ECOLOGICAL CHEMISTRY

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Summary

Ecological chemistry may be defined as the whole spectrum of physico-chemical and biological processes that jointly determine the fate of a chemical in the environment and its potential for affecting ecosystems. As such, ecological chemistry determines the ecological stress posed upon ecosystems by the presence of chemicals in the

environment. Risk assessment is usually done on the basis of the causality chain. Within the causality chain the following elements are linked: emissions → environmental behavior/fate determining processes → exposure of species to (bio)available fractions → uptake (accumulation), metabolism, distribution in organisms and subsequent toxic effects. Ecological chemistry plays an essential role in this interplay as it determines the truly bioavailable fraction, and hence the extent of effective exposure of biotic species to chemicals. The physico-chemical and biological processes that jointly determine the fate of a chemical in the environment are the topic of interest of this contribution. Amongst others, the main characteristics of chemicals emitted into the environment are discussed, followed by a more detailed discussion of the processes of interest. This includes the impact of external factors like pH, temperature and redox conditions, and methodologies for predicting rate constants for transfer and degradation processes. Physico-chemical processes discussed include partitioning, intermedia transfer and removal by chemical or biological processes. Along the lines of the causality chain, biological availability of organic compounds will be touched upon. Toxicity at any biological integration level is not dealt with. The focus of this contribution is on organic substances, inorganic compounds will not be dealt with. Finally, a multimedia modeling approach is discussed in which all processes of interest are integrated to enable the estimation of the environmental fate of a chemical.

1. Introduction

Ecosystems are exposed to a large number of hazards. These hazards include acidification, eutrophication, dehydration, fragmentation and disruption. In addition there is chronic, diffuse environmental stress caused by a combination of substances which, if taken separately, are present in relatively low concentrations. The latter type of stress is also referred to as toxic stress. Strongly increased levels of natural and man-made chemicals are often present at local and regional scales and may exert strong adverse effects on the carrying capacity of ecosystems. As a consequence, the composition of the ecosystem in terms of numbers of individual organisms, but also in terms of higher biological integration levels (population and community level) may be subject to (irreversible) change. Hence the natural biodiversity of ecosystems that are subject to one or more of the stresses mentioned is at risk, and ecosystems might develop in which a limited number of the least sensitive organisms will survive.

On the other hand, it is almost impossible to imagine present-day society without pollution induced toxic stress. The effects of pollution in general are perceptible in many distinct sectors of society. Reduction of pollution and coping with the hazards of pollution affects the policies of a number of governmental departments. Man-made chemicals are found in all shapes and sizes. On the one hand there is peak time overloading restricted to one specific location, on the other hand there is the widespread chemical veils of pollution consisting of a whole range of man-made substances, each of which are often present at relatively low concentrations. Moreover, these types of pollution are chronic with a tendency to expand.

Two types of toxic stress may be distinguished: ecosystem effects due to the immission of xenobiotic compounds, and effects due to increased levels of naturally occurring substances. Representatives of the latter category include organic and inorganic

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chemicals. Examples of naturally occurring organic chemicals include Polycyclic Aromatic Hydrocarbons (PAHs), which are emitted as the consequence of natural combustion processes like volcanic activities and forest fires, and low molecular weight halogenated hydrocarbons like bromoform. All metals and large number of organo-metallic compounds are found in the earth crust. With regard to effects on various levels of biological integration, a clear distinction needs to be made between metals that are essential for optimal functioning of species and processes within ecosystems, and non-essential elements. The biodiversity of natural ecosystems is directly related to the levels of essential metals present and any shift, be it natural or man-induced, will directly affect the (natural) composition of ecosystems and their functioning. It should be noted, however, that conditions in natural ecosystems are thus that a large fraction of species present may be at risk due to non-optimal levels of essential elements. This effect usually is considered to be permitted from a legislative point of view.

Apart from classifying chemicals as naturally occurring, xenobiotic, essential or non-essential substances, further classification on the basis of their inherent chemical properties and toxicity characteristics, is possible. Current international focus is on persistent organic pollutants (POPs), a diverse category of bioaccumulative and toxic organic compounds of natural or anthropogenic origin that resist photolytic, chemical, and biological degradation (see *Persistent Organic Wastes*). They are characterized by low water solubility and high lipid solubility, resulting in bioaccumulation in fatty tissues of living organisms. POPs may be transported in the environment at low concentrations by movement of fresh and marine waters, whereas recent evidence has shown that because of their semi-volatility, POPs are also transported long distances in the atmosphere, resulting in widespread distribution around the earth (see *Pathways of Organic Chemical Contamination in Ecosystems*). This includes regions where they never have been produced or used, like arctic regions. Concern on possible long-term adverse effects on human health and the environment, has initiated international negotiations within the United Nations Economic Commission for Europe (UNECE) about an 'International Legally Binding Instrument for Implementing International Action on Certain Persistent Organic Pollutants'. In 1996. these negotiations have resulted in the formulation of UNECE convention text in which twelve persistent organic pollutants have been identified as priority POPs, which require immediate legislative action. These substances are listed in Figure 1. The sources, uses and properties of the priority POPs are given in Table 1. Most of the priority POPs have half-lives on the order of a week or more in air and months to years in water and soil. The half-lives given in Table 1 should be regarded as tentative because they vary with environmental conditions as redox, temperature, pH. The list of priority POPs contains eight pesticides, two industrial chemicals (hexachlorobenzene and polychlorinated biphenyls (PCBs)), and two by-products of natural origin and human activity (chlorinated dioxins and furans). Several of the priority POPs are mixtures of different substances with different individual properties. Some of these properties are difficult to measure, especially when values are extreme (e.g.: high octanol-water partition coefficient) and reported data typically cover a wide range. The values given in Table 1 should be treated as approximate rather than as accurate. PCBs consist of potentially 209 congeners obtained by chlorinating biphenyl with from one to ten chlorines. They are probably the most studied and monitored POPs. Commercial mixtures (also known as Arochlors) are widely used; their properties vary greatly depending on the number

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and position of the chlorine substituents. The lower chlorine-number PCBs are fairly volatile and are widely distributed in the global atmosphere. PCBs are very hydrophobic. Chlorinated dioxins and furans are formed in small quantities when organic matter is combusted in the presence of chlorine, like incineration of waste and combustion processes ranging from auto emissions to forest fires. In addition, they are also produced during pulp bleaching. Dioxins and furans consist of 135 potential chlorinated dibenzofurans and 75 chlorinated dibenzo-*p*-dioxins with from one to eight chlorine substituents. As with PCBs they vary in hydrophobicity and volatility. The tetrachlorinated 2,3,7,8-congeners are regarded as particularly toxic.

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Substance	**Sources/Uses**	**Properties**			**Half-lives**	**Characteristic environmental**
		K_{ow}	K_{aw}	K_{oa}	(hours)	behavior
Aldrin	Insecticide	~ $10^{6.5}$	~ $10^{-1.4}$	~ $10^{7.9}$	Air: <10 Water: 10 000 – 30 000 Soil: 10 000 – 30 000	Persistent in water and soil
Chlordane	Insecticide, mixture of cis- and trans-isomers	~ $10^{6.0}$	~ $10^{-2.9}$	~ $10^{8.9}$	Air: 30 – 100 Water: 10 000 – 30 000 Soil: 10 000 – 30 000	Persistent in water and soil
Dichlorodiphenyltrichloroethane (DDT)	Widely used insecticide, degrades quickly to dichlorodiphenyldichloroethylene (DDE)	~ $10^{6.2}$	~ $10^{-3.2}$	~ $10^{9.4}$	Air: 100 – 300 Water: 3000 – 10 000 Soil: 10 000 – 30 000	Especially persistent in soil
Dieldrin	Insecticide	~ $10^{5.2}$	~ $10^{-3.3}$	~ $10^{8.5}$	Air: 30 –100 Water: 10 000 – 30 000 Soil: 10 000 – 30 000	Persistent in water and soil
Endrin	Insecticide	~ $10^{5.2}$	~ $10^{-4.9}$	~ $10^{10.1}$	Conflicting values reported	Insufficient information
Heptachlor	Insecticide	~ $10^{5.3}$	~ $10^{-0.9}$	~ $10^{6.1}$	Air: 30 –100 Water: 300 –1000 Soil: 1000 – 3000	Fairly persistent
Hexachlorobenzene	Fungicide and byproduct in synthesis of other organochlorine compounds	~ $10^{5.5}$	~ $10^{-1.3}$	~ $10^{6.8}$	Air: 10 000 – 30 000 Water: >30 000 Soil: > 30 000	Susceptible to long range transport

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Mirex	Insecticide	~ $10^{6.9}$	~ $10^{-0.5}$	~ $10^{7.4}$	Air: 100 – 300 Water: 3000 – 10 000 Soil: > 30 000	Persists in water and soil
Polychlorinated biphenyls (PCBs)	Heat transfer, dielectric fluid, plasticizer, capacitors, copy paper. Properties dependent on number/position Cl substituents	~ $10^{6.5}$	~ $10^{-2.3}$	~ $10^{8.8}$	Air: 100 Water: 50 000 Soil: 10 000	Persistent in water and soil
Polychlorinated dioxins	Byproduct of natural origin and human activity, formed during combustion processes, but also during bleaching	~ $10^{6.9}$	~ $10^{-2.9}$	~ $10^{9.7}$	Air: 100 – 300 Water: 1000 – 3000 Soil: 3000 – 10 000	2,3,7,8,-congeners especially toxic
Polychlorinated furans	Byproduct of natural origin and human activity, formed during combustion processes, but also during bleaching	~ $10^{6.1}$	~ $10^{-3.2}$	~ $10^{9.3}$	Air: 100 – 300 Water: 1000 – 3000 Soil: 10 000 – 30 000	2,3,7,8,-congeners especially toxic
Toxaphene	Insecticide, mixture consisting of large number of congeners	~ $10^{5.5}$	~ $10^{-3.5}$	~ $10^{9.0}$	Air: 100 – 300 Water: 1000 – 3000 Soil: 10 000 – 30 000	Fairly volatile, chemical analysis difficult

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Table 1. The sources, the uses, some of the physico-chemical properties, the half-lives in the environmental compartments air, water and soil, and a general description of the characteristic environmental behavior of the priority persistent organic pollutants identified by the United Nations Economic Commission for Europe. $K_{\text{ow}} =$ octanol-water partition coefficient, $K_{\text{aw}} =$ air-water partition coefficient, $K_{\text{oa}} =$ octanol-air partition coefficient. The properties are taken from Mackay D., Shiu W.Y., Ma K.C. (1999). *Physical-chemical properties and environmental fate degradation handbook*. (CD-ROM). Boca Raton, FL, USA: Chapman & Hall C-RCnetBASE, CRC.

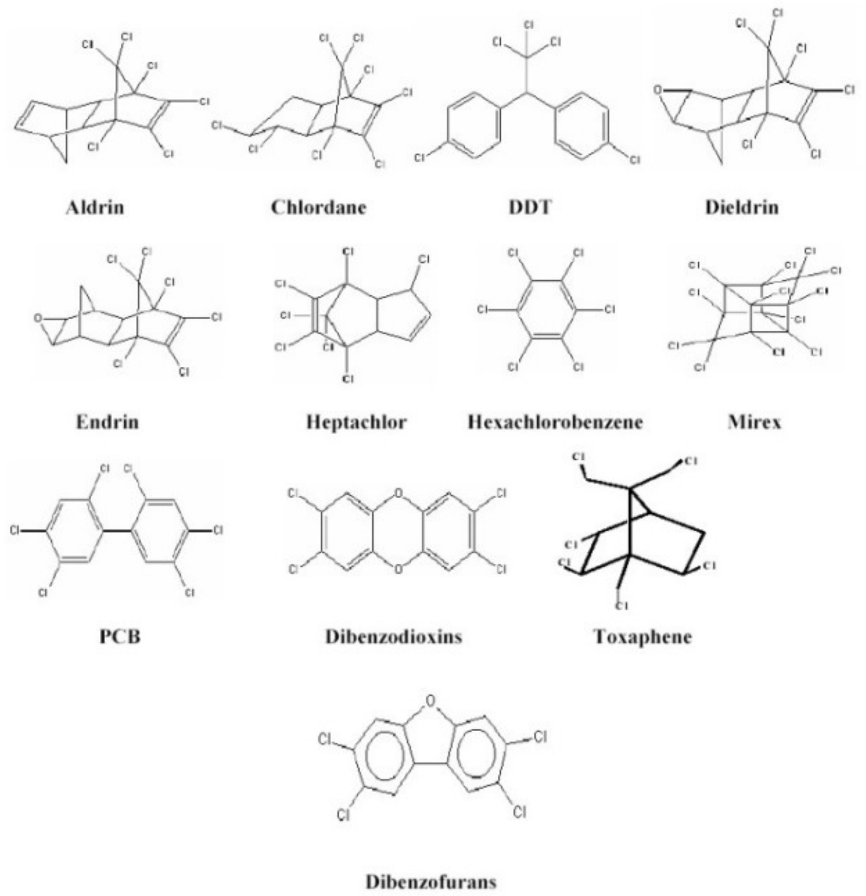

Figure 1. Priority persistent organic pollutants, as identified by the United Nations Economic Commission for Europe.

Physico-chemical and biological processes modify the availability of persistent and non-persistent natural and man-made chemicals for uptake by organisms and plants and subsequent adverse effects. Hence, these processes determine the ecological stress posed upon ecosystems by the presence of chemicals in the environment. Generic risk assessment aims at assessing the potential risks imposed by the presence of increased levels specific chemicals at regional and national scales. Site-specific risk assessment is aimed at assessing actual risks and quantifying adverse effects on a local or regional scale. This is usually done on the basis of the causality chain. Within the causality chain the following elements are linked: emissions → environmental behavior/fate determining processes → exposure of species to (bio)available fractions → uptake and toxic effects (see *Assessment of Contaminated Soils*). Ecological chemistry plays an essential role in this interplay as it determines the truly bioavailable fraction, and hence the extent of effective exposure of biotic species to chemicals. Ecological chemistry may be defined as the whole spectrum of physico-chemical and biological processes that jointly determine the fate of a chemical in the environment and its potential for affecting ecosystems. In this contribution, the main fate-determining processes will be discussed. Amongst others, the main characteristics of chemicals emitted into the environment will be discussed, followed by a discussion of the processes determining the environmental behavior and fate of chemicals. This will include the impact of external factors like pH, temperature and redox conditions, and methodologies for predicting rate constants for transfer and degradation processes, mostly based upon chemical structure. Processes discussed include partitioning, inter-media transfer, and removal by chemical or biological processes. Along the lines of the causality chain, biological availability of organic and inorganic compounds will be touched upon. Toxicity at any biological integration level will not be dealt with.

2. Release of Chemicals in the Environment

Chemical substances can originate from natural sources, from combustion and degradation processes, or they can be man-made.

1. Substances from natural origin can further be subdivided into:
    - Substances from lifeless materials as minerals and ores. Examples include metals in rock, salts in seawater and inert gases in air. Many of these natural resources are exploited and utilized by man and in many cases transformed into other substances.
    - Substances present in fossil fuels – mainly organic hydrocarbons. Apart from being used for heating, electricity generation and in combustion engines for transport, fossil fuels are also the basis for the production of a wide range of man-made synthetic organic substances.
    - Substances from organisms and plants. Organisms and plants consist predominantly of substances formed by biochemical reactions, and organisms and plants are at the basis of a wide range of different types of compounds, and produce for instance the building blocks for the agricultural industry. Many substances originating from plants and (micro) organisms are utilized directly by man as food, medicines, dyes, clothing materials, etc., or are chemically modified. As a general rule of thumb, substances produced by organisms and plants are easily transformed into other substances and upon release in the environment they are generally biodegradable.
2. Combustion and degradation processes may either have a natural origin (like forest fires, but also biodegradation processes) or they may be man-induced (like waste incineration).
3. There are millions of man-made substances resulting from chemical synthesis, many of which are xenobiotics. Typically, many by-products may be formed in chemical synthesis and therefore substances may also be categorized as being either desirable (produced intentionally by man) or undesirable. Well-known examples of chemicals produced unintentionally include the dioxin 2,3,7,8-TCDD (2,3,7,8-tetrachloro dibenzo-*p*-dioxin, produced for instance as a by-product in the synthesis of compounds like pentachlorophenol and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), but also during waste incineration under non-optimal conditions). Polychlorinated biphenyls (PCBs) are another example of compounds that are produced unintentionally during waste incineration. On the other hand, however, PCBs have been produced intentionally in view of their specific properties, and thus they provide an example of classes of substances that are produced both desirably and undesirably. Metals provide another example of a class of dually produced chemicals: cadmium produced from zinc ores is desirable, cadmium released during the processing of phosphate ores is undesirable.

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Emissions can take place at any stage of the life cycle of substances, be it during production or formation, formulation, processing, use, recovery, or in the waste. Emissions are also directly related to the way man handles resources. Emissions occur in many different ways: for short periods of time or continuously, and may be at fixed levels or with wide fluctuations (block emissions versus peak emissions). In addition, they may be from distinct point sources or from diffuse sources. It should be noted that it is dependent on the scale whether sources are to be considered as point sources or as diffuse sources. Hence, a number of local point sources may be considered diffusive sources on a regional scale. Continuous diffusive emissions produce a veil of substances at concentrations that may be considered as average background or ambient concentrations for chronic exposure. Application of pesticides is often linked to one or more of the seasons and may be considered as peak emissions at a local scale or even as block emissions on a regional or national scale.

It is important to distinguish between emissions and the load to an environmental compartment where the actual exposure occurs. The load to air, water and soil is the result not only of direct emissions but also of transport, degradation and distribution processes in the environment. A schematic overview of the processes governing the environmental fate of chemicals is given in Figure 2.

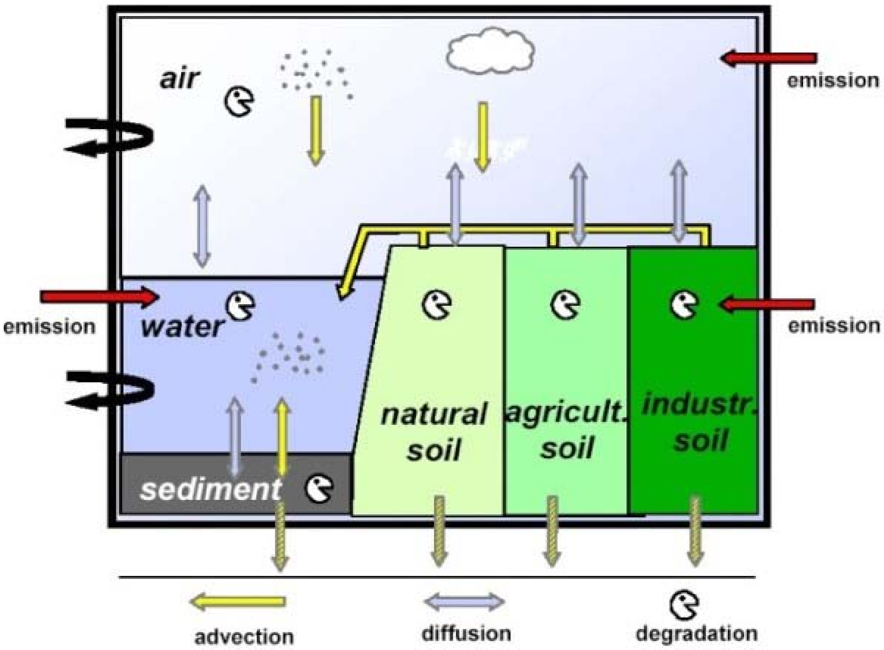

Figure 2. Schematic overview of the processes governing the environmental fate of chemicals

Volatile solvents that are emitted to soil or surface water will for instance end up in the air compartment and will contribute to the chemical load in air. On the other hand, many substances reach the soil due to wet and dry deposition from the air. This load is an indirect result of emissions to the air. In terms of risk assessment, local point sources are often the most significant. Surface waters may contain various levels of a plethora of chemicals. Often, however, a small river in which a point source is discharging, is more significant in terms of local exposure and possible adverse effects. Although air is renewed quickly, it is local pollution that may give rise to significant risks: traffic emissions may lead to effects on human during rush hours in a busy street. The latter example also shows the effect of time dependency.

Prevention and reduction measures are usually put in place when risk assessment shows that preset risk limits are exceeded. Three types of measures can be taken:

- End-of-pipe treatment: this is the traditional method applied to reduce emissions.
- Process optimization: this is increasingly seen as the best alternative.
- Recycling.

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Biographical Sketch

Dr. Willie Peijnenburg is an environmental chemist whose research interests include: the implementation of bioavailability of heavy metals in risk assessment procedures, the development and application of quantitative structure-activity relationships (QSARs) for the estimation of physical-chemical properties and transformation rates of chemical substances in the environment, and the study of biotic and abiotic transformation processes of chemical substances in natural ecosystems. He completed his Ph.D. study in 1988 at the Eindhoven University of Technology. The topic of this research was on mechanisms of photochemically induced sigmatropic shifts. Currently, Dr. Peijnenburg is employed at the National Institute of Public Health and the Environment (RIVM) in Bilthoven, the Netherlands. He is currently editor of Environmental Chemistry section of the Environmental Toxicology and Chemistry journal, Editor-in-Chief of the 'Journal of Soils and Sediments', and editor of the 'Bulletin Chemical Society Ethiopia' and "Environmental Pollution".

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