

# Persistent, ecotoxic, and bioaccumulative compounds and their possible environmental effects

Karlheinz Ballschmiter

*University of Ulm, Department of Analytical and Environmental Chemistry, Albert-Einstein-Allee 11 D-89069 Ulm*

**Abstract:** The relationship between physico-chemical properties, environmental distribution and effects of organochlorine compounds as a major class of persistent organic pollutants (POPs) are discussed. The environmental fate of a compound includes its transport and dispersion in the environment as well as its accumulation and transformation in defined environmental compartments. Accumulation and transformation as the result of environmental distribution may have long-term consequences; this is indicated by the ultimate accumulation and long-term bioactivity of several widely spread organochlorines, and is clearly evident in the decomposition of chlorofluorocarbons in the stratosphere.

Depending on the order of trophic levels biomagnification factors of 10 000 up to 100 000 are encountered for persistent semivolatile organochlorines like 4,4'-DDE, PCB congeners or some Toxaphene constituents. Mammals show intra-species pollutant transfer during the lactation period. While the mother animal is partly depleting its body burden the calve accumulates in a critical period of its life via the milk a concentrated input of persistent organochlorines. A similar depletion phenomenon is also found for fish and crustacean which enrich in the eggs a substantial part of the accumulated body burden of the female.

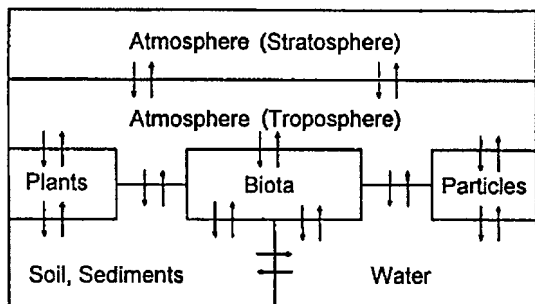
The air skimming of semivolatiles by plant surfaces leads to surprisingly high levels of pollutants in the upper soil layers of forests that otherwise would be considered pristine in terms of human activities.

## ENVIRONMENTAL DISTRIBUTION

The role of chemistry in the environment of our soon-to-be global industrial society increasingly requires, besides a regional discussion, a global and long term perspective for the evaluation of the input, transport, transformation, and accumulation of chemical compounds in the environment. Where do organics go when they apparently disappear with the air of the wind or the water of the rivers?

This chapter emphasizes the relationship between physico-chemical properties, environmental distribution and effects of organochlorine compounds as a major class of persistent organic pollutants (POPs). Mainly, it focusses on the atmospheric transport and the marine pollution from land based sources. As an important environmental effect the magnification of persistent compounds in the food chain is discussed. Bioaccumulation has to be considered as a most critical starting point for long term ecotoxicological effects. General toxicology defines the toxicity of a single compound in terms of a quantal dose-response relationship for a single biological system or a specific animal (like rat or man). In contrast to this, ecotoxicology widens the definition of targets for adverse effects of chemicals from microorganisms to whole ecosystems and the interactions therein. The problem remains to distinguish the not always short term effects of natural stress factors like drought, floods, or temperature extremes from the long term effects of low doses of mixtures of chemicals as they are constantly encountered in the environment. Therefore, bioaccumulation or biomagnification can be most relevant for long term effects, as it increases critical concentrations at possibly sensitive target areas.

The global fate of a compound includes the transport and general dispersion as well as its accumulation as the result of equilibria (Fig. 1) and its transformation in defined environmental compartments. Accumulation and transformation as the result of environmental distribution may have long-term consequences;



**Fig. 1** Model of a local, regional or global multiphase distribution of an environmental chemical. The preference for one of the four major compartment is called geo-, bio- aquo- or aero-accumulation. For transport in the atmosphere and the hydrosphere, equilibria with the respective particulate phase play an important role.

this is indicated by the ultimate accumulation and long-term bioactivity of polychlorobiphenyls and analogous compounds in marine mammals and the deep-sea fauna, and is clearly evident in the decomposition of chlorofluorocarbons in the stratosphere.

The overall residence time  $t_{i, \text{total}}$  of a compound  $i$  in an environmental compartment (atmosphere, surface water, sediment or biota) is controlled by the process with the shortest specific residence time  $t_{i1}$ ,  $t_{i2}$  or highest output rate. In reality, the overall residence time of a compound can only be partly split into specific residence times. However, in most cases one can calculate the output of a compound as the sum of physical (transportation) and chemical processes (transformation) (eqn 1):

$$\text{output} = 1/t_{i, \text{total}} = 1/t_{\text{phys}} + 1/t_{\text{chem}} \quad [1]$$

Studies of the environmental distribution of organic molecules have to include both the stability of the respective compound and its physical chemical properties, and secondly the dependence of the spreading of the compounds in air and water as dictated by the general circulation in the troposphere or the surface and deep sea currents of the oceans.

The atmospheric deposition of organochlorine contaminants to the Arctic originating from the lower latitudes of the Eurasian continent has been estimated by Cotham & Bidleman [1]. Particularly in winter, due to the Siberian high pressure region a south to north flow pattern is encountered in the lower troposphere, which transports air from the Eurasian continent directly to the Arctic. The general aspects of the transport and the fate of organic molecules in the global environment have recently been reviewed [2–5].

### Modeling of environmental multiphase distribution

The fugacity concept of Mackay (i.e. generalizing the physical-chemical properties of a compound) is a valuable tool for predicting and understanding a multiphase distribution of a specific compound or of sets of specific compound parameters [6]. Table 1 summarizes as a general example compounds of changing preferences of the four basic environmental compartments (air, water, soil, and biota).

An extended collection of specific data in multiphase distribution, including organochlorines like chlorobenzenes, polychlorinated biphenyls, dibenzofurans, dibenzo-*p*-dioxins, and several volatile chlorinated and brominated C1-C4-hydrocarbons, is given by Mackay in three monographies [7].

Recent studies indicate how the temperature regulates the concentrations of semivolatile organic compounds (SOCs) in the lower troposphere by influencing the equilibrium between air and surface ocean water [8,9] or between air and the complex surface of leaves/needles/soil/rocks of the continents [10–15]. Wania & Mackay have forwarded a global model that consists of nine meridional segments, each subdivided into four environmental compartments, which includes the temperature dependence of the multiphase distribution as a major parameter [16].

### Environmental distribution: What does it depend on in reality?

Modeling of the environmental fate will never be able to describe the regional heterogeneity of the real world; its strength is the prediction of a generalized scenario. What are the factors which describe the reality?

The molecular parameters of environmental distribution in the real world are:

- production amounts (regional, global);
- composition of technical mixtures;
- water solubility and vapor pressure;
- distribution coefficients:  $K_{\text{gas/water}}$ ,  $K_{\text{gas/octanol}}$ ,  $K_{\text{octanol/water}}$ ;
- $K_{\text{oc}}$  for the adsorption on sediments, air/particle distribution in air;

**Table 1** Multiphase equilibrium distribution (Level I).

	Air	Mass % water	Solids	Distribution category
CCl <sub>4</sub>	99.80	0.19	0.02	A
CCl <sub>2</sub> =CCl <sub>2</sub>	99.45	0.40	0.15	A
Hexachlorobutadiene	78.02	2.06	19.93	AS
Pentachlorobenzene	48.10	2.10	49.81	AS
HCB	10.11	0.39	89.50	AS
<i>p,p'</i> -DDT	0.40	0.42	99.18	S
alpha-HCH	0.28	50.67	49.05	WS
beta-HCH	0.00	50.81	49.19	WS
gamma-HCH	0.58	47.66	51.76	WS
Phthalates:				
Diethyl-	1.50	95.94	2.55	W
Di- <i>n</i> -butyl-	0.38	9.52	90.1	WS
Di-(2-ethyl-hexyl)-	1.62	4.74	93.65	S
Atrazin	0.01	93.15	6.84	W
Nitrobenzene	30.49	68.04	1.47	AW
3,4-Dichloroaniline	37.07	46.84	16.09	AWS

A = air; W = water; S = solid (sediment, surface, biota); HCB = Hexachlorobenzene; HCH = Hexachlorocyclohexane.

- according to the Junge–Pankow equation;
- stability towards air and water chemistry:  $\cdot\text{OH}/\cdot\text{NO}_3/\cdot\text{O}_2\text{H}/\text{O}_3$ ; hv;  $\text{H}_2\text{O}/\text{H}^+$ ;
- stability towards biotic chemistry: microbial transformation;
- microbial degradation, specific transformation in insects, fish, birds and mammals;
- isomer-specific and even enantiomer-specific regulation of transformation reactions.

The environmental parameters that are relevant to the environmental fate of a compound are:

- sources: point sources, nonpoint sources, general use, transport routes;
- dedicated spatial and temporal applications in health care, plant protection, and animal care;
- global mass flow: atmosphere: general circulation, interhemispheric crossing;
- oceanic system: surface currents, and subsurface currents;
- environmental exchange processes;
- water surface  $\leftrightarrow$  air; gasphase  $\leftrightarrow$  particulates; soil/leave surfaces  $\leftrightarrow$  air;
- particulate organic matter (POM)  $\leftrightarrow$  water;
- accumulation in biota (fish, birds, mammals, and man) and;
- abiotic compartments (stratosphere; sediments).
- multimedia distribution in general.

If, not only the products with highest stability and high annual production are to be investigated one has to be absolutely aware that only methods of extreme trace organic analysis (in terms of sensitivity and selectivity) can elucidate the global spreading organics. The necessary tools have been developed and are used by the analytical environmental chemists.

## Transport and accumulation in the environment

The apparent disappearance of stable chlorinated organic compounds during their transport in the mass flow of the atmosphere and the hydrosphere can be categorized into general transport pathways and into equilibria in the multiphase system of the environment that consists of atmosphere, oceans, ice cover, land and plant surfaces, and biota. The global transport in the atmosphere is given by winds, areas of descending air (high pressure, anticyclones) and ascending air in low atmospheric pressure regions (cyclones), and in the hydrosphere by rivers, circulation of water in lakes, and surface and subsurface currents in the oceans

[3]. These mass flows would account solely for the spreading of organic compounds if they were indefinitely stable and molecularly distributed in air and water. For most organic compounds the ultimate environmental fate is however, determined by complex sorption/desorption processes on finely dispersed particle phases in the air (aerosols) and water environment (detritus, marine snow), as well as by abiotic and biotic transformations [3–5].

In more specific terms: final distribution is regulated by the interaction of physical-chemical properties of a compound, and properties of the media of the global mass flow in the atmosphere, the global oceanic system, and the food webs. The general trend towards dispersion is partly counteracted by accumulation in preferred environments. We clearly observe aero-accumulation, aquo-accumulation, geo-accumulation, and—which may be most important—bio-accumulation. Each type of enrichment is depending on the physical-chemical properties of the specific xenobiotic.

A rather defined preference of a global environmental compartment for the volatile organochlorines is the atmosphere. A similar preference is found for the semivolatiles in the lipophilic phase of biota and by their adsorption to surfaces. Compounds like the chlorobenzenes and the hexachlorocyclohexanes give a much more differentiated behavior in terms of distribution (Table 1).

The complexity of environmental pollution emerging from the mixing and separation processes which are possible in the environment is further compounded by the wide range of physico-chemical and chemical properties of the many compounds that can be regarded as chlorinated xenobiotics. These range from the halomethanes to the  $C_{25}$  chlorinated paraffins. Classical tracers in terms of specific aspects of global distribution are, among others, the chlorinated ethanes and ethenes [17], the hexachlorocyclohexane isomers [18–20], and the polychlorinated biphenyls [9,19,21–25], respectively.

An ideal region to study equilibria between the atmosphere and the ocean water in a global scale is a meridional transect through an ocean. The land masses of the northern hemisphere act, for most of the VOCs and the SOCs, as a source while the oceans, particularly of the southern hemisphere, more or less function as a dilution and equilibration space for the overspill of VOCs and SOCs from the northern hemisphere.

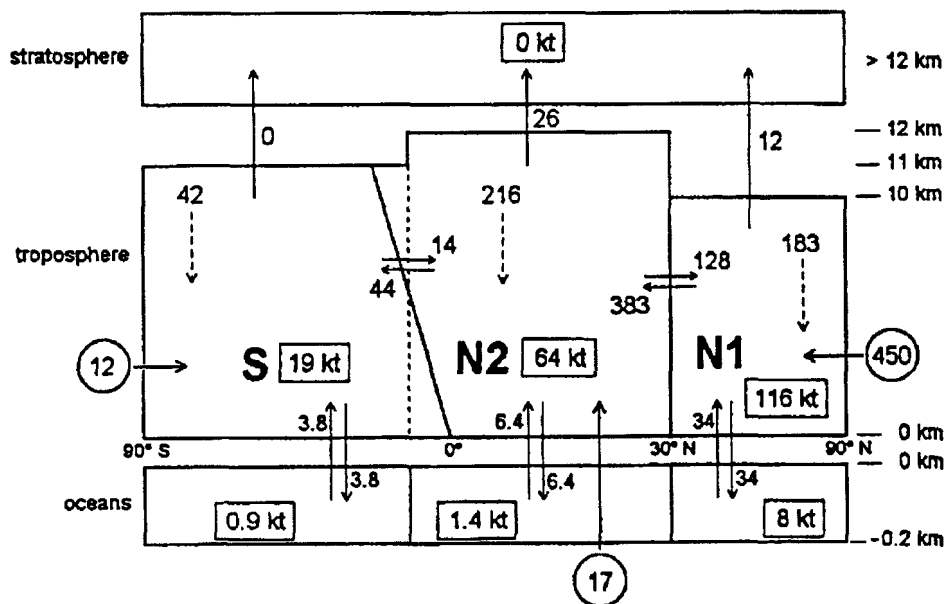


Fig. 2 Estimations of global mass flow of tetrachloroethene based on global analytical measurements and a three box model for the atmosphere. All mass flow figures are given in kt/year; standing burdens of tetrachloroethene in the atmosphere and the oceanic system are given as marked in kt. The basis of the model is the world production of tetrachlorethene in the year 1988.

**Table 2** Compounds similar to PCBs in environmental fate

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Polychlorinated diphenylethers (PCDE – 209 congeners)
Polychlorinated naphthalines (PCN – 75 congeners)
Polychlorinated arenes (Phenanthrenes, Pyrenes, ...)
Polychlorinated dibenzofuranes (PCDF – 135 congeners)
Polychlorinated dibenzothiophenes (PCTP – 135 congeners)
Polychlorinated dibenzo-p-dioxins (PCDD – 75 congeners)
Polychlorinated phenoxathiines (PCOT 75 congeners)
Polychlorinated thianthrenes (PCTT 75 congeners)
Polychlorinated benzo-naphthofuranes (PCBNF)
including the bromo-chloro- and bromo- congeners of the above groups as well as methyl-substituted congeners
Chlorinated benzenes
Chlorinated paraffines (C12 – C30)
Chlorinated triphenylmethanes
Tetrachlorobenzyltoluenes (Ugilec) (TCBT – 96 isomers)
Chlorinated diphenylethanes (DDT-group)
Chlorinated pesticides and their metabolites: toxaphene, chlordanes-group, endosulfane, and others.
Halogenated phenyl-methyl ethers (biogenic source)

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## ENVIRONMENTAL FATE OF ORGANOCHLORINES

### Tetrachloroethene (C<sub>2</sub>Cl<sub>4</sub>) as a model compound

The modeling of the multiphase distribution of tetrachloroethene predicts a presence in the air of 99.45% (Table 1). The output of tetrachloroethene from the atmosphere is mainly a result of its reaction with OH radicals, leading to reaction products like trichloroacetic acid and hydrochloric acid with phosgen as an intermediate. Only by considering the all of the chemical reactions and products one comes to the necessary comprehensive assessment of the environmental fate of a compound. The discussion of the environmental fate has to include the final chemical fate.

By combining the measurements of its environmental concentration on a global scale with the reactivities and transport in a three box model of the atmosphere that approximates the general circulation in the troposphere, can lead to a modeling of the global spreading of the semistable tetrachloroethene [17]. Figure 2 summarizes the results of this approach. It can easily be extended to other volatiles if the respective analytical data are collected.

### PCBs (C<sub>12</sub>H<sub>10-x</sub>Cl<sub>x</sub>) as model compounds

Polychlorinated biphenyls (PCBs) can be considered as classical model compounds for the group of semivolatiles in global environmental chemistry. The global occurrence is well established in the troposphere, and in ocean ecosystems [21,23,26–30]. The production and release has been worldwide over decades. Typically one deals with nonpoint sources, though point sources can still be observed for PCB emissions. The main difference between mixtures is the average degree of chlorination. Despite a wide variety of technical blends, the composition of the technical mixtures of the same degree of chlorination are very similar [31–34]. The application of the main technical blends varied over time [35] and interesting enough the composition of the applied technical blends also varied between the US and Europe. This defines at least two different continental nonpoint sources for the northern hemisphere [9,25].

About 130 of 209 possible congeners are found in the environment. High resolution gas chromatography and sensitive detection in the lower picogram range by ECD and MSD are available [36–41]. The congeners found in the environment cover a wide range of physical-chemical constants: orders of magnitude difference are observed in water solubility  $S_{H_2O}$ , vapor pressure  $p_{oL}$ , and octanol-water partition coefficient  $K_{ow}$ . These are the parameters that basically drive the environmental partitioning [7,42,43]. In spite

of a general chemical stability, the biotransformation of PCBs to hydroxylated metabolites is strictly congener specific. It leads, in part, to persistent chlorobenzoic acids as a dead-end pathway [44–47]. The results observed for the PCBs can mostly be generalized in one way or the other to the other groups of chlorinated semivolatile organic compounds (SOCs). Classes of organochlorine compounds of which the environmental fate is or will be about similar to that of the PCBs are summarized in Table 2.

## AIR–SEA EXCHANGE AS A SINK AND A SOURCE OF POPs

### Hexachlorocyclohexane isomers ( $C_6H_6Cl_6$ )

The two hexachlorocyclohexane (alpha- and gamma-HCH) isomers are the the most abundant semivolatiles of the organochlorines in the atmosphere of the northern hemisphere. A particle attached portion of < 1% in the atmosphere suggests that besides dilution by HCH depleted air, the decrease of atmospheric concentrations is mainly governed by gas dry deposition and by reaction with OH radicals [20]. In the tropics and subtropics—representing more than 50% of the global atmosphere—OH radicals have a continuously high average concentration. A rate constant for the reaction of gamma-HCH with OH-radicals of  $0.6 \times 10^{-12}$  cm<sup>3</sup>/s has been measured by Zetsch, and estimates are that this value is the same for alpha-HCH. A diurnal concentration of  $3 \times 10^6$  OH-radicals/cm<sup>3</sup> in the tropics leads to a lifetime  $t_{OH}$  of 13 days for HCH in the atmosphere of the tropics. Atkinson estimated the reaction rate constant to be  $6.9 \times 10^{-12}$  cm<sup>3</sup>/s [48]. This value would require a photooxidation lifetime of only about 1.2 days for the HCHs in the tropics. The photolysis of HCH in the atmosphere will be a process of minor importance in respect to the removal from the atmosphere, as the absorption spectrum of HCH does not extend into the region of the sun light.

Despite the necessary decline of HCH in the air of the southern trades as a result of dry and wet deposition and degradation by OH radicals, an increase of the concentration of the HCHs in air flowing to lower latitudes is observed. It is the result of the temperature dependence of the gas–water equilibrium between the marine air and the surface water of the South Atlantic [20]. A seasonality of air–water fluxes has been measured in a regional scale for hexachlorocyclohexanes in Lake Ontario [49]. Bidleman reported similar results for the Arctic Ocean [30]. The eastern North Atlantic water is clearly undersaturated with the HCHs relative to the overlaying air, especially if inflowing air of the ‘Lindane-source’ Europe is present [20].

The changing levels of HCH in marine air are due to temporal and spatial differences of the input from continental anthropogenic sources, the air–sea exchange equilibrium, and the removal from the atmosphere by chemical and physical processes.

### Polychlorinated biphenyls ( $C_{12}H_{10-x}Cl_x$ )

Polychlorinated biphenyls, PCBs, like the polychlorinated dioxins and other organochlorines are part of the emissions of modern technical civilization. As part of the chemistry of uncomplete combustion dioxins have been formed for long at baseline levels. The combustion of wood alone can form low levels of dioxins. Various sources of the chlorine chemistry have added dioxins to this quasi geogenic input. The mean levels of polychlorinated dioxins in environmental samples from air to mothermilk are known [50].

PCBs are definitely technical products and thus around in the environment only since their production started in 1929. In contrary to the chlorinated pesticides they have never deliberately spread out into the environment. From millions of minute sources they ended up as global pollutants. They are true chemical indicators of our industrial civilization.

PCBs are found in air, water, biota, and sediments despite of their apparant non volatility and their apparant water insolubility. For the large group of the semivolatile organic compounds (SOCs) (Table 2) they can be taken as model or indicator compounds.

The pattern of concentrations of the more than 100 PCBs present in the marine air relative to the underlying water surface of the global oceanic system representing about 70% of the globes surface can be discussed either as

- 1 a stochastic schlieren model, or as
- 2 an oscillating or constant flux model, or as
- 3 an equilibrium model with relaxation phases.

The role of the air/water interface and the environmental implication of an air–water interfacial parti-

tioning have been discussed by Mackay [51,52].

In spite of differences in the aerial input of the pattern of PCB congeners from the American and the European continents, a distinct clean marine air pattern is found north and south of the equator [25]. If we assume an air/sea exchange close to equilibrium as the relevant source of PCBs in air of the open ocean a decline to higher latitudes should be given as the result of the temperature dependence of the  $K_{gw}$  value. Such a correlation between the levels of the lower chlorinated congeners in air over the South Atlantic and the water temperature has been observed [9]. The levels of the trichlorobiphenyls (PCB 28) and (PCB 31) in air decrease from a sample in the tropics (9°S 31°W) to a sample in the colder regions of the West wind drift (50°S 3°W) by one order of magnitude. The decrease in water temperature is nearly 25 °C leading to a decrease of  $K_{gw}$  by a factor of ten. The measured reduction of the PCBs in air is in this range. The plot of  $\ln c_{air}$  vs. the inverse of the absolute temperature for the tetrachlorobiphenyl (PCB 52) measured in the South Atlantic leads via the slope of the equation to a value of the air/water distribution enthalpy of  $dH_{gw} = 40$  (east) and 44 (west) kJ/mol, respectively, [9]. This is close to values measured in laboratory experiments of 52 kJ/mol [53]. Schreitmüller calculated a relaxation time of 6–12 days for the air/water equilibrium depending on the wind speed and the temperature [54].

Particularly under conditions of a diminishing input of SOCs from continental sources, the air/surface water equilibrium will give the global oceanic system the function of a reservoir of anthropogenic compounds for the marine air. It will finally feed the continental air and rain for a long time. The air–sea exchange equilibrium can be regarded as the general and unavoidable nonpoint source for the occurrence of the SOCs in the air of pristine marine regions. Similar to catching fish, which provides a back flow of persistent lipophilic, mostly chlorinated xenobiotics in the food of men, the air–sea equilibrium will feed air and rain reaching the continents.

## BIOACCUMULATION OF PERSISTENT ORGANOCHLORINES

### Basic principles of bioaccumulation

Studies of the phenomenon of bioaccumulation date back to the turn of the century when the narcotic effects of compound on organisms were studied. At that time it became already evident that the narcotic action correlated to the lipid to water partition coefficient. Hansch & Leo normalized the general property of lipophilicity or hydrophobicity by using the octanol–water pair as the standard system for measuring this important compound property. They went on to propose quantitative structure activity relationships (QSAR) for toxicity, that are still the basis of modern computer studies.

In the early 1970s researchers following Hansch's proposal began to use the octanol–water partition coefficient  $K_{ow}$  as the molecular parameter to quantify the bioaccumulation capacity of persistent organochlorines. With an increasing degree of chlorination of a carbon skeleton  $K_{ow}$  increases as the water solubility decreases, and thus increases the capacity for bioaccumulation. Biotic as abiotic persistence increases with the degree of chlorination therefore favoring long term bioaccumulation. In spite of this general rule, there can be a wide interspecies variability. The well known 2,3,7,8-tetrachlorodibenzo-p-dioxin has a half life of a few weeks for rats while for humans it is 7–9 years. Connel has summarized in a very comprehensive way the theoretical and experimental work about the relationships between octanol–water partition coefficient and other physical-chemical parameters and the bioaccumulation of persistent compounds [55]. Recently the molecular connectivity index (MCI) has been used instead  $K_{ow}$  as a predictor of chemical biotransfer from environmental media into an animal. The molecular connectivity index can be calculated from molecular increments thus avoiding the bias of the measuring the  $K_{ow}$  experimentally [56].

The bioconcentration factor (BCF,  $K_b$ ) is clearly defined only for biota living in an aquatic environment, like fish. For various biota a rather constant and direct functionality between  $\log K_{ow}$  covering a range of 3.0–7.0 and the bioconcentration factor  $\log K_b$  has been observed:

$$\log K_b = (0.85 \dots 1.00) \log K_{ow} - (1.06 \dots 1.36)$$

The biomagnification factor (BF) includes besides the single species bioconcentration also the uptake via the food or the various food chains if one discusses predators. In most cases the more general term bioaccumulation is used summarizing all bioconcentration steps [55,57].

## Bioaccumulation and ecotoxic effects

In terms of an assessment of the ecotoxicology of a compound its biomagnification is most relevant. It can be discussed for the terrestrial and the aquatic environment.

A typical transfer of increasing importance in the terrestrial environment is the air ↔ soil transfer [58,59] and the so called skimming of air constituents by plant surfaces [60–63]. The air skimming by plant surfaces, normally not considered as bioaccumulation, leads to surprisingly high levels of pollutants in the upper soil layers of forests that otherwise would be considered as pristine in terms of human activities. The baseline PCDD/PCDF content is in the range of 0.5–3 ng ITE/kg in farm land; it easily reaches levels of 15–30 ng ITE/kg for the upper forest soils in central Europe [51]. Next in relevance to this somewhat surprising air-leaves-soil biomagnification effect is the biomagnification in terrestrial and aquatic food chains. It is the still classical question of inter-species pollution transfer or bioaccumulation studied in broadness since the early 1960s [64–66].

Depending on the order of trophic levels biomagnification factors of 10 000 up to 100 000 are encountered for persistent organochlorines like 4,4'-DDE, PCB congeners or some Toxaphene constituents. Bioaccumulation within several trophic levels can be studied by stable isotope analysis [66]. In general,  $^{15}\text{N}$  abundance enriches relative to  $^{14}\text{N} \approx 3\text{--}5\text{‰}$  per trophic level. The role of trophic levels is even visible for marine mammals with different feeding habits. Baleen whale which skim the water for plankton are less contaminated than predatory species living in the same region [67].

Bioaccumulation in bone marrow [68] as the blood renewing tissue and in brain tissue [69,70] as the central steering unit of man and animals must warrant more concern than the same levels of POPs in blubber. Mammals show important intra-species pollutant transfer during the lactation period. While the mother animal is partly depleting its body burden the calve accumulates in a critical period of its life via the milk a concentrated input of persistent organochlorines. The Striped Dolphin female loses during the 18 months long lactation period close to 85% of its body burden to the calve. A similar depletion phenomenon is also found for birds, fish and crustacean which enrich in eggs a substantial part of the accumulated body burden of the female [71]. In term of ecotoxicological relevance this will be one of the most critical areas of the bioaccumulation phenomena for persistent organochlorines besides the observed accumulation in brain and bone marrow tissue of man and mammals.

More recently the oestrogenic effects of several organochlorine compounds came under discussion [72,73]. *p,p'*-DDE has found to be a potent androgen receptor antagonist [74]. Male alligators in Lake Apopka in Florida contain high levels of *p,p'*-DDE and have abnormally small penises and other reproductive disorders [75]. Besides a femalelization of the male physiology changes in the behavioural pattern may lead to non-materialized effects of low dose long term exposition to the reproduction chain.

## OUTLOOK

The role of chemistry in the environment in our soon to be global economy increasingly requires besides a regional perspective a globally oriented discussion for the evaluation of the input, transport, transformation, and accumulation of persistent chemical compounds. It is becoming evident that the natural breakdown of organics has a limit to its capabilities. It has as the converse of biosynthesis maintained the carbon cycle since the beginning of evolution. The time scale of low dose long term effects of persistent compounds has to be taken into account. The biological and with it the chemical evolution has avoided to introduce chemical compounds that are not capable of being broken down again into the basic building blocks. The scientific community has a duty to take note of the presence throughout the world of chemicals that it has produced either directly or indirectly. Local pollution can easily be controlled, but already a regional pollution is difficult to be cleared off and in any case global contamination is out of control of men.

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