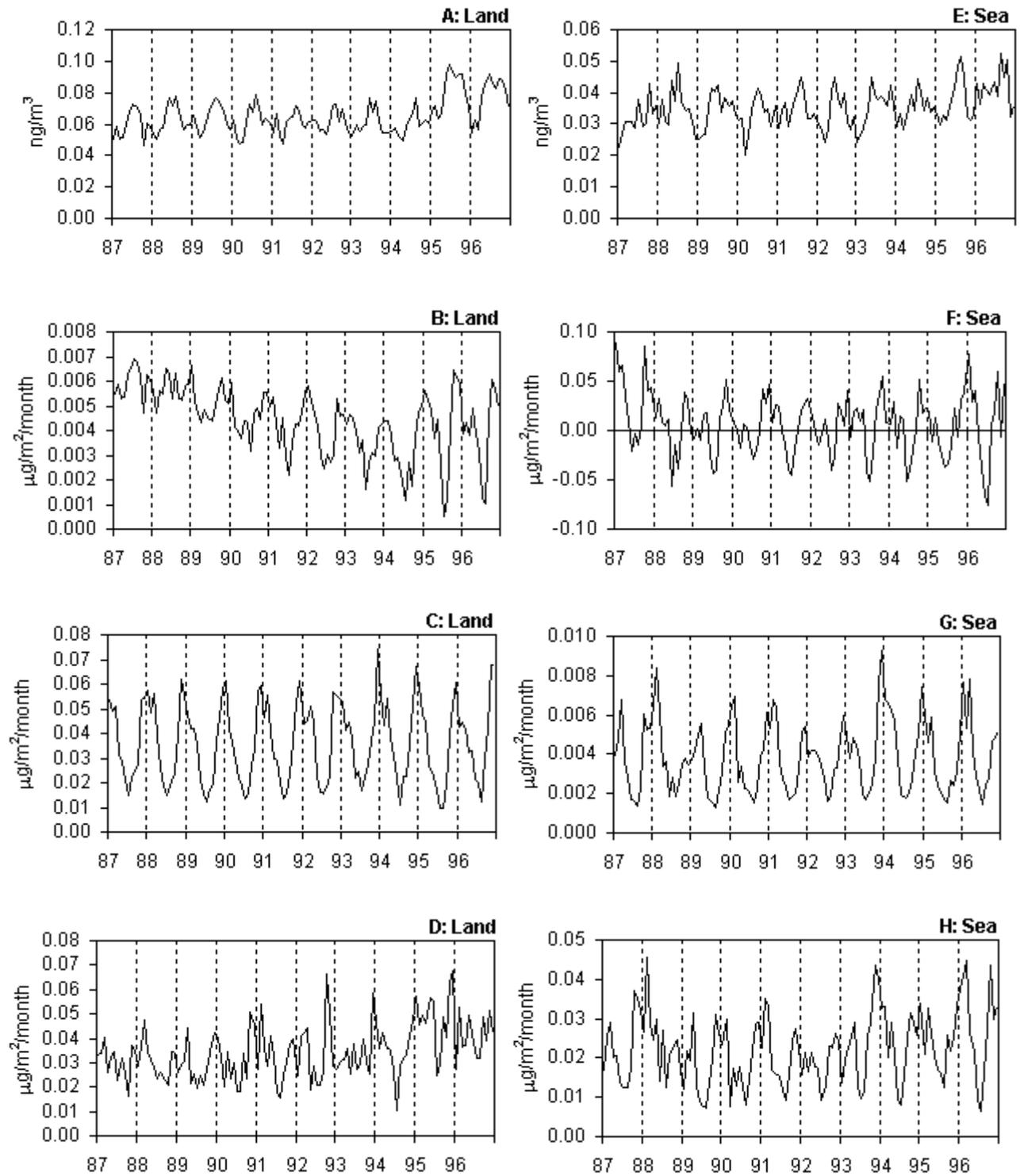


**Figure 7.14.** PCB deposition onto MDT, kg/yr

For example, dry deposition flux of the aerosol phase decreases in summer and increases in winter because at high temperatures PCB-153 exists in air mainly in the gas-phase and at low temperatures – mainly in the aerosol phase. Net gaseous flux over sea becomes negative in summer because at high temperatures Henry's law constant increases and PCB is evaporated from 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



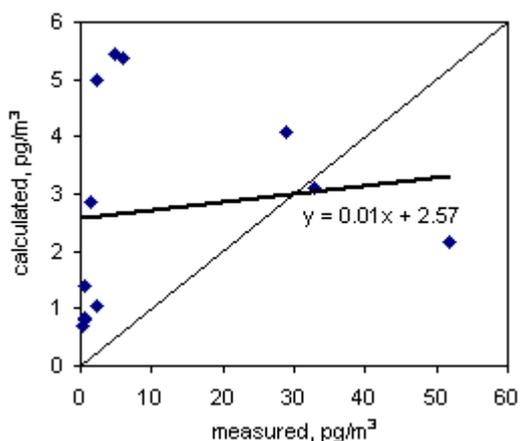
**Figure 7.16.** Monthly averaged air concentration (A and E), monthly net gaseous flux (B and F), monthly aerosol phase dry deposition flux (C and G) and wet deposition (D and H) of PCBs

### Comparison with measurement data

For the comparison with modelling results measurement data on PCB-153 were used. Modelling results of total PCB were recalculated for PCB-153 using coefficient 0.04 (expert estimates of PCB-153 fraction in the total PCB emission).

Fig.7.17 shows the comparison of calculated and measured data of PCB in air,  $\text{pg}/\text{m}^3$ . Calculated values of PCB-153 air concentrations are 4 times less than measured ones.

Station	Year	Measured, $\text{pg}/\text{m}^3$	Calculated, $\text{pg}/\text{m}^3$
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



Concentrations in precipitation are available only for 2 stations: DE9 (1996), and IS91 (1995, 1996). Wet deposition is available at 4 stations, which are listed below along with measured and calculated wet deposition values,  $\text{ng}/\text{m}^2/\text{year}$ :

**Figure 7.17.** PCB-153 concentration in air,  $\text{pg}/\text{m}^3$  (comparison of measured data and calculated results)

Station code	Year	Measured, $\text{ng}/\text{m}^2/\text{year}$	Calculated, $\text{ng}/\text{m}^2/\text{year}$
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

Calculated values of PCB-153 concentrations in precipitation are 3 times less than measured ones.

## Chapter 8. CONCLUSIONS

1. Physical-chemical properties of lindane, PCB, B(a)P, HCB available in literature are summarized in this paper. It should be noted that estimates of a number of parameters vary within a wide range leading to uncertainties in calculations.
2. There are scarce official data on emissions from Mediterranean countries. In this study a wide spectrum of expert estimates of emission is presented. In calculation assessments of TNO (UBA project) were used.
3. The analysis of measurements indicated their paucity for MDT and they are of a campaign character. In this connection available data for Europe and other regions were used.
4. For the evaluation of the Mediterranean pollution by lindane and PCBs 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 dependent on temperature and aerosol concentration in air.
5. Calculation results of lindane concentrations in air and in precipitation are in a reasonable agreement with available measurements carried out on a regular basis in Europe.
6. On the basis of calculation results it can be concluded that:
  - Lindane deposition on the Mediterranean Sea is about 4% of total European emission;
  - PCB deposition on the Mediterranean Sea is about 1% of total European emission;
  - Mean annual air concentration of lindane over the Mediterranean Sea is about  $0.5 \text{ ng/m}^3$ , and of PCBs –  $0.1 \text{ ng/m}^3$ .
  - Total (dry and wet) deposition density of lindane over Mediterranean Sea is about  $16 \text{ } \mu\text{g/m}^2$  per year, and of PCBs –  $0.3 \text{ } \mu\text{g/m}^2$  per year.
  - Maximum depositions are obtained for the northern coastal region of the Mediterranean: subbasins MT5, MT2, MT8, MT4, MT6.
7. Countries of the Mediterranean region make a considerable contribution to the deposition on the Mediterranean Sea.
8. The analysis of 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 lindane and PCB deposition on the subbasins, which are probably connected with a variability of meteorological situation.

9. The marine compartment to a considerable degree accumulates POPs and after accumulation re-emits POPs back to the atmosphere. The ability to re-emission from sea to air of PCBs exceeds that of lindane.
10. Comparison with experimental data shows that the model needs to be further improved namely:
  - Improvement of the emission data;
  - Improvement the modelling of the removal processes from the atmosphere to underlying surface. These processes are: gas exchange with the surface, dry deposition of particle bounded POPs onto the surface, precipitation scavenging of gas and aerosol phases of POPs, degradation in air;
  - Consideration of processes which are not included the model, namely POP absorption by plants, sedimentation inside sea bodies, runoff from watershed;
  - More accurate parameterization of physical-chemical properties.

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